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Determination of tert-Butylhydroquinone Using a Nanostructured Sensor Based on CdO/SWCNTs and ionic liquid

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Tert-Butylhydroquinone (TBHQ) is common antioxidant in food and cosmetics industries, yet it has side-effects and can lead to disadvantages to humans. Hence the determination of different concentrations of this material is various samples is of importance and in this light the present work was focused on the voltammetric analysis of the electro-oxidation behavior of TBHQ. Accordingly a composite of CdO and single wall carbon nanotubes (SWCNTs) was prepared and used to modify an ionic liquid carbon paste electrode (ILCPE) and the resulting electrode was used for the determination of TBHQ. Structure and morphology of the composite was also evaluated through XRD method. Assessments of the electro-oxidation properties of unmodified electrodes and those modifiesed with CdO/SWCNTs and 1,3-dipropylimidazolium bromide (CdO/SWCNTs-1,3-DPIBr-ILCPEs) proved the modification to lead to enhanced sensitivity and selectivity. The CdO/SWCNTs-1,3-DPIBr-ILCPEs had a linear response range and detection limit of 0.1–750 μmol L^{-1} and 0.05 μmol L^{-1} and were applied to the determination of tert-Butylhydroquinone in oil samples.

Keywords: 1,3-dipropylimidazolium bromide, CdO/SWCNTs nanocomposite, tert-Butylhydroquinone analysis, Antioxidant

1. INTRODUCTION

TBHQ is a common antioxidant in food and cosmetic products like, edible oil, eye shadows, blushers, etc. [1, 2] used for increasing the oxidative stability of products. The compound is widely used in various edible products ranging from crackers, crisps to fast foods. TBHQ has also been further suggested as an antioxidant for biodiesel and explosive compounds [3]. Yet the risks associated with the side-effects of TBHQ outweigh its benefits and this compound is hence considered a highly unsafe preservative ingredient. Monitoring the concentration of TBHQ is various samples has been reported using different techniques like jigh-performance liquid chromatography (HPLC) [4], Fourier transform infrared (FTIR) spectroscopy [5], capillary electrophoresis [6], gas chromatography [7] and various electrochemical methods [8-15]. Electrochemical techniques are known to offer advantages like high sensitivity and selectivity, fast response, and low costs as opposed to other techniques used for the analysis of foods, pollutants, drugs and biological samples [16-30]. This technique has been suggested by many scientists for rapid analysis of different types of analytes [31-45]. The variety of electrochemical methods as well as the possibility of using different sensors have made these techniques a great tool for measuring various compounds [46-55].

On the other hand, nanostructured materials have been widely used in analytical sensors, super-capacitors, drug delivery, removal process and catalysts due to the advantageous qualities they offer [56-65]. The high surface areas of these materials and their good electrical conductivity have hanged them to candidates for modifying electrodes intended for trace analyses [66-72]. Also room temperature ionic liquid (RTILs) are known as compounds with high electrical conductivity which can be used as binders, with modifying properties, for use in electrochemical sensor [73-77].

Given the above and in continues of our group works for food additive and other important biological compounds analysis [78-83], this study was focused on the preparation of a CdO/SWCNTs-1,3-DPIBr modified ILCPE and its evaluation as an electrochemical sensor for the determination of TBHQ in pure form and real food samples.

2. EXPERIMENTAL PART

2.1. Reagents and materials

The stock 10^{-2} M solutions of tert-Butylhydroquinone (Merck) were through dissolving TBHQ in a buffer solution (pH=7.5). Paraffin oil, cadmium acetate dehydrate, sodium hydroxide, and ethanol were from Merck. Phosphoric acid, and graphite powder (<50 µm) were supplied by Sigma-Aldrich. All operations were performed using double-distilled water.

2.2. Apparatus

A µ-Autolab PGSTAT (Eco Chemie, Utrecht, the Netherlands) was used for the electrochemical analyses. The three-electrode set-up used included an auxiliary electrode (a platinum wire), the modified electrode (CdO/SWCNTs-1,3-DPIBr-ILCPE) as the working electrode and an Ag/AgCl reference electrode. The XRD characterization of the CdO/SWCNTs composites was performed using a STOE diffractometer.

2.3. Preparation of CdO/SWCNTs-1,3-DPIBr-ILCPEs

The modified electrodes were prepared through mixing 0.15 gr of 1,3-DPIBr, 0.85 gr of the paraffin oil, 0.1 gr of CdO/SWCNTs, and 0.9 g of graphite powder and the resulting paste was filled into a glass tube and a copper wire was inserted into the paste from the other side of the tube to act as an electrical contact.

2.4. Preparation of the real samples

To obtain the samples for analyses, 10.0 gr of the oil samples was transferred into 200 mL of an Erlenmeyer flask, where they were mixed with 10.0 mL of methanol for extraction. Next the samples were shaken for 50 min, followed by 20 minutes of centrifugation at 2000 rpm. Eventually the resulting extracts were transferred to a 50 mL volumetric flask and diluted to the mark using methanol.

3. RESULTS AND DISCUSSION

3.1. Characterization of the CdO/SWCNT nano-composites

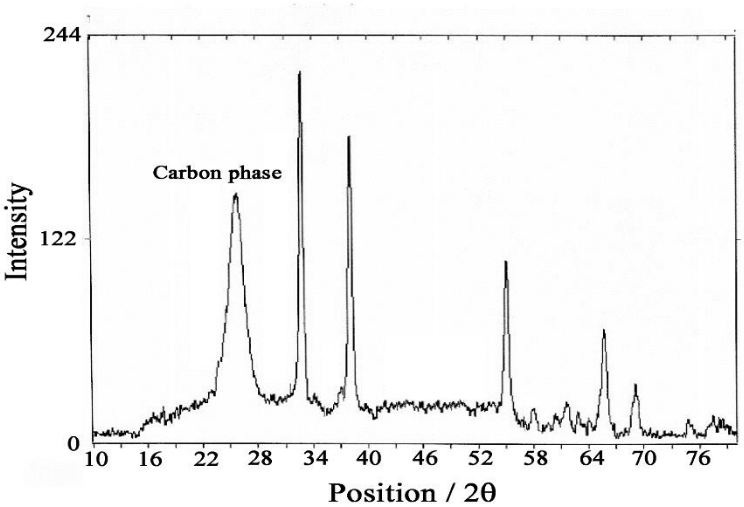


Figure 1. XRD patterns recorded for synthesized CdO/SWCNTs nanocomposite.

The structure of CdO/SWCNTs analyses were performed through XRD studies and the results (Fig. 1) indicated the presence of CdO nanoparticle and SWCNTs (carbon phase ~26^0) [84]. The average crystallite size ~32 nM was calculated using XRD pattern in Figure 1and scherrer's equation.

3.2. Electrochemical behavior of the analytes at CdO/SWCNTs-1,3-DPIBr-ILCPEs

The electro-active areas of CdO/SWCNTs-1,3-DPIBr-ILCPE, CdO/SWCNTs–ILCPE, 1,3-DPIBr-ILCPE and ILCPE were determined ~0.24, 0.19, 0.13 and 0.09 cm^2 using randles sevcik equation [85].

Since the electro-oxidation of TBHQ can be influenced by pH of the sample solutions (scheme 1) [86] the voltamogramms of a 500 μmol L^{-1} solution of TBHQ were obtained in the pH range of 4.5–8.5 (Fig. 2 insert).

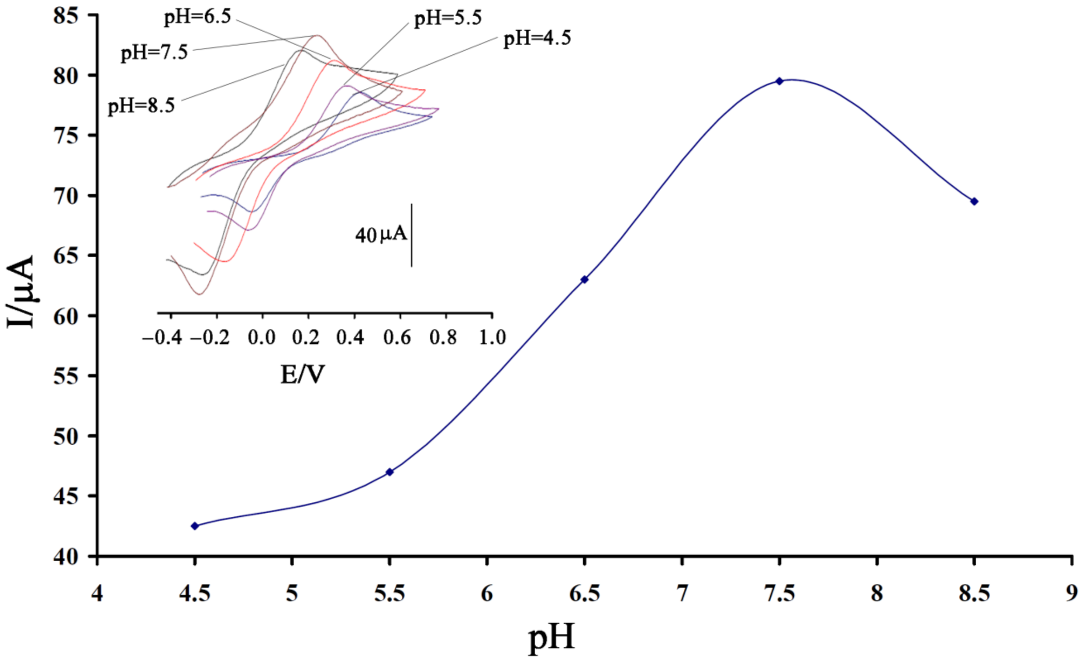


Figure 2. Current–pH curve for electro-oxidation of 500 μM TBHQ at CdO/SWCNTs-1,3-DPIBr-CPE. Inset: influence of pH on cyclic voltammograms of TBHQ at a surface of the CdO/SWCNTs-1,3-DPIBr-CPE, (pH 4.5, 5.5, 6.7, 7.5 and 8.5, respectively).

The i_{pa} *vs.* pH and E_{pa} *vs.* pH plots (Figures 2 and 3) were also recorded. Since the highest peak current could be observed at pH=7.5 (Fig. 2), this pH was selected as the optimal value and used in other studies. Further, according to figure 3, increasing the pH led to shifts in the oxidation peak potentials towards more negative values and the resulting plot had a slope of 65 mV/pH, which is close to the Nernstian value of 59 mV/pH for two electron and two protons that shows in scheme 1 [86].

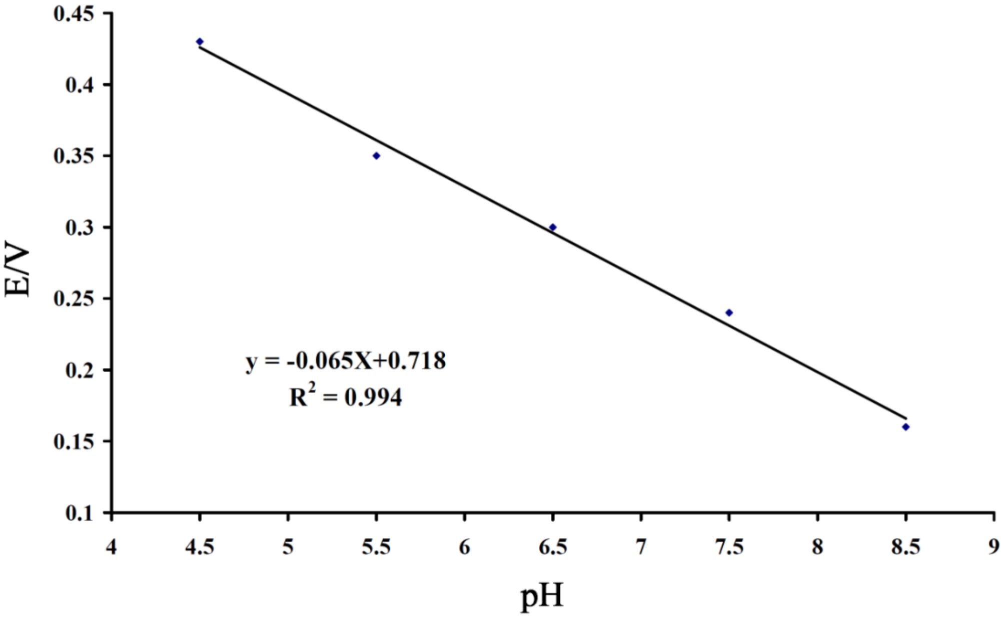
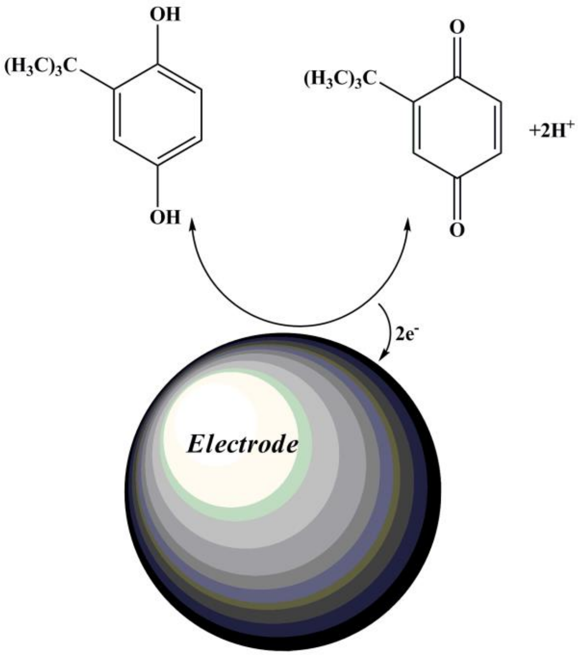


Figure 3. Potential-pH curve for electro oxidation of 500 µM TBHQ at CdO/SWCNTs-1,3-DPIBr-CPE with a scan rate of 100 mV s^{-1}.



Scheme 1. Electro-oxidation reaction of tert-Butylhydroquinone.

According to Fig.4, the voltamogramms obtained using CdO/SWCNTs-1,3-DPIBr-ILCPE (curve a), 1,3-DPIBr-CPE (curve b), CdO/SWCNTs –CPE (curve c), and CPE (curve d) as the working electrodes in the three-electrode set-up showed the highest peak current (and hence sensitivity) to be obtained in the case of CdO/SWCNTs-1,3-DPIBr-ILCPE (Fig. 4) as reflected by the increase in the peak current and decrease in the overvoltage, as opposed to ILCPEs .

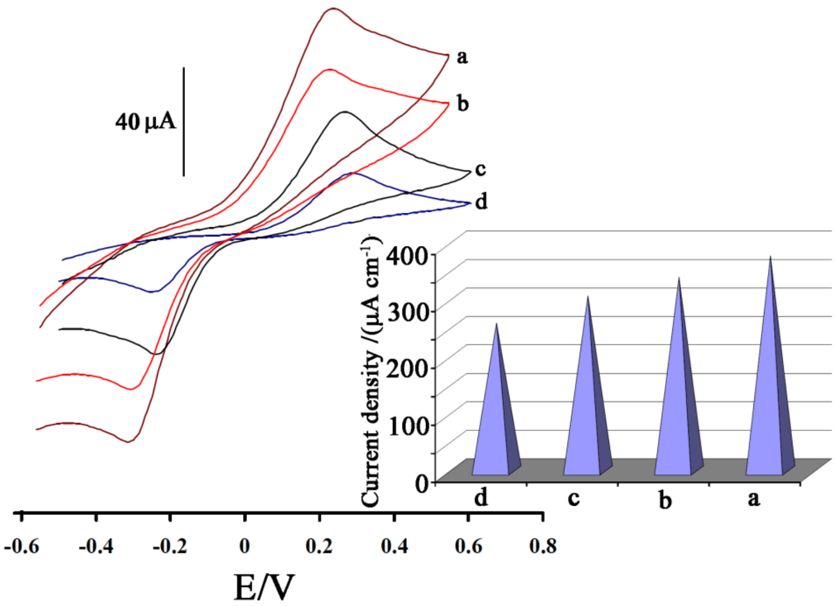


Figure 4. Cyclic voltammograms of (a) CdO/SWCNTs-1,3-DPIBr-CPE, (b) 1,3-DPIBr-CPE, (c) CdO/SWCNTs-CPE and (d) CPE in presence of 500 µM TBHQ at a pH 7.5, respectively. Inset: the current density derived from cyclic voltammograms.

The CdO/SWCNTs-1,3-DPIBr-CPE exhibited a large oxidation current of 82.5 µA (curve a) at around 220 mV. On the other hand, we detected oxidation potential ~300 mV and oxidation current ~25.2 µA at surface of CPE at same condition. The result indicated that, using the CdO/SWCNTs-1,3-DPIBr-CPE, the oxidation peak potential of TBHQ is about 80 mV less than that at the surface of the CPE. This improving is relative to role IL and nanocomposite in electrode surface [87-89]

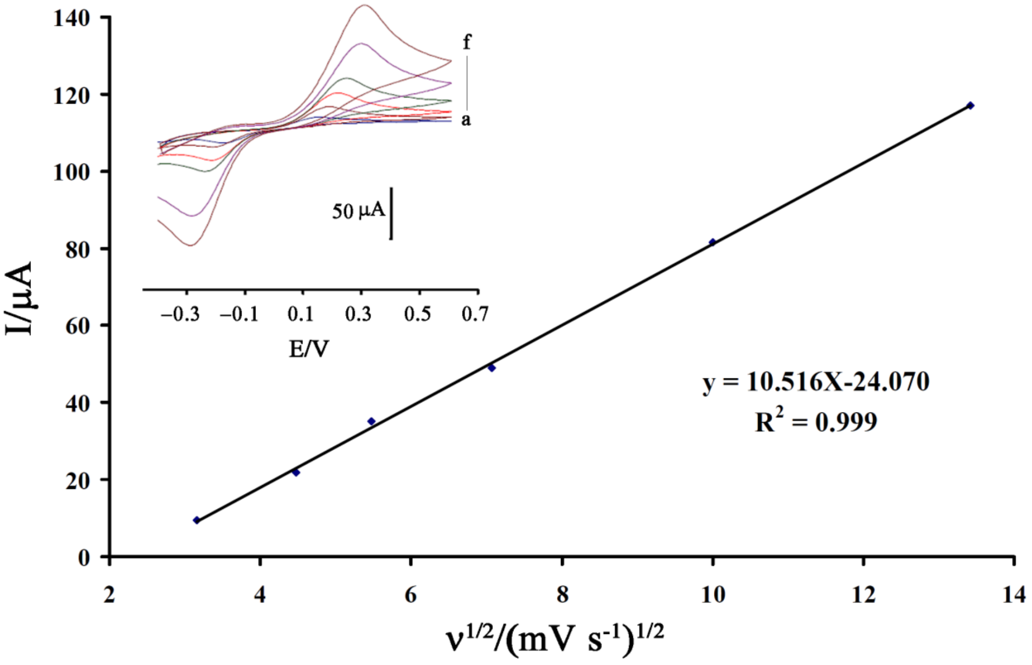


Figure 5. Plot of I_{pa} versus $\nu^{1/2}$ for the oxidation of TBHQ at CdO/SWCNTs-1,3-DPIBr-CPE. Inset shows cyclic voltammograms of TBHQ at CdO/SWCNTs-1,3-DPIBr-CPE at different scan rates of a) 10, b) 30, c) 30, d) 50, e) 100 and f) 180 mV s^{-1}1 in 0.1 M phosphate buffer, pH 7.5.

The changes in the electrochemical behavior of a 500 µmol L^{-1} solution of TBHQ, on the surface of CdO/SWCNTs-1,3-DPIBr-CPE, with varying the scan rate are illustrated in Fig. 5, which indicates a linear relationship of I_{pa} vs. $\nu^{1/2}$. This confirms the electcro-oxidation of TBHQ on the surface of CdO/SWCNTs-1,3-DPIBr-CPE to be a diffusion-controlled process [89-94].

It was also found that the electro-oxidation of TBHQ is also dependent on the scan rate (Figure 6), and using the plot of E_p as a function of ln υ, the value for α was calculated to be 0.9.

CdO/SWCNTs-1,3-DPIBr-ILCPEs were also used in the chronoamperometric determination of TBHQ at 0.4 V (Figure 7A), and the experimental plots of I *vs.* $t^{-1/2}$ with the best fits for different concentrations of TBHQ were applied. Based on the obtained slopes and the Cottrell equation the mean value for D was determined to be 3.7×10^{-5} cm^2 s^{-1} [86].

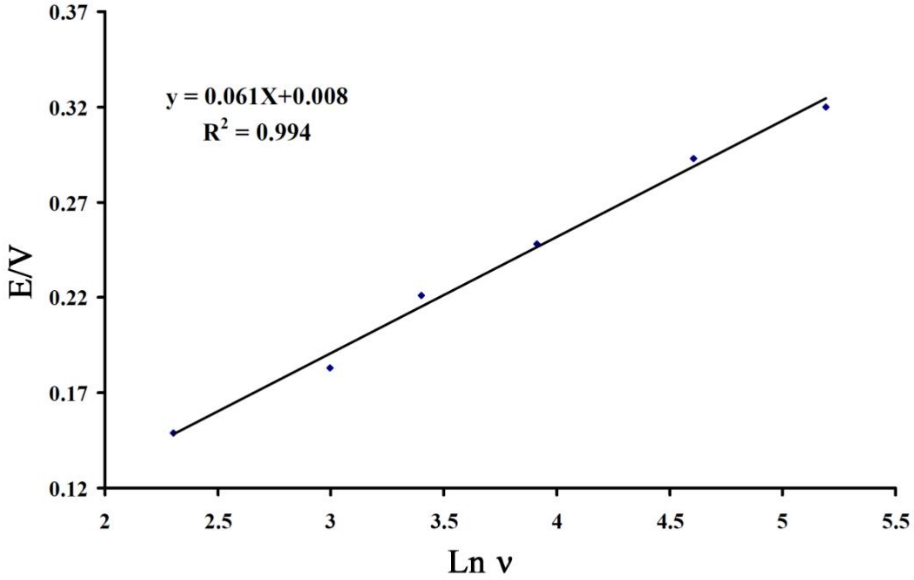


Figure 6. E vs. Ln ν plot for CdO/SWCNTs-1,3-DPIBr-CPE in the presence of TBHQ.

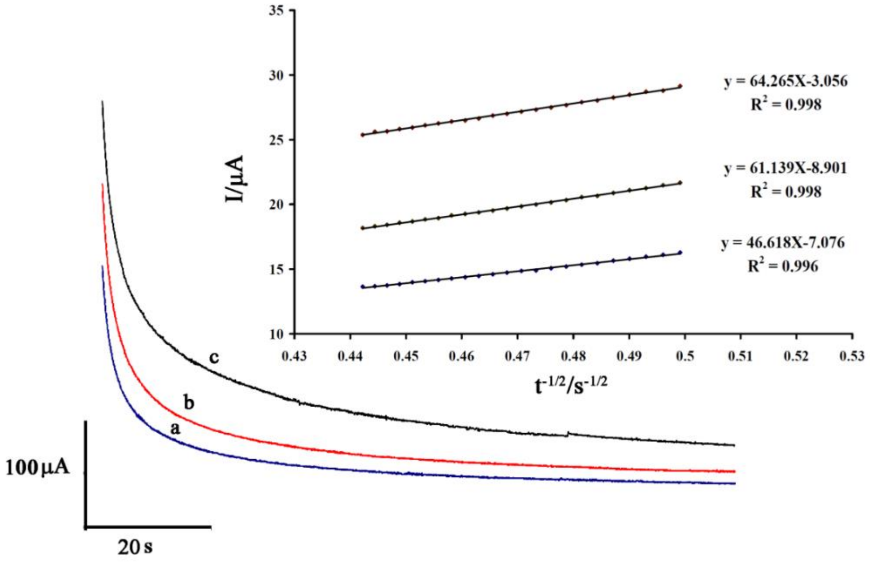


Figure 7. A) Chronoamperograms of CdO/SWCNTs-1,3-DPIBr-CPE in the presence of a) 300, b) 400 and b) 500 µM TBHQ. B) Cottrell's plot for the data from the chronoamperograms.

Also square wave voltammetric (SWV) analyses were performed using CdO/SWCNTs-1,3-DPIBr-CPE and the results (Fig. 8 insert) showed a linear peak current/concentration behavior in the range of 0.1-750.0 µmol L^{-1}, which was according to the following equation:

$I_p(\mu A) = 0.3185\ C_{TBHQ} + 11.815$

The detection limit was also determined to be 0.05 µmol L^{-1} for $Y_{LOD} = Y_B + 3\sigma$.

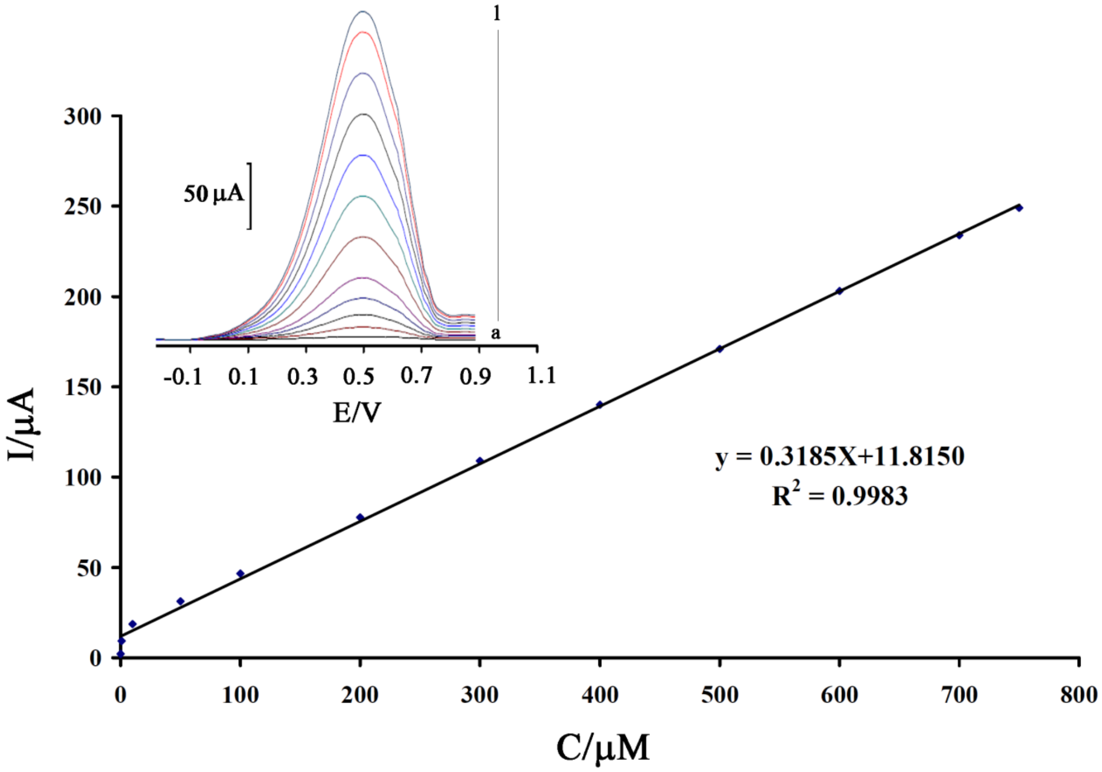


Figure 8. The plots of I_{pa} *vs*. TBHQ concentration. Inset shows the SWVs of CdO/SWCNTs-1,3-DPIBr-CPE containing different concentrations of TBHQ. The a-l correspond to 0.1, 1.0, 10.0, 50.0, 100.0, 200.0, 300.0, 400.0, 500.0, 600.0, 700.0 and 750.0 µmol L^{-1} of TBHQ.

The stability of the CdO/SWCNTs-1,3-DPIBr-ILCPEs was evaluated through maintaining the electrodes at pH=7.5 for 30 days and performing SWVs analyses with them. The obtained results were compared with those recorded before the immersion and it was found that the peak currents decreased only by 3.45% reflecting the good stability of the modified electrodes. Further seven CdO/SWCNTs-1,3-DPIBr-ILCPEs were prepared and used for the determination of a 100 µmol L^{-1} TBHQ solution, as a means for determining the reproducibility of the electrodes and the RSD of the obtained electrode peak currents (n=8) was found to equal 3.0%.

3.3. Interference studies

The influence of the presence of foreign species on the electro-oxidation peak current and potential response of the modified electrodes towards TBHQ was evaluated and no interference effects were observed upon adding 1000-fold excess of glucose, fructose, lactose, sucrose, 900-fold excess of

Br^{-},Na^{+}, K^{+}, Ca^{2+}, Mg^{2+}, Ba^{2+}, Li^{+}, Cl^{-}, SO_4^{2-}, Al^{3+}, $NH_4^{+}$and F^{-}; 800-fold excess of alanine, glycine, phenyl alanine and methionine in a buffered 10.0 µmol L^{-1} solution of TBHQ (pH 7.5).

3.4. Analysis of real samples

The applicability of the CdO/SWCNTs-1,3-DPIBr-ILCPEs was further validated through comparing their results with those obtained using HPLC (UV–vis detection at 280 nm; mobile phase: (A) methanol and (B) 0.01 mol L^{-1} NaH_2PO_4) (Table 1). The results revealed that the amount of TBHQ with the electrodes agrees with those obtain by the control method.

Table 1. Determination of TBHQ in food samples (n=3).

Sample	Added (µmol L^{-1})	Expected (µmol L^{-1})	Founded (µmol L^{-1})	HPLC method (µmol L^{-1})	F_{ex}	F_{tab}	t_{ex}	$t_{tab(95\%)}$
Sesame oil	—	—	8.65±0.22	8.95±0.82	6.5	19	1.5	3.8
	1.35	10.00	10.33±0.47	9.79±0.96	8.5	19	2.2	3.8
Soybean oil	—	—	7.50±0.33	7.94±0.75	7.8	19	2.0	3.8
	7.50	15.0	14.74±0.51	15.86±0.97	11.8	19	3.1	3.8
Colza oil	—	—	12.54±0.50	12.86±0.86	10.7	19	2.9	3.8

4. CONCLUSION

A modified electrode based on an ionic liquid based CPE modified with CdO/SWCNTs and 1,3-DPIBr was evaluated as an electrode for TBHQ. The characterization of the CdO/SWCNT nanocomposites was performed using TEM and XRD. The redox reaction of TBHQ at the surface of CdO/SWCNTs-1,3-DPIBr-CPE was monitored through cyclic voltammetry and SWV. The experiments proved that the presence of ionic liquids and the CdO/SWCNTs nanocomposite helped TBHQ have a favored orientation and lowered the effective electron transfer distance. As opposed to the results obtained using CPE, the overpotential of the electro-oxidation of the analyte was found to be about 80 mV less and the peak currents were 3.27-folds enhanced using the CdO/SWCNTs-1,3-DPIBr-ILCPEs.

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