

Electrochemical detection of phenolic estrogenic compounds at clay modified carbon paste electrode

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Abstract. A simple and sensitive electroanalytical method was developed to determine the Endocrine Disrupting chemical 4-tert-octylphenol on clay modified carbon paste electrode (Clay/CPE). The electrochemical response of the proposed electrode was studied by means of cyclic and square wave voltammetry. It has found that the oxidation of 4-tert-octylphenol on the clay/CPE displayed a well-defined oxidation peak. Under these optimal conditions, a linear relation between concentrations of 4-tert-octylphenol current response was obtained over range of 7.26×10^{-6} to 3.87×10^{-7} with a detection and quantification limit of 9.2×10^{-7} M and 3.06×10^{-6} M, respectively. The correlation coefficient is 0.9963. The modified electrode showed suitable sensitivity, high stability and an accurate detection of 4-tert-octylphenol. The modified electrode also relevant suitable selectivity for various phenolic estrogenic compounds.

1. Introduction

Since the middle of the last decade, a variety of adverse effects of endocrine disrupting chemicals (EDCs) on the endocrine systems of human and animals have been observed. Alkylphenols are released into the aquatic environment primarily as major metabolites of alkyl phenol ethoxylates. For example, 4-tert-octylphenol is one of the most important substances and intermediates. They are ubiquitous in the environment because of their large domestic, industrial and agricultural use [1]. Currently LC-MS and HPLC has demonstrated to be a useful technique for the analysis of EDCs in environmental and biological samples [2]. In recent years, some phenols have been successfully detected by using electrochemical methods [3, 4]. However, carbon nanotube (CNT) film was used for the detection of 4-tert-Octylphenol [5]. As shown previously, the clay modified electrodes are types of chemical modified electrodes and their potential use for electroanalysis [6]. In this study, cyclic and square wave voltammetry on disposable carbon paste electrodes (CPE), bare or modified with clay, were used for direct electrochemical detection of the 4-tert-octylphenol.

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2. EXPERIMENTAL

2.1. Reagents

All chemicals were of analytical grade and have been used as received without any further purification. All solutions were prepared in double distilled water. 4-*tert*-Octylphenol was purchased from Sigma-Aldrich (USA) with the purity of 97%. The commercial graphite powder was supplied from France (Carbone, Lorraine, ref 9900). The clay samples employed in the research were taken from the Natural Resources of Cameroon, more precisely from the town of Garoua, in the region of North Cameroon. The samples were washed with deionized water several times with constant stirring. After being dried at 900 °C for 1 hour, the samples were crushed, and finally sieved into different particle size ranging $\leq 125 \mu\text{m}$. The natural phosphate used in this work is collected from the Province of Khouribga in Morocco.

2.1. Instrument

Cyclic and square wave voltammetry were carried out with a voltalab potentiostat (model PGSTAT 100, Ecochemie B.V., Utrecht, The Netherlands) driven by the general purpose of the electrochemical systems data processing software (voltalab master 4 software). The electrochemical cell was configured to work with three electrodes by using Clay/CPE as the working electrode, platinum plate for counter and saturated calomel electrode(SCE) as reference electrodes. The surface area of the working electrode is about 0.12cm^2 .

2.3. Synthesis of working electrode

The carbon paste electrodes were prepared by mixing high purity graphite powder and a Cameroon's clay with paraffin oil. That mixture named clay/CPE was then compacted carefully in the electrode cavity. The electrical connection was provided by a bar of carbon.

2.4. Analytical procedure

The initial procedure consisted in measuring the electrochemical response at the clay/CPE electrode at a fixed concentration of 4-*tert*-octylphenol. Standard solution of 4-*tert*-octylphenol was added into the electrochemical cell containing 0.1 M of the supporting electrolyte (Na_2SO_4). The 4-*tert*-octylphenolcontaining supporting electrolyte was kept 20 s at open circuit before performing the voltammetric measurements. The square wave voltammetry was recorded in the range from -1.5 V to 1.5 V with a scan rate of 50 mV.s^{-1} , a step potential of 50 mV, the amplitude of 2 mV and 0.1s duration. Optimum conditions were established by measuring the peak currents versus various investigated parameters such as preconcentration time, scan rate and concentration. All the experiments were performed at room temperature (25°C).

3. Results and discussion

3.1. Electrochemical impedance spectroscopy (EIS)

Electrochemical impedance spectroscopy (EIS) has been proven to be one of the most powerful tools for probing the features of surface-modified electrodes. EIS measurements, shown in figure 1, were performed in the presence of $26.6 \times 10^{-6} \text{ M}$ of 4-*tert*-octylphenol in 0.1 M Na_2SO_4 and the frequency range is from 0.1 to 10^5 Hz . Here Z_r and Z_i are the real and imaginary parts of experimental data. At the higher frequencies, squeezed semicircles represent an electron transfer-limited process, followed by a diffusion ally limited electron transfer process at the lower frequencies [7]. The diameter of this semicircle in the Nyquist plot, which exhibits the electron transfer resistance (R_{ct}) of the layer, can be used to describe the interface properties of the electrode for each immobilization step [8, 9]. The charge-transfer resistance (R_{ct}) values are calculated from the difference in impedance at lower and higher frequencies, as suggested by Tsuru et al [10]. To obtain the double layer capacitance (C_{dl}) the

frequency at which the imaginary component of the impedance is maximal ($-Z_{max}$) is found as represented in the equation (1):

$$C_{dl} = \frac{1}{\omega R_{ct}} \text{ where } \omega = 2\pi f_{(-Z_{max})} \quad (1)$$

With $f_{(-Z_{max})} = 100 \text{ mHz}$

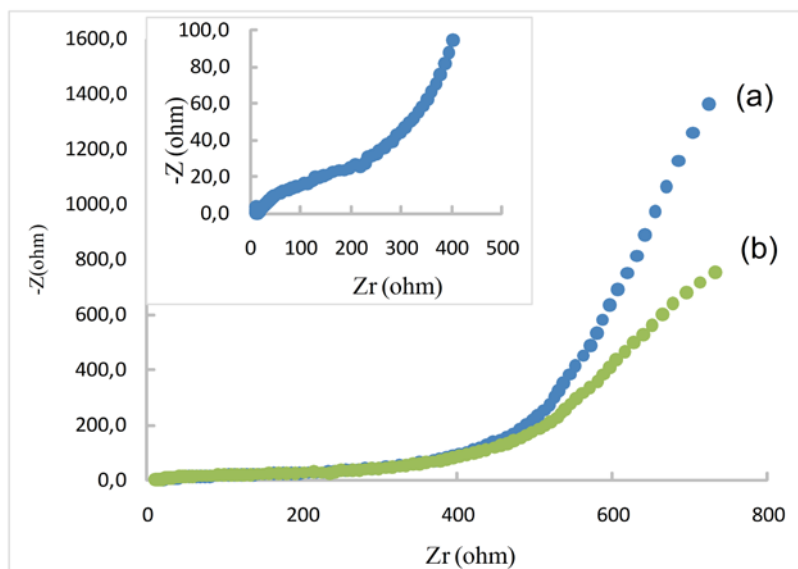


Figure 1. Nyquist plots obtained for Clay/CPE (a), Clay/CPE/4-tert-octylphenol (b). EIS measurements were carried out in $26.6 \times 10^{-6} \text{ M}$ of 4-tert-octylphenol containing 0.1 M of Na_2SO_4

The impedance diagrams were obtained for the frequencies ranging from 100 kHz to 100 mHz . The values of the charge-transfer resistance (R_{ct}) and those of double-layer capacitance (C_{dl}) are given in table 1. As shown in Figure 1, A semicircle with a large diameter is observed at the unmodified electrode, indicating the high charge resistance of CPE ($189 \Omega \cdot \text{cm}^2$) and it is difficult for the electron transfer at electrode surface. However, the diameter of semicircle diminishes significantly at clay/CPE/4-tert-octylphenol. It was obvious that charge transfer resistance ($140 \Omega \cdot \text{cm}^2$) of the electrode surface decreased, which indicated that the presence of products exhibited good conductivity and the electron transfer rate at the electrode/solution interface was greatly increased. This result is similar to that obtained by Xia Li et al [11]. Further, the C_{dl} value for the Clay/CPE/4-tert-octylphenol electrode is much higher than that for the CPE revealing that the 4-tert-octylphenol can easily diffuse through the clay/CPE electrode layer.

Table 1. Electrical parameters calculated from the impedance spectra carried out in 0.1 M Na_2SO_4 on the clay/CPE and clay/CPE/4-tert-octylphenol.

Electrode	$R_{ct} (\Omega \cdot \text{cm}^2)$	$C_{dl} (\mu\text{F}/\text{cm}^2)$
Clay/CPE	189	42.4
Clay/CPE/4-tert-octylphenol	140	35.1

3.2. Cyclic voltammetry measurements

The cyclic voltammograms have been recorded Clay/CPE. Measurements have been performed with the modified carbon paste electrodes before and after incubation with 4-tert-octylphenol. The results are presented in Figure 2. In the blank electrolyte i.e. in absence of 4-tert-octylphenol precisely in the electrolyte, no anodic oxidation peak is observed on clay/CPE electrodes. Only an anodic peak on clay/CPE at $\sim 0.75\text{V}$ is seen after adding the 4-tert-octylphenol.

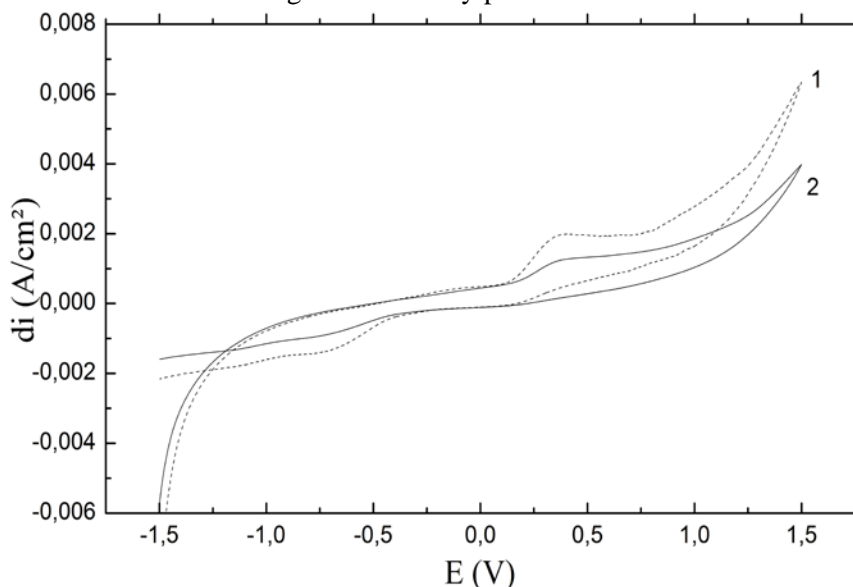


Figure 2. Cyclic voltammograms recorded on the clay/CPE containing $0.1\text{ M Na}_2\text{SO}_4$ at a scan rate of 50 mV/s : (1) in absence and (2) in presence of 4-tert-octylphenol.

3.3. Calibration curve

The square wave voltammetry was performed in figure 3 and a well-defined 4-tert-octylphenol's oxidation peak was obtained. In its inset, a linear evolution of the peak current density towards the 4-tert-octylphenol concentration was reached. As it is obtained, the oxidation peak current (I_p) is proportional to 4-tert-octylphenol concentration in the range of $7.26 \times 10^{-6}\text{ M}$ to $38.7 \times 10^{-6}\text{ M}$ with a detection and quantification limit of $9.2 \times 10^{-7}\text{ M}$ and $3.06 \times 10^{-6}\text{ M}$, respectively.

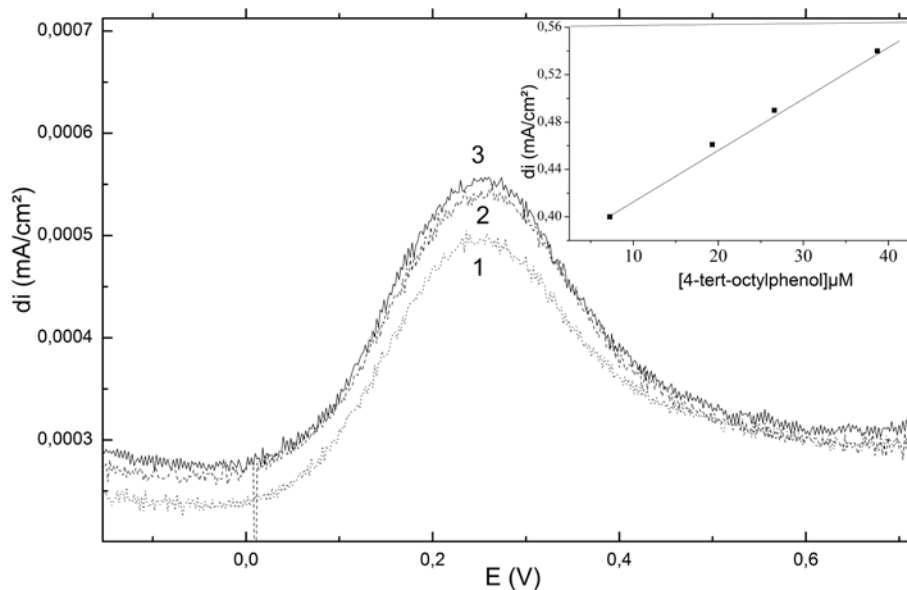


Figure 3. Square wave voltammograms at clay/CPE in $0.1\text{ M Na}_2\text{SO}_4$ for different concentrations of 4-tert-octylphenol; (1) $7.26 \times 10^{-6}\text{ M}$, (2) $19.3 \times 10^{-6}\text{ M}$, (3) $26.6 \times 10^{-6}\text{ M}$.

The relative standard deviation is less than 3.8 % for 26.6×10^{-6} M 4-tert-octylphenol (for four analysis), which shows good reproducibility.

3.4. Comparison of the activities of the prepared electrode towards several endocrine disrupting chemicals

The comparison of a cyclic voltammograms obtained at a Clay/CPE; a natural phosphate /CPE at an unmodified CPE for 26.6×10^{-6} M solutions of 4-tert-Octylphenol, 4-Nonylphenol and Bisphenol A shown, respectively, a well-defined oxidation peaks at 0.5V, 0.35 V and at 0.33V at the Clay/CPE, whose peak currents are considerably larger than those obtained at the bare CPE with the exception of 4-tert-octylphenol. These results indicated the electrocatalytic activity of the clay modified carbon paste electrodes towards all the estrogenic compounds. The relative standard deviation (RSD %) (S/N=3) is 2.04 % for 1.81×10^{-6} M 4-nonylphenol and 3.4 % for 8.76×10^{-6} M Bisphenol A. So the repeatability of electrode like its reproducibility is good.

4. Conclusion

In the current study, a simple and sensitive electrochemical method was proposed for the determination of 4-tert-octylphenol based on Clay/CPE. The modification of the carbon paste electrode with clay produced, an enhancement of the electrochemical oxidation responses obtained for phenolic estrogenic compounds.

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