Fe₃O₄/GO nanocomposite modified glassy carbon electrode as a novel voltammetric sensor for determination of bisphenol A

Fariba Beigmoradi¹ and Hadi Beitollahi²,✉ A new voltammetric sensor is proposed for the determination of bisphenol A, using a glassy carbon electrode (GCE) modified with Fe₃O₄/graphene oxide (GO) nanocomposite. The modification of the electrode surface was performed by dispersion drop-casting. The electrochemical behavior of bisphenol A was evaluated by cyclic voltammetry (CV). The oxidation peak was observed during the anodic potential scan at potentials of 0.45 V. Higher anodic peak currents (Iₚa) were observed at Fe₃O₄/GO/GCE modified electrode than at bare GCE. The electrochemical determination by differential pulse voltammetry (DPV) revealed a linear response in the concentration range of 1.0×10⁻⁷ to 5.0×10⁻⁵ M, with a detection limit of 9.0×10⁻⁸ M. The proposed method was successfully applied using water samples, with good recoveries.

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Abstract
A new voltammetric sensor is proposed for the determination of bisphenol A, using a glassy carbon electrode (GCE) modified with Fe₃O₄/graphene oxide (GO) nanocomposite. The modification of the electrode surface was performed by dispersion drop-casting. The electrochemical behavior of bisphenol A was evaluated by cyclic voltammetry (CV). The oxidation peak was observed during the anodic potential scan at potentials of 0.45 V. Higher anodic peak currents (Iₚa) were observed at Fe₃O₄/GO/GCE modified electrode than at bare GCE. The electrochemical determination by differential pulse voltammetry (DPV) revealed a linear response in the concentration range of 1.0×10⁻⁷ to 5.0×10⁻⁵ M, with a detection limit of 9.0×10⁻⁸ M. The proposed method was successfully applied using water samples, with good recoveries.

Keywords
Modified electrode, water samples; differential pulse voltammetry; high repeatability

Introduction
Bisphenol A (BPA) is a polyphenol used in the production of polycarbonates and epoxy resins, and then it can be found in plastic packaging and canning coatings [1]. Because of its large-scale use and physicochemical properties, there is a risk of contamination of food or water by bisphenol migration from the packages. Bisphenol A shows estrogenic effects for humans, and it may increase...
the probability of developing prostate cancer and decrease fertility in animals, among other diseases [2]. As an emerging pollutant, threshold limits have not been established by environmental regulations. Still, bisphenol A was included as a future substance in the “list of 33 priority substances” in Annex II of the 2008/105/EC. Moreover, the European community has established a maximum daily intake of 0.05 mg kg$^{-1}$ of body weight [3-5]. Because of these health concerns, bisphenol A has been determined in urine, river, sea, and tap waters [6-8]. Thus, the development of a sensitive and selective method for the detection of bisphenol A is very important for both human health and environmental protection. Methods that have been used to monitor these analytes include electrochemical sensors, mass spectrometry (GC/MS) and high-performance liquid chromatography (HPLC) with detection by fluorescence or spectrophotometry (UV), or mass spectrometry (LC/MS or LC/MS/MS) [9-14].

Electrochemical methods have the advantages of being simpler and more sensitive, offering excellent repeatability and short analysis times, and are less expensive compared to traditional methods [15-31].

Glassy carbon (GC) is a type of non-graphitic carbon formed by the pyrolysis of certain polymeric precursors. The microstructure of GC is composed of discrete fragments of curved carbon planes, like imperfect fullerene-related nanoparticles. GC synthesized at high temperatures above 2000 °C exhibits a network of stacked graphite-like ribbon molecules. Entities of polyhedral graphite crystals were also detected in commercial glassy carbon, as used in our studies [32]. The network of randomly and tangled carbon planes forms a dense carbon structure. Due to the low reactivity, high hardness, impermeability and good electrical conductivity of GC, it is commonly employed as an electrode material for electroanalysis [33,34]. Due to the assumed chemical inertness, it is also often used as a substrate to cast powder catalysts in order to evaluate their catalytic performance in electrochemical reactions.

However, the response signal of conventional sensors toward analytes detection is quite weak, making it very difficult to achieve accurate measurements of analytes. Therefore, in order to improve the response signal of the analyte determination, electrochemical sensors are modified with various materials [35-47].

Nanomaterials have unique physicochemical properties, such as a large surface area to mass ratio, ultra-small size and high reactivity, which differ from bulk materials with the same composition. The unique property or desirable characteristics of nanomaterials decide its potential application in many fields [48-64].

Owing to its superior electronic, thermal and mechanical properties as well as chemical stability, graphene, as a well-defined, two-dimensional honeycomb structure of carbon materials, has been attracting more and more attention from both experimental and theoretical scientific communities [65,66]. Graphene and graphene oxide (GO) are potential nanoscale building blocks for new hybrid materials because of their layered structure and special surface properties [67-69]. It is believed that the composites of metal oxides and graphene would have better functionalities and performances in their applications. Among those hybrid materials, the ones with the magnetic nanoparticles (e.g., Fe$_3$O$_4$, Fe$_2$O$_3$) are an important class of materials due to their numerous applications in various technological fields [70]. Magnetite (Fe$_3$O$_4$) nanoparticles (NPs) have attracted worldwide research attention not only because of their unique size- and morphology-dependent physical and chemical properties but also for their potential applications in many fields, including magnetic storage, biosensors, communication materials, magnetic resonance imaging and as materials for microwave absorbing and shielding research [71-73].
According to the previous points, it is important to create suitable conditions for the analysis of bisphenol A in real samples. In this study, we describe the application of Fe₃O₄/GO nanocomposite as a nanostructure sensor for the voltammetric determination of bisphenol A. The proposed sensor showed a good electrocatalytic effect on bisphenol A. The modified electrode shows advantages in terms of reproducibility and sensitivity. Eventually, we evaluate the analytical performance of the suggested sensor for bisphenol A determination in water samples.

Experimental

Chemicals and apparatus

The electrochemical measurements were performed with an Autolab potentiostat/galvanostat (PGSTAT 302N, Eco Chemie, the Netherlands). The experimental conditions were controlled with General Purpose Electrochemical System (GPES) software. A conventional three electrodes cell was used at 25 ± 1 °C. An Ag/AgCl/KCl (3.0 M) electrode, a platinum wire, and the Fe₃O₄/GO/GCE were used as the reference, auxiliary and working electrodes, respectively. A Metrohm 710 pH meter was employed for pH measurements.

Bisphenol A and all other reagents were analytical grade and were purchased from Merck (Darmstadt, Germany). Phosphate buffer solution (PBS) was prepared with phosphoric acid and adjusted by NaOH to the desired pH value in the range of 2.0–9.0.

Preparation of the modified electrode

The bare glassy carbon electrode was coated with Fe₃O₄/GO nanocomposite according to the following simple procedure. 1 mg Fe₃O₄/GO nanocomposite was dispersed in 1 mL aqueous solution within 45 min ultrasonication. Then, 5 µl of the prepared suspension was dropped on the surface of carbon working electrodes. It remains at room temperature until it becomes dry.

The surface areas of the Fe₃O₄/GO/GCE and the unmodified electrode were obtained by CV using 1 mM K₃Fe(CN)₆ at various scan rates. Using Randles-Ševčík formula [74], in Fe₃O₄/GO/GCE, the electrode surface was found 0.13 cm² which was approximately 4.1 times greater than the unmodified electrode.

Result and discussion

Electrochemical profile of the bisphenol A on the Fe₃O₄/GO/GCE

To study the electrochemical behaviour of bisphenol A which is pH-dependent, it is necessary to obtain the optimized pH value to achieve accurate results. By performing the experiments using modified electrodes at various pH values ranging from 2.0–9.0, it was revealed that the best results for electrooxidation of bisphenol A occur at pH 7.0. Scheme 1 demonstrates the electrooxidation process of bisphenol A.
The obtained cyclic voltammograms in the presence of 30.0 μM bisphenol A using the Fe₃O₄/GO/GCE (trace a) and unmodified GCE (trace b) are shown in Figure 1. According to CV results, the oxidation current peak of bisphenol A on the Fe₃O₄/GO/GCE appears at 450 mV, which is about 150 mV more negative compared with unmodified GCE.

**Effect of scan rate on the results**

Increasing scan rate leads to enhanced oxidation peak current according to the obtained results from the study of the effect of potential scan rates on the oxidation currents of bisphenol A, Figure 2. In addition, there is a linear relationship between $I_p$ and the square root of the potential scan rate ($\nu^{1/2}$), demonstrating the diffusion control of analyte oxidation.
Figure 2. LSVs of Fe₃O₄/GO/GCE in 0.1 M PBS (pH 7.0) containing 15.0 μM bisphenol A at various scan rates; numbers 1-8 correspond to 10, 20, 40, 60, 80, 100, 200 and 300 mV s⁻¹. Inset: Variation of Ipa vs. νⁱ/₂

Chronoamperometric analysis

The chronoamperometry analysis for bisphenol A samples was performed using of Fe₃O₄/GO/GCE vs. Ag/AgCl/KCl (3.0 M) at 0.5 V. The results of different concentrations of bisphenol A sample in PBS (pH 7.0) are demonstrated in Figure 3.

Figure 3. Chronoamperograms obtained at Fe₃O₄/GO/GCE in 0.1 M PBS (pH 7.0) for different concentrations of bisphenol A. The numbers 1-4 correspond to 0.1, 0.5, 1.5 and 3.0 mM. (A) Plots of I vs. t⁻¹/₂ obtained from chronoamperograms 1-4. (B) Plot of the slope of the straight lines against bisphenol A concentration

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According to the Cotrell equation (equation 1) [68], experimental results of $I$ vs. $t^{-1/2}$ were plotted in Figure 3A, with the best fits for different concentrations of bisphenol A. The resulting slopes corresponding to straight lines in Figure 3A were then plotted against the concentration of bisphenol A (Figure 3B). The mean value of $D$ was determined to be $4.6 \times 10^{-5}$ cm$^2$ s$^{-1}$.

$$I = nFAD^{1/2}C_0\pi^{1/2}t^{-1/2}$$

(1)

**Calibration curves**

Based on the resulting peak currents of bisphenol A using Fe$_3$O$_4$/GO/GCE, the quantitative analysis of bisphenol A was done in water solutions. The modified electrode (Fe$_3$O$_4$/GO/GCE) as a working electrode in the range of bisphenol A concentration in 0.1 M PBS was used in DPV due to the advantages of DPV, including the improved sensitivity and better performance in analytical applications (Figure 4). According to the results, a linear relationship exists between the peak currents and concentrations of bisphenol A within the concentration range of 0.1-50.0 µM with a correlation coefficient of 0.999. The limit of detection, $C_m$, of bisphenol A was calculated using equation (2):

$$C_m = 3S_b/m$$

(2)

where, $m$ is the slope of the calibration plot (0.1508 µA µM$^{-1}$) and $S_b$ is the standard deviation of the blank response obtained from 15 replicate measurements of the blank solution. The detection limit for determination of bisphenol A using this method 0.09 µM was obtained.

![Figure 4. DPVs of Fe$_3$O$_4$/GO/GCE in 0.1 M PBS (pH 7.0) containing different concentrations of bisphenol A. Numbers 1–9 correspond to 0.1, 0.5, 1.0, 5.0, 10.0, 20.0, 30.0, 40.0 and 50.0 µM. Inset: Plot of $I$ vs. bisphenol A concentrations. In all cases the scan rate was 50 mV s$^{-1}$. Step potential 0.01 V and pulse amplitude 0.025 V](image)

Also, Table 1. shows a comparison of the analytical features of merit of the proposed electrochemical method with a different reported modifier for the determination of bisphenol A [75-79].

<table>
<thead>
<tr>
<th>Modifier</th>
<th>LOD, nM</th>
<th>LDR, µM</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Multiwalled carbon nanotube and gold nanoparticle</td>
<td>4.0</td>
<td>0.01-0.7</td>
<td>75</td>
</tr>
<tr>
<td>Reduced graphene oxide-silver/poly-l-lysine nanocomposites</td>
<td>540</td>
<td>1.0-80.0</td>
<td>76</td>
</tr>
<tr>
<td>Graphene oxide and cuprous oxide nanocomposite</td>
<td>53</td>
<td>0.1-80.0</td>
<td>77</td>
</tr>
</tbody>
</table>
Reduced graphene oxide-multi-walled carbon nanotubes 1 0.005-20.0 [78]
AuPd nanoparticles-loaded graphene nanosheets 8.0 nM 0.5-10.0 [79]
Fe₃O₄/GO nanocomposite 90 0.1-50.0 This work

**Analysis of real samples**

The applicability of this modified electrode in the determination of real samples was assessed through the determination of bisphenol A in water samples using the described method. In order to perform this analysis, the standard addition method was employed and the results are listed in Table 2.

**Table 2. The application of Fe₃O₄/GO/GCE for the determination of bisphenol A in water samples (n = 5)**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Spiked / µM</th>
<th>Found / µM</th>
<th>Recovery, %</th>
<th>RSD, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Well water</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7.5</td>
<td>7.6</td>
<td>101.3</td>
<td>1.7</td>
<td></td>
</tr>
<tr>
<td>12.5</td>
<td>12.4</td>
<td>99.2</td>
<td>2.2</td>
<td></td>
</tr>
<tr>
<td>17.5</td>
<td>17.3</td>
<td>98.9</td>
<td>3.1</td>
<td></td>
</tr>
<tr>
<td>22.5</td>
<td>23.1</td>
<td>102.7</td>
<td>2.9</td>
<td></td>
</tr>
<tr>
<td>River water</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10.0</td>
<td>9.9</td>
<td>99.0</td>
<td>2.5</td>
<td></td>
</tr>
<tr>
<td>15.0</td>
<td>15.3</td>
<td>102.0</td>
<td>3.1</td>
<td></td>
</tr>
<tr>
<td>20.0</td>
<td>19.5</td>
<td>97.5</td>
<td>3.2</td>
<td></td>
</tr>
<tr>
<td>25.0</td>
<td>25.9</td>
<td>103.6</td>
<td>1.9</td>
<td></td>
</tr>
</tbody>
</table>

Accordingly, the results of bisphenol A recovery are satisfactory and the reproducibility of the results is proved by the mean relative standard deviation (RSD).

**Conclusions**

The Fe₃O₄/GO/GCE sensor showed excellent performance in the determination of bisphenol A, offering an alternative analytical technique that is reliable, effective, and inexpensive. Modifying the electrode surface with Fe₃O₄/GO nanocomposite resulted in the combination of a large surface area and high conductivity, providing high catalytic activity, highly reproducible and repeatable electrochemical measurements, and satisfactory results in the analysis of water matrices, with recoveries close to 100 %. The detection limit for bisphenol A using Fe₃O₄/GO/GCE, 0.09 µM was obtained.

**References**


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