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RESEARCH ARTICLE

Electrochemical Determination of Bisphenol A Based on Poly(Chromotropic Acid) Modified Glassy Carbon Electrode

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Abstract: ***Background:*** A new modified electrode based on the poly(chromotropic acid) (4,5-dihydroxynaphthalene-2,7-disulfonic acid) film was developed by electrochemical polymerization to explore its voltammetric behavior. The electrochemical synthesis of poly(chromotropic acid) was accomplished by applying an aqueous solution of sodium hydroxide as a supporting electrolyte (0.1 M). The electrochemical behaviors of BPA on poly(chromotropic acid) modified glassy carbon electrode (poly(CTA)/GCE) were researched by cyclic voltammetry, square wave voltammetry, and chronoamperometry.

Methods: The analytical performances of the developed method were carefully examined. When the concentration of BPA changed from 0.1 μM to 20 μM, the current response of BPA was linearly related to the concentration over the range of 0.1–2 μM and 2.0–20 μM, respectively and the detection limit of the suggested method was found to be 0.06 μM. The feasibility of the detector was successfully demonstrated for BPA detection in various real samples.

Results: The suggested methodology was applied for the detection of BPA in different real samples (bottled water, tap water and honey sample). The samples were prepared as described above and these aforesaid samples were analyzed directly. Since no BPA was detected in these samples, standard addition method was employed. The percent recovery tests were also investigated by measuring the current responses to the samples in which the known concentrations of BPA standard solution were spiked. Thus, the spikes are subjected to similar matrix effects. The percent recoveries in the range of 94.0%–103% were obtained. These consequences indicated that the poly(CTA)/GCE has adequate electroanalytical efficiency and it can be a feasible sensor for detection of BPA in different samples.

Conclusion: A new voltammetric sensor for the detection of BPA was developed based on a very simple preparation scheme consisting in the direct electropolymerization of poly(CTA) films on GCE. The proposed poly(CTA)/GCE displays a helpful and easy method for observing of BPA in real aqueous samples exhibiting an adequate electroanalytical performance (linearity, detection limit, sensitivity, and selectivity) due to its stability and reproducibility associated with an effortless and speedy fabrication, and low cost. This new method could offer a charming approach for on-site detection of trace BPA contamination in aqueous samples.

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1. INTRODUCTION

Bisphenol A (2,2'-bis(4-hydroxyphenyl) propane, BPA) is used as a monomer in the formation of polycarbonate plastic (PC) for different applications [1]. This material has been widely used for food and beverage product containers because it is a clear, strong, and lightweight plastic. Nowadays, drinking bottled water packaged in plastic bottles. For this reason, BPA may be found in many daily use items such as plastic bottles, food, toys, metal food cans, cosmetics, and pesticides. BPA is a potentially harmful endocrine disruptor and it's possible adverse effects on human health [2, 3]. BPA, as xenoestrogen lipophilic compound, accumulates into adipose tissue. The subjects with higher BPA plasma values presented markers of low-grade inflammation, higher visceral adiposity and higher prevalence of MS and insulin resistance [4]. Consequently, it is indispensable to research a sensitive, rapid, and precise sensors able to monitor the BPA concentration in water and food samples.

Nowadays, diverse analytical procedures have been improved and employed for the detection of BPA, including gas and liquid chromatography–mass spectrometry (GC–MS, LC–MS), capillary electrophoresis, spectrophotometric, chemiluminescence detection, immunoassay detection and

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electrochemical sensor [5]. However, some of these methods are costly, poor sensitivity and largely require time-consuming complicated sample pretreatment. In the past, varied types of the electrochemical sensor with forward materials have been arranged to increase the open region of the electrode to enhance electrochemical currents. To improve the current intensity of BPA, varied types of nanomaterials or their hybrids have been implemented for surface alteration of bare electrode [5, 6]. In this setting, varied type sensors have been produced and employed for the detection of BPA [6-9]. At present, various sensors have been reported to monitor BPA such as molecularly imprinted polymer sensors [10-14], carbon-nanotube (CNT) based sensors [15-18], graphene-based sensors [19-23], quantum-dot-based sensors [24], metal composite based sensors [25-28], and nanocomposite-based sensors [29-33]. Another recent tendency for electrochemical estimation is the growth of disposable and miniature sensors. A disposable BPA sensor was constructed with commercial art paper as a working electrode. Art paper with convenient roughness was coated with gold nanoparticles by a simple physical vapor deposition (PVD) method and thereafter paper surface coated with multi-walled carbon nanotubes (MWCNTs) [34]. The non-returnable sensor indicated good resistance versus interferences and the suggested detector was implemented to estimate BPA extracted from real plastic samples. Eventually, an unmodified B-doped diamond electrode was employed for the estimation of BPA. As a consequence, the bare B-doped diamond electrode significantly reformed sensitivity the current intensity of target analyte [35]. Nowadays, a new and label-free electrochemical immune sensor for sensitive detection of bisphenol A using rutin as the redox probe was reported [36]. Another report showed the electrochemical determination of BPA with pencil graphite electrodes modified with Co(II), Ni(II), Cu(II) and Fe(II) phthalocyanine tetrasulfonate [37].

Conductive polymer based sensors are one class of chemically modified electrodes, wherein polymer films are used to improve electrocatalytic properties, the sensibility, the constancy and the reproducibility of electrodes [38,39]. Among the different approaches available to deposit the polymer film on the electrode surface, electropolymerization has been set up to be the most convenient. Electropolymerization of monomer offers the advantages of simplicity, uniform and controlled film thickness and deposition can be set as needed by changing electrochemical parameters [40,41]. Recently, Mazzotta *et al.* [42] synthesized a conductive polymer (poly(3,4-ethylenedioxythiophene) to modify GCEs (PEDOT/GCE) by an electropolymerization process for the estimation of BPA using cyclic voltammetry.

Chromotropic acid is an important dihydroxy naphthalene derivative. Although it is a well-known complexing agent, its polymeric feature is still not reported [43]. However,, no study of the electrochemical behavior of CTA in aqueous solution has ever been described thus far. The current work focuses on the voltammetric detection of BPA on a GCE modified by an electropolymerized poly(CTA) film. Importantly, the preferred method is very simple, consisting of a one-step preparation requiring only a short time for film formation. Likewise, we choose CTA reagent as the surface modifier because it is inexpensive and commercially available. The poly (CTA) is a conjugated conducting polymer that can be readily made by electrochemical polymerization producing steady films on the bare electrode surface. The electropolymerization of CTA has not been described beforehand, and no voltammetric research of the poly(CTA) was reported in the literature by the researchers. The practice of the suggested sensor in terms of sensitivity, selectivity, concentration range, and the detection limit was itemized. Finally, the voltammetric estimation of BPA and feasibility to real drinking water and honey samples are also reported.

2. EXPERIMENTAL

2.1. Reagents and Instruments

Electrochemical essays were realized in a 10-mL glass voltammetric cell at room temperature. The stock solutions of BPA (obtained from Merck) and CTA (purchased from Sigma-Aldrich) (1.0×10^{-3} M) were prepared with ethanol and kept in darkness at 4°C.

Buffer solutions with different pH values were prepared by mixing the solutions of 0.1 M CH_3-COOH/0.1 CH_3-COONa (pH=3.6-6.0) (AcB), 0.1 M CH_3-$COONH_4$ (pH=7) (NH_4AcB), and 0.1 M NH_3/0.1 M NH_4Cl (pH=8-10) (AmB). Solutions were prepared using distilled water, except where indicated differently. Voltammetric essays were performed on Gamry Reference 600 potentiostat system (Gamry, USA) with a three-electrode configuration which occurred off the poly (CTA) film modified GCE as working electrode, a platinum wire auxiliary electrode, and an Ag/AgCl wire reference electrode. The voltammetric measurements were performed in a 0.1 M AcB solution. All chemicals used were of analytical grade and employed as received.

2.2. Preparation of Real Samples

Honey sample (1.0 g) was mixed with 100 mL AcB solution (pH= 5), and the solution was stirred vigorously at room temperature for 5 minutes. After 5 min stirring, resulted from colorless homogeneous solution. All the honey samples were placed in the dark at 4 °C. A percentage of the resulting solution (1.0 mL) was then brought out and serviced as the sample for the detection of BPA using SWV.

Tap water samples were collected from our own laboratory. The bottled drinking water samples were bought from the local store, including three different brands. The real water samples were directly assayed or stored at 4 °C for use. An 8-ml aliquot of these samples was analyzed. The pH of samples was adjusted with AcB (pH 5) and final solution (10 ml) was subjected to the voltammetric procedure.

2.3. Preparation of the Modified Electrodes

Cyclic voltammetry was employed to form an electropolymerized film. Before beginning each experiment, the unmodified GCE surface was polished to a mirror finished on chemical, mechanical polishing pads with alumina suspensions and the electrode cleaned thoroughly with ethanol and distilled water and dried at ambient temperature. The poly(CTA) film-coated electrodes were generated by a potential scan rate of 50 mV s^{-1} in the potential range of -0.5 to 1.2 V (vs. Ag/AgCl) in 0.1 M NaOH containing 0.1 mM CTA. Unless otherwise specified, the poly(CTA) coated

electrodes with cyclic scans of 25 times were realized. After polymerization, the obtained poly (CTA) /GCE was rinsed carefully with distilled water and the prepared modified electrode was used for electrochemical detection of BPA.

The poly(CTA)/GCE was placed in 0.1 M AcB solution (pH = 5) containing the desired concentration of BPS for 5 min at open circuit potential. Next, the SWV evaluation was realized with the scanning range from –1.0 V to 1.2 V. The optimized values of the SWV parameters that were employed in the remaining studies are: frequency 40 Hz, step size 10 mV, and pulse size 100 mV.

3. RESULTS AND DISCUSSION

3.1. Preparation of Poly (CTA) Modified Glassy Carbon Electrode

The surface accumulation layer of the electroactive moieties within the poly (CTA) films could be controlled by appropriately selecting the routine of the cyclic scans. The bare electrode was subsequently immersed in a solution containing 0.1 M NaOH and 0.1 mM CTA and the cyclic potential sweep were applied in the range of -1.0 to +1.2 V at a scan rate of 50 mV s^{-1} for 25 times. After 25 cycles, it was observed that the peak currents started to decrease; this was owing to the active electrode surface area which does not replace significantly after 25 cycles and the polymer thickness increases, which obstructs the electron transfer rate. After polymerization, the poly (CTA) modified GCE was treated with distilled water to eliminate the physically adsorbed CTA and then it was allowed to dry at 25^0C for 5 min and the resultant electrode was used as working electrode. Fig. (**1**) displays cyclic voltammograms of CTA in 0.1 M NaOH solution containing 0.1 mM CTA with a scan rate of 150 mV s^{-1} for 25 cycles. CTA has the two hydroxyl and two sulfonate groups. A pair of oxidation (occurred around -0.248 V) and reduction (occurred around -0.414 V) peak currents was obtained in each round. Additionally, a second irreversible cathodic peak, at approximately + 0.342 V (vs. Ag/AgCl), was appeared. As can be seen in Fig. (**1**), the intensity of the three peaks increased gradually with cyclic time increasing and remained static for more than 25 rounds. The latter observation indicates the growth of CTA film on GCE due to electropolymerization. The fashion of electropolymerization of CTA is similar to the oxidation coupling polymerization of naphthol. The oxidative *phenol coupling reaction* involves mainly C-O coupling, whereas that of naphthol or derivatives involves C-C coupling [44]. Grounded along the above results, the plausible polymerization mechanism of the CTA was proffered as shown in Fig. (**2**).

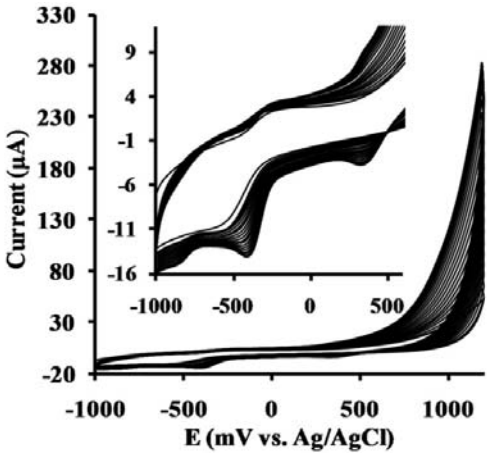

Fig. (1). Cyclic voltammograms (between –1.0 and +1.2 V) for electropolymerization of chromotropic acid on GCE (diameter: 3 mm) in 0.1 M NaOH solution (pH 13) containing 0.1 chromotropic acid. Potential scan rate: 150 mV s^{-1}. Inset: Cyclic voltammograms of BAP between -1.0 and +0.6 V.

3.2. Characterization of Poly(CTA)/GCE

Electrochemical and morphological characterization of the bare GCE and poly(CTA)/GCE was assessed by cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), scanning electron microscopy (SEM) and FTIR.

Cyclic voltammetry can ensure interface knowledge of the electrode surface during the alteration process. The electrochemical behaviors of 0.1 mM $(Fe(CN)_6)^{3-/4-}$ containing 0.1 M KCl at diverse electrodes were examined at a potential scan rate of 50 mV s^{-1}. As indicated schematically in Fig. (**3A**), on the bare GCE (curve a), the cathodic and anodic peak potential separation (ΔEp) was 0.707 V with poor redox peak currents. On the poly(CTA) film coated electrode (curve b), a pair of redox peaks obtained and the redox peak currents increased clearly. As a result, the ΔEp apparently decreased to 0.083 V, which was due to the grand surface area and perfect electrical conductivity of poly (CTA) existing on the electrode surface.

EIS is a robust tool to explore the surface properties of electrode substrates. The Nyquist diagrams for $(Fe(CN)_6)^{3-/4-}$ (5.0 mM) at GCE and poly(CTA) are shown in Fig. (**3B**). The frequency range selected in the experimental studies was from 0.1 Hz to 0.1 MHz. As can be seen from the Fig. (**3B**), the characteristic semicircles were observed and the semicircle diameter decreases in going from GCE to poly(CTA). The charge transfer resistance (R_{ct}) values are 371 Ω and 48 Ω for bare GCE and poly(CTA)/GCE, respectively. The R_{ct}

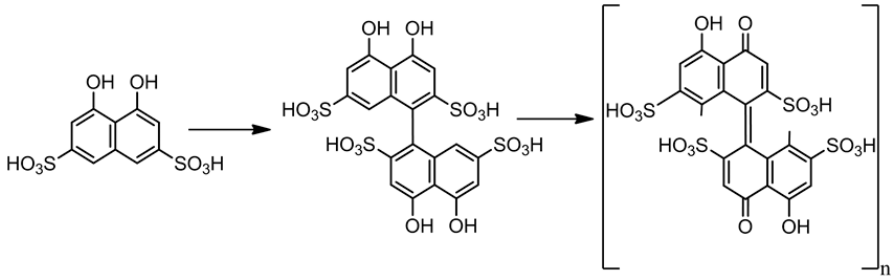

Fig. (2). Plausible electrochemical polimerization mechanism of CTA.

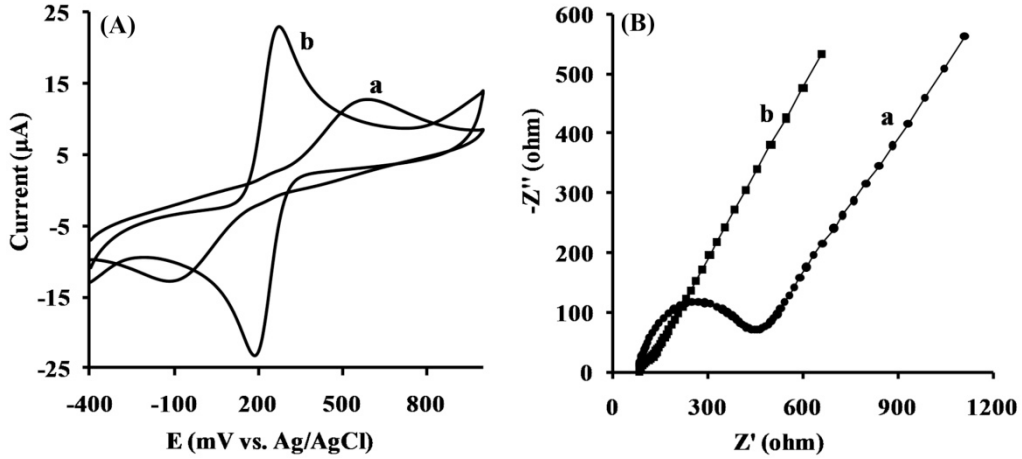

Fig. (3). (**A**) CVs of (**a**) bare GCE, and (**b**) poly(CTA)/GCE in 0.1 M phosphate buffer containing 0.1 mM $(Fe(CN)_6)^{3-/4-}$ and 0.1 M KCl solution in the potential range of -0.4 to 0.9 V. Scan rate: 50 mV s^{-1}. (**B**). Nyquist plots of the different electrodes in a 5.0 mM $(Fe(CN)_6)^{3-/4-}$ containing 0.1 M KCl solution. The frequency range was from 0.1 Hz to 0.1 MHz with perturbation amplitude of 5 mV. (**a**) Blank GC electrode and (**b**) poly(CTA) film GC electrode.

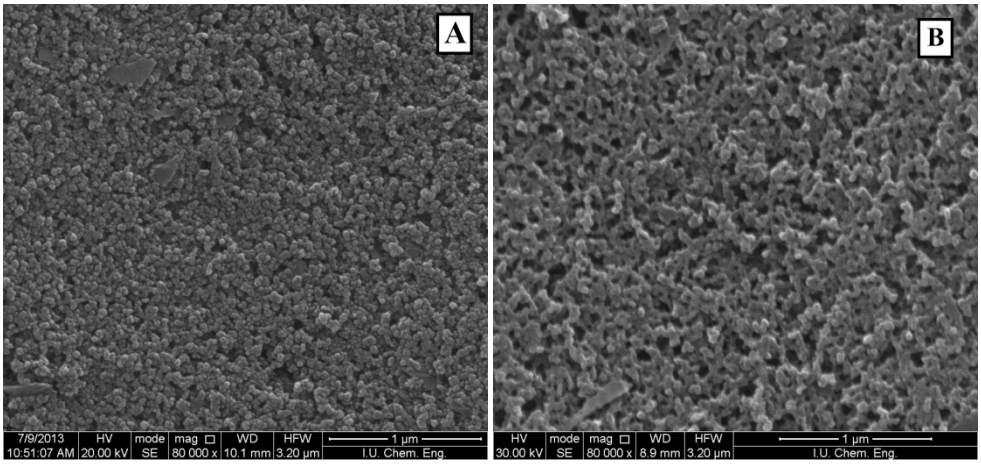

Fig. (4). SEM images of bare SPCE (**A**) and poly(CTA) modified SPCE (**B**).

value of poly(CTA) modified electrode was nearly 8 times higher than that of unmodified GCE. Based on EIS results, the electron transfer resistance decreased when GCE surface was altered with poly(CTA) film, which facilitated the charge transfer reaction of $(Fe(CN)_6)^{3-/4-}$ reaction. These outcomes further indicated that poly(CTA) was successfully deposited onto the GCE surface.

Figure **4B** shows the SEM image of the poly (CTA) film on the screen-printed carbon electrode (SPCE). As shown in Fig. (**4B**), the poly(CTA) film (after 25 cycles) has a nearly porous structure and roughness. These images show mostly rod-like or papilla structures of various lengths and this structure provide easy access and quicker transport of species at the electrode/electrolyte interface, which is an important feature for the faradaic charge-transfer reactions. The high specific surface area of poly(CTA) will boost the electrochemical performance of GCE.

Figure **5a** represents the ATR-FTIR spectrum of pure CTA where a sharp band at 3415 cm^{-1} was recorded which could be attributed to the *ν*(OH) stretching vibration of the free OH of CTA. A spitted band at 3120, 2728 and 2184 cm^{-1} was observed and attributed to *ν*(OHO) hydrogen bond of CTA. Figure **5b** represents the FTIR spectrum of poly(CTA) where a sharp band at 3423 cm^{-1} was observed corresponding to free OH stretching vibration.

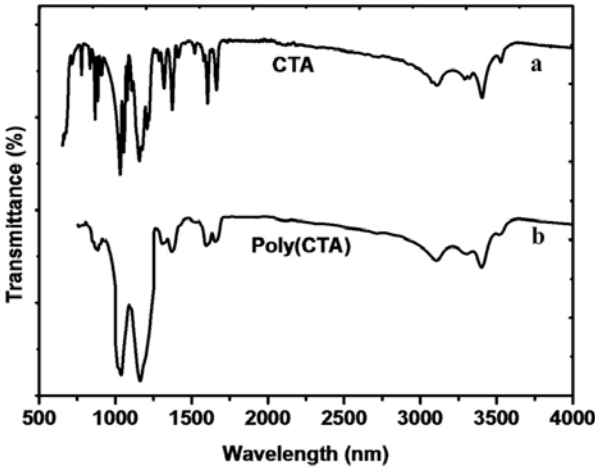

Fig. (5). ATR-FTIR spectra of CTA (**a**) and poly(CTA) (**b**).

3.3. Electrochemical Behavior of BPA at Poly(CTA)/GCE

The voltammetric characteristic of BPA at poly(CTA)/ GCE was also studied by CV. Figure **6** indicates the cyclic voltammograms (CVs) obtained for 0.1 mM BPA at bare GCE (curve a) and poly(CTA) (curve b) coated electrode in 0.1 M AcB solution (pH 5.0). As indicated, the poor electroactivity of BPA led to weak and negligible current peaks at bare GCE (curve a). By contrast, the poly(CTA) film coated electrode increased the voltammetric signals of BPA (curve b). Notably, the poly(CTA) functionalized GCE exhibited the highest oxidation responses with the most negatively shifted potentials with respect to the unmodified electrode. As a consequence, it is illustrated that the poly(CTA) film coated electrode possesses the most distinguished electrocatalytic capacity toward target analyte.

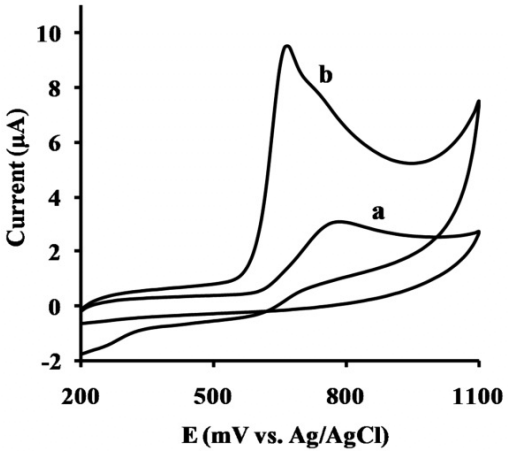

Fig. (6). CV curves of 0.1 mM BPA at the (**a**) bare GCE, (**b**) poly(CTA)/GCE in 0.1 M acetate buffer (pH 5) at a scan rate 50 mV s^{-1}.

3.4. Effect of Scan Rate

The dependence of scan rate was realized by recording cyclic voltammograms in the potential range 0.2 to 1.1 V s^{-1} for the poly(CTA) coated electrode immersed in AcB (pH 5.0) solution loaded with 0.1 mM BPA. The oxidation response to BPA increases while increasing the scan rates. When the scan rates of BPA were increased from 10 to 500 mV s^{-1}, the oxidation responses of BPA were increased linearly with the correlation coefficient of 0.9969. The equation is described as I(μA) = 0.0747 *v* (mV s^{-1}) + 2.9511, and this result indicates that the oxidation process is controlled by the adsorption of BPA (Fig. **7**).

3.5. Effect of pH

The influence of pH on the current responses of BPA in 0.1 M buffer solution in the pH range from 3.6 to 10 (AcB, NH_4AcB), and AmB) at the functionalized electrode was examined (Fig. **8**). The outcomes exhibited that the oxidation potentials of BPA changed toward a negative direction with the change of buffer pH. The consequences demonstrated that the protons took part in the electrode reaction. Moreover, the oxidation response of BPA increases until the pH value reaches 5.0 and then decreased slightly and remained almost constant in the pH range of 6.0–9.0. According to the

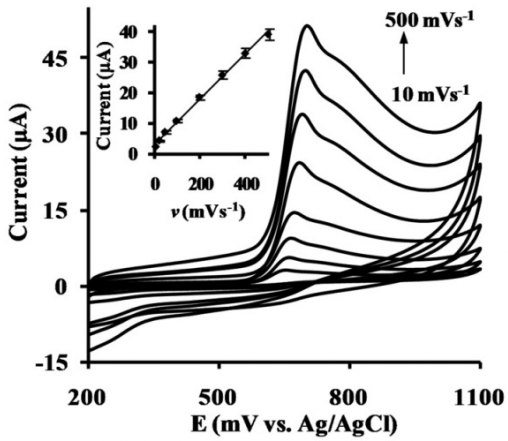

Fig. (7). CV curves of 0.1 mM BPA at poly(CTA)/GCE in 0.1 M acetate buffer solution with scan rate ranging from 10, 25, 50, 100, 200, 300, 400, and 500 mV s^{-1}.

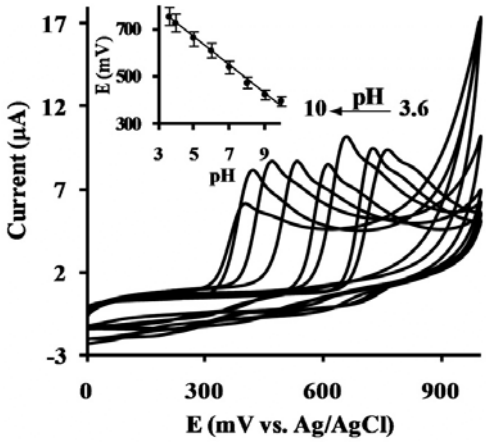

Fig. (8). Cyclic voltammograms of poly(CTA)/GCE to 0.1 mM BPA in 0.1 M (AcB, NH_4AcB, and AmB) different pH: 3.6, 4.0, 5.0, 6.0, 7.0, 8.0, 9.0, and 10. Insets: Effects of pH on the peak current. Scan rate: 50 mV s^{-1}.

result, the pH 5.0 was chosen as the ideal pH for further studies. In addition, the pH of the analyte solution was lower or higher than the value (pH 5), the oxidation response of BPA decreased. Moreover, the oxidation response decreased sharply when the pH value of analyte solution was above 9.0. In this context, the functionalized electrode surface had a more negative charge when pH was higher than 9.0 (For BPA; pKa_1 =9.6 and pKa_2 =10.2) [38]. The negative charge on the poly(CTA) functionalized electrode surface was increased with increasing pH, so more BPA molecules were fascinated to the functionalized electrode surface. Furthermore, in the pH range from 5.0 to 9.0, the hydrophobic interaction between the poly(CTA) film (the pKa_1 and pKa_2 of CTA are 5.3 and 15.6, respectively [34]) and BPA molecules was the major factor. As can be observed in Fig. (**8**) (inset), the slope value of the Ep/pH plots was found to be approximate -58 mV/pH for BPA. This date indicated that an equal number of protons and electrons (two protons and two electrons) were concerned in the electrochemical oxidation processes of BPA based on the Nernst Equation. The probable electrode reaction is shown in Fig. (**9**).

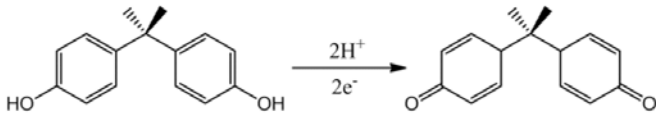

Fig. (9). Oxidation reaction of bisphenol-A on electrode surface during electrochemical sensing.

3.6. Chronoamperometric Measurements

The chronoamperometry was used along with other electrochemical methods for the examination of electrode processes at chemically altered electrodes. This is a single potential step experiment. Figure **10A** shows single potential step chronoamperograms of poly(CTA)/GCE in 0.1M AcB solution in the absence (curve a) and presence (curves b–f) of BPA. The analysis of chronoamperometry data is based on the Cottrell equation:

$$I = nFAC^{\circ}D^{1/2}\pi^{-1/2}t^{-1/2}$$

where n = stoichiometric number of electrons involved in the reaction; F = Faraday's constant, A = electrode area (cm^2), C^0 = concentration (M), and D^0 = diffusion constant (cm^2/s). As can be observed in Fig. (**10B**), the experimental plots (I *vs* $t^{-1/2}$) were arranged for different concentrations of BPA. After that, the slopes of the resulting straight lines were then plotted versus the BPA concentration. According to this equation, the diffusion constant of BPA was found to be approximately 7.0×10^{-6} cm^2 s^{-1}.

Additionally, the catalytic rate constant (k_{cat}) was investigated by chronoamperometry and the catalytic rate constant was calculated using the following equation [42]:

$$I_{cat}/I_L = \pi^{1/2}(k_{cat}C_0t)^{1/2},$$

where I_{cat}= the current response in the presence of the analyte, I_L= the current response in the absence of the analyte, k_{cat}= catalytic rate constant (M^{-1} s^{-1}), C_0= bulk concentration (M) of the analyte, t= elapsed time (s). Based on the slope of the I_{cat}/I_L versus $t^{1/2}$ plot (Fig. **10C**.), the average value of k_{cat} for the electrooxidation of BPA was calculated to be approximately 2.84×10^4 M^{-1} s^{-1} when the BPA concentration was 2.0×10^{-4} M. The result implies that the poly(CTA)/GCE can be efficiently used as the voltammetric sensor for BPA detection.

3.7. Analytical Parameters

The effects of various SWV parameters were optimized in order to achieve a good analytical response, using 10 µM BPA in 0.1 M AcB. Thus, all SWV experiments in this work were performed using a frequency 40 Hz, step size 10 mV, and pulse size 100 mV.

The calibration curve of the BPA sensor was derived from the SWVs obtained on the poly(CTA)/GCE in 0.1 M AcB (pH 5.0) under the optimum conditions. As can be illustrated in Fig. (**11A**), the current response increases linearly with the increase of the BPA concentration. According to the

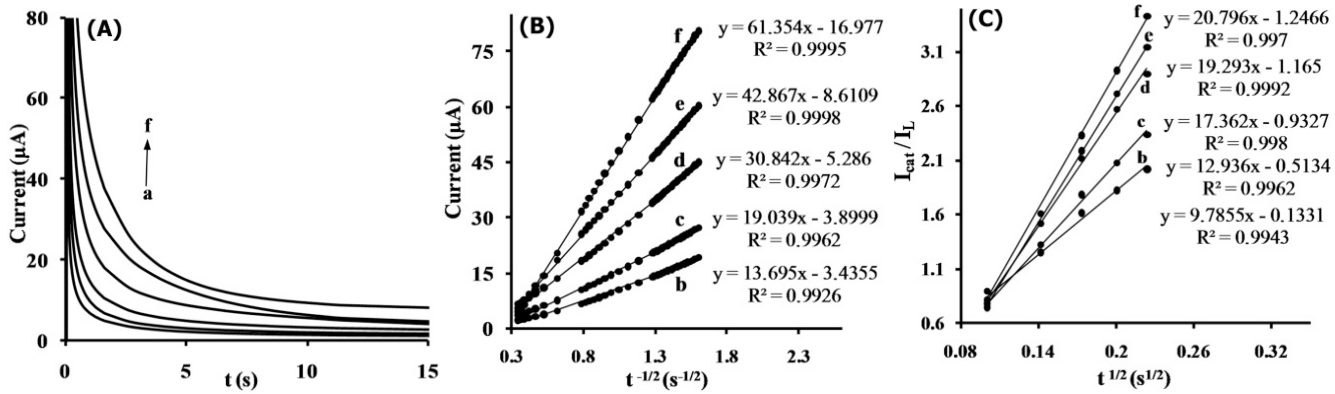

Fig. (10). (**A**). Chronoamperograms of poly(CTA)/GCE in AcB (pH 5.0) in the presence of: (a) 0.0; (b) 0.1; (c) 0.2; (d) 0.5; (e) 1.0; (f) 1.5 mM of BPA. (**B**) shows current response (b-f) versus $t^{1/2}$. (**C**) shows dependence (b-f) of I_{cat}/I_L on the $t^{1/2}$ derived from the chronoamperogram data.

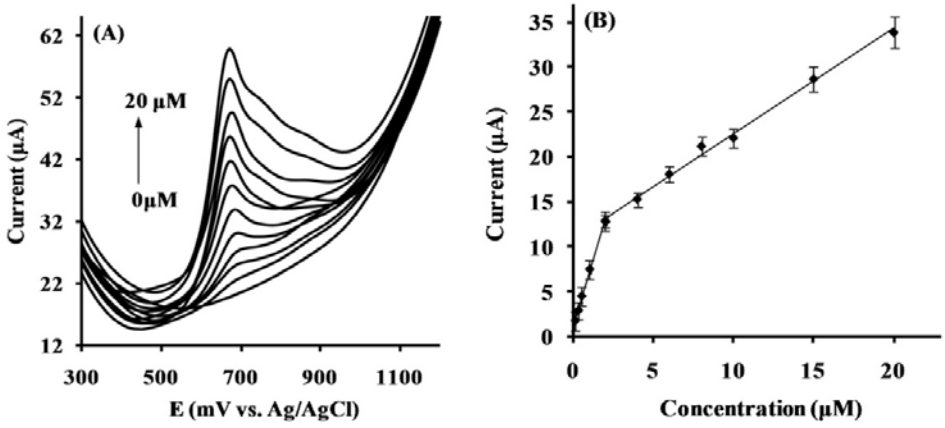

Fig. (11). (**A**). SWVs at the poly(CTA) coated electrode for different BPA concentrations in 0.1 M AcB: 0, 0.1, 0.3, 0.5, 1, 2, 4, 6, 8, 10, 15, and 20 µM BPA. (**B**) shows the corresponding analytical curve (peak currents versus BPA concentrations).

Table 1. Features of various sensors developed for the analysis of BPA.

Electrode	Linear Range (μM)	Detection limit (μM)	Reference
2-Aminothiophenol /GNPs	8 –2000	0.138	[10]
E-MIP	0–12000	420	[11]
BPA imprinted polymer	0.1–1	0.02	[12]
Chitosan/acetylene black paste electrode	0.008–1	0.006	[13]
TiO_2 nanotubes/polypyrrole	0.0045–0.108	0.002	[14]
MWCNT-GNPs/GCE	0.08–20	0.001	[15]
SWCNTs/b-cyclodextrin	0.0054–0.03	0.001	[16]
Carboxylated MWCNTs	0.01–0.104	0.005	[17]
MWCNTs	0.05–20	0.02	[18]
Graphene – Potassium ferricyanide	0.05–1	0.005	[19]
Exfoliated graphene electrode	1.56–50	0.76	[20]
Nitrogen-doped graphene /chitosan	0.01–1.3	0.005	[21]
Graphene-CNTs nanocomposite	0.06–10	0.0042	[22]
Graphene nanofibers/AuNPs	0.08–250	0.0035	[23]
CoTe QDs/PAMAM dendrimer	0.0013–9.89	0.001	[24]
Cobalt phthalocyanine	0.00875–12.5	0.001	[25]
Mesoporous silica MCM-41	0.22–8.8	0.0038	[26]
Mg–Al layered double hydroxide (LDH)	0.01–1.05	0.005	[27]
Amorphous hydroxy iron/β-cyclodextrin (BCD)	0.1–50	NR	[28]
PAMAM–Fe_3O_4	0.01–3.07	0.005	[29]
Chitosan–Fe3O4	0.05–30	0.008	[30]
MWCNTs-GNPs	0.113–8200	0.0036	[31]
PAMAM-AuNPs-SF	0.001–1.3	0.0005	[32]
MNPs/Reduced Graphene oxide	0.06–11	0.017	[33]
Disposable paper-basedsensor	0.877–87.7	0.13	[34]
Boron doped diamond electrode	0.44–5.2	0.21	[35]
PEDOT/GCE	40–410	22	[40]
Poly(CTA)	0.1–20	0.01	This work

obtained results, the calibration curve exhibited two linear ranges (Fig. **11B**). The first part is in the range of 0.1 to 2 μM of BPA by a calibration equation of I (μA) = 5.854 C + 1.324 (R^2 = 0.9966) and the coefficient of determination of R^2=0.9966 and the second part contains the range of 2 to 20 μM by a calibration equation of I (μA)= 1.1703 C (μM) + 10.843 and the coefficient of determination of R^2= 0.9946 and the detection limit (S/N = 3) was estimated to be 0.06 μM.

3.8. Comparison with Other Works

In order to show the newness and advantage of our work, the response characteristics of the poly(CTA)/GCE were compared with other sensors in beforehand published works. To date, conducting polymer based sensor has been rarely reported for the determination of BPA by electrochemical methods. A voltammetric sensor for the determination of BPA was developed at a GCE modified with a conductive polymer PEDOT [42]. The electroanalytical platform allows a sensitive determination of BPA in the range of 40–410 μM with a detection limit of 22 μM. The poly (CTA) functionalized GCE has the excellent sensitivity (linear range: 0.1–20 μM and limit of detection: 0.06 μM). All the other electrodes reported in the literature are modified ones, some by very complex methods. Most of the materials that modified the electrode were carbon materials and nanocomposite. Apparently, the suggested procedure is cheaper when compared to other electrochemical sensors involving expensive modifiers (graphene, CNTs, nanocomposite, quantum-dot, metal composite) [10-35] (Table **1**). Moreover, this suggested method shows a considerable progress in simplifying electrode preparation, saving analysis time, and lowing cost.

3.9. Reproducibility, Repeatability, and Stability

SWV experiments were realized using the poly(CTA)/GCE at the same experimental conditions. To appraise the reproducibility of the recommended method, the relative standard deviation (RSD) of five times parallel measurements of 5.0 μM BPA at the poly(CTA)/GCE was found to be ± 3.9 %, which indicated the good reproducibility of the

method. Moreover, under the same preparing conditions, for five different poly(CTA)/GCEs, the relative standard deviation (RSD) of the current response to 5 μM was 4.2%, revealing good fabrication reproducibility. The long-term stability of poly(CTA)/GCE was also examined. Before each examination, the poly(CTA)/GCE was preserved at 4°C in a refrigerator for 7 days. The response of BPA did not change for seven days, and the RSD was calculated to be 2.95% for five times parallel estimation of 5.0 μM BPA. As a result, the poly(CTA)/GCE has an elevated stability.

3.10. Specificity

The specificity of this poly(CTA) sensor was further studied by detecting bisphenol B (BPB), bisphenol S (BPS), bisphenol AF (6F-BPA) and bisphenol valeric acid (BVA) at the same concentration of BPA, respectively. In fact, BPA and BPB have very similar molecular structures. Thus, the oxidation peak current for BPA is seriously overlapped by the oxidation peak of BPB. It was found that these compounds (BPS, 6F-BPA, and BVA) did not interfere with the results of the proposed methods. As a result, the method is specific because the aforesaid molecules (*i.e.* a structure analog of BPA) do not interfere with BPA determination.

3.11. Selectivity

The selectivity properties of the poly(CTA)/GCE for BPA detection was essayed by adding various invasive species into AcB (pH 5.0) containing 5 μM BPA. As a consequence, 100-fold Al^{3+}, Cu^{2+}, Fe^{3+}, Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, SO_4^{2-}, PO_4^{3-} Cl^{-}, NO_3^{-}, 100-fold Bisphenol S, 50-fold glucose and 10 fold of catechol, hydroquinone, and phenol did not impress the detection of BPA (< 5% of current change). These consequences demonstrated the good selectivity of the fabricated electrochemical detector.

3.12. Stability of BPA

The thermal stability of BPA was determined by measuring the concentration of BPA (10 μM) in the solution samples. Firstly, the stability of the sample solution was established by storage of the sample solution in refrigerator (4°C) for 10 days. The outcomes from the solution stability experiments confirmed that the sample solution was stable for up to 10 days at the refrigerator and during assay determination. The peak current value of BPA has not changed significantly. The solution of BPA was kept at room temperature for 24 h and the current response showed a 4.8 % decrease compared to the original value. It has been observed that BPA in water was degraded progressively. On the other hand, the aqueous solution is gently warmed to about 50°C for 1 h, the current response was not received. It is thought that BPA is degraded to BPA-quinone, probably via catechol followed by the formation of semiquinone [45,46]. As a consequence, the compound was very unstable at high temperature and in aqueous solution. It can be found that the thermal stability of BPA decreased as the reaction temperature increased, and the degradation rate was accelerated. Briefly, BPA is unstable in solution when exposed to direct daylight and more so when kept at high room temperature. BPA is expected to be rapidly degraded in aquatic and other environments. These notices are in concord with the report from the European Union [47]. As an average, the half-life for BPA in water and soil would be expected to be very short (1-5 days).

3.13. Applications

The suggested methodology was applied for the detection of BPA in different real samples (bottled water, tap water, and honey sample). The samples were prepared as described above and these aforesaid samples were analyzed directly. Since no BPA was detected in these samples, standard addition method was employed. The percent recovery tests were also investigated by measuring the current responses to the samples in which the known concentrations of BPA standard solution were spiked. Thus, the spikes are subjected to similar matrix effects. As illustrated in Table **2**, the percent recoveries in the range of 94.0%–103% were obtained. These consequences indicated that the poly(CTA)/GCE has adequate electroanalytical efficiency and it can be a feasible sensor for detection of BPA in different samples.

Table 2. Recovery study of BPA in bottled water, tap water, and honey sample (n = 3).

Sample	Spiked (μM)	Found (μM)	Recovery (%)
Bottled water	–	< LOD	–
	1	1.02±0.4	102
	2	2.03±0.7	101
	4	4.15±0.5	103
Tap water	–	< LOD	–
	5	4.7±1.4	94
	10	9.6±2.2	96
	15	14.3±1.2	95
Honey	–	< LOD	–
	1	96±0.2	96
	2	1.95±0.8	98
	3	2.85±0.4	95

4. CONCLUSION

A new voltammetric sensor for detection of BPA was developed based on a very simple preparation scheme consisting in the direct electropolymerization of poly(CTA) films on GCE. The proposed poly(CTA)/GCE displays a helpful and easy method for observing of BPA in real aqueous samples exhibiting an adequate electroanalytical performance (linearity, detection limit, sensitivity, and selectivity) due to its stability and reproducibility associated with an effortless and speedy fabrication, and low cost. This new method could offer a charming approach for on-site detection of trace BPA contamination in aqueous samples.

CONFLICT OF INTEREST

Asiye Aslıhan Avan declares no conflict of interest.

Ethical Approval: This article does not contain any studies with human participants or animals performed by any of the authors.

Informed Consent: Human and/or animal were not used in this work.

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