DETERMINATION OF BISPHENOL A AS AN ENVIRONMENTAL POLLUTANT USING A NANO SENSOR

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ABSTRACT
A novel carbon paste electrode modified with ZrO_2 nanoparticles and ionic liquid was fabricated and used for the electrochemical study of bisphenol A. This modified electrode offers a considerable improvement in voltammetric sensitivity toward bisphenol A, compared to the bare electrode. Square wave voltammetry (SWV) exhibits a linear dynamic range from 1.0×10^{-7} to 3.0×10^{-4} M and a detection limit of 50.0 nM for bisphenol A. Finally, the proposed method was successfully applied to the determination of bisphenol A in real samples.

KEYWORDS: Environmental pollutants, Water analysis, Bisphenol A. ZrO_2 nanoparticles.

INTRODUCTION

Bisphenol A (scheme 1) is an important chemical used principally as a monomer in the manufacture of a multitude of chemical products including epoxy resins and polycarbonate. Epoxy resins are used for the lining of food cans, dental sealants, paints and adhesives. Polycarbonate are utilized in food packaging, coatings for PVC water pipe walls, plastic bottles for water, baby bottles and etc. (Staples *et al.* 1998). During the manufacturing process of these products, some bisphenol A can be inadvertently released into the environment to contaminate rivers and ground waters. Moreover, bisphenol A can also migrate into food and drinking water from nursing bottle, food can linings and beverage container (Brotons *et al.* 1995; Biles *et al.* 1997). Recently it was reported that bisphenol A is one of a number of potential endocrine disruptors which may alter normal hormone function. As a result, bisphenol A not only is postulated to antagonize the effect of endogenous estrogens, but also it could cause cancer, reduce immune function and impair reproduction of wild animals and humans (Yoshida *et al.* 2001; Vom Saal and Hughes 2005; Gupta 2000). Therefore, an efficient determination method is required for monitoring the levels of bisphenol A in environment.

Various analytical methods have been investigated to determine bisphenol A in environmental water, air and plastic waste including gas chromatography-mass spectrometry (GC–MS) (Lambert *et al.* 1997), fluorimetry Wang *et al.* (2006), liquid chromatography (HPLC) (Zhao *et al.* 2009), gas chromatography (GC) Shin *et al.* (2001), enzyme-linked immunosorbent assay (ELISA) Kuruto-Niwa *et al.* (2007) and electrochemical methods (Liu *et al.* 2014; Andreescu and Sadik 2004). However, there are only a few easy and sensitive methods for the determination of a trace amount of bisphenol A in water and serum samples. So, they are inappropriate for online or field monitoring (Inoue *et al.* 2000). Among them, electrochemical methods have attracted more and more attentions due to the advantages of fast response, inexpensiveness, simple operation, high sensitivity, timesaving and real-time detection in situ condition (Foroughi *et al.* 2014).

Carbon paste electrodes (CPEs), due to their ease of construction, low cost, low background current, relatively wider potential windows, renewability, and compatibility with various types of modifiers, have been widely used as suitable matrixes for preparation of modified electrodes (Deylova *et al.* 2014; Kang *et al.* 2013). The common carbon paste electrodes (CPE) usually employ organic liquids such as nujol, paraffin and so on as binder. These nonpolar pasting liquids fulfill some of the important criteria for a suitable electrode, such as chemical inertness, insulating property, and water immiscibility. But these binders are not component-fixed since it is involved in various refining of petroleum and processing of crude oil, and some unaccounted ingredients may engender unpredictable influences on detection and analysis. Also, these binders are not conductive, which to some extent weakens the electrochemical response of CPE, and especially are disadvantageous to traces of detection. Therefore, another successful class of binders is room temperature ionic liquids (RTILs). They have been developed and received much attention in many areas of chemistry and electrochemical industry (Liua *et al.* 2005). RTILs are usually organic or mixed organicinorganic salts that have melting points less than 100 °C, which are considered as green solvents due to their vapor pressure and resulting ease of containment. The acknowledged advantages of these RTILs include good chemical and thermal stability, almost negligible vapor pressure, good ionic conductivity, and wide electrochemical windows etc (Li *et al.* 2005; Liu *et al.*

2005). But direct detection of bisphenol A using CPE electrode is rare because the response of bisphenol A is poor (Yin *et al.* 2011). Due to the unique and special properties of nanoparticles, they have been applied in various fields of science and technology. In order to increase the response signal, sensitivity and to achieve a better reproducibility the fabrication of carbon paste electrodes modified with nanoparticles has been the focus of recent attention. The large surface area to volume ratio of the nanomaterial has increased the quantity of binding sites for detection of a specific analyte, hence lowering the detection limit (Yu *et al.* 2013).

In the present work, we describe the preparation of a new carbon paste electrode modified with an ionic liquid and ZrO_2 nanoparticles (ILZNCPE) and investigate its performance for the determination of bisphenol A in aqueous solutions.

EXPERIMENTAL
Apparatus and chemicals
The electrochemical measurements were performed with an Autolab potentiostat/galvanostat (PGSTAT 12N, Eco Chemie, the Netherlands). The experimental conditions were controlled with General Purpose Electrochemical System (GPES) software. A conventional three electrode cell was used at 25 ± 1 °C. An Ag/AgCl/KCl (3.0 M) electrode, a platinum wire, and ILZNCPE were used as the reference, auxiliary and working electrodes, respectively. A Metrohm 710 pH meter was used for pH measurements.

Bisphenol A and all of the other reagents were of analytical grade and were obtained from Sigma Aldrich. The buffer solutions were prepared from orthophosphoric acid and its salts.

Preparation of the electrode
ILZNCPEs were prepared by mixing 0.05 g of ZrO_2 nanoparticles with 0.95 g graphite powder and approximately, ~ 0.8 mL of ionic liquids with a mortar and pestle. The paste was then packed into the end of a glass tube. A copper wire inserted into the carbon paste provided the electrical contact.

For comparison, ionic liquid/carbon paste electrode in the absence of ZrO_2 nanoparticles (ILCPE), ZrO_2 nanoparticles carbon paste electrode (ZNCPE) consistent of ZrO_2 nanoparticles and paraffin oil, and bare carbon paste electrode (CPE) consistent of graphite powder and paraffin oil were also prepared in the same way.

RESULT AND DISCUSSION
Electrochemical behavior of bisphenol A at the surface of various electrodes
Fig. 1 displays cyclic voltammetric responses from the electrochemical oxidation of 200.0 μM bisphenol A at the surface of ILZNPE (curve d), ILCPE (curve c), ZNCPE (curve b) and bare CPE (curve a). The results showed that the oxidation of bisphenol A is very weak at the surface of the bare CPE, but in the presence of ILs in CPE could enhance the peak current and decrease the oxidation potential (decreasing the overpotential). A substantial negative shift of the currents starting from oxidation potential for bisphenol A and dramatic increase of the current indicates the catalytic ability of ILZNPE (curve d) and ILCPE (curve c) to bisphenol A oxidation. The results showed that the combination of ZrO_2 nanoparticles and the ionic liquid (curve d) definitely improved the characteristics of bisphenol A oxidation. However, ILZNPE shows much higher anodic peak current for the oxidation of bisphenol A compared to ILCPE, indicating that the combination of graphene oxide nano sheets and IL has significantly improved the performance of the electrode toward bisphenol A oxidation.

Effect of scan rate
The effect of potential scan rates on the oxidation current of bisphenol A has been studied (Fig. 2). The results showed that increasing in the potential scan rate induced an increase in the peak current. In addition, the oxidation process is diffusion controlled as deduced from the linear dependence of the anodic peak current (I_p) on the square root of the potential scan rate ($v^{1/2}$) over a wide range from 10 to 150 mV s^{-1} (Fig. 3).

Chronoamperometric measurements
Chronoamperometric measurements of bisphenol A at ILZNPE were carried out by setting the working electrode potential at 0.6 V vs. Ag/AgCl/KCl (3.0 M) for the various concentrations of bisphenol A in PBS (pH 7.0) (Fig. 4). For

an electroactive material (bisphenol A in this case) with a diffusion coefficient of D, the current observed for the electrochemical reaction at the mass transport limited condition is described by the Cottrell equation (Bard and Faulkner 2001). Experimental plots of I vs. $t^{-1/2}$ were employed, with the best fits for different concentrations of bisphenol A (Fig. 5). The slopes of the resulting straight lines were then plotted vs. bisphenol A concentration (Fig. 6). From the resulting slope and Cottrell equation the mean value of the D was found to be 3.95×10^{-6} cm^2/s.

Calibration plot and limit of detection
The peak current of bisphenol A oxidation at the surface of the modified electrode can be used for determination of bisphenol A in solution. Therefore, square wave voltammetry (SWV) experiments were done for different concentrations of bisphenol A (Fig. 7) The oxidation peak currents of bisphenol A at the surface of a modified electrode were proportional to the concentration of the bisphenol A within the ranges 1.0×10^{-8} to 3.0×10^{-4} M with detection limit (3σ) of 50.0 nM (Fig. 8).

Real sample analysis
In order to evaluate the analytical applicability of the proposed method, also it was applied to the determination of bisphenol A in some water samples. The results are given in table 1.
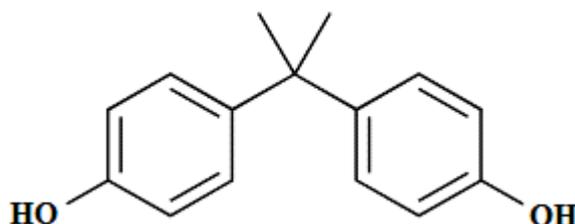
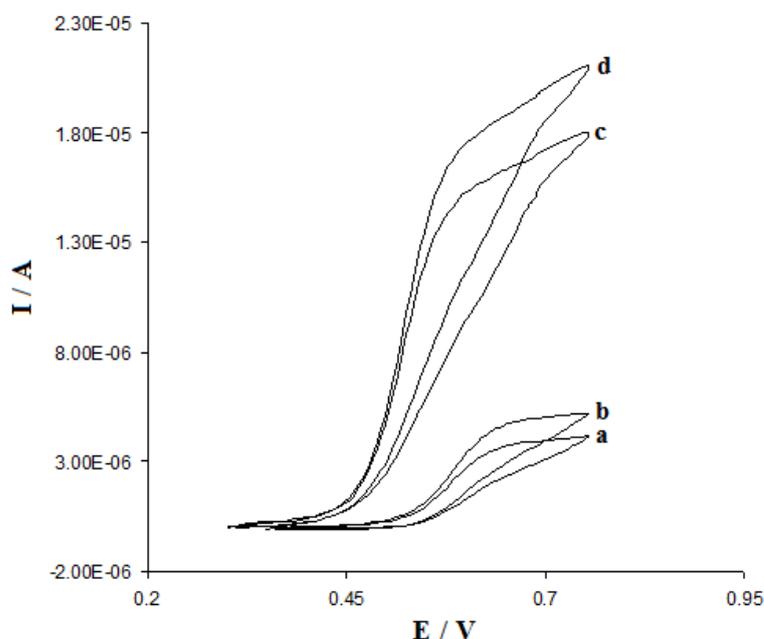**Scheme 1.** Chemical structure of Bisphenol A

Fig. 1. CVs of a) CPE, b) ZNCPE, c) ILCPE and d) ILZNPE in the presence of 200.0 μM bisphenol A at a pH 7.0, respectively. In all cases the scan rate was 50 mV s^{-1}.
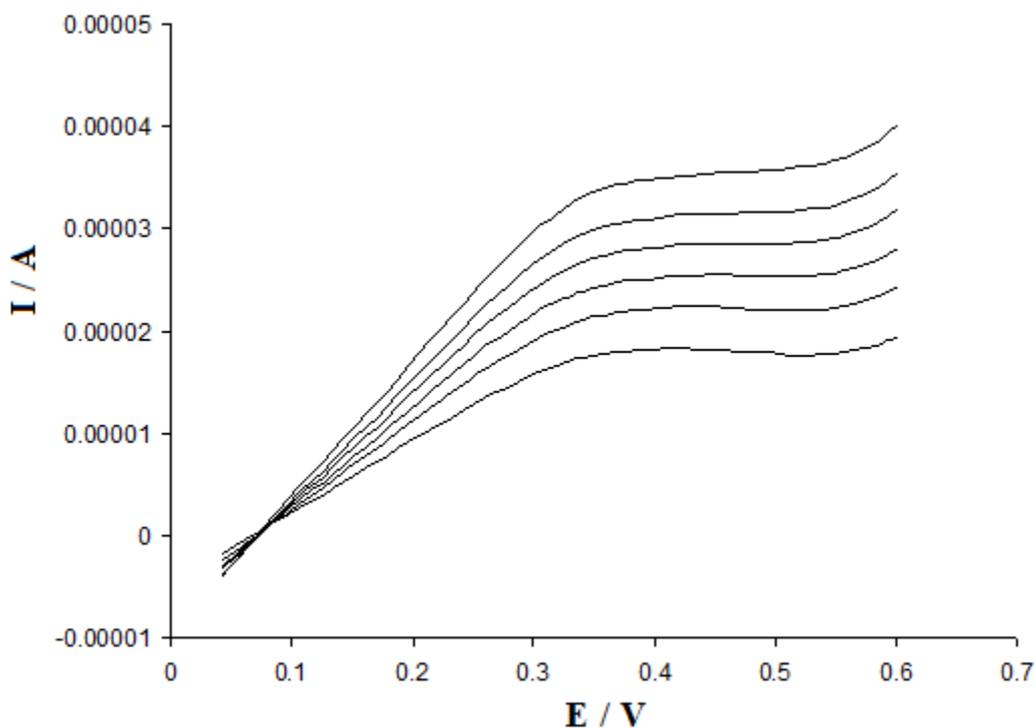
Fig. 2. LSVs of ILZNPE in 0.1 M PBS (pH 7.0) containing 200.0 μM bisphenol A at various scan rates; (10, 30, 50, 75, 100 and 150 mV s^{-1}).
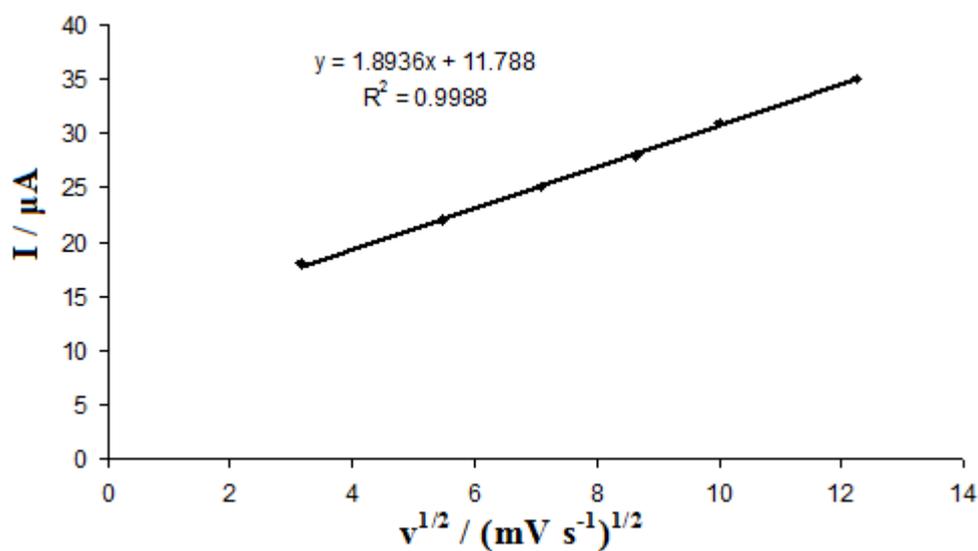

Fig. 3. Variation of anodic peak current *vs*. square root of scan rate from LSVs of Fig. 2.
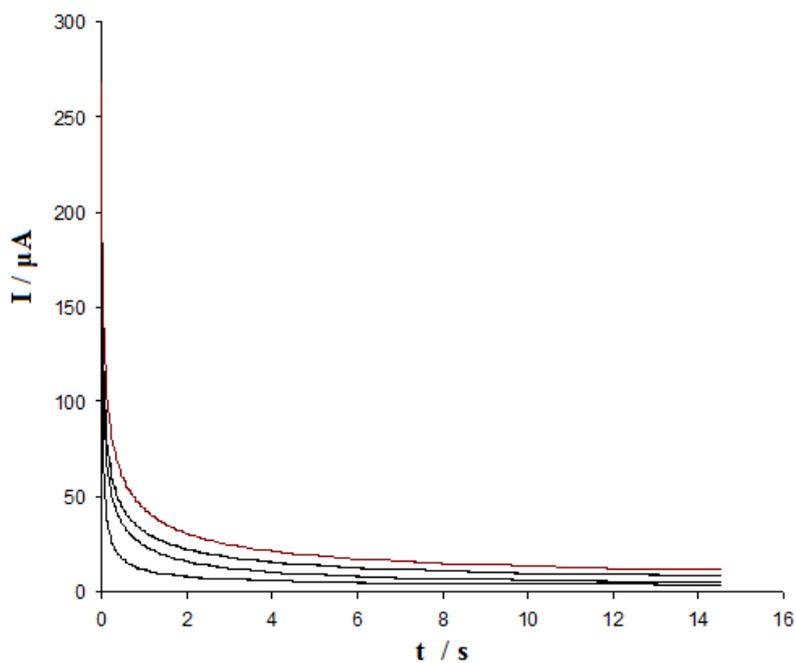
Fig. 4. Chronoamperograms obtained at ILZNPE in 0.1 M PBS (pH 7.0) for different concentration of bisphenol A. (0.1, 0.75, 1.0 and 1.5 mM of bisphenol A).
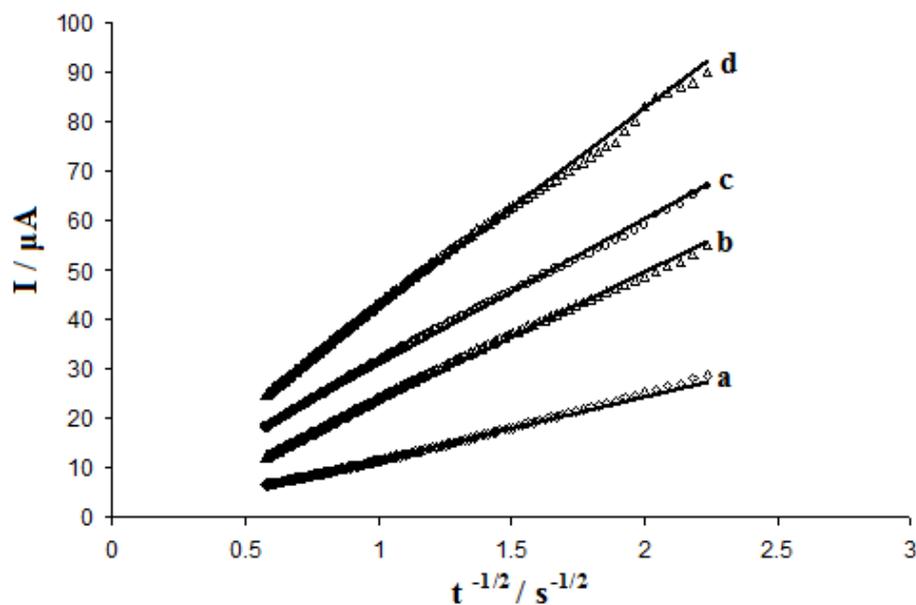

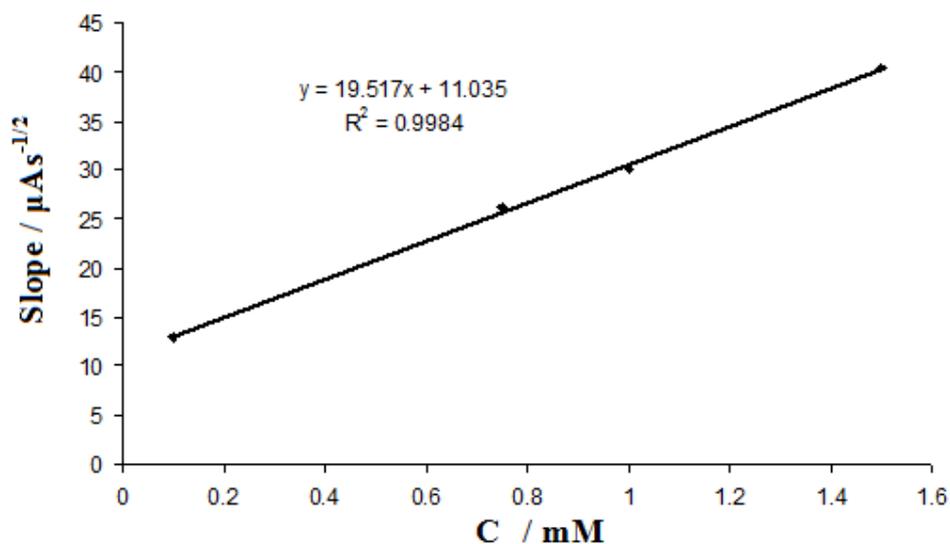**Fig. 5.** Plots of I vs. $t^{-1/2}$ obtained from chronoamperograms.

Fig. 6. Plot of the slope of the straight lines against bisphenol A concentration.
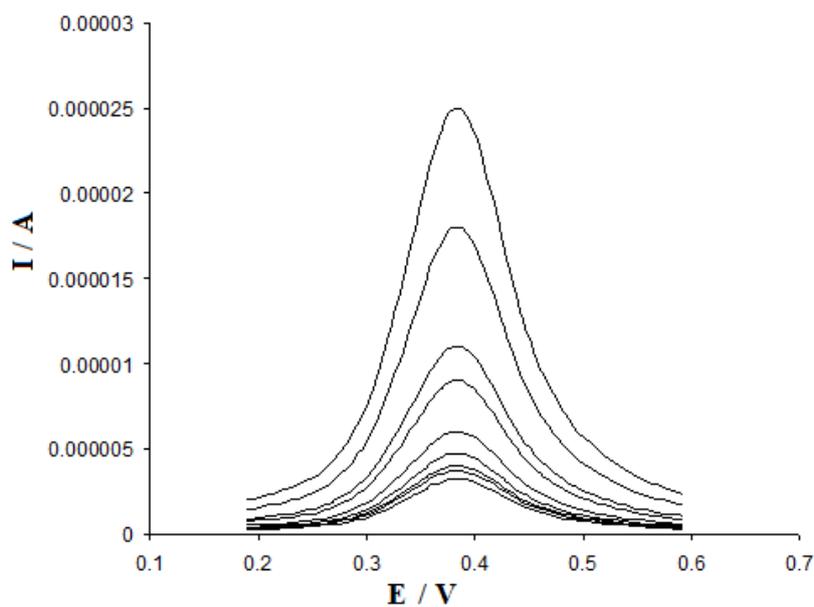

Fig. 7. SWVs of ILZNPE in 0.1 M PBS (pH 7.0) containing different concentrations of bisphenol A. (0.1, 1.0, 5.0, 10.0, 30.0, 70.0, 100.0, 200.0 and 300.0 µM of bisphenol A).
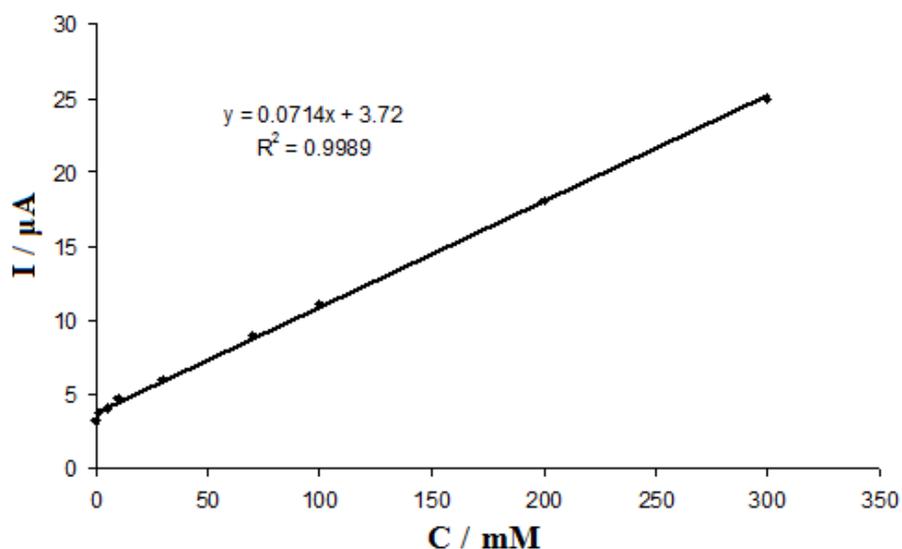
Fig. 8. Inset shows the plots of the peak current as a function of bisphenol A concentration in the range of 0.1-300.0 μM.

Table 1. Determination of bisphenol A in water samples. All the concentrations are in μM (n=5).

Sample	Spiked	Found	Recovery (%)	R.S.D. (%)
Drinking water	0	ND	-	**-**
	10.0	10.3	103.0	**3.3**
	20.0	19.8	99.0	**2.8**
	30.0	30.3	101.0	**2.9**
	40.0	38.9	97.2	**1.7**
River water	0	ND	-	**-**
	15.0	14.8	98.7	**1.9**
	25.0	25.5	102.0	**2.7**
	35.0	34.8	99.4	**2.4**
	45.0	45.5	101.1	**3.2**
Waste water	0	ND	-	**-**
	5.0	5.1	102.0	**2.9**
	15.0	14.7	98.0	**2.8**
	25.0	25.2	100.8	**3.1**
	35.0	**35.6**	**101.7**	**1.7**

CONCLUSION

Electrochemical behavior of bisphenol A was studied for the first time at the surface of a ZrO_2 nanoparticles/ionic liquid carbon paste electrode. The proposed modified electrode presented a low detection limit and good linear range and reproducibility which make it a suitable bisphenol A sensor for practical applications.

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