

A Simple and Sensitive Non Modified Acetylene Black-Polyurethane Composite Electrode in the Determination of Bisphenol-A in Water Samples

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A new composite based on acetylene black (AB) and vegetable derivative polyurethane (PU) was prepared and evaluated in the determination of bisphenol A (BPA) in water samples using a differential pulse voltammetric procedure (DPV). DPV pulse amplitude of 50 mV, 10 mV s⁻¹ scan rate and 0.10 mol L⁻¹ phosphate buffer were selected for the analytical studies. An analytical curve was obtained with linear range of 0.1-10 μmol L⁻¹ BPA and a limit of detection of 14.1 nmol L⁻¹. The proposed electrode was used without modifiers and with high sensitivity and low-cost preparation in the determination of BPA in both tap and artesian well waters spiked with 0.30 μmol L⁻¹, with relative errors of 0.81 and 1.0% and recoveries of 102 and 105%, respectively. Interferences from oxytetracycline, furosemide, catechol, methyl viologen chloride and fenitrothion could be overcome by appropriate current measuring, while diclofenac did not interfere.

Keywords: composite electrode, bisphenol-A, voltammetric determination, endocrine disruptor

Introduction

Composites based on carbon materials agglutinated by polymers offer low-cost alternatives for electrode materials, once they are robust and easy to assemble at the same time that they present increased sensitivity, large surface area, and easiness of surface renovation associated with the possibility of incorporating modifiers to improve selectivity and sensitivity. They can also be prepared in several forms, including imprinting and 3D technologies.^{1,2}

Since the earlier 2000, our group has been working on the development of composite electrodes based on graphite agglutinated by polyurethane (PU),³ silicone rubber⁴ and epoxy resin⁵ both as bare electrodes as well as modified ones that had been applied in the determination of several analytes.¹

Recently, we proposed a new composite electrode material based on acetylene black (AB) as a conducting phase agglutinated by a castor oil derivative PU.⁶ In addition to the advantages described above, the PU binder derived from castor oil presents a quickly curing at room temperature, is highly hydrophobic what prevents swelling in aqueous media, and is provenient from a renewable resource.⁷

The AB is a kind of carbon black constituted of nanoscale acinoform particles with high porous surface, which is prepared by the exothermic decomposition of acetylene in controlled atmosphere.⁸ Its properties, such as high catalytic and electrical conductivity properties, large surface area and adsorptive properties have resulted in its use as a conducting phase in components of batteries and fuel cells,⁹⁻¹² and in much less extension in the development of electrochemical and electroanalytical sensors.¹³⁻¹⁶

On the other hand, nowadays there is an increasing concern regarding phenolic compounds considered emerging pollutants, putting them among the main organic contaminants bioaccumulated in plants, animals and humans.^{17,18} One of these substances is the diphenolic endocrine disruptor bisphenol-A (BPA, 2,2-bis(4-hydroxyphenyl)propane, Figure 1).¹⁹

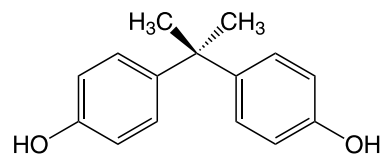


Figure 1. Structural formula of bisphenol-A (BPA).

BPA is quickly absorbed into the bloodstream and results in bioaccumulation in adipic tissue, thus affecting adipocytes metabolism and inflammatory functions, once the molecular structure of BPA is analogous to endocrine

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steroid hormones.^{20,21} Their estrogenic activity enables a binding to estrogen receptors, causing dysfunctions in the endocrine system and development of some diseases, such as diabetes, obesity, infertility, cardiovascular diseases, carcinogenicity, polycystic ovarian syndrome and other conditions.^{22,23}

As BPA is frequently used as a plasticizer for the large scale production of some polymers (e.g., polycarbonate, polyacrylate, polysulfonate, epoxy and polyester styrene resins) that are used in the manufacture of common and daily use products in contemporary society, this results in its accumulation in the environment and justifies the search for detection and quantification of this environmental contaminant.^{24,25}

Thus, fluorimetric,²⁵ high performance liquid chromatographic (HPLC),²⁶ gas chromatographic (GC),²⁷ chemiluminescent,²⁸ bioluminescent²⁹ and hyphenated analytical procedures³⁰⁻³² for BPA quantification are frequently found in the literature. Recently, Huelsmann *et al.*³³ presented a review article with modern strategies for the chromatographic determination of BPA based on molecularly imprinted polymers (MIP), metal and covalent organic frameworks, ionic liquids and magnetic ionic liquids and deep eutectic solvents.

Electrochemical procedures represent an interesting alternative to the determination of organic pollutants once they present relatively high sensitivity, selectivity, analytical frequency, low limit of detection and the possibility of analyzing complex samples *in situ* with few, or even without sample pre-treatment.³⁴

Regarding the electroanalytical determination of BPA, several kinds of electrodes and voltammetric techniques were presented by Gugoasa.³⁵ Particularly concerning the use of composite electrodes, there are examples of carbon pastes in which AB is the conducting phase modified with chitosan,³⁶ graphene,³⁷ salicylaldehyde-modified chitosan,³⁸ graphene, 4-vinylpyridine-MIP,³⁹ chitosan-MIP and graphene.⁴⁰

AB composites prepared by casting on electrode surfaces can also be found. Examples include AB composites modified with chitosan-MIP,⁴¹ dihexadecylhydrogen phosphate,⁴² chitosan and gold nanoparticles.⁴³ The use of such different devices and techniques resulted in a variety of limits of detection and linear range response, depending on the modifiers used as will be discussed later in this text.

In the present work, a solid composite electrode based on AB and PU derived from a vegetable oil (ABPUE) without modifier was evaluated regarding its performance in the determination of BPA in water samples without the need of solvent use and sample preparation with relatively high sensitivity and low cost. Up to our knowledge, this is

the first attempt at using this new composite device in the quantification of BPA in water samples.

Experimental

Reagents and solutions

All reagents were of analytical grade and used as received. Solutions were prepared with water treated in an OS 10 LZ reverse osmosis system (GEHAKA, São Paulo, Brazil) and then purified in a Barnstead D13321 EasyPure RoDi® system (Thermo Scientific, Dubuque, USA) with resistivity ≥ 18.2 M Ω cm.

Potassium chloride (Sigma-Aldrich, Burlington, USA), potassium ferricyanide, potassium ferrocyanide (Merck, Darmstadt, Germany), monobasic potassium phosphate, dibasic potassium phosphate, and sodium hydroxide (Spectrum, New Brunswick, USA) were also used to prepare electrolyte solutions with pH adjusted to the desired values.

BPA (Sigma-Aldrich, Burlington, USA) 1.00×10^{-3} mol L⁻¹ stock solution was prepared every day in a water and ethanol (Tedia, Fairfield, USA) mixture 1:1 (v/v).

AB, surface area of 80.0 m² g⁻¹ and 42.0 nm average particle size, (Strem Chemicals, Boston, USA) and the PU resin consisting of 4,4-diphenylmethane diisocyanate (MDI) and castor oil (both from Univar, Paulínia, Brazil) were used to manufacture the composites.

Instrumentation

Electrochemical experiments were performed in an Autolab PGSTAT 204 potentiostat/galvanostat, coupled to a microcomputer and controlled by the NOVA® v. 2.1.3 software (both from Metrohm, Herisau, Switzerland). Data processing was performed with OriginPro 2016⁴⁴ software.

Voltammetric curves were obtained in a glass cell with 25.0 mL full capacity using the ABPUE (diameter = 3.0 mm, geometric area of 0.071 cm²) as a working electrode, a platinum foil (0.55 cm²) as auxiliary electrode and a saturated calomel electrode (SCE) as reference. All measurements were performed at room temperature.

The pH measurements were performed in an 827 pH Lab digital pHmeter coupled to a 6.0228.010 Ag/AgCl/KCl (3.0 mol L⁻¹) combined glass electrode (both from Metrohm, Herisau, Switzerland).

Composite electrode fabrication

As observed in previous works,^{3,6} the proportion of

60% of AB as conducting phase and 40% of agglutinant material (m/m) presented the best composition regarding the percolation threshold and mechanical stability. Thus, this was the proportion used for AB and PU resin, being 0.60 g of AB powder and 0.40 g of PU (44.5% polyol and 55.5% isocyanate, m/m).

The materials were weighed directly in a glass mortar and homogenized for 2 min. The mixture was extruded in a manual press as rods with 3 mm diameter and ca. 50 mm length. The pressure applied was estimated as ca. 10 kgf cm⁻². All this procedure was done in approximately 10 min, when the curing of PU started. After curing at room temperature for 24 h, the rods were cut in pieces of 10 mm long and connected to copper wires with Conductive Silver Epoxy Kit (Electron Microscopy Sciences, Hatfield, USA) and left to dry for another 24 h. The copper wire/composite assemblies were fixed inside a glass tube (6 mm inner diameter, 70 mm longer), filled with Silaex 6400 epoxy resin (Silaex, São Paulo, Brazil) and left to cure for 24 h. Finally, the composite electrode surface was sanded in 2000-grit sandpaper before each working day in an APL-02 motorized polishing wheel (Arotec, Cotia, Brazil) to remove excess epoxy resin from the surface. After sanding, the working electrode was sonicated in deionized water in MaxiClean 750 ultrasonic bath (Unique, Indaiatuba, Brazil) for 3 min.

Analytical procedure

Cyclic voltammograms (CV) were obtained in a mixture of 1.0 mmol L⁻¹ K₄[Fe(CN)₆]/K₃[Fe(CN)₆] each in 0.5 mol L⁻¹ KCl solution in order to evaluate the electrochemical behavior of the ABPUE composite (60% AB:40% PU, m/m) in comparison with glassy carbon electrode (GCE).

The effect of scan rate in the anodic response of BPA was evaluated from cyclic voltammograms obtained using 1.0 × 10⁻⁴ mol L⁻¹ BPA in 0.10 mol L⁻¹ phosphate buffer pH = 7.0. Scan rates of 10.0, 20.0, 30.0, 40.0, 50.0, 60.0, 70.0, 80.0, 90.0 and 100 mV s⁻¹ were used and peak currents taken at the potential of maximum current intensities. Only oxidation currents were measured once the BPA presented an irreversible behavior.

The differential pulse voltammetric procedure (DPV) experiments were performed in phosphate solution pH 3.0-11.0 in order to determine the best electrolytic medium. After that, DPV parameters such as scan rate (*v*) and pulse amplitude (*a*) were optimized using a 2ⁿ factorial planning. The variables were 50 mV, 20 mV (pulse amplitude) and 20 and 10 mV s⁻¹ (scan rate), totaling 4 experiments. The best conditions in terms of peak current

intensity (*I_p*) of BPA oxidation were used to obtain the analytical curve and the detection of BPA in water samples.

Thus, defined amounts of BPA stock solution were diluted in 10.0 mL of phosphate buffer pH = 7.0 resulting in concentrations from 0.100 to 10.0 mmol L⁻¹. From the analytical curve, the limits of detection (LOD) and quantification (LOQ) were calculated using the following relationships: LOD = (3 × SD)/*s* and LOQ = (10 × SD)/*s*, where *s* is the slope of the analytical curve and SD is the standard deviation of the intercept.⁴⁵

BPA detection was also evaluated in the presence of different compounds, including oxytetracycline (antibiotic), catechol (polyphenol), furosemide (diuretic), fenitrothion (insecticide), viologen (herbicide) and diclofenac (anti-inflammatory) under the same optimized conditions to evaluate possible interferences. The standard addition method was used, in which the spiked concentration of BPA was fixed at 0.30 mmol L⁻¹ in 0.10 mol L⁻¹ phosphate buffer pH = 7.0 and the added concentrations of interferents were 0.20, 0.40 and 0.60 mmol L⁻¹.

Water samples preparation

Artesian well water and public supply tap water samples from the city of Potirendaba, State of São Paulo, Brazil (21°02'51.1"S; 49°24'00.0"W) were collected in polypropylene bottles and did not receive treatment before the voltammetric analysis. They were spiked with BPA solution in order to reach 0.30 mmol L⁻¹ of the analyte and stored in a refrigerator at 3-4 °C until the analysis.

Suitable amounts of potassium monobasic phosphate and sodium dibasic phosphate was directly dissolved in 100.0 mL of BPA free and BPA spiked water (0.3 mmol L⁻¹) samples resulting in a 0.10 mol L⁻¹ total phosphate concentration and adjusted to pH = 7.0. Then, 10.0 mL of these samples were transferred into the electrochemical cell and DPV voltammograms were obtained under the optimized conditions for the analytical curve in triplicate for each sample and after each standard addition. The standard addition procedure was used for both determinations of BPA and recovery evaluations.

Results and Discussion

A complete chemical and morphological characterization of the ABPUE, including the best composition and electrochemical response, using scanning electron microscopy, thermogravimetry and spectroscopic techniques, as well as the surface area, reproducibility and stability of this electrode in electroanalysis has already been discussed in a previous work.⁶

Electrochemical response of ABPUE

The electrochemical behavior of $1.0 \text{ mmol L}^{-1} \text{ K}_4[\text{Fe}(\text{CN})_6]/\text{K}_3[\text{Fe}(\text{CN})_6]$ in $0.5 \text{ mol L}^{-1} \text{ KCl}$ solution at ABPUE and GCE electrodes in cyclic voltammetry are presented in Figure 2. The higher peak current observed in the ABPUE voltammogram is due to the smaller particle size of AB regarding graphite and surface porosity, which makes the effective area of the electrode higher as previously described.⁶ It also suggests a higher surface activity of ABPUE due to the use of the smaller AB particles, resulting in a greater degree of aggregation between particles and facilitating electronic transport and reactivity in the bulk and onto the electrodic surface in redox reactions.⁴⁶

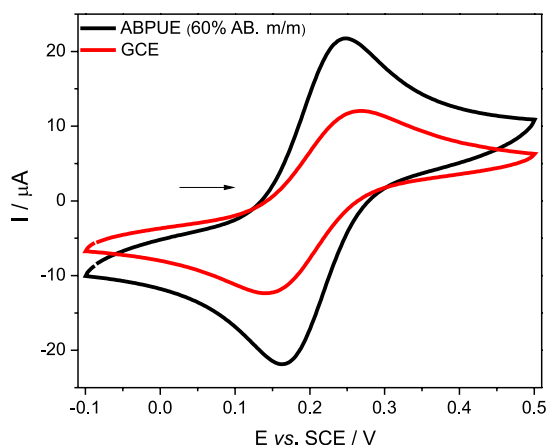


Figure 2. Cyclic voltammograms of $1.0 \text{ mmol L}^{-1} \text{ K}_4[\text{Fe}(\text{CN})_6]/\text{K}_3[\text{Fe}(\text{CN})_6]$ in $0.5 \text{ mol L}^{-1} \text{ KCl}$ solution at ABPUE composite (60% AB, m/m) and at GCE for comparison obtained at $\nu = 25 \text{ mV s}^{-1}$.

A capital challenge in the manufacture of this composite material was to provide an effective electrical contact between the conductive particles inside the agglutinant matrix. Once AB particles are relatively small, they present the tendency of do not uniformly disperse in contact with the agglutinant. On the other hand, edge sites are 10-100 times more reactive than basal sites, which promotes greater reactivity of these formed clusters, determining their connection potential and flexibility in making them compatible with numerous arrays.^{46,47} Thus, it was necessary to apply a considerable pressure to compact the composite before extrusion of the rods. Another noticeable characteristic of the ABPUE is its high surface area and active surface area, classifying it as a porous electrode.⁶

Electroanalytical behavior of BPA at ABPUE

Cyclic voltammograms of $1.0 \times 10^{-4} \text{ mol L}^{-1}$ BPA in 0.10 mol L^{-1} phosphate buffer pH 7.0 in different scan

rates from 10 to 100 mV s^{-1} are presented in Figure 3. At ABPUE, the BPA presented an irreversible peak between 0.50 to 0.55 V (vs. SCE), suggesting a limitation by the kinetic of charge transfer.

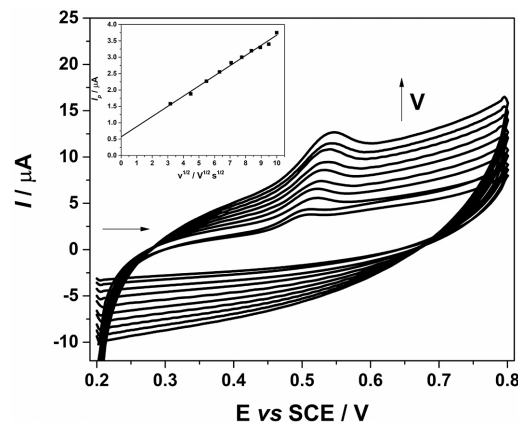


Figure 3. Cyclic voltammograms of $1.0 \times 10^{-4} \text{ mol L}^{-1}$ BPA in 0.10 mol L^{-1} phosphate buffer pH 7.0 in different scan rates: 10.0, 20.0, 30.0, 40.0, 50.0, 60.0, 70.0, 80.0, 90.0 and 100 mV s^{-1} at the ABPUE. In the inset the dependence of the peak currents with $\nu^{1/2}$.

However, the peak current was linearly proportional to the square root of scan rate (inset in Figure 3; $y = 5.71 \times 10^{-7} \text{ A} + 3.71 \times 10^{-7} \text{ A V}^{-1/2} \text{ s}^{-1/2}$; $R^2 = 0.9922$; $n = 10$), revealing a diffusional control of the mass transport process. As the redox behavior of BPA is irreversible, only the anodic current was presented in the inset.

Analytical evaluation of the ABPUE in BPA determination

Optimization of DPV parameters

DPV was used to detect and quantify BPA, after optimizing parameters such as scan rate (ν) and pulse amplitude (a) (Figure 4).

The voltammograms using scan rate of 10 mV s^{-1} and pulse amplitude of 50 mV presented the highest intensity

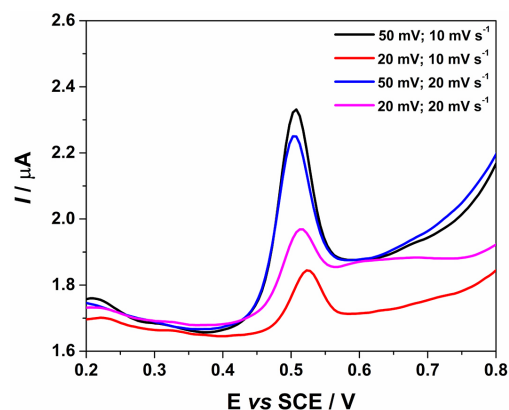


Figure 4. DPV voltammograms of 5.0 mmol L^{-1} BPA in 0.10 mol L^{-1} phosphate buffer pH = 7.0 at ABPUE composite with pulse amplitude and scan rate variation.

and a better voltammetric profile, being chosen for the next analysis.

In order to find the best pH for BPA determination, a study of the pH effect in DPV was performed using $0.5 \mu\text{mol L}^{-1}$ BPA in phosphate solution in pH = 3.0-11.0 at ABPUE. Results are presented in Figure 5a.

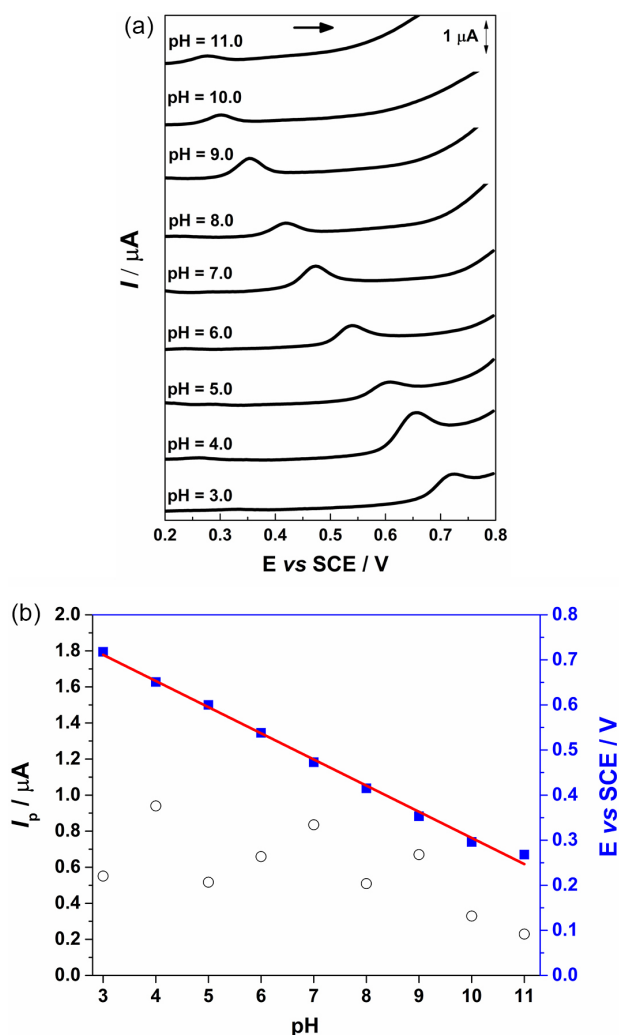


Figure 5. (a) DPV voltammograms of 0.50 mmol L^{-1} BPA in phosphate solution in different pH values at ABPUE composite and (b) dependence of peak current (○) and peak potential (■) of BPA with pH. $a = 50 \text{ mV}$, $v = 10 \text{ mV s}^{-1}$.

The use of phosphate as an electrolyte medium for the determination of BPA was based on previous reports^{5,20,28} in which the authors found relatively high sensitivity and well-defined peaks for the analyte in a wide range of pH. This is in agreement with the voltammograms in Figure 5a. These voltammograms revealed a displacement of the BPA peak potential to more negative potentials as pH increased. As H^+ are released during the electroic oxidation of BPA, when the pH is increased, the BPA oxidation peak shifts to lower potentials with increasing pH.⁴⁸ A linear relationship

in the range pH = 3.0-11.0 (Figure 5b) and the anodic peak potential of BPA at ABPUE was obtained, as presented in equation 1.

$$y = 0.88 - 0.058 \text{ pH} \quad (R^2 = 0.9961; n = 9) \quad (1)$$

The slope of $(-0.058 \pm 0.001) \text{ V pH}^{-1}$ is close to the theoretical value of 59 mV pH^{-1} , indicating that the same number of electrons and protons take part of the oxidation reaction of BPA, in agreement with the previous report⁴¹ regarding the mechanism of BPA redox behavior.

Although a slightly higher anodic oxidation peak current was observed for BPA at pH = 4 in comparison with the pH = 7.0 (Figure 5b), we decided using pH = 7.0 in further studies due to its proximity of physiological pH and once the peak potential is close to the electrolyte discharge, with a considerable contribution of the capacitive current to the peak current.

The composite material demonstrated to be robust and stable for at least 6 months.⁶ A single electrode could be used to obtain all the data presented in this work, with an intraday repeatability of $(1.69 \pm 0.01) \times 10^{-1} \mu\text{A}$ ($n = 7$) at the ABPUE in DPV under the optimized conditions, for a $5.00 \times 10^{-6} \text{ mol L}^{-1}$ BPA in 0.10 mol L^{-1} phosphate buffer pH = 7.0. As the surface is usually renewed interday evaluation was not performed. The variability between different electrodes was observed and depend on the composition of the composite and uniformity of such composition. However, it is constant along the rod and proportional to all the measurements performed with each device.

Analytical curve

DPV voltammograms were obtained using the previously optimized parameters at ABPUE for concentrations ranging from 0.10 to 10.0 mmol L^{-1} BPA. Figure 6a presents the voltammograms that resulted in linear analytical range, while Figure 6b presents the analytical curve for all concentrations, and the linear range in the detail.

A linear response range between 0.10 and 1.0 mmol L^{-1} BPA was observed, according to the equation 2, with limit of detection of 14.1 nmol L^{-1} and $R = 0.9995$.

$$I_p (\mu\text{A}) = 0.088 (\mu\text{A mol}^{-1} \text{L})c + 0.00261 (\mu\text{A}) \quad (2)$$

The LOD was determined as three times the standard deviation of the intercept, divided by the slope of the straight line.⁴⁵ The peak currents of the voltammograms obtained from BPA were measured at a fixed potential of 0.48 V (vs. SCE), discounting the residual current in each case.

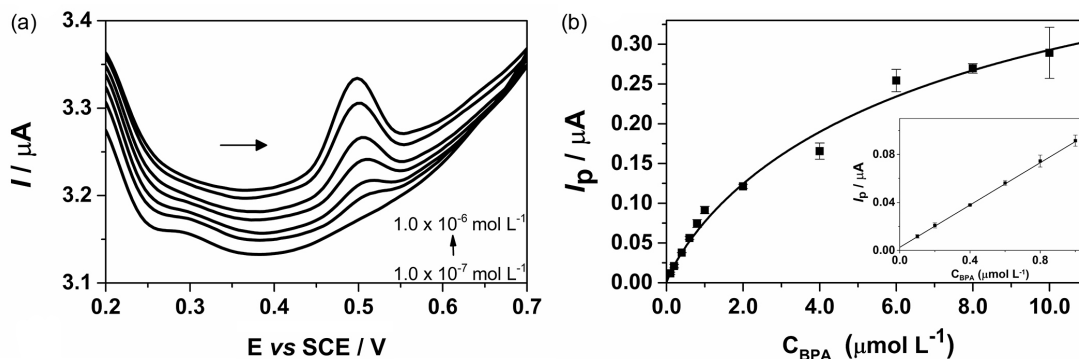


Figure 6. (a) DPV voltammograms that resulted in linear range obtained at ABPUE composite with $a = 50$ mV, $v = 10$ mV s⁻¹. (b) Analytical curve from 0.1 to 10.0 mmol L⁻¹ BPA, in phosphate buffer pH = 7.0 at ABPUE composite. In the inset the linear response range.

The analytical curve presented a linear response up to 1.0 mmol L⁻¹ BPA and then a typical saturation profile for higher concentrations. The shape of the analytical curve can be associate to a saturation of active sites of the electrode in higher concentrations, probably due to a limitation in the kinetic of charge transfer, thus explaining the non-linear response above 1.0 μ mol L⁻¹ BPA concentration. This can be justified by the cyclic voltammograms in different scan rates presented in Figure 3 which revealed that the mass transport is limited by diffusion of the analyte concomitant, but with a displacement of the peak potential towards higher potentials at higher scan rates.

Some works³⁶⁻⁴³ previously reported the determination of BPA at composite electrodes in which AB is the conductive phase as presented in Table 1. Some other examples of unmodified electrodes were included⁴⁹⁻⁵² in this table for comparison.

If compared to the unmodified electrodes prepared with different strategies, the ABPUE composite presented a similar performance regarding linear range; however, with lower limit of detection, except for carbon paste electrode (CPE). When compared with the modified devices based on AB as a conductive phase, there are a variety of wider linear ranges and lower limits of detection.

Table 1. Characteristics of previous devices described in the literature for the determination of BPA based on composites in which AB is used as conductive phase and unmodified electrode materials for comparison

Electrode	Linear range / (mmol L ⁻¹)	LOD / (mmol L ⁻¹)	Analytical technique	Reference
Composite electrodes				
MIP/ABPE ^a	0.08-10.0	0.06	LSV	36
GR/ABPE ^b	0.0008-100.0	0.0006	LSV	37
S-CHIT/ABPE ^c	0.04-10.0	0.02	LSV	38
Gr/MIPs/ABPE ^d	0.0000014-1200	0.00000042	DPV	39
MIP-GR/ABPE ^e	0.008-20.0	0.006	LSV	40
MIPs-AB/GCE ^f	0.005-0.2; 0.5-10.0	0.002	DPV	41
AB-DHP/GCE ^g	0.02-5.0	0.006	DPV	42
AB-CS-AU ^h	0.0075-1.0	0.0064	DPV	43
Unmodified electrodes				
CPE ⁱ	0.025-1.0	0.0079	DPV	49
ITO ^j	5.0-120.0	0.29	DPV	50
BDD ^k	0.44-5.2	0.21	DPV	51
EG ^l	1.56-50.0	0.76	DPV	52
This work				
ABPUE ^m	0.10-1.0	0.014	DPV	–

^aCarbon paste electrode based on acetylene black-chitosan; ^bcarbon paste electrode based on acetylene black-graphene; ^ccarbon paste electrode based on salicylaldehyde-modified chitosan; ^dcarbon paste electrode based on acetylene black-graphene-4-vinyl pyridine-chitosan; ^ecarbon paste electrode based on acetylene black-chitosan-graphene; ^facetylene black-chitosan on glassy carbon electrode; ^gacetylene black-dihexadecyl hydrogen phosphate on glassy carbon electrode; ^hacetylene black-chitosan-gold nanoparticles on glassy carbon electrode; ⁱcarbon paste electrode based on graphite and paraffin oil; ^jindium tin oxide electrode; ^kboron-doped diamond electrode; ^lexfoliated graphite electrode; ^macetylene black polyurethane electrode. DPV: differential pulse voltammetric procedure; LSV: linear sweep voltammetry.

However, the use of modifiers requires synthesis and use of not always environmentally friendly chemicals. Thus, considering the performances presented in Table 1, the ABPUE can be considered an interesting alternative for BPA electroanalytical determination. Modifiers can also be incorporated in the ABPUE matrix in the future to improve its analytical features as sensitivity and selectivity.

Determination of BPA in water samples

The ABPUE electrode was used for the determination of BPA in tap and artesian water samples by standard addition method according to the Experimental section. The water samples were spiked with 0.300 mmol L⁻¹ in both cases, and the standard addition procedure resulted in BPA concentrations of 0.303 ± 0.004 mmol L⁻¹ (R² = 0.9997) and 0.297 ± 0.01 mmol L⁻¹ (R² = 0.9991) with relative errors of 0.81 and 1.01% for the tap and artesian well water samples, respectively. Recovery tests were also performed and the results are presented in Table 2.

According to the Student's *t*-test, the average concentration values determined in Table 2 are in agreement with the spiked values within 95% confidence interval, while recoveries ranging from 97.5 to 115.0% were found.

According to these values, it is suggested that the ABPU castor oil-based composite electrode can be used for the determination of BPA in water samples in phosphate buffer pH = 7.0 without matrix effect and that the concomitants present in such samples do not interfere in the determinations.

Effect of possible interferents

An interference study was performed to evaluate the effect of the presence of some pharmaceuticals and pesticides as possible contaminants found in waters as a result of agriculture, industry and domestic wastes. Table 3 shows the oxidation peak currents of 0.30 mmol L⁻¹ BPA

spiked in 0.10 mol L⁻¹ phosphate buffer pH = 7.0 and the changes in such currents when three concentrations of interferents 0.15, 0.30 and 0.60 mmol L⁻¹ were added.

As can be seen, oxytetracycline, furoseamide and catechol presented negative interference in the BPA peak current when the background subtraction was used. However, when measuring the absolute current values, the interference was reduced drastically, indicating that these substances alter the base line of the voltammograms changing it to higher values. Using methyl viologen dichloride and fenitrothion, the opposite occurred and positive interference was observed. Thus, the current measuring must be carefully performed in the presence of such substances. Diclofenac did not interfere when the background subtraction procedure was used. None of these analytes presented peaks in the same potential as BPA.

Conclusions

The unmodified ABPUE composite electrode is a promising device in the determination of BPA in water samples by a relatively fast, simple, repeatable and sensitive voltammetric procedure, without the need of sample preparation, pre-concentration steps or resurfacing between measurements.

The electrode is easy to assemble with environmentally friendly chemicals, robust and long lasting once a single one was used in all the analytical procedures reported in this work. Considering sensitivity, the proposed device presents similar performance to other common unmodified electrode materials, however presented a lower limit of detection, as well as regarding some modified ones.

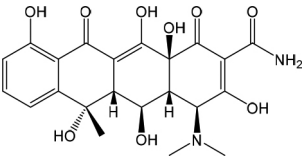
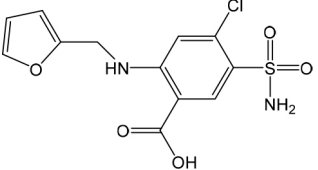
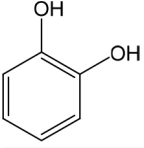
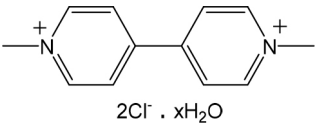
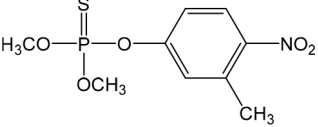
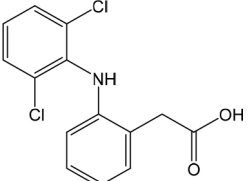
Application in water samples revealed recoveries of almost 100%, without interference from the natural concomitants in tap and artesian well samples. Interference from some analytes was observed, but could be overcome by careful measuring of the peak currents.

Table 2. Results for the determination and recoveries of BPA in the spiked tap and artesian well water samples at ABPUE in the DPV procedure

Water samples	Addition	Added / (mmol L ⁻¹)	Found / (mmol L ⁻¹)	Recovery ^a / %
Tap	1	0.20	0.22 ± 0.03	110
	2	0.40	0.39 ± 0.02	97.5
	3	0.60	0.60 ± 0.01	100
	Average ± SD ^a			102 ± 5
Artesian well	1	0.20	0.23 ± 0.02	115
	2	0.40	0.40 ± 0.01	100
	3	0.60	0.60 ± 0.00 ₄	100
	Average ± SD ^a			105 ± 7

^aAverage ± standard deviation (SD), n = 3.

Table 3. Study of interferences of oxytetracycline, diclofenac, furosemide, catechol, methyl viologen and fenitrothion in the determination of 0.30 $\mu\text{mol L}^{-1}$ BPA in phosphate buffer pH 7.0 at ABPUE

Interferent	$C_{\text{interf}} / (\text{mmol L}^{-1})$	$I_p / \mu\text{A}$		Interference ^b / %	
		BPA	BPA + interferent ^a	A	B
 Oxytetracycline	0.15		0.035 \pm 0.001	-17	0.0
	0.30	0.042 \pm 0.002	0.033 \pm 0.0003	-21	+0.2
	0.60		0.032 \pm 0.0001	-24	+0.9
 Furosemide	0.15		0.039 \pm 0.001	-7.1	+1.2
	0.30	0.042 \pm 0.001	0.036 \pm 0.001	-14	+2.0
	0.60		0.033 \pm 0.001	-21	+3.2
 Catechol	0.15		0.038 \pm 0.0002	-7.9	+2.8
	0.30	0.042 \pm 0.001	0.035 \pm 0.001	-17	+4.7
	0.60		0.034 \pm 0.001	-19	+6.1
 Methyl viologen dichloride	0.15		0.066 \pm 0.001	+57	+2.8
	0.30	0.042 \pm 0.002	0.070 \pm 0.002	+67	+5.4
	0.60		0.072 \pm 0.0005	+72	+7.5
 Fenitrothion	0.15		0.042 \pm 0.001	+2.4	3.6
	0.30	0.041 \pm 0.001	0.052 \pm 0.001	+27	7.2
	0.60		0.066 \pm 0.002	+61	14.1
 Diclofenac	0.15		0.042 \pm 0.001	-	-
	0.30	0.042 \pm 0.001	0.042 \pm 0.001	-	-
	0.60		0.042 \pm 0.001	-	-

^aAverage \pm standard deviation; n = 3; background subtraction at peak potential; ^bA: when current was measured by background subtraction at the peak potential; B: when the absolute current, without background subtraction was measured at the peak potential. C_{interf} : concentration of interferent; BPA: bisphenol A; I_p : peak current.

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