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Synergistic Effect of Lithium Perchlorate and Sodium Hydroxide in the Preparation of Electrochemically Treated Pencil Graphite Electrodes for Selective and Sensitive Bisphenol A Detection in Water Samples

Ali Özcan*[a]

Abstract: In this study, pencil graphite electrodes were activated electrochemically in the presence of different supporting electrolytes and used for the selective and sensitive determination of bisphenol A (BPA) in water samples. Synergistic effects of both $LiClO_4$ and NaOH supporting electrolytes on the performance of the electrochemically treated pencil graphite electrode (ETPGE) were demonstrated in the oxidation of BPA. The electrochemical behavior of BPA on the ETPGE showed two irreversible oxidation peaks at 0.744 V and 0.877 V (vs. SCE). The detection limit was determined to be 3.1 nM. This single-use electrode is a very promising candidate to overcome the passivation problems arising from the oxidation of BPA. The analytical application of the ETPGE was performed in tap and river water samples.

Keywords: Bisphenol A · Pencil graphite · Voltammetry · Tap water · River water

1 Introduction

Bisphenol A (BPA) is one of the endocrine disrupting hormones which mimic the endogenous hormones and has some adverse health effects such as impaired brain development and sexual differentiation [1–4]. It is also pointed out that BPA increases cancer risk [5], and decreases sperm quality in humans [6]. Furthermore, it prevents the action of thyroid hormone [7]. BPA is heavily used in the manufacturing process of epoxy resins and polycarbonate plastics. While most of the food and beverage cans use epoxy resins as the inner coatings, many plastic products such as water and baby bottles, eyeglass lenses, and electronic equipment are made of polycarbonate plastics. These products release BPA during their use. The release of BPA in the canned soft drinks was determined in the frame of a research performed in Canada [8] and use of BPA containing substances in the production of baby bottles was banned in this country in 2010 [9]. Moreover, BPA is used for the processing of poly(vinyl chloride) (PVC) plastics and some other polymers that are used in dental applications. Because of its widespread use, the BPA levels continuously increase in the environment. Therefore, the BPA level should be very closely monitored in many areas and applications. Different analytical methods based on high performance liquid chromatography (HPLC), fluorimetry and gas chromatography-mass spectrometry (GC-MS) analyses have been employed in the determination of BPA in water samples [10–13]. However, these methods are time consuming and require qualified staff and high cost equipment.

It is known that electrochemical methods are very promising in the determination of environment pollutants because these methods have more advantages over the analytical methods such as fast response time, low cost, ease of miniaturization, high sensitivity, high selectivity and suitability for real-time monitoring. However, the electrochemical determination of BPA is difficult with bare electrodes due to their poor responses and high over-potentials. To overcome these limitations, modification of electrode surfaces using different approaches has been performed lately. In this context, Mg-Al-CO_3 layered double hydroxide [14], the imprinted sol-gel [15], MWCNT-melamine complex [16], fullerene-C_{60} [1], N-doped graphene sheets [17], SWCNT-cyclodextrin [18] and arginine functionalized nanocomposite graphene [19] have been employed in the modification of glassy carbon electrodes. Moreover, boron doped diamond electrode [20], mesoporous silica modified carbon paste electrodes [21] and polyaniline nanorods-multiwalled carbon nanotube modified basal plane pencil graphite [22] were also employed in the determination of BPA. But the surface regeneration problems restrict the application of modified carbon electrodes if the analyte molecules have high adsorption affinity toward the electrode surface. Moreover,

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[a] A. Özcan
Anadolu University, Faculty of Science, Department of Chemistry
26470 Eskisehir, Turkey
tel: +905333807975, fax: +902223204910
*e-mail: aozcan3@anadolu.edu.tr

Supporting Information for this article is available on the WWW under http://dx.doi.org/10.1002/elan.201400082 analyte molecules containing phenolic groups may polymerize on the electrode surface and this drawback is a challenge for the BPA determination because it contains two phenolic moieties. To overcome these restrictions, the single-use electrodes can be used as alternatives for the modified and unmodified glassy carbon electrodes. Therefore, pencil graphite can be considered an important single-use electrode material for the electroanalytical applications due to its low cost and commercial availability. The pencil graphite electrode (PGE) has been recently tested in numerous electroanalytical applications [23–27]. The electrochemical behavior of a PGE mainly depends on its surface functionality and the electron transfer rate. Moreover, its electrochemical activity can be improved in many ways. One of them is the electrochemical treatment of the electrodes which relies on the electrochemical oxidation or reduction of PGE at certain conditions. This treatment can drastically change the electrochemical properties and the surface area of PGE relative to the untreated ones. Previous studies present that these properties strictly depend on the electrochemical treatment conditions such as applied potential interval, supporting electrolyte, potential scan rate and so on [27c]. These studies also showed that the selectivity and sensitivity of the electrochemically treated electrodes varied with the nature of both analytes and supporting electrolytes used during the electrode preparations. For example, an ETPGE showed high affinity towards dopamine oxidation when the electrochemical treatment was conducted in phosphoric acid solution [27c]. In another example, an ETPGE had high affinity towards uric acid oxidation when the electrochemical treatment was carried out in a solution containing lithium perchlorate and sodium carbonate [27d]. Therefore, it can be concluded that the supporting electrolyte present in the electrochemical treatment medium induces different selectivity and catalytic properties to a PGE. Thus, the effects of the supporting electrolytes on the selectivity and sensitivity of a PGE have to be optimized for every type analyte molecules.

In this study, the electrochemical treatment of PGE was carried out in the presence of different supporting electrolytes with the intention to have electrodes highly selective and sensitive single-use ETPGE for the BPA determination in water. The proposed ETPGE presents an alternative solution for the passivation of electrode resulting from the oxidation of BPA. To the best of my knowledge, this is the first study that deals with the application of the ETPGE in the determination of BPA. The study showed that the ETPGE had an electro-catalytic effect on the BPA oxidation when it was prepared in a solution containing $LiClO_4$ and NaOH as supporting electrolytes. Further studies were performed for the optimization of the electrochemical treatment conditions. Moreover, the effects of experimental variables such as the pH of the medium, the accumulation time and effects of interfering molecules on the voltammetric response of BPA were thoroughly examined. Finally, the analytical application of the ETPGE was successfully tested for the BPA determination in tap and river water samples.

2 Experimental

2.1 Chemicals and Apparatus

Bisphenol A (BPA, 99%) was obtained from Aldrich. Aqueous solutions were prepared with ultra-pure deionized water supplied by a Sartorius ultra-pure water system (Germany). The BPA stock solutions were prepared in water and stored at +4 °C. Phosphate buffered solutions (PBS) were prepared using a stock solution of 0.10 M KH_2PO_4 (99%, Fluka) and pH values of the buffered solutions were adjusted to desired value by adding aliquots from 0.10 M H_3PO_4 (85% in H_2O, Aldrich) or 0.10 M NaOH (99.99%, Aldrich). Sodium sulfate (≥99.0%), lithium perchlorate (99.99%), potassium ferricyanide (99%), potassium ferrocyanide trihydrate (99.5%) and sodium carbonate (99.999%) were obtained from Sigma-Aldrich and used without any treatment. Hexamineruthenium(III) complex was prepared by dissolving ruthenium(III) chloride (99%, Aldrich) in a minimum amount of concentrated ammonia (28% in H_2O, Aldrich) and diluted to a desired value with deionized water.

A three-electrode system was employed in the electrochemical experiments. A saturated calomel electrode (Gammry Instruments, USA) and a platinum wire were used as the reference and auxiliary electrodes, respectively. Working electrode was a PGE or a ETPGE. A Voltalab PGZ402 model potentiostat equipped with a VoltaMaster 4 software (Radiometer Analytical, Australia) was used in the preparation of the ETPGE. The voltammetric responses of the PGE and ETPGE were tested by an Autolab PGSTAT 100 model potentiostat (Eco Chemie, The Netherlands).

Electrochemical impedance spectroscopy (EIS) measurements were performed by a CHI 660D Electrochemical Workstation equipped CHI model 680 Amp Booster (Shanghai Chenhua Co., China).

Pencil-lead rods (0.5×60 mm, diameter×length) were obtained from a local supplier with a brand name of Tombow (Tombow Pencil Co., Ltd., Japan). The PGE was prepared by cutting the rods into 3.0 cm long sticks and 1.0 cm of these sticks was used as a rod electrode. A home-made holder was prepared by soldering a metallic wire to the metallic part of a pen to ensure electrical contact with the PGE.

pH measurements were conducted by an IONcheck45 model (Radiometer) pH-Ion meter calibrated with standard buffers at pH values of 4.0, 7.0 and 10.0.

Scanning electron micrograph (SEM) of the PGE and ETPGE were performed by using Ultra High Resolution Field Emission Scanning Electron Microscope (ULTRA-FE-SEM) (Zeiss-Ultraplus).

2.2 Preparation of the ETPGE

The ETPGE was prepared by the potential cycling in a definite potential interval in aqueous solutions containing different supporting electrolytes. The supporting electrolytes were 0.10 M H_3PO_4 (pH 1.81), 0.10 M $LiClO_4$ (pH 7.39), 0.10 M NaOH (pH 12.56), 0.10 M Na_2CO_3 (pH 11.10) and 0.10 M PBS (pH 8.5). The prepared electrodes in the presence of these supporting electrolytes were donated as ETPGE-PA, ETPGE-LP, ETPGE-SH, ETPGE-SC and ETPGE-PB, respectively. The binary mixtures of these supporting electrolytes such as Na_2SO_4-NaOH (pH 12.61), $LiClO_4$-Na_2CO_3 (pH 10.90), $LiClO_4$-PBS (pH 8.5), and $LiClO_4$-NaOH (pH 12.46) were also tested. The prepared electrodes were abbreviated as ETPGE-SS/SH, ETPGE-LP/SC, ETPGE-LP/PB and ETPGE-LP/SH, respectively. The potential sweeping was carried out for 3 scans with a scan rate of 50 mV s^{-1} during the electrochemical treatment process. Finally, prepared ETPGE was washed with deionized water and used in the following experiments.

2.3 Adsorptive Stripping Differential Pulse Voltammetry (ASDPV) Measurements

Adsorptive stripping differential pulse voltammetry (ASDPV) measurements were used to determine the analytical parameters of the proposed method. The ASDPV measurements are generally performed in two steps. First step is the accumulation of analyte molecules on the surface of the working electrode and next step is the stripping of the accumulated analytes by the potential scanning. Either a PGE or ETPGE was immersed in the stirred solution of BPA in a definite period of time to permit the accumulation of BPA molecules. After that, the electrode was maintained for 2 s without stirring in the same medium. Next, the stripping of adsorbed BPA was performed by DPV measurements in the same medium. Measurements were repeated three times using fresh electrodes each time.

3 Results and Discussion

3.1 Selection of Supporting Electrolyte for the Preparation of ETPGE for the BPA Determination

The electrochemical treatment of the PGE was performed in the presence of different supporting electrolytes under the same conditions. The electrochemical activities of the prepared electrodes were determined by ASDPV measurements of 5.0 μM BPA in PBS (pH 7.4). The oxidation current values of BPA are given in Figure 1. The voltammetric responses of the ETPGE-SC, ETPGE-PA and ETPGE-SH were almost the same as that of the untreated PGE. However, the voltammetric responses of the other ETPGEs were significantly higher than that of the untreated PGE. The highest voltammetric response was obtained by the ETPGE-LP/SH. It is important to note that the sum of the oxidation peak currents of BPA obtained by ETPGE-LP and ETPGE-SH was much smaller than that of the ETPGE-LP/SH. It can be concluded that the mixture of $LiClO_4$ and NaOH electrolytes used during the electrochemical treatment of the PGE showed a synergistic effect on the performance of the electrode on the BPA oxidation. This effect can also be easily seen in Figure 2. Moreover, the oxidation potential of BPA shifted to more cathodic values at the ETPGEs. This shift was the highest in the case of the ETPGE-LP/SH (~70.0 mV). According to these results, the aqueous mixture of $LiClO_4$ and NaOH was chosen as the electrochemical treatment medium for the preparation of the ETPGE-LP/SH and the optimization studies were proceeded by using this mixture.

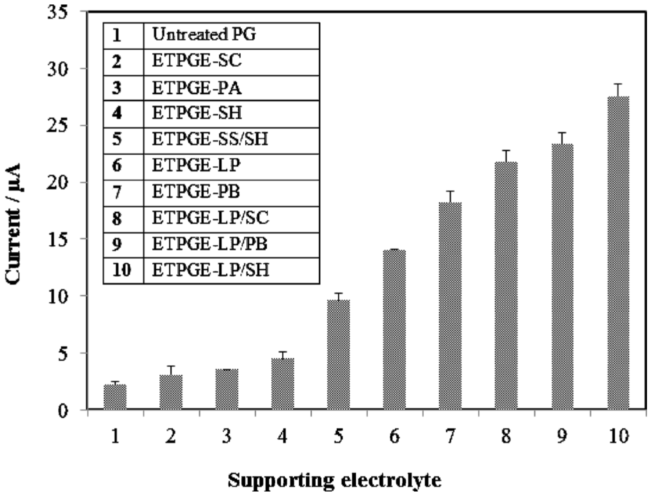

Fig. 1. The oxidation peak current values of 5.0 μM BPA in PBS (pH 7.4) obtained by the untreated PGE and ETPGE prepared in the presence of different supporting electrolytes. Accumulation time: 120 s, stirring rate: 250 rpm.

3.2 Characterization of ETPGEs

A synergistic effect was seen in the oxidation of BPA when the ETPGEs were prepared in the mixture of $LiClO_4$ and NaOH. Therefore, characterization studies were mostly focused on the ETPGE prepared in this mixture and individual solutions of these supporting electrolytes. The characterization of the prepared ETPGE-LP, ETPGE-SH and ETPGE-LP/SH was conducted by different techniques such as cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and scanning electron microscopy (SEM).

The $Fe(CN)_6^{3-/4-}$ and $Ru(NH_3)_6^{3+/2+}$ redox couples are commonly used to determine the electrochemical activity of modified electrodes. Firstly, the CV measurements were performed in 0.1 M KCl solution containing 2.5 mM $Fe(CN)_6^{3-/4-}$ and the results were shown in Figure 3a. The separation of anodic and cathodic peaks of $Fe(CN)_6^{3-/4-}$ is 0.093 V, 0.098 V and 0.102 V for untreated PGE (A), ETPGE-SH (B) and ETPGE-LP/SH (C), re-

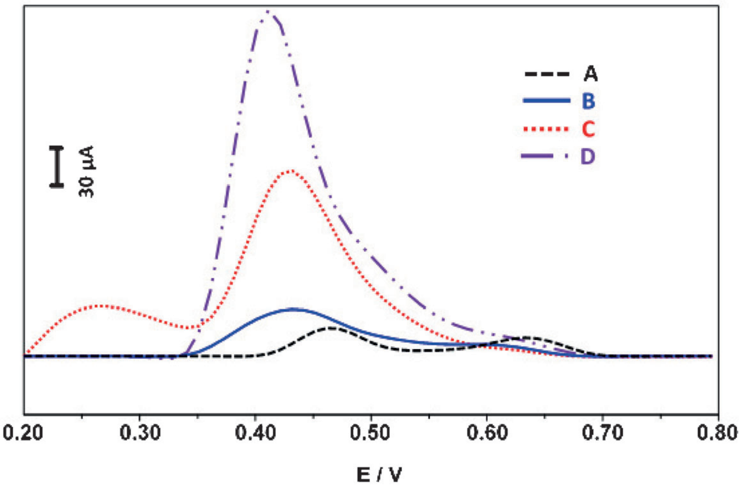

Fig. 2. The baseline-corrected ASDPVs of 5.0 µM BPA obtained in PBS (pH 7.4) by untreated PGE (A), ETPGE-SH (B), ETPGE-LP (C), and ETPGE-LP/SH (D). Accumulation time: 120 s, stirring rate: 250 rpm.

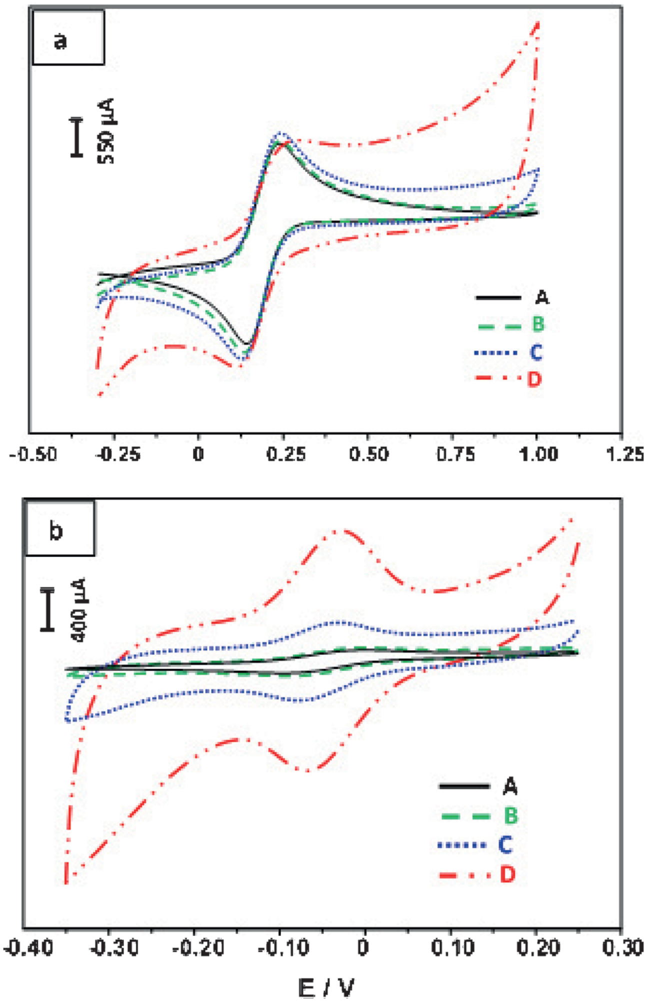

Fig. 3. The CVs of 2.5 mM $Fe(CN)_6^{3-/4-}$ (a) and 1.0 mM $Ru(NH_3)_6^{3+}$ (b) obtained in 0.1 M KCl by the untreated PGE (A), ETPGE-SH (B), ETPGE-LP/SH (C) and ETPGE-LP (D).

spectively. The ratio of peak currents is virtually one indicating similar electrochemical behavior of these electrodes. On the other hand, $Fe(CN)_6^{3-/4-}$ exhibited 0.127 V peak separation at ETPGE-LP and the ratio of peak currents (i_{pa}/i_{pc}) is 0.85 for this electrode. In addition, the peak currents of $Fe(CN)_6^{3-/4-}$ decreased in the case of ETPGE-LP. The electrochemical characterization of ETPGEs was continued using $Ru(NH_3)_6^{3+/2+}$ redox couple (Figure 3b). As can be seen, $Ru(NH_3)_6^{3+/2+}$ redox couple showed broad peaks at untreated PGE (A) and ETPG-SH (B) giving the peak separation values of 0.073 V and 0.063 V, respectively. Peak currents were the smallest for these electrodes. The redox characteristics of $Ru(NH_3)_6^{3+/2+}$ increased at ETPGE-LP/SH (C) with a peak separation value of 0.030 V. The highest response was obtained at ETPGE-LP (D) with a peak separation value of 0.034 V. These results indicate that the preparation of ETPGE in NaOH solution had no effect on the electrochemical behavior of the prepared electrodes. On the other hand, use of $LiClO_4$ as supporting electrolyte in the preparation of ETPGE had a prominent effect on the electrochemical behavior of the prepared electrodes. It can be also concluded that ETPGE-LP/SH showed different characteristics from individual solutions of these supporting electrolytes. It can be inferred from the results that ETPGEs prepared in the presence of different supporting electrolytes have different surface functionalities. The lowest current values of $Fe(CN)_6^{3-/4-}$ and the highest current values of $Ru(NH_3)_6^{3+/2+}$ at ETPGE-LP show that the surface of this electrode is most negative of all.

The electrochemical impedance spectroscopy is an effective way for the characterization of modified electrodes. Nyquist plots of PGE, ETPGE-SH, ETPGE-LP and ETPGE-LP/SH were given in Figure 4A. The impedance data best fit to an electrical equivalent circuit of $R_s(C\text{-}[R_{ct}W])$ including the solution resistance (R_s), the charge-transfer resistance (R_{ct}), the Warburg element, and the charge of constant phase element (C). The R_{ct} values

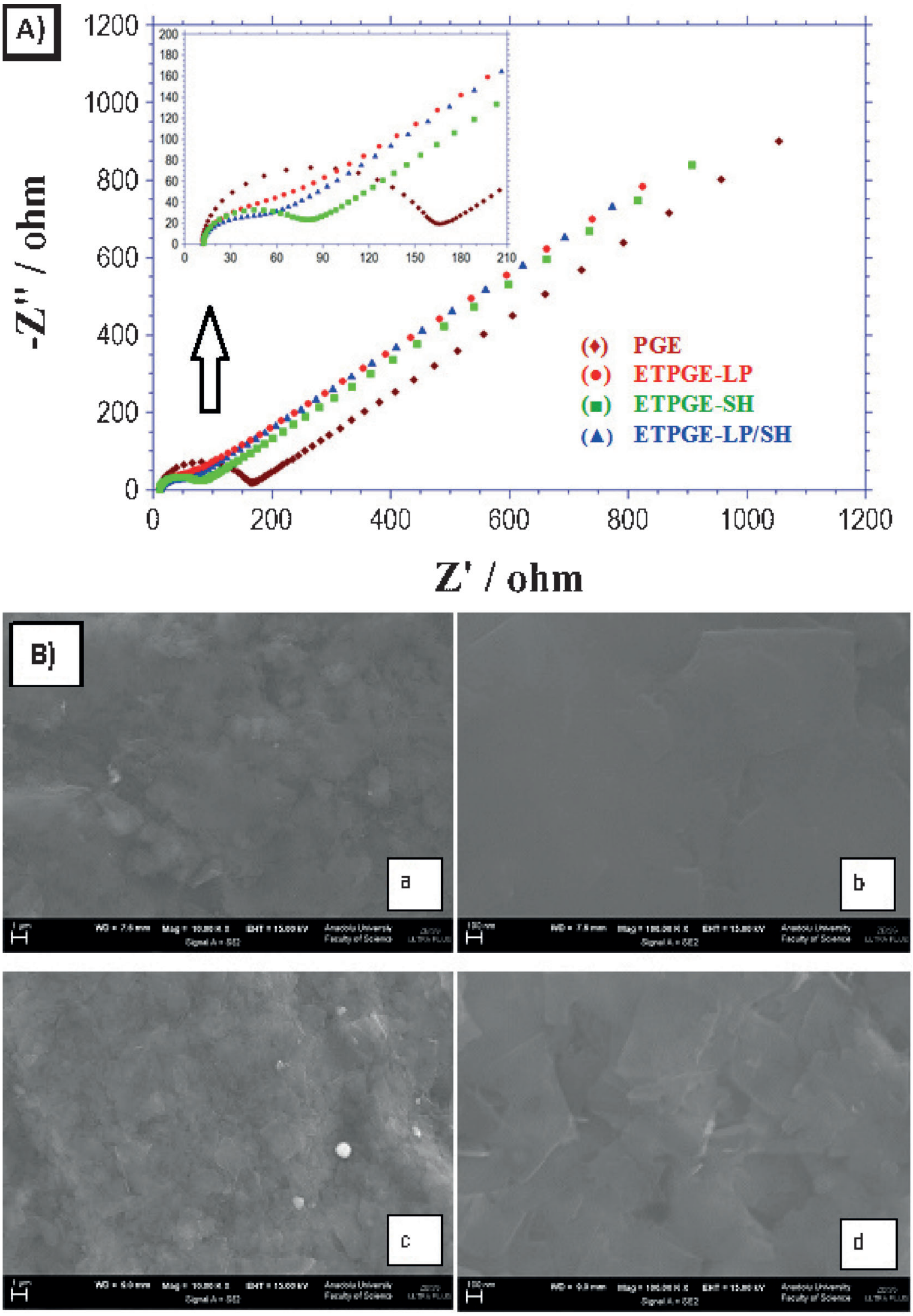

Fig. 4. A) Nyquist plots of PGE (◆), ETPGE-LP (●), ETPGE-SH (■) and ETPGE-LP/SH (▲) in a 0.1 M PBS (pH 7.4) containing 5.0 mM $Fe(CN)_6^{3-/4-}$ and 0.1 M KCl at the formal potential of +0.25 V. The frequency was scanned from 0.01 Hz to 100 kHz with the AC amplitude of 10 mV. B) The SEM images of PGE (a, b) and ETPGE-LP-SH (c, d) at 10.000 (a, c) and 100.000 (b, d) magnification.

which are the measure of the electron transfer rate at the electrode/electrolyte interface were determined from the diameter of the semi-circular parts in a Nyquist plot. The R_{ct} values of PGE, ETPGE-SH, ETPGE-LP and ETPGE-LP/SH were 143.2 Ω, 58.99 Ω, 43.87 Ω, and 36.07 Ω, respectively. These values indicate that the electrochemical treatment greatly decreases the R_{ct} values indicating the increase of the electron transfer rate. This increase was the highest in the case of ETPGE-LP/SH. Here, ETPGEs showed different electrochemical impedimetric behaviors relative to the electrochemically treated GC electrodes. It was mentioned that the R_{ct} values increased after the electrochemical treatment according to bare GC electrode indicating the formation of a membrane on the electrode surface that inhibits the electron transfer [28,29].

The morphologies of the PGE and ETPGE-LP/SH were investigated by the SEM analysis (Figure 4B). As can be seen, untreated PGE showed smooth surface morphology (Figure 4B-a,b), whereas ETPGE-LP/SH showed porous structure (Figure 4B-c,d) indicating that electrochemical treatment process increased the surface roughness. This may arise from the broken of the graphite layers into smaller parts during the electrochemical treatment process. This situation increases the effective surface area of the ETPGE-LP/SH leading to high peak currents during the electrochemical reactions. The ETPGE-LP and ETPGE-SH also showed comparable surface morphologies (data not shown) to that of ETPGE-LP/SH. In can be inferred from the SEM analysis, the effective surface area was increased during all electrochemical treatment processes. The different electrochemical behavior of the prepared ETPGEs may arise from the discrete surface functionalities. Nagaoka and Yoshino (1986) reported that the formation of different oxygen containing groups (such as carbonyl, carboxyl, hydroxyl, etc) on the glassy carbon (GC) electrode surface during the electrochemical treatment process [30]. The amount of these functional groups depends on the electrochemical treatment conditions and electrode materials. The synergistic effect of the mixture of supporting electrolytes of NaOH and $LiClO_4$ may be attributed to the formation these functional groups on the electrode surface. The increase of the hydrophilic character of the electrodes after the electrochemical treatment indicates the entrance of oxygen into the electrode structure. The added oxygen can be found in the form of hydroxyl, carbonyl and carboxyl on the electrode surface [30]. Their relative amounts determine the selectivity of the prepared electrodes. The high ratio of carboxyl groups give a negative character to the electrode and this electrode repels negatively charged molecules and attracts positively charged molecules. The carbonyl and hydroxyl groups do not change so much the charge of the surface, but they affect the adsorption characteristics of the electrode. The behavior of the ETPGE-LP/SH during the characterization studies indicates that these functional groups may be phenol-like and quinone-like structures. These structures can interact with BPA and increase the adsorption characteristics since it contains two phenolic groups. The phenol-like and quinone-like structures also increased the electron transfer rate for ETPGE-LP/SH gaining an electro-catalytic property to the electrode. The main functional groups on ETPGE-LP can be found in the form of carboxyl which gives the negative character to the electrode surface. The ETPGE-SH showed almost identical behavior with PGE during the characterization studies. This suggests that the electrochemical treatment in NaOH medium does not change so much the surface functionality of the electrode surface. On the other hand, the mixture of these supporting electrolytes has a noticeable effect on the electrochemical behavior of ETPGE.

3.3 Optimization of Electrochemical Treatment Conditions for the Preparation of ETPGE-LP/SH

The effect of the electrochemical treatment potential interval on the voltammetric responses of the ETPGE-LP/SH was investigated for the electrodes prepared in the aqueous mixture of 0.10 M NaOH and 0.10 M $LiClO_4$ at different potential intervals. The voltammetric response of BPA increased gradually after increasing the potential upper limit up to 2.0 V and then a gradual decrease in the response was observed (Figure S1, Supporting Information). Therefore, the potential interval between -0.3 V and $+2.0$ V was determined as the optimal range and this range was applied in the rest of the study. These results were consistent with the literature values [27a].

The effect of the concentration of the supporting electrolytes of $LiClO_4$ and NaOH on the voltammetric response of the ETPGE-LP/SH was examined to determine the optimal concentration values. For this purpose, the ETPGE-LP/SH were prepared in different concentrations of $LiClO_4$ and NaOH solutions and their voltammetric responses were tested in BPA solution (Figure S2, Supporting Information). First, the effect of the variation of the concentration of NaOH solution was investigated in the constant concentration of 0.10 M $LiClO_4$. When the concentration of NaOH in the solution increased to 0.025 M, the voltammetric response of the ETPGE-LP/SH increased. The highest response value was achieved in the presence of 0.50 M NaOH and 0.10 M $LiClO_4$. Next, the effect of concentration of $LiClO_4$ solution on the voltammetric response of the ETPGE-LP/SH was studied in the same way as in the variation of NaOH concentration case. A sudden increase in the response of the ETPGE-LP/SH was observed in the mixture of 0.05 M $LiClO_4$ and 0.50 M NaOH, and a gradual increase in the response was observed when the concentration of $LiClO_4$ was 0.10 M. Beyond this value, variation in its concentration had no noticeable effect on the oxidation peak current values of BPA. It appears that 0.10 M is optimal supporting electrolyte concentration of $LiClO_4$ in the electrode response.

The ETPGE-LP/SH can be prepared either potential cycling between a pre-determined potential range or applying a constant potential for a definite time period. To evaluate the efficiencies of these two methods, the ETPGE-LP/SH were prepared by both potential sweeping between -0.3 V and $+2.0$ V and applying a constant potential of $+2.0$ V for 60 s in the mixture of 0.1 M $LiClO_4$ and 0.5 M NaOH. The performance of the prepared electrodes was tested in 1.0 μM BPA solution (Figure S3, Suporting Information). The ETPGE-LP/SH prepared in the former method showed almost ten times higher oxidation currents for BPA oxidation than ETPGE-LP/SH prepared in the latter method. Therefore, the former method was chosen as the electrochemical treatment method and used in the rest of the study.

3.4 pH Effect on the Electrochemical Behavior of BPA

The effect of pH on the voltammetric response of the ETPGE-LP/SH was investigated in 5.0 μM BPA solutions at different pH values. The oxidation potential and current values were plotted against the pH (Figure S4, Supporting Information). A linear relationship was observed for the oxidation potential values vs. pH in the studied pH range yielding a slope of -56.1 mV pH^{-1}. This value indicates that equal numbers of electrons and hydronium ions take place in the electrochemical oxidation mechanism of BPA. On the other hand, the oxidation current values of BPA first decreased with the increase in pH from 2.0 to 4.0, then increased gradually up to pH value of 8.5. The highest voltammetric response was achieved at pH 2.0 which was chosen and maintained as the pH of the medium in the rest of the study.

3.5 Optimization of the Accumulation Time of BPA on the ETPGE-LP/SH

The magnitude of the oxidation peak current of BPA increased with the increasing surface concentration of BPA on the ETPGE-LP/SH which is mainly dependent on the contact time of the ETPGE-LP/SH with BPA solution. As the accumulation time of BPA on the voltammetric response of the ETPGE-LP/SH prolonged, the current values increased gradually up to 120 s contact time (Figure S5, Supporting Information). Beyond 120 s the magnitudes of responses were almost the same, thus, the optimal contact time value was determined as 120 s.

3.6 Electrochemical Behavior of BPA

The electrochemical behaviors of the untreated PGE and ETPGE-LP/SH were examined by cyclic voltammetry measurements in the absence (Figure 5A and 5B) and presence of 25.0 μM BPA (Figure 5C and 5D) in PBS at pH 2. The untreated PGE and ETPGE-LP/SH showed no electrochemical activity in the absence of BPA in the studied potential interval. The background current values of the ETPGE-LP/SH (Figure 5B) were significantly higher than those of the untreated PGE (Figure 5A). This situation results from the high surface area of the ETPGE-LP/SH compared to that of the untreated PGE. In the presence of 25.0 μM BPA two oxidation peaks were observed in the forward scans of cyclic voltammograms obtained for both the untreated PGE (Figure 5C) and ETPGE-LP/SH (Figure 5D). The oxidation of BPA took place at the potentials of 0.774 V and 0.874 V for the untreated PGE. On the other hand, the oxidation of BPA was observed at the potentials of 0.744 V and 0.887 V for the ETPGE-LP/SH.

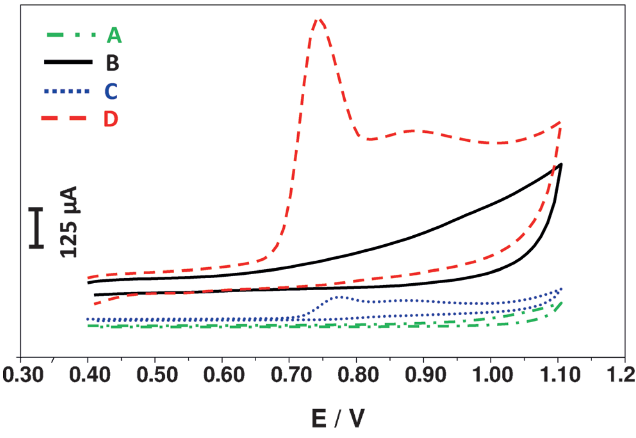

Fig. 5. The cyclic voltammograms of the untreated PGE (A and C) and ETPGE-LP/SH (B and D) in the absence (A and B) and in the presence of 25.0 μM BPA (C and D) in PBS (pH 2). Scan rate: 50 mV s^{-1}, Accumulation time: 120 s, Stirring rate: 250 rpm

In the reverse scans, there were no electroactivity for both electrodes. This finding indicates that the oxidation of BPA on both electrodes was irreversible. It can be easily inferred from Figure 5 that the ETPGE-LP/SH shows an electrocatalytic effect on the oxidation of BPA by decreasing the oxidation potential of BPA. Moreover, the oxidation peak current values increased tremendously in the case of the ETPGE-LP/SH. This situation may arise from the high surface area and mainly functionality of the ETPGE-LP/SH which are either lower or absent in the untreated PGE [27a].

3.7 Interference Studies

The effect of possible interfering molecules was performed by ASDPV measurements of 1.0 μM BPA in the absence and presence of interfering molecules. Sodium chloride, citric acid, sodium nitrate, sodium sulfate, and methanol are electroinactive molecules. It was observed that there was no electroactivity for these molecules and no change in the voltammetric response of 1.0 μM BPA in the presence of a thousand-time excess concentration (1000.0 μM) of these molecules. Other molecules such as phenol, 1–4-hydroquinone, p-benzoquinone, catechol, p-nitrophenol, o-nitrophenol and m-nitrophenol that investigated as possible interfering molecules are electroactive molecules. The oxidation of 1–4-hydroquinone, p-benzoquinone and catechol took place at potential values lower than +0.5 V which is the lower limit of the studied potential interval. The oxidation of nitrophenols isomers required potential values higher than +0.9 V which is the upper limit of studied potential interval. As a result, there were also no electroactivity in the studied potential interval of +0.5 V and +0.9 V. Peak currents of BPA (1.0 μM) were almost same in the presence of 100.0 μM concentrations of these molecules. The only molecule that showed electroactivity in the studied potential interval was phenol. The oxidation potential values of BPA and phenol were 0.722 V and 0.842 V, respectively. The potential discrimination between phenol and BPA is 0.12 V. As can be seen, this potential difference is enough to determine BPA in the presence of phenol. The tolerance level for phenol was also 100.0 µM. In the light of the presented results, it can be concluded that the prepared ETPGE-LP/SH has high selectivity for BPA oxidation.

3.8 Analytical Parameters

The relationship between the oxidation current values and BPA concentration was determined by performing ASDPV measurements in the presence of different amount of BPA in PBS at pH 2 (Figure S6, Supporting Information). Two linear regions were observed in the calibration plot. The first linear region which fits an equation of I (µA) $= 6.71\ C_{BPA}$ (µM) ($R^2 = 0.9972$) was observed in the concentration range between 0.05 µM and 5.0 µM of BPA. The second linear region fitting an equation of I (µA) $= 4.86\ C_{BPA}$ (µM) $+ 9.78$ ($R^2 = 0.9976$) was obtained in the concentration range of 5.0 µM and 10.0 µM of BPA. The reason why two linear regions present in the calibration plot is not known, but it may be due to the adsorption characteristics of BPA. The detection limit of the proposed method was calculated as 0.0031 µM using S/N ratio as 3. Table 1 gives the obtained analytical parameters in this study and those reported previously. The linear range and the detection limit values obtained with the ETPGE-LP/SH were comparable to those reported in the literature.

Table 1. Comparison of the proposed method with some of the previously reported ones. GC-F-C_{60}: glassy carbon fullerene-C_{60}, GC-MgAlCO_3-LDH: glassy carbon Mg-Al-CO_3-layered double hydroxide, Au-MWCNT-ISG: gold multiwalled carbon nanotube imprinted sol-gel, GC-MWCNT-MC: glassy carbon multiwalled carbon nanotubes/melamine complex, GC-N-GS-CS: glassy carbon N-doped graphene sheets (N-GS) and chitosan, GC-SWCNT-CD: glassy carbon single walled carbon nanotube and cyclodextrin, GC-AFNCGF: glassy carbon arginine functionalized graphene film, BDD: boron doped diamond, CP-MPS: carbon paste mesoporous silica.

Electrode	Linear range (µM)	Detection limit (µM)	Reference
GC-F-C_{60}	0.074–0.23	0.0037	[1]
GC-MgAlCO_3-LDH	0.01–1.05	0.005	[14]
Au-MWCNT-ISG	0.113–8210	0.0036	[15]
GC-MWCNT-MC	0.01–40.8	0.005	[16]
GC-N-GS-CS	0.01–1.3	0.005	[17]
GC-SWCNT-CD	0.0108–18.5	0.001	[18]
GC-AFNCGF	0.005–0.040	0.001	[19]
BDD	0.44–5.2	0.21	[20]
CP-MPS	0.22–8.8	0.038	[21]
ETPGE-LP/SH	0.05–5.0	0.0031	This study

Table 2. The BPA content and recovery percent values determined by the proposed method in tap water samples.

Sample	[BPA] (µM)			
	Initial	Added	Found	Recovery (%)
A	0.00	0.100	0.097	97.00
B	0.00	0.500	0.490	99.80
C	0.00	0.750	0.748	99.73
D	0.00	1.000	0.985	98.50

The fabrication reproducibility of ETPGE-LP/SH was tested by taking ASDPV measurements of 1.0 µM BPA in PBS (pH 2). A relative standard deviation (*RSD*) value of 2.76 % was observed for ten different ETPGE-LP/SH prepared in the same way.

3.9 Analytical Applications

The analytical applications of the ETPGE-LP/SH were tested in the determination of BPA in water samples. First, determinations of BPA in tap water samples from different sources were performed. The samples were analyzed for BPA using the ETPGE-LP/SH. The recovery values of BPA concentrations are shown in Table 2 and recovery percentages were very satisfactory yielding results in the range of 97.00 % and 99.80 %. Next, determination of BPA was investigated by the ETPGE-LP/SH in river water samples. River water samples were filtered before the measurements. 1.0 mL of the filtered river water sample was transferred into electrochemical cell and diluted ten times with PBS (pH 2). After that, the ASDPV measurements were performed (Figure 6). As can be seen, there was no voltammetric response in the case of bare sample. This indicates that there is no BPA

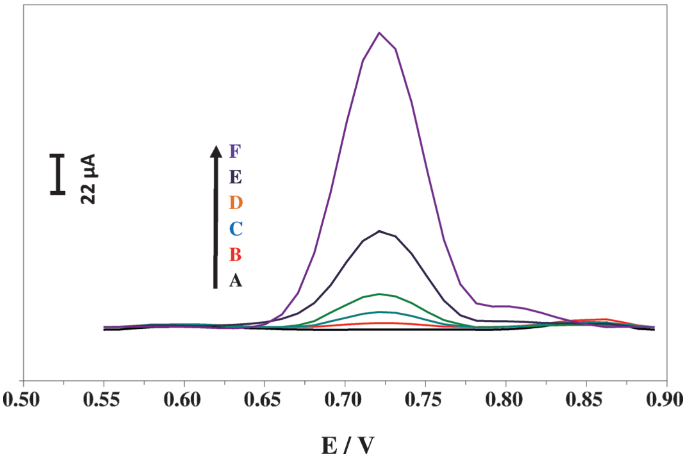

Fig. 6. The baseline-corrected ASDPVs of ten-times diluted a river water sample in the presence of 0.0 µM (A), 0.1 µM (B), 0.25 µM (C), 0.50 µM (D), 1.0 µM (E), and 2.5 µM (F) BPA. Accumulation time: 120 s, Stirring rate: 250 rpm. Dilution was made with PBS (pH 2).

in the original sample. When the concentration of BPA was increased gradually in the medium, the current values of BPA increased proportionally. This result indicates that the ETPGE-LP/SH is very promising in the determination of BPA in water samples.

4 Conclusions

The selectivity and sensitivity of the ETPGE-LP/SH depend on mainly the preparation conditions and the nature of the analyte molecules. The ETPGE-LP/SH prepared in the aqueous mixture of $LiClO_4$ and NaOH showed the highest voltammetric response for the oxidation of BPA. A voltammetric method was proposed for the determination of BPA in water samples based on the so prepared single-use ETPGE-LP/SH. This single-use electrode system brings an alternative way to overcome the electrode passivation resulting from the formation of dimers during the oxidation of BPA. It was observed that the potential interval and the concentrations of $LiClO_4$ and NaOH were also prominent effect on the voltammetric response of ETPGE-LP/SH. The optimization of the parameters that affect the voltammetric determination of BPA were optimized. The detection limit of the proposed method is lower than those of the most literature reports. The analytical application showed that the proposed method can be successfully applied in the determination of BPA in environmental water samples.

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References

[1] J. A. Rather, K. D. Wael, *Sens. Actuators B* **2013**, *176*, 110–117.
[2] A. Krishnan, P. Stathis, S. Permuth, L. Tokes, D. Feldman, *Endocrinology* **1993**, *132*, 2279–2286.
[3] P. Palanzaa, L. Gioiosaa, F. S. vom Saalb, S. Parmigiania, *Environ. Res.* **2008**, *108*, 150–157.
[4] J. Y. Youn, H. Y. Park, J. W. Lee, I. O. Jung, K. H. Choi, K. Kim, K. H. Cho, *Arch. Pharm. Res.* **2002**, *25*, 946–953.
[5] A. M. Soto, C. Sonnenschein, *Nat. Rev. Endocrinol.* **2010**, *6*, 363–370.
[6] S. H. Safe, *Environ. Health Perspect.* **2000**, *108*, 487–493
[7] R. T. Zoeller, R. Bansal, C. Parris, *Endocrinology* **2005**, *146*, 607–612.
[8] A. Goodson, W. Summerfield, I. Cooper, *Food Addit. Contam.* **2002**, *19*, 796–802.
[9] http://www.theglobeandmail.com/news/national/ canada-first-to-declarebisphenol-a-toxic/article1755272/
[10] A. Ballesteros-Gómez, S. Rubio, D. Pérez-Bendito, *J. Chromatogr. A* **2009**, *1216*, 449–469.
[11] G. Gatidou, N. S. Thomaidis, A. S. Stasinakis, T. D. Lekkas, *J. Chromatogr. A* **2007**, *1138*, 32–41.
[12] X. Wang, H. Zeng, L. Zhao, J. M. Lin, *Anal. Chim. Acta* **2006**, *556*, 313–318.
[13] J. J. Ou, L. H. Hu, L. G. Hu, X. Li, H. F. Zou, *Talanta* **2006**, *69*, 1001–1006.
[14] H. Yin, L. Cui, S. Ai, H. Fan, L. Zhu, *Electrochim. Acta* **2010**, *55*, 603–610.
[15] J. Huang, X. Zhang, Q. Lin, X. He, X. Xing, H. Huai, *Food Control* **2011**, *22*, 786–791.
[16] Y. Li, Y. Gao, Y. Cao, H. Li, *Sens. Actuators B* **2012**, *171–172*, 726–733.
[17] H. Fan, Y. Li, D. Wu, H. Ma, K. Mao, D. Fan, B. Du, H. Li, Q. Wei, *Anal. Chim. Acta* **2012**, *711*, 24–28.
[18] Y. Gao, Y. Cao, D. Yang, X. Luo, Y. Tang, H. Li, *J. Hazard. Mater.* **2012**, *199–200*, 111–118.
[19] Y. Zhang, L. Wang, D. Lu, X. Shi, C. Wang, X. Duan, *Electrochim. Acta* **2012**, *80*, 77–83.
[20] G. F. Pereira, L. S. Andrade, R. C. Rocha-Filho, N. Bocchi, S. R. Biaggio, *Electrochim. Acta* **2012**, *82*, 3–8.
[21] F. Wang, J. Yang, K. Wu, *Anal. Chim. Acta* **2009**, *638*, 23–28.
[22] S. Poorahong, C. Thammakhet, P. Thavarungkul, W. Limbut, A. Numnuam, P. Kanatharana, *Microchim. Acta* **2012**, *176,* 91–99.
[23] A. N. Kawde, M. C. Rodriguez, T. M. H. Lee, J. Wang, *Electrochem. Commun.* **2005**, 7, 537–541.
[24] Y. Dilgin, B. Kızılkaya, D. G. Dilgin, H. İ. Gokçel, L. Gorton, *Colloids Surf. B:* **2013**, *102*, 816–821.
[25] A. Özcan, Y. Şahin, M. Özsöz, S. Turan, *Electroanalysis* **2007**, *19*, 2208–2216.
[26] L. Özcan, Y. Şahin, H. Türk, *Biosens. Bioelectron.* **2008**, *24*, 512–517.
[27] a) A. Özcan, Y. Şahin, *Anal. Chim. Acta* **2011**, *685*, 9–14; b) A. Özcan, Y. Şahin, *Biosens. Bioelectron.*, **2012**, *31*, 26–31; c) A. Özcan, Y. Şahin, *Electroanalysis* **2009**, *21*, 2363–2370; d) A. Özcan, Y. Şahin, *Biosens. Bioelectron.* **2010**, *25*, 2497–2502.
[28] J. X. Qiao, H. Q. Luo, N. B. Li, *Colloids Surf. B* **2008**, *62*, 31–35.
[29] W. Geremedhin, M. Amare, S. Admasssie, *Electrochim. Acta* **2013**, *87*, 749–755.
[30] T. Nagaoka, T. Yoshino, *Anal. Chem.* **1986**, *58*, 1037–1042.

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