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## Electrochemical Analysis of Endocrine Disrupting Chemicals over Carbon Electrode Modified with Cameroon's Clay

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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. The structural morphology of the modified electrode was characterized by SEM/EDX and XRD techniques. It has been found that the oxidation of 4-tert-octylphenol on the clay/CPE displayed a well-defined oxidation peak. Factors influencing the detection processes were optimized. 4-tert-octylphenol oxidation occurred through a surface process involving its adsorption on the clay/CPE. Under these optimal conditions, a linear relation between concentrations of 4-tert-octylphenol and current response was obtained over the range of  $7.26 \times 10^{-6}$  to  $3.87 \times 10^{-7}$  with a detection limit and a quantification limit of  $9.2 \times 10^{-7}$  M and  $3.06 \times 10^{-6}$  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 such as 4-Nonylphenol and Bisphenol A.

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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. Their release in the environment without treatment is of a particular environmental concern.<sup>1,2</sup> In recent years, both detection and treatment of these endocrine disrupting chemicals have become one of the main topics of research in the field of environmental sciences.<sup>3</sup> Alkylphenolic compounds are one of the most important groups of EDCs. Indeed, 4-nonylphenol, 4-tert-octylphenol and Bisphenol A belong to category 1 of the endocrine disrupter priority list and present clear endocrine disrupting effects in wildlife and humans. The effects of those observed compounds include reduced fertility, feminization, reproductive organ anomalies and changes in the sexual behavior of various aquatic organisms (fish, algae, frogs, benthic organisms, etc).<sup>4</sup> Alkylphenols are released into the aquatic environment primarily as major metabolites of alkylphenol ethoxylates. They are non-ionic surfactants with are widely used in a variety of industrial, household and commercial application.<sup>5</sup> Moreover, the usage in the production of Phenol/formaldehyde-based resins might also contribute to 4-tert-octylphenol occurrence in environment.<sup>6</sup> For example, 4-tert-octylphenol (4-(1,1,3,3-tetramethylbutyl phenol) as one of the most important substances and intermediates, had a consumption of approximately 23,000 tons in 2001 within the European Union.<sup>7</sup> It is known that the presence of 4-tert-octylphenol in water will lead to estrogenic activity.<sup>8-12</sup> The predicted no-effect concentration of 4-tert-octylphenol in fresh water on aquatic organisms is 0.6 nM. They are ubiquitous in the environment because of their large domestic, industrial and agricultural use.<sup>13</sup> Thus, the willpower of these compounds from water samples is of major concern in environmental monitoring<sup>14-16</sup> in order to plan their removal from the environment. Some analytical techniques reported for EDCs detection are the chromatographic methods which are the major choice in determination of phenol and its derivatives in environmental water samples,<sup>17,18</sup> the reverse osmosis also may be an effective means among ozonation, microfiltration and nanofiltration for removing a wider range of hormones and pharmaceutically active residuals from treated wastewater.<sup>19</sup> Though these techniques have high sensitivity and low detection limit, some factors, such as expensive, complicated and time-consuming restricted their application. Currently Liquid chromatography coupled with mass spectrometry (LC-MS) has

demonstrated to be a useful technique for the analysis of phenolic estrogenic compounds in environmental and biological samples.<sup>20-23</sup> Also, fluorescence<sup>24</sup> and UV<sup>25</sup> have been used as detection modes. HPLC with coulometric detection has been successfully applied for the determination of bisphenol A (BPA) in human serum<sup>26</sup> and urine.<sup>27</sup>

In recent years, electrochemical methods have been received considerable attention because of their high sensitivity, excellent selectivity, low cost, fast response, timesaving and simple operation.<sup>28</sup> Moreover, some phenols have been successfully detected by using electrochemical methods.<sup>29,30</sup>

The voltammetric behavior of xenoestrogens 4-nonylphenol (NP) and BPA at a platinum electrode has been compared with that of  $\beta$ -estradiol and other natural hormones.<sup>31</sup> Moreover, the electrooxidation of BPA was also studied at a glassy carbon electrode.<sup>32</sup> Carbon fiber electrodes were used to carry out the electrochemical removal of NP<sup>33</sup> and BPA.<sup>34</sup> However, carbon nanotube (CNT) film and further cover the CNT film coated electrode with a conducting polymer film was used for the detection of 4-tert-Octylphenol.<sup>35</sup> Due to their unique characteristics like high surface area, special conducting properties, anelectrocatalytic effect, carbon and/or modified carbon electrodes are also used in order to develop more sensitive voltammetric detection methods for different like phenols.<sup>29,30,36-38</sup>

As shown previously, The clay modified electrodes are types of chemical modified electrodes and their potential use in selective analysis<sup>39,40</sup> for electroanalysis<sup>41,42</sup> and as support matrices for catalysis<sup>43,44</sup> was reported. The Cameroon clay is very used in the adsorption of many heavy metals such as Lead<sup>45</sup> and Mercury.<sup>46</sup> Electrodes modified by porous material films, such as clays, have been a very active research area.<sup>47-53</sup> Despite their low electrical conductivity, some properties of the clays such as their ionic exchange capacity, good catalytic support, large surface area, mechanical stability and low cost<sup>54,55</sup> make them suitable as electrode surface modifiers. In particular, it has been shown in our laboratory<sup>56-59</sup> that the electrode surface can be advantageously modified by clay-suspensions with the aim of developing novel electrochemical sensors. In these cases the clay suspension has been entrapped by casting onto the surface. Modified electrodes may be also prepared by simply adding the modifier directly to a carbon paste electrode (CPE). CPE is a mixture of an electrically conducting graphite powder and a pasting liquid. It has been widely used as modified electrode for electrochemical and electroanalytical applications. It shows various advantageous attributes such as stability over a wide potential range with high over potentials for water decomposition reactions, simple and fast preparation,

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convenient surface renewal, porous surface and low residual current, besides low cost. However, the sensitivity of bare CPE is relatively poor for determination of inorganic and organic species.

In this study, cyclic and square wave voltammetry on disposable carbon paste electrodes (CPE), bare or modified with Cameroon's clay, were used for direct electrochemical detection of the 4-tert-octylphenol. Factors influencing the detection processes, such as potential scan rates and accumulation time were investigated and optimized.

### Experimental

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.

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 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.

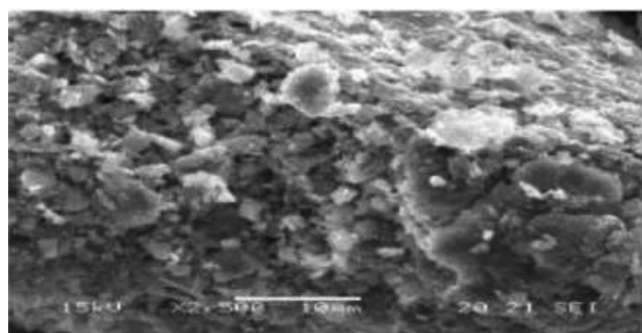
The initial procedure consisted in measuring the electrochemical response at the clay/CPE electrode at a fixed concentration of 4-tert-octylphenol. Standard solution of 4-tert-octylphenol was added into the electrochemical cell containing 0.1 M of the supporting electrolyte ( $\text{Na}_2\text{SO}_4$ ). The 4-tert-octylphenol-containing supporting electrolyte was kept 20 s at open circuit before performing the voltammetric measurements. The square wave voltammetry was recorded in the range from  $-1.5 \text{ V}$  to  $1.5 \text{ V}$  with a scan rate of  $50 \text{ mV}\cdot\text{s}^{-1}$ , a step potential of  $50 \text{ mV}$ , the amplitude of  $2 \text{ mV}$  and  $0.1 \text{ s}$  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 ( $25^\circ\text{C}$ ).

### Results and Discussion

*Surface chemical characterization.*— Table I shows the chemical composition of major elements of the six clay samples from the town

**Table I. Chemical and physical proprieties of Cameroon clay.**<sup>60</sup>

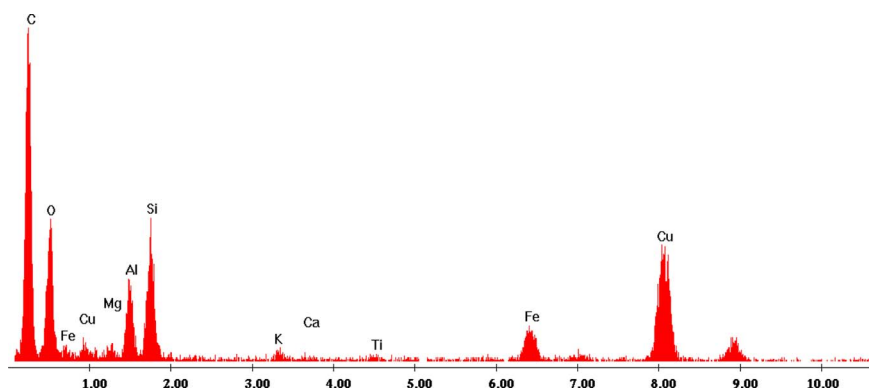
Parameters	Values
pH	5.28
Particle size ( $\mu\text{m}$ )	$\leq 125$
$\text{SiO}_2$ (%)	68.23
$\text{Al}_2\text{O}_3$ (%)	13.57
$\text{Fe}_2\text{O}_3$ (%)	6.60
MnO (%)	0.01
MgO (%)	0.44
CaO (%)	0.68
$\text{Na}_2\text{O}$ (%)	0.21
$\text{K}_2\text{O}$ (%)	0.44
$\text{TiO}_2$ (%)	0.21
$\text{SiO}_2/\text{Al}_2\text{O}_3$ (%)	5.03
SSA ( $\text{m}^2/\text{g}$ )	90
CEC (meq/100g)	42



**Figure 1.** SEM image of the clay/CPE.

of Garoua. The most abundant oxides are  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$  whereas  $\text{K}_2\text{O}$ ,  $\text{CaO}$ ,  $\text{Na}_2\text{O}$ ,  $\text{MgO}$ ,  $\text{TiO}_2$  and  $\text{MnO}$  are present only in small quantities.  $\text{SiO}_2$  value is equal to 66.23.  $\text{Al}_2\text{O}_3$  content is equal to 13.57. The specific surface area of the clay is equal to  $90 \text{ m}^2/\text{g}$ . Finally, the pH value (Table I) is equal to 5.28 indicating an acid character of the clays and the absence of carbonates.

The surface morphology of the clay/CPE electrode was carried out by SEM/EDX and XRD measurements. The obtained results were depicted in Figures 1 and 3 respectively for SEM/EDX and XRD. SEM analysis of the clay/CPE revealed layered surface as commonly obtained with clay. It presented rough and porous surface like carbons.<sup>61</sup> The average clay particle size is between 1 and  $15 \mu\text{m}$ . The elemental composition of the Cameroon clay given by EDAX measurements, in Figure 2, showed high and sharp peaks indicating that the surface of the electrode is composed of carbon (C), oxygen (O), magnesium (Mg), aluminum (Al), potassium (K), calcium (Ca), titanium (Ti), iron (Fe), silicon (Si), copper (Cu) and several metals in the range of ppm. The percentage of this composition is also shown in Table I. The XRD



**Figure 2.** EDAX spectrum of the clay/CPE.

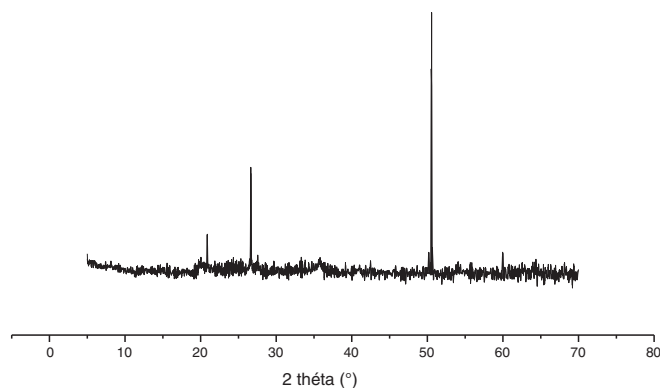


Figure 3. X-ray diffraction diagram Clay/CPE electrode.

diagram showed three sharp peaks at around  $20^\circ$ ,  $27^\circ$  and  $50^\circ$ . The peaks located at  $20^\circ$ , and  $50^\circ$  indicate the presence of Quartz where as that located at  $27^\circ$  is characteristic of carbon.

The polarization curves recorded on the clay modified carbon paste electrode before and after adding  $26.6 \times 10^{-6}$  M of 4-tert-Octylphenol into the electrolyte is shown in Figure 4. In the presence of 4-tert-octylphenol, a decrease in the current densities is observed. It indicates probably that the electrochemical oxidation of 4-tert-octylphenol on the Clay/CPE electrode is controlled by adsorption as reported by Qijin et al.<sup>7</sup> The collected parameters which are deduced from the polarization curves such as rest potential ( $E_{\text{corr}}$ ), exchange current density ( $j_{\text{corr}}$ ), cathodic and anodic Tafel slopes ( $\beta_c$  and  $\beta_a$ ) are shown in Table II. With regard to this table, it seems that the rest potential ( $E(i=0)$  mV) is more negative in terms of 4-tert-octylphenol containing electrolyte. One also observes an increase in the polarization resistance, a decrease in the corrosion current density. All these findings indicate that another reaction takes place at the electrode material surface in presence of 4-tert-octylphenols. The 4-tert-Octylphenol consists of a hydroxyl group (OH) bonded directly to an aromatic hydrocarbon group. It is expected to oxidize electrochemically.<sup>62-64</sup>

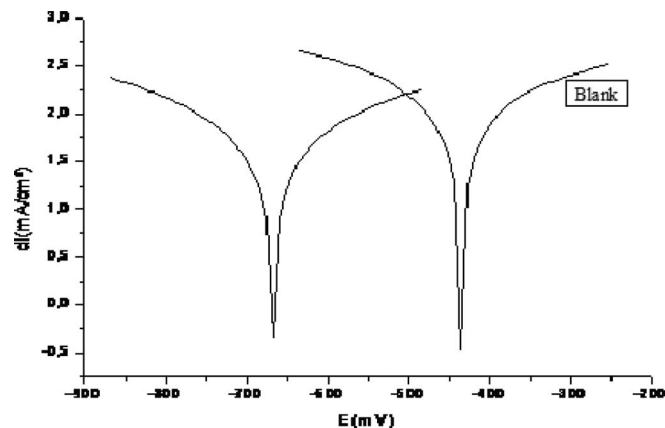


Figure 4. Tafel plot performed on Clay/CPE in absence and in presence of 4-tert-octylphenol.

*Surface electrochemical characterization.*— The cyclic voltammograms have been recorded on unmodified and modified clay carbon paste electrode. Measurements have been performed with the modified carbon paste electrodes before and after incubation with 4-tert-octylphenol. The results are presented in Figure 5. In the blank electrolyte i.e. in absence of 4-tert-octylphenol precisely in the electrolyte, no anodic oxidation peak is observed on both CPE and clay/CPE electrodes. Only an anodic peak on clay/CPE at  $\sim 0.75$  V is seen after adding the 4-tert-octylphenol.

The effect of pre-concentration time on the voltammetric response for  $26.6 \times 10^{-6}$  M of 4-tert-octylphenol using clay/CPE electrode, is shown in Figure 6. The response current increased as deposition time increased from 0 to 10 min. After this period, the peak current did not change significantly with time. Besides, these results indicate that the sorption process can be considered very fast within the first 10 min of adsorption. This phenomenon can be attributed to the saturation of 4-tert-octylphenol at the electrode surface. Taking into account the sensitivity and the efficiency, accumulation time was 10 min in the following experiments.

Table II. Electrochemical parameters.

	$E(i=0)$ mV	$R_p$ (ohm; $\text{cm}^2$ )	$i_{\text{corr}}$ ( $\mu\text{A}/\text{cm}^2$ )	$B_a$ (mV/dec)	$\beta_c$ (mV/dec)	Correlation Coefficient	$ \beta_a/\beta_c $
Clay/CPE	-435.3	462.17	105.85	364.4	-287.8	0.993	1.26
Clay/CPE/4-tert-Octylphenol	-667.9	1000	52.38	328.4	-296.7	0.995	1.1

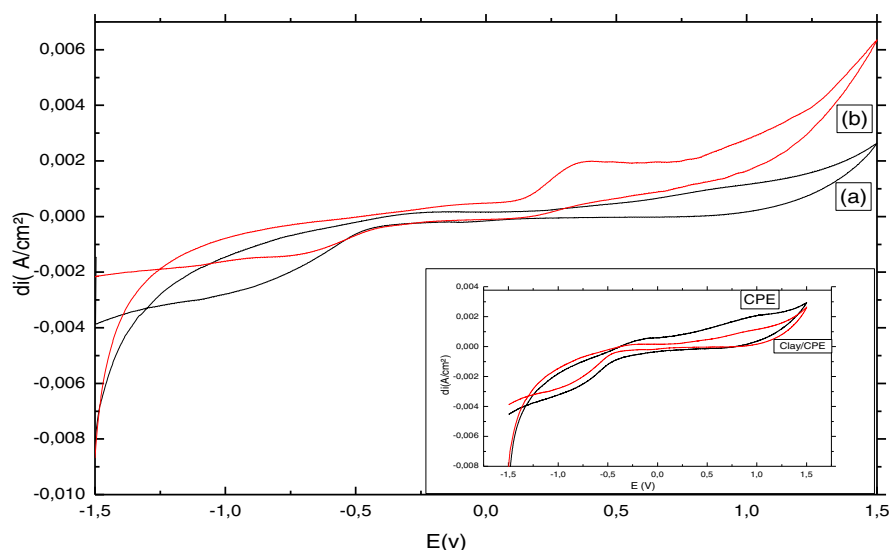
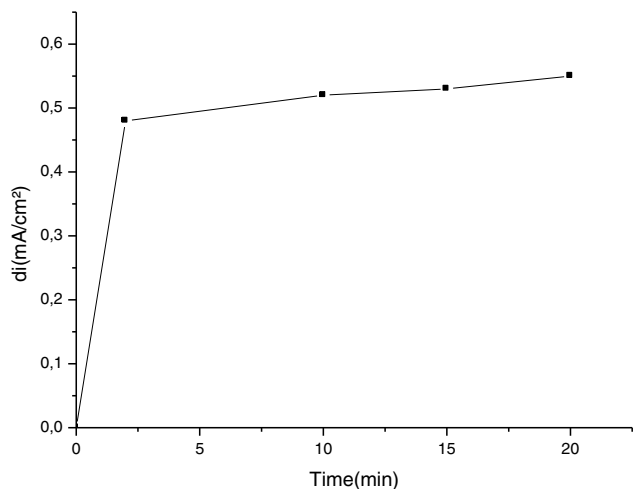
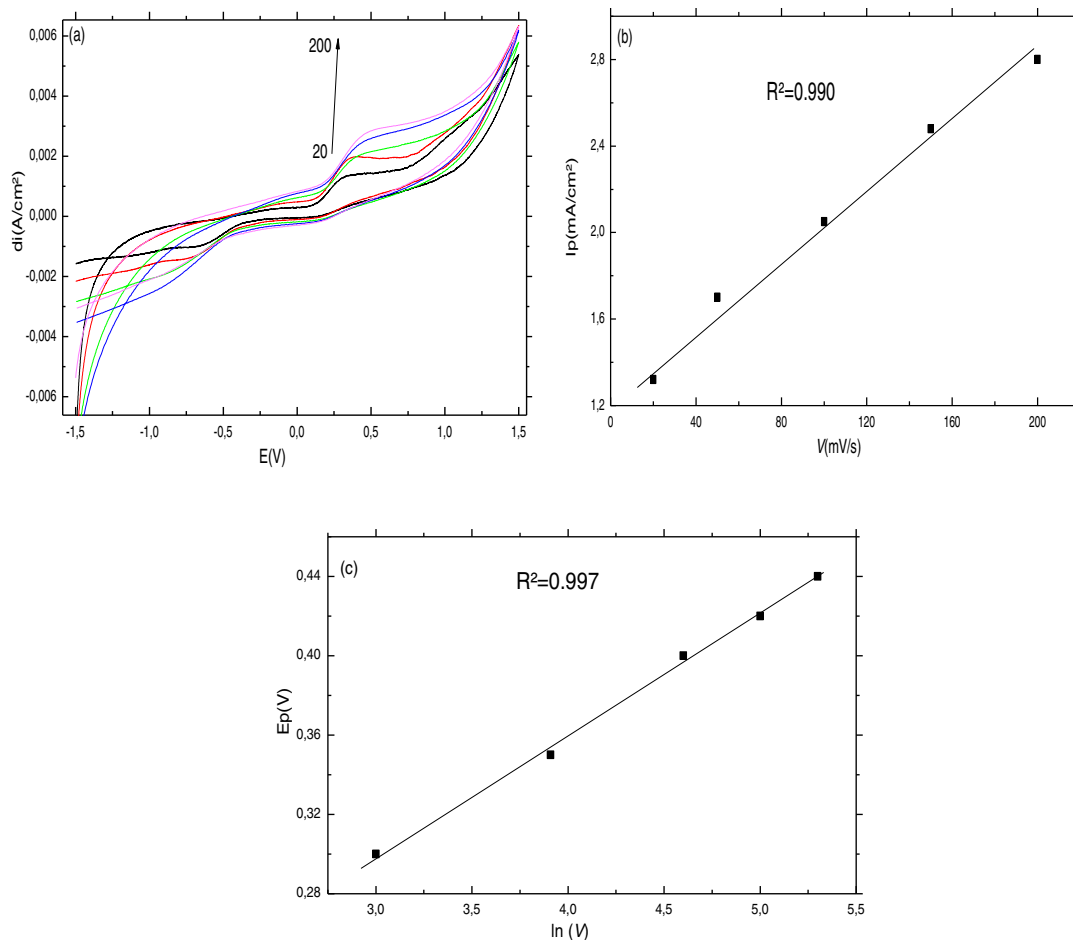


Figure 5. Cyclic voltammograms recorded on the clay/CPE containing 0.1 M  $\text{Na}_2\text{SO}_4$  at a scan rate of 50 mV/s: (a) in absence and (b) in presence of 4-tert-octylphenol. (Inset): Voltammograms of CPE and clay/CPE in 0.1 M  $\text{Na}_2\text{SO}_4$ .



**Figure 6.** Curve of the octylphenol's oxidation peak current density against its accumulation time on the clay/CPE electrode.  $26.6 \times 10^{-6}$  M of 4-tert-octylphenol in 0.1 M  $\text{Na}_2\text{SO}_4$  has been used for the measurements.

In order to investigate the 4-tert-octylphenol's oxidation mechanism at the clay modified carbon paste electrode in aqueous solution, cyclic voltammetry was recorded in  $26.6 \times 10^{-6}$  M of 4-tert-octylphenol at various potential scan rates ranging from 20 to 200 mV/s. The obtained voltammograms are shown in Figure 7.



**Figure 7.** (a) Cyclic voltammograms acquired on Clay/CPE with  $26.6 \times 10^{-6}$  M of 4-tert-octylphenol in 0.1 M  $\text{Na}_2\text{SO}_4$  supporting electrolyte at different scan rates from 20 to 200 mV/s, (b) plot of the oxidation peak current density against the potential scan rates and (c) The plot for the relationship between  $E_p$  and  $\ln v$ .

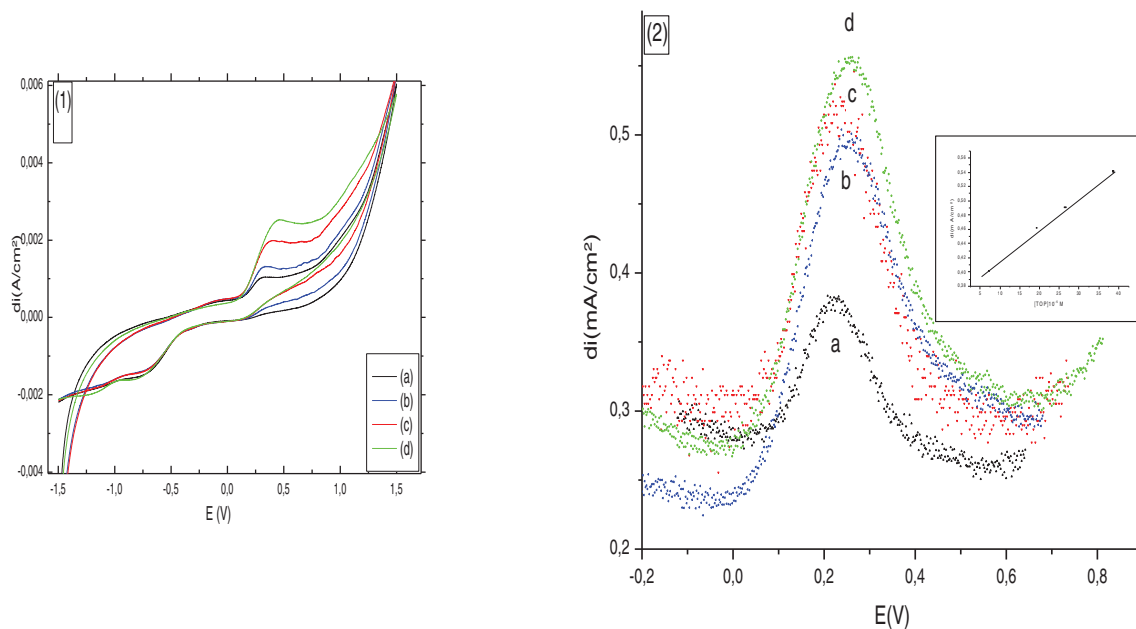
In Figure 7a, it is noticed that the 4-tert-octylphenol's oxidation peak increases with the potential scan rates. A linear dependency of the anodic current peak on the scan rate was observed from the plot of  $i_{p_a}$  versus the potential scan rates in Figure 7b. The correlation coefficient of the obtained straight line is about 0.99. Hence it can be deduced from the obtained result that a surface process involving adsorption of 4-tert-octylphenol occurs prior to its oxidation. The finding such as the characteristic of the surface adsorbed species owing the linearity between  $I_p$  and the potential scan rates.<sup>65</sup> Although the peak current augmented with the increase of scan rate, the background current was enhanced as well. The high scan rate was not suitable for the measurement of the peak current. In addition, the scan rate of  $150 \text{ mV s}^{-1}$  was chosen for quantitative analysis of 4-tert-octylphenol. The oxidation peak potential shifted positively with the increase of the scan rate. A good linear relationship between the peak potential and the natural logarithm of the scan rate was obtained in Figure 7c. The regression equation can be expressed as:

$$E_p = 0.061 \ln v + 0.114 \quad (R^2 = 0.997 \quad E_p \text{ in V and } v \text{ in } \text{mV s}^{-1}) \quad [1]$$

In the case of a controlled adsorption as well as the totally irreversible electrode process, referenced to Laviron,<sup>66</sup>  $E_p$  could be defined by the equation as follows:

$$E_p = E^0 + \frac{RT}{\alpha n F} \ln \left[ \left( \frac{RTk^0}{\alpha n F} \right) \right] + \frac{RT}{\alpha n F} \ln v \quad [2]$$

Where  $E^0$  is the formal potential,  $T$  is the temperature,  $\alpha$  is the transfer coefficient and  $n$  is the number of the electron transfer in the rate-determining step.  $k^0$  is the electron-transfer rate constant,  $v$  is scan



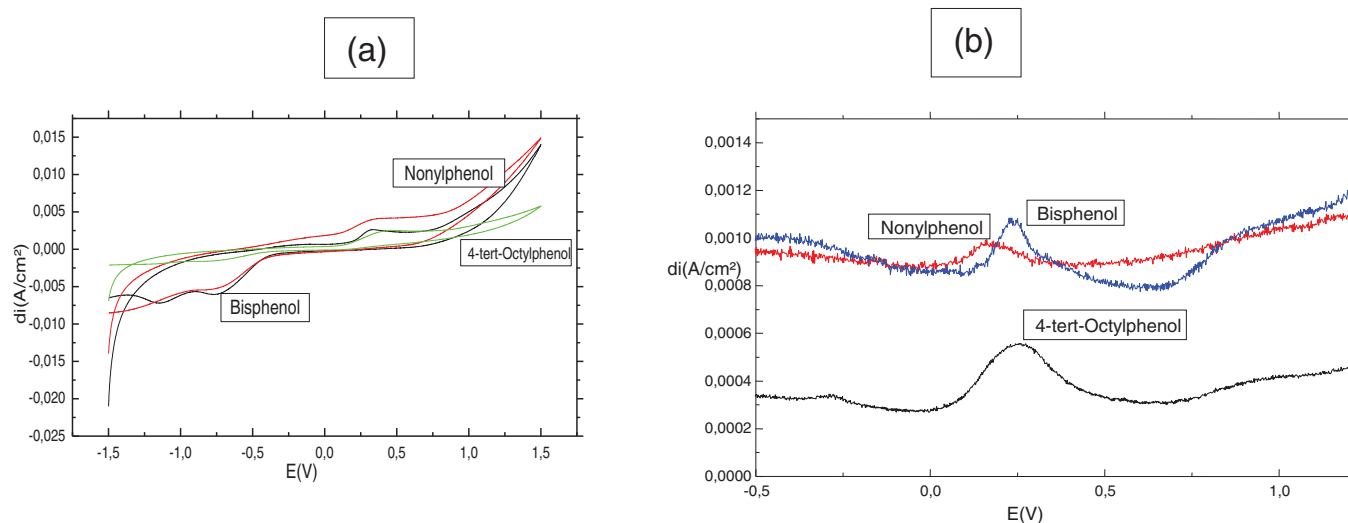
**Figure 8.** Cyclic (1) and (2) Square wave voltammograms at clay modified carbon paste electrode in 0,1 M  $\text{Na}_2\text{SO}_4$  for different concentrations of 4-tert-octylphenol; (a)  $7.26 \times 10^{-6}$  M, (b)  $19.3 \times 10^{-6}$  M, (c)  $26.6 \times 10^{-6}$  M, (d)  $38.7 \times 10^{-6}$  M.

rate, and  $F$  is the Faraday constant. From Eqs. 1 and 2, the calculated value of  $E_p$  is equal to 0.42. It is known that in a weak acidic medium, 4-tert-octylphenol is irreversibly oxidized in a one electron transfer process ( $n = 1$ ) instead of a two-electron process which take place in basic medium.<sup>63,64,67</sup>

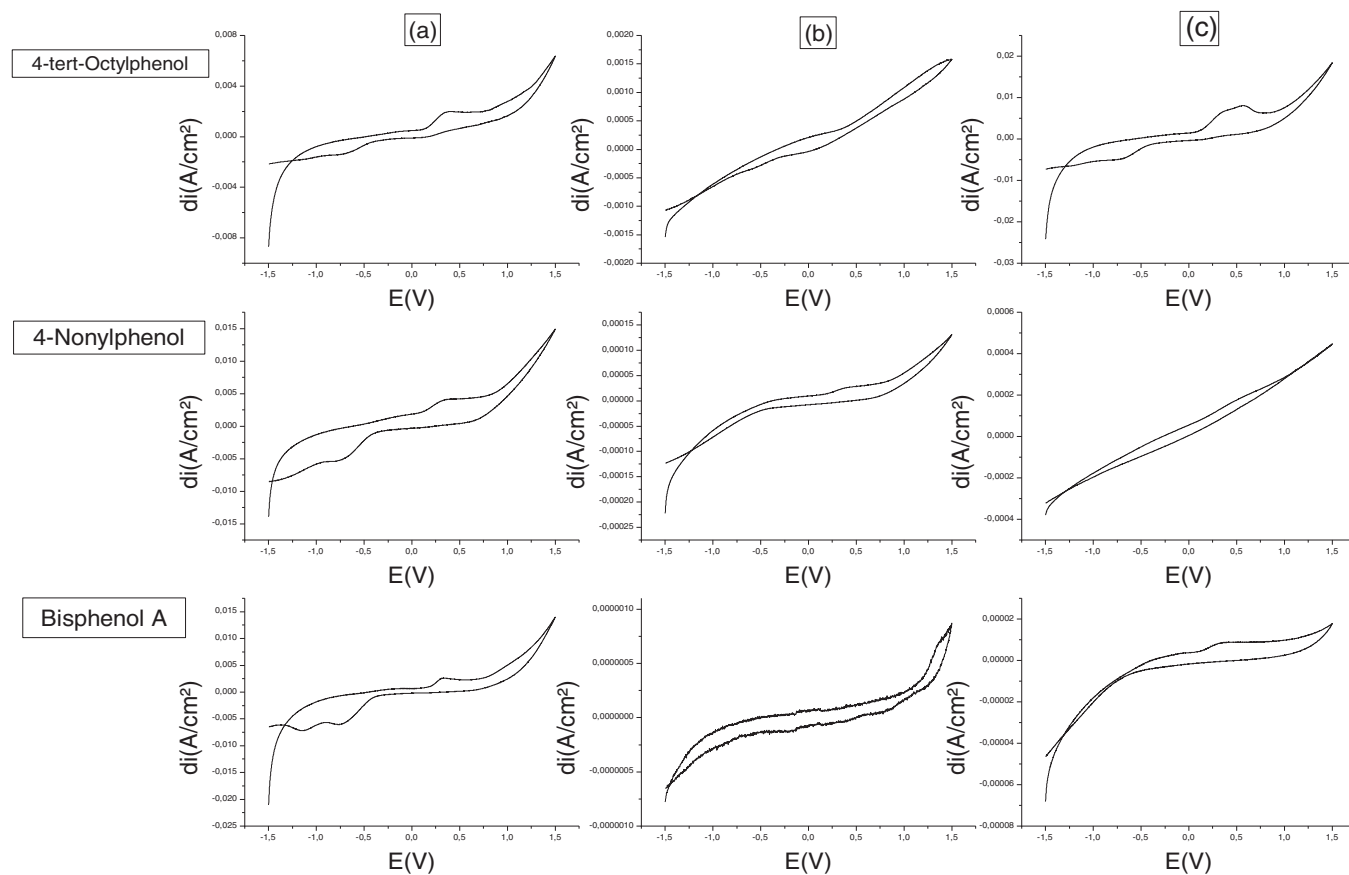
The determination of 4-tert-octylphenol at the Clay/CPE was performed by using cyclic (CV) and square wave voltammetry (SQW). The results are presented in Figure 8. Figure 8(1) and Figure 8(2) show the CV and the SQW measurements, respectively. Through the CV measurements, it is observed that the 4-tert-octylphenol's oxidation peak current density increases as the concentration of 4-tert-octylphenol is increased. For more accurate assessment of the 4-tert-octylphenol concentration, SQW was performed and the obtained well-defined 4-tert-octylphenol's oxidation peak are depicted in Figure 8(2). In its inset, a linear evolution of the peak current density toward 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  $7.26 \times 10^{-6}$  M to  $38.7 \times 10^{-6}$  M with a detection limit (DL, 3 SD) of  $9.2 \times 10^{-7}$  M and a quantification limit (QL, 10 SD) of  $3.06 \times 10^{-6}$  M. Under the optimized conditions, the relationship between the peak current density of 4-tert-octylphenol and its concentration is linear with a regression equation of  $I(\text{mA}) = 0.0044 [4\text{-tert-octylphenol}] + 0.371$  ( $R^2 = 0.9963$ ). The relative standard deviation (RSD%) is less than 3.8% for  $26.6 \times 10^{-6}$  M 4-tert-octylphenol (for four analysis), which shows good reproducibility.

*Electrode sensitivity and selectivity.*— Figure 9 shows the cyclic and the SQW voltammograms recorded at clay-CPE, after preconcentration performed in different solutions containing three endocrine disrupting chemicals such as Bisphenol, 4-tert-Octylphenol and Nonylphenol. In Figure 9a, the cyclic voltammetric



**Figure 9.** Cyclic (a) and Square (b) wave voltammograms at clay modified carbon paste electrode in 0.1 M  $\text{Na}_2\text{SO}_4$  for  $26 \times 10^{-6}$  M of Bisphenol, 4-tert-Octylphenol and Nonylphenol.



**Figure 10.** Cyclic voltammograms at a Clay/CPE (a), at a Natural Phosphate/CPE (b) and at a bare CPE (c) for  $26.6 \times 10^{-6}$  M 4-tert-Octylphenol, bisphenol A and 4-nonylphenol in 0.1 M  $\text{Na}_2\text{SO}_4$  solution;  $\nu = 50 \text{ mVs}^{-1}$ .

measurements indicated that the three compounds are oxidized in the potential domain between  $-0.25 \text{ V}$  and  $+0.75 \text{ V}$ . For more accurate detection of those compounds, square wave voltammetry was carried out. The recorded voltammograms show peaks related to the oxidation of those organic compounds at  $0.17 \text{ V}$ ;  $0.25 \text{ V}$  and  $0.30 \text{ V}$  respectively for Nonylphenol, Bisphenol A and 4-tert-octylphenol. The same electrode can oxidize all three compounds and most likely not only them.

The comparison of a cyclic voltammograms obtained at a Clay/CPE; a natural phosphate/CPE at an unmodified CPE for  $26.6 \times 10^{-6}$  M solutions of 4-tert-Octylphenol, Bisphenol A and 4-Nonylphenol in 0.1 M of  $\text{Na}_2\text{SO}_4$  is shown in Figure 10. Voltammetric parameters for 4-tert-Octylphenol, Bisphenol A and Nonylphenol at the Clay/CPE were also compared with those obtained in experiments or reported in the literature by using other different electrode materials is listed in Table III. With reference to the voltammograms, these products exhibit well-defined oxidation peaks at  $0.5 \text{ V}$  (4-tert-Octylphenol), at  $0.35 \text{ V}$  (4-Nonylphenol) and at  $0.33 \text{ V}$  (Bisphenol A) at the Clay/CPE, whose peak currents are considerably larger than those obtained at the bare CPE with the exception of 4-tert-octylphenol. With the natural Phosphate/CPE, no apparent oxidation peak was noticed on the voltammograms. Moreover, a slight potential shift toward less positive potentials is also obtained with the Clay/CPE in Table III. These results indicated the electrocatalytic activity of the clay modified carbon paste electrodes toward all the estrogenic compounds. In addition, the cyclic voltammogram for 4-Nonylphenol and Bisphenol A showed a small cathodic peak at  $-0.74 \text{ V}$  and  $-0.7 \text{ V}$  respectively on the clay modified carbon paste electrodes. The high sensitivity shown in Figure 9 and 10 can be indicates that the oxidation processes of phenolic compounds at clay-modified CPE electrodes are independent and that the simultaneous or independent measurements of this analytes are, therefore, possible without any interference. Then you can analysis all this compounds in the same time. Although, this

electrode didn't selectively sensitive to different analytes, this clay-modified CPE electrode can be very useful in electrochemical sensors.

The clay modified carbon paste electrode showed better electrocatalytic behavior toward 4-tert-Octylphenol, Bisphenol A and Nonylphenol than platinum electrode (PtE) and carbon felt electrode (CFE) owing to the low oxidation potential of these compounds seen on the clay modified carbon paste electrode. These findings allow us to examine the capability of the studied electrode for accurate determination of the compounds selectively. The calibration curves shown in Figure 11 for Bisphenol A and Nonylphenol using the peak areas as the analytical signals, exhibited the analytical characteristics summarized in Table IV. The detection and quantification limits were calculated. From the obtained results, no interference was found and the prepared electrode (Clay/CPE) seems to be selective for each of the investigation phenolic estrogenic compounds.

The relative standard deviation (RSD%) ( $S/N = 3$ ) is 2.04% for  $1.81 \times 10^{-6}$  M 4-nonylphenol and 3.4% for  $8.76 \times 10^{-6}$  M Bisphenol

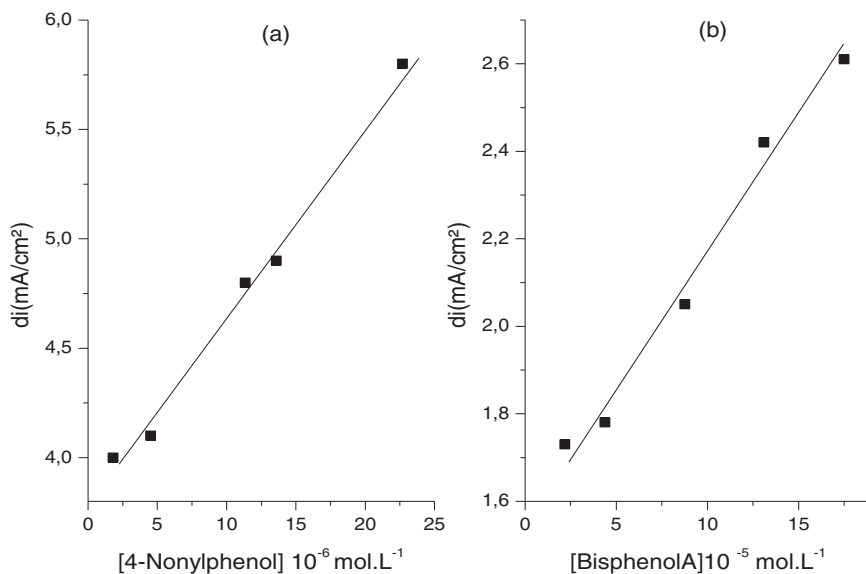
**Table III.** Peak potential values (V) and current densities ( $\text{mA/cm}^2$ ) deduced from the voltammetric oxidation of some phenolic xenoestrogens at different electrode materials.

Electrode	4-tert-Octylphenol	4-Nonylphenol	Bisphenol A
Clay/CPE	+0.50 <sup>a</sup> (1.9)	+0.35 <sup>a</sup> (4.1)	+0.33 <sup>c</sup> (2.6)
CPE	+0.53 <sup>a</sup> (7.9)	-	+0.32 <sup>c</sup> ( $8.4 \times 10^{-3}$ )
PtE <sup>68</sup>	-	+1.05 <sup>b</sup> ( $1.7 \times 10^5$ ) <sup>c</sup>	+0.90 <sup>b</sup> ( $1.0 \times 10^5$ ) <sup>c</sup>
CFE <sup>69</sup>	+0.60 <sup>b</sup> ( $2.2 \times 10^6$ ) <sup>c</sup>	+0.51 <sup>b</sup> ( $9.3 \times 10^6$ ) <sup>c</sup>	+0.54 <sup>b</sup> ( $3.8 \times 10^6$ ) <sup>c</sup>

<sup>a</sup>0,1M  $\text{Na}_2\text{SO}_4$ .

<sup>b</sup>0.05 M TBA/ $\text{H}_2\text{O}$ /acetonitrile (50:50).

<sup>c</sup>( $\mu\text{A/cm}^2 \text{ M}$ ).



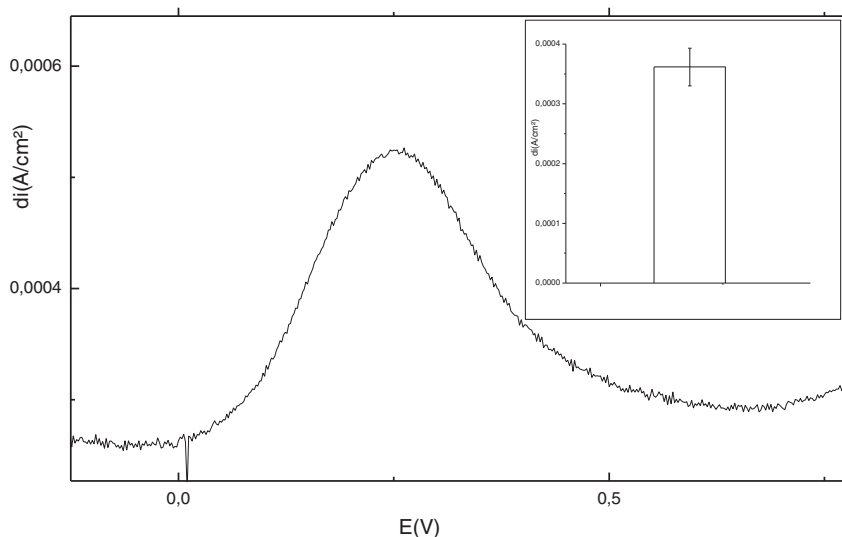
**Figure 11.** Calibration curve of 4-Nonylphenol (a) and Bisphenol (b).

**Table IV.** Limit of detection and limit of quantification of studied phenol compounds.

	4-tert-Octylphenol	4-Nonylphenol	Bisphenol
Linear range $10^{-6}$ M	7.26–38.7	1.81–22.69	2.19–17,5
Equation ( $\text{mA}/\text{cm}^2$ )	$Y = 0.004X + 0.37$	$Y = 0.092 X + 3.74$	$Y = 0.061X + 1.55$
detection limit (DL) $10^{-6}$ M	0.92	0.32	1.08
Quantification limit(QL) $10^{-6}$ M	3.06	1.01	0.32
$R^2$	0,996	0,989	0,984

A. The results confirm that electrochemical monitoring of EDCs with the clay modified carbon paste electrode is sensitive and reproducible. Peak area is especially useful because peaks may be tailed. In our case, because peak heights may vary (although area will remain constant), area values are more repeatable. The selectivity of the proposed electrode was conducted by interference of some phenolics compounds such as Nonylphenol and Bisphenol A. It was found that no effect on the determination of the 4-tert-octylphenol. These substances have no significance effect on standard signal of 4-tert-octylphenol (without interferences). Also, under the obtained experimental conditions did not interfere with the determination of 4-tert-octylphenol. Thus, it seems demonstrated that the proposed procedure was able to sense all the three compounds with high sensitive. Comparing the peak current and peak potential of 4-tert-octylphenol on Clay/CPE with those on other electrodes such polymer/CNT film coated electrode,<sup>7</sup> one can

say that the detection of 4-tert-octylphenol on clay modified carbon paste electrode has higher current and low potential to be realized with good sensitivity. The stability of the modified electrode was good. No obvious changes were observed in the peak currents for the same sample concentration after several runs of the SWV when the modified electrode was kept at a room temperature of about 25°C for one month. In fact, the performance of the modified electrode completely depends on the yield of surface modification with Clay/CPE. Furthermore, electrode preparation is a critical measurement step. But the preparation procedure is repeatable and the relative standard deviation (RSD%) is less than 3.8%. Figure 12 shows the 4-tert-octylphenol oxidation signal measured by clay/CPE. The oxidation peak of 4-tert-octylphenol was observed at +0.25 V with the average magnitude of 0.00052 A /cm<sup>2</sup> with RSD = 3.8% (n = 4). The results show that there is no significant difference between different days preparation



**Figure 12.** Square wave voltammogram and inset (histogram) presenting the  $26.6 \times 10^{-6}$  M of 4-tert-octylphenol oxidation signal (n = 4) for RSD = 3.8% obtained at clay/CPE.



electrode. So the repeatability of electrode like its reproducibility is good.

### Conclusions

In the current study, a simple and sensitive electrochemical method was proposed for the determination of 4-tert-octylphenol based on Clay/CPE. The electrochemical results discussed above demonstrate the electrochemical response of 4-tert-octylphenol on the Cameroon's clay modified carbon paste electrode. The key reason for those measurements is that this type of modified electrode marries electronic properties of carbon (e.g. larger surface area, special conducting properties and electrocatalytic effect etc.) (e.g. larger surface area, high catalytic activity, etc.) with clay (e.g. porous structures, low electrical conductivity, ionic exchange capacity, large surface area, mechanical stability etc.). The method exhibited some obvious advantages, such as simple preparation process, high sensitivity, and suitable stability. It suggests that it has a potential application for trace 4-tert-octylphenol detection in the environment. 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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