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Selective electrochemical sensor for bisphenol A quantification on carbon electrodes modified with graphitic mesoporous carbon

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Abstract

Owing to the unique electronic properties, high electrical conductivity, and high adsorption capacity of graphitic mesoporous carbon (GMC), a simple strategy was developed to alter the surface of glassy carbon electrodes with a thin layer of GMC. These modified electrodes were applied to detect bisphenol A (BPA) in wastewater samples due to the strong attraction between the GMC-modified surface and BPA. Electrochemical BPA sensing processes were evaluated using different electrochemical techniques, such as differential pulse voltammetry and cyclic voltammetry. For all electrochemical experiments, a distinguished anodic peak at ~ 0.55 V was observed, which was attributed to the enhanced electrochemical BPA oxidation on the surface of the GMC-modified electrode. In addition, the influence of scan rate and electrolyte pH on the electrochemical oxidation of BPA were studied in detail. The electrochemical sensor exhibited a reliable quantification of BPA in a wide range of BPA concentrations (i.e., 20 – 300 μM) and pH (i.e., 5.5 – 8.9) with a sensitivity of 2.93 μA μM^{-1} cm^{-2} and a detection limit of 59 nM. Finally, the pre-determined parameters were applied for the quantification of BPA in secondary-treated sewage. The results showed that the developed electrochemical sensor exhibited high BPA recovery in the range of 98.13 – 100.36 %. In summary, the developed electrochemical sensor showed satisfactory reproducibility and sensitivity for accurate BPA detection even in complex matrices, such as sewage.

Keywords: Electrochemical sensor; Bisphenol A; Graphitic mesoporous carbon; Glassy carbon electrode; Differential pulse voltammetry; Sewage

1. Introduction

Although conventional domestic wastewater treatment plants (WWTPs), such as activated sludge process, are efficient at removing the majority of biodegradable organics, suspended solids, and nutrients, they do not have the capability to efficiently remove recalcitrant pollutants, which are not easily biodegradable and are toxic to microorganisms [1,2]. Recalcitrant pollutants, which are a wide group of contaminants of emerging concern, such as pharmaceuticals, endocrine disruptors, chlorinated compounds, polycyclic aromatic hydrocarbons, and antibiotics, remain biologically active and possess a harmful influence on the environment even at trace concentrations [3]. Bisphenol A (BPA) is one of the extensively used chemicals in several industries with estrogenic potency, resulting in its leaching into the environment, including water, air, soil, and human tissues, which causes severe diseases and hazards (such as carcinogenicity, brain-function disorders, and obesity prevalence) [2, 4-8]. Owing to its hydrophobic nature and low sorption potential, BPA is commonly detected in the treated effluent of WWTPs and sewage sludge [9-11].

Although different tools, such as gas chromatography (GC) [14], high-performance liquid chromatography (HPLC) [15], gas chromatography-mass spectrometry [16], and liquid chromatography-mass spectrometry [17], have been extensively used to detect BPA with high sensitivity and selectivity, these analytical tools require sophisticated instrumentation, high cost and long time associated with its use, and highly-skilled personals. Recently, electrochemical sensors have been emerged as an alternative option to replace the commonly-used instrumental technologies for the quantification of several organic contaminants, including BPA, owing to their simplicity, fast and accurate response, and relatively low cost [18-20]. Despite the advantages of using bare carbon electrodes,

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such as glassy carbon electrodes, to detect BPA, it requires high overpotential to directly oxidize BPA on the electrode surface, resulting in low sensitivity and selectivity [21]. Recently, there are different strategies to alter the surface of carbon electrodes by coating them with bimetallic cobalt–iron diselenide nanorod [22], carbon black [23], Poly(4-amino-3-hydroxynaphthalene-1-sulfonic acid) [24], BaO nanorods [25], flavin adenine dinucleotide/poly(3,4-ethylenedioxythiophene) (PEDOT) [26], and layered double hydroxide and anionic surfactant [27] for sensitive detection of organic compounds, including BPA. Although electrode modification methods significantly improved the detection sensitivity and selectivity, these methods usually require long-time and sophisticated procedures.

Owing to its high electrical conductivity, large surface area, and high corrosion resistance, graphitic mesoporous carbon (GMC), which has mono-dispersed mesopores with pore size greater than 2 nm, has been recently used in different applications, such as direct methanol fuel cells and microbial fuel cells [28,29]. In addition, high-quality mesoporous carbon materials have the capability of allowing faster mass transport and high accessibility of electrochemically-active substances within their pores compared to other carbon materials with micropores, such as activated carbons [28]. These features make GMC a suitable candidate for the improvement of BPA oxidation, resulting in the highly selective and sensitive detection of BPA.

The present work described a simple deposition method of GMC film on the glassy-carbon electrodes (GCE) and evaluated the feasibility of employing the modified GCE for selective, accurate quantification of BPA. The electrochemical detection of BPA was evaluated by cyclic voltammetry and differential pulse voltammetry by studying the influence of pH and substrate concentration on the sensitivity of the electrochemical sensors as well as its detection limit and selectivity. Finally, the chronoamperometric technique, CV, and DPV were used to detect BPA using real wastewater.

2. Experimental

2.1. Chemicals

All chemicals were of analytical grade and obtained from Sigma Aldrich (Steinheim, Germany). They were used without purification except for GMC, which was treated in an acid bath containing 8 M sulfuric acid (H_2SO_4) and 8 M nitric acid (HNO_3) (1:1 *v:v*) for 4 hours. Following this pre-treatment step, GMC was filtered, washed with DI water, and, dried at 80 °C for 16 h.

2.2. Preparation of electrochemical sensor

Before depositing GMC on the GCE surface, GCE (electroactive surface area = 0.196 cm^2) was polished with alumina powder on a polishing pad and washed with deionized water. The GMC ink solution was prepared by mixing 8 mg of GMC in 0.5 mL of 0.5 % Nafion solution, 1 mL ethanol, and 0.5 mL deionized water, and then ultrasonicated for 20 min to obtain a homogeneous ink. Finally, a thin layer of GMC ink solution (i.e., 8 μL) was drop-casted on the GCE and left to dry at room temperature for 16 hours.

2.3 Electrochemical Measurement of BPA

Electrochemical analyses were performed in triplicate by performing cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), differential pulse voltammetry (DPV), and chronoamperometry in 0.1 M phosphate buffer electrolyte (PBS) at room temperature (24 ± 2 °C) using a VSP electrochemical workstation (Bio-Logic, Clarix, France). Typically, either the bare GCE or GMC-modified GCE was used as a working electrode. An Ag/AgCl electrode and a Pt wire were used as reference and counter electrodes, respectively. Potential values were reported versus the standard hydrogen electrode (SHE) unless otherwise stated.

The electrochemical quantification of BPA in real secondary-treated sewage samples, which were collected from the Zenin wastewater treatment plant (WWTP) (Cairo, Egypt), were analyzed by chronoamperometric technique as well as DPV by spiking BPA standard solutions in order to obtain the desired BPA concentration of 300 μM. BPA concentration was also quantified using a UV-Vis spectrophotometer (Labomed Inc., Los Angeles, CA, USA).

3. Results and discussion

3.1. Electrochemical properties of GMC-modified GCE

The electrochemical properties of the modified GCE were evaluated by performing CV in 10 mM $[Fe(CN)_6]^{3-/4-}$ solution at a scan rate of 25 mV sec^{-1} (Figure 1a). The bare GCE exhibited a very low current production with no-redox peaks, indicating a sluggish electron transfer process and irreversible electrochemical reactions. However, the GMC-modified GCE had pronounced oxidation and reduction peaks at ~ + 0.424 V and – 0.323 V, respectively, with a peak separation of 101 mV, implying an enhanced electron transfer process and quasi-reversible electrochemical reactions [30]. This improvement in the electrochemical response was most likely due to the unique electronic properties and high electrical conductivity of GMC [28]. EIS was also used to characterize the electrochemical response of GMC-modified GCE within a frequency range of 0.1 – 10,000 Hz and data was fitted by as a Randles equivalent circuit (Figure 1b) [31]. The R_{ct} for the bare GCE was 446 Ω, a value 1.42-fold higher than the GMC-modified GCE (i.e., 313 Ω), implying that the GCE modification with GMC enhanced the electron transfer process.

In addition, the electrochemical active surface area (A) of the bare GCE as well as the GMC-modified GCE were estimated according to the Anson relationship [32]:

$$Q\ (t) = 2\,n\,F\,A\,C\,D^{\frac{1}{2}}\pi^{-\frac{1}{2}}\,t^{\frac{1}{2}} + Q_{dl} + Q_{ads} \qquad (1)$$

where Q is the charge transferred (C), n is the number of electrons involved in the reaction, F is the Faraday constant (96,485 C mol−1), C is the electrolyte concentration, t is time (s), D is diffusion coefficient (i.e., 7.6×10^{-6} cm^{2} s^{-1}) [33], Q_{dl} is the double-layer charge, and Q_{ads} is the Faradic charge.

Figure 1c represents the linear relationship between Q versus the square root of time ($t^{1/2}$). The electrochemical active surface area was estimated to be 0.012 and 0.023 cm^{2} for the bare GCE and the GMC-modified GCE, respectively, indicating that the electrochemical active surface area was almost doubled after modifying the surface of GCE with GMC. Consequently, the increase in the electroactive surface area would improve the BPA adsorption capacity, mainly due to the strong interaction between BPA and GMC, resulting in a much better electrochemical response and sensitivity of the electrochemical sensor for BPA detection.

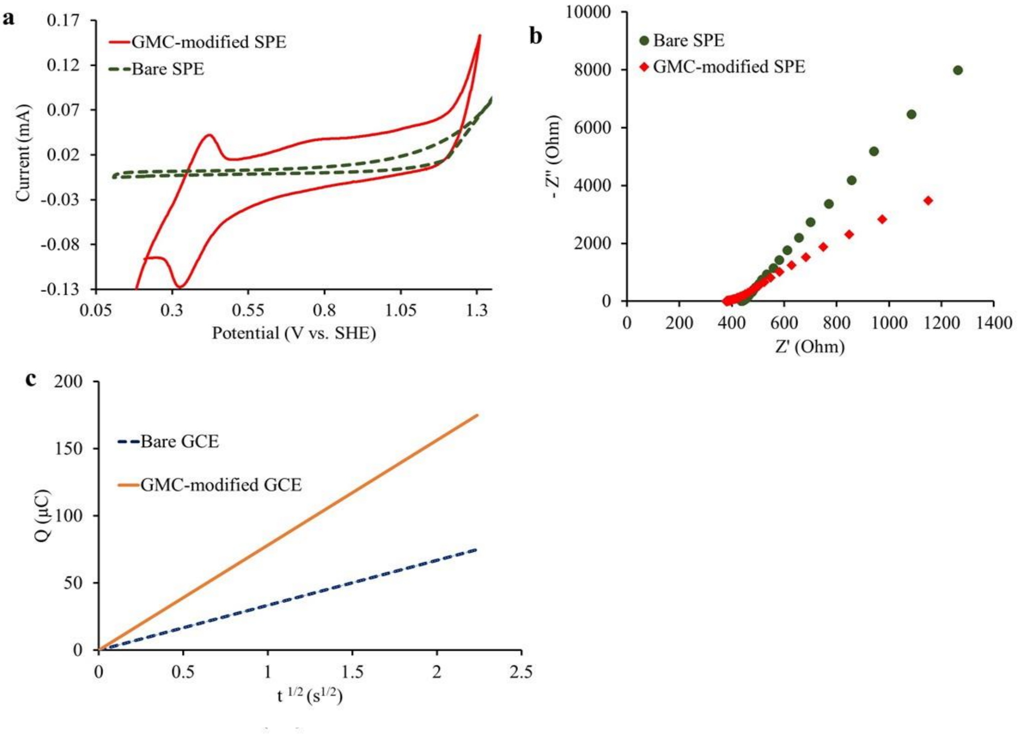

Figure 1. (a) CV, (b) EIS, and (c) the Anson plot of bare and GMC-modified GCEs in 10 mM $[Fe(CN)_6]^{3-/4-}$ electrolyte. The inset in Figure 1a shows the Randles equivalent circuit.

3.2. CV response of BPA

Figure 2a displays the CV plots of GMC-modified and bare GCE in 0.1 M PBS (pH = 7.2) containing 300 µM BPA. Compared to the bare GCE, the modified GCE had a distinguished oxidation peak at approximately 0.55 V, suggesting that the BPA electrochemical oxidation is mainly an irreversible electrochemical process. Owing to the high electroactive surface area and conductivity as well as the existence of oxygen-containing functional groups on the GMC surface are most likely the main reason for enhancing the direct interaction of BPA with GCE, resulting in efficient electrocatalytic BPA oxidation [31,34].

Figure 2b shows that CV plots of GMC-modified and bare GCE in the presence of BPA at different scan rates (v). The results revealed that the electrochemical response was enhanced as the scan rate increased within the tested range (i.e., 25 to 250 mV s^{-1}). Within the scan rates used in this study, the peak current was linearly increased with $v^{½}$ with a high R^2 value of 0.9765 (Figure 2c), indicating that BPA oxidation on the GMC-modified GCE is an ideal diffusion-controlled electrochemical process. Furthermore, the CV analysis was used to evaluate the electrochemical kinetics and the number of electrons transferred during the electrochemical oxidation of BPA from the Laviron relationship, which represents a relationship between the natural logarithm of *v* and the oxidation potential peak (E_{pa}) as follows:

$$E_{pa} = E^0 + \left(\frac{RT}{\alpha nF}\right) \ln\left(\frac{RTk^0}{\alpha nF}\right) + \left(\frac{RT}{\alpha nF}\right) \ln v \qquad (2)$$

where E^0 is the formal potential (V), R is the gas constant (8.314 J K^{-1} mol^{-1}), T is the absolute temperature (K), α is the transfer coefficient (= 0.5 for irreversible electrochemical reactions [35]), and k^0 is the reaction rate constant.

As shown in Figure 2d, the oxidation peak potential had a linear relationship with ln *v* (R^2 = 0.9481) with the number of electrons involved in the BPA oxidation of approximately 2. Therefore, the BPA electrochemical oxidation on the GMC-modified GCE proceeded via 2-electron and 2-proton process (Figure 2e).

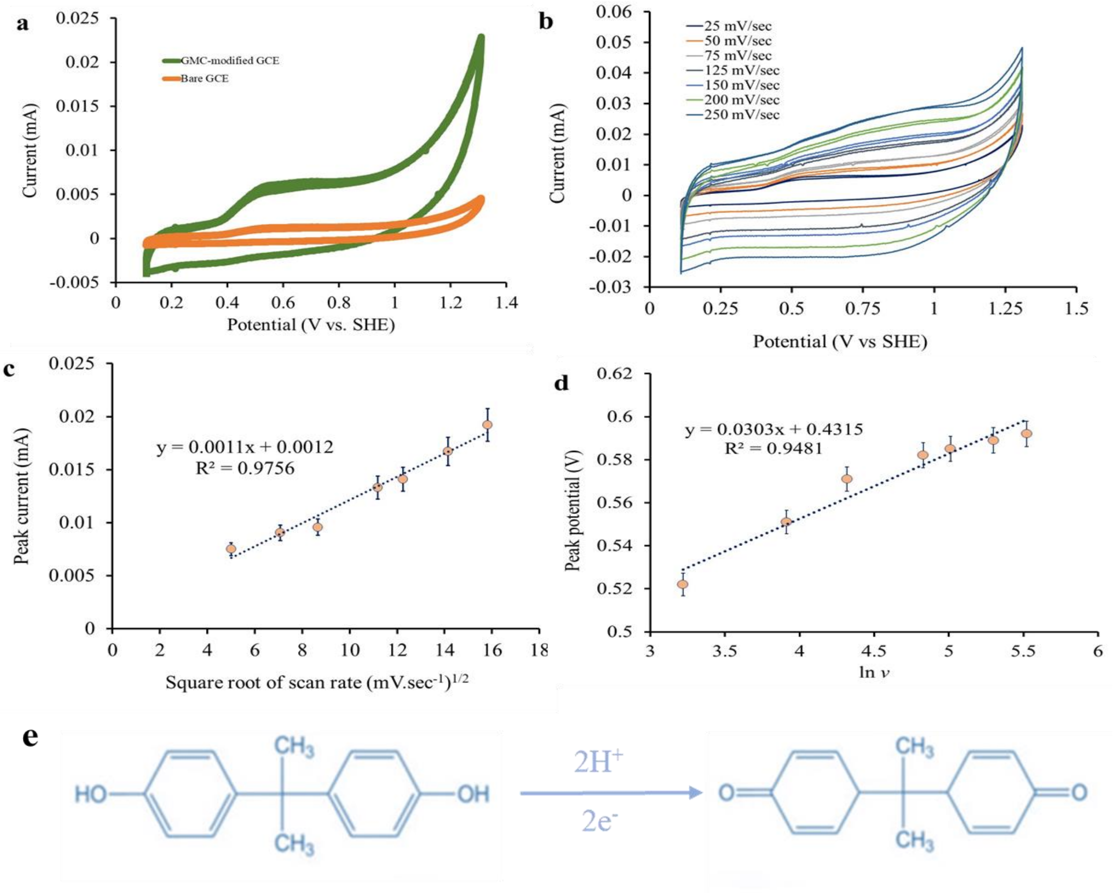

Figure 2. (a) CV plots of bare and GMC-modified GCE in 100 mM PBS containing 300 µM BPA at a scan rate of 25 mV s^{-1}, (b) CV plots of the GMC-modified GCE in the presence of BPA (300 µM) at different scan, (c) relationship between the square root of *v* versus peak current, (d) relationship between ln *v* versus peak potential, and (e) the proposed mechanism of BPA oxidation.

3.3. Effect of pH

The influence of pH on the electrochemical response of GMC-modified GCE towards BPA oxidation was evaluated by altering the electrolyte pH in the range of 5.5 – 8.9 (Figure 3a). The results show that the peak current significantly increased as the electrolyte pH increased from 5.5 to 7.2. Further increase in the BPA electrolyte pH resulted in a sharp decline in the peak current, confirming that protons actively participated in the electrochemical oxidation of BPA [36]. A possible reason for reaching the highest current value at pH = 7.2, which is much lower than the pKa of BPA of 9.73, is that the non-protonated BPA has much better adsorption on the GCE surface compared to its protonated forms, resulting in higher sensitivity and selectivity of the electrochemical sensor at near-neutral pH, which was selected in the subsequent experiments. Figure 3b shows the relationship between the oxidation Epa and the BPA solution pH. Within the selected pH values, the oxidation E_{pa} was inversely proportional to the electrolyte pH with a plot slope of 62 mV, a value close to the theoretical value of 57.6 mV per pH according to the Nernst equation, implying that an equal number of electrons and protons are transferred during the electrochemical oxidation of BPA, which is in agreement with the proposed mechanism shown in Figure 2e [37].

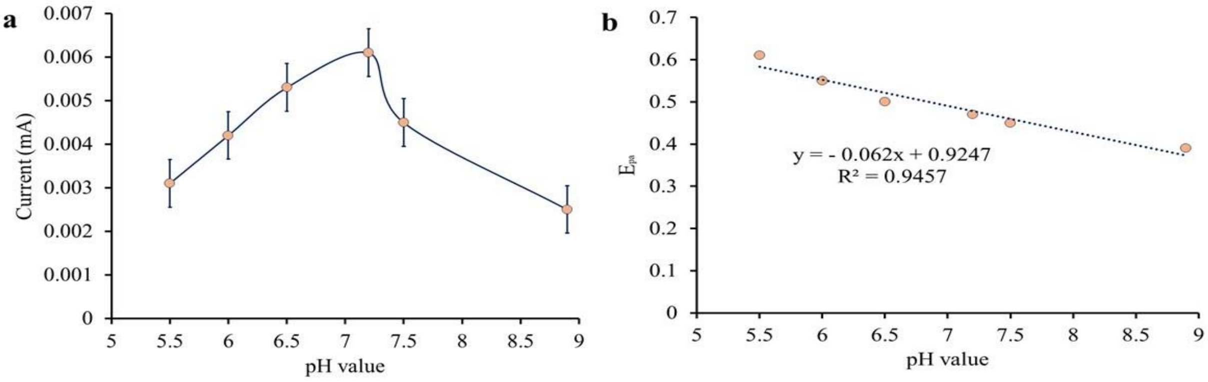

Figure 3. The influence of the electrolyte pH on (a) BPA oxidation peak current and (b) BPA oxidation peak potential.

3.4. Determination of BPA by differential pulse voltammetry

Owing to the higher sensitivity and selectivity of the DPV technique compared to CV, it was used to quantitatively analyzed BPA with different initial concentrations (i.e., 20 to 300 µM). DPV responses were recorded using the following parameters: pH = 7.2; amplitude = 50 mV; v = 25 mV s^{-1}; pulse width = 200 ms; and pulse period = 500 ms. The DPV plots exhibited a distinguished anodic peak for BPA oxidation at about 0.57 V, which its peak current significantly increased as a response to increasing the initial BPA from 0 to 300 µM (data not shown). Figure 4 shows the calibration plot between the peak current (I_p) and the BPA concentration (C), which could be represented by the following equation: $I_p = 7 \times 10^{-5} C + 0.017$ ($R^2 = 0.9587$) with a sensitivity of 2.93 µA μM^{-1} cm^{-2}, which is consistent with previous studies [38 – 40]. In addition, the detection limit was estimated to be 59 nM with high reproducibility and reliability. The GMC-modified GCE exhibited a relative standard deviation (RSD) of 2.25 ± 0.12 %, indicating that electrochemical detection of BPA using the modified GCE is highly reproducible.

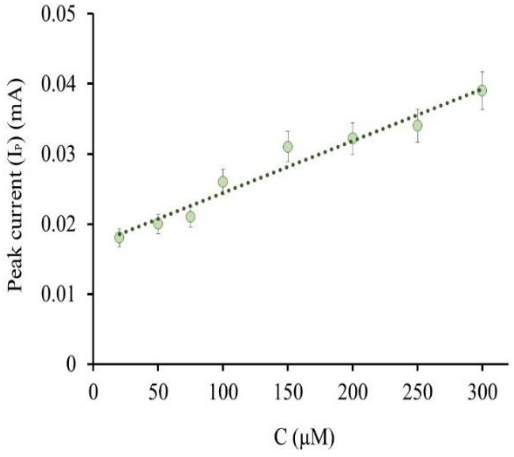

Figure 4. The Calibration plot of GMC-modified GCE in PBS containing different initial BPA concentrations.

3.5. Selectivity and stability of GMC-modified electrochemical sensor for BPA quantification in complex matrices

The selectivity of GMC-modified GCE was evaluated by performing DPV in PBS electrolyte containing BPA as well as different concentrations of interfering substances (i.e., phenol, hydroquinone, and glucose), and the current response was converted to the corresponding BPA concentration using the developed calibration curve. The results revealed that BPA quantification was significantly unaffected as evidenced by having less than 5% change in the peak current values, implying that the developed electrochemical sensor had high tolerance limit towards BPA detection in the presence of interfering compounds. In addition, the developed electrochemical sensor exhibited long-term stability for BPA detection. The peak current was only reduced by less than 14% over 30 days of operation.

The pre-determined parameters were used for the quantification of BPA in secondary-treated sewage that was collected from the Zenin WWTP (Cairo, Egypt). Interestingly, sewage samples did not exhibit any response signal using chronoamperometric and DPV techniques. Sewage samples were spiked with BPA standard solution to reach different final BPA concentrations and used chronoamperometric and DPV techniques to detect BPA in sewage samples. Table 1 shows the results of a standard addition method to evaluate the electrochemical sensor efficiency. The electrochemical sensor exhibited high BPA recovery in the range of 98.13 – 100.36 % in this complex matrix, indicating the feasibility of using the developed electrochemical sensor for accurate BPA detection even in complex matrices, such as sewage.

Table 1. Electrochemical determination of BPA in treated sewage samples (n = 4)

Sample	Spiked BPA (μM)	Detected BPA (μM)	Recovery (%)	RSD (%)
1	0	-	-	-
2	10	9.85	98.5	2.91
3	30	29.44	98.13	2.66
4	40	40.59	101.48	1.98
5	50	50.68	101.36	3.21

4. Conclusions

In this study, a disposable, simple electrochemical sensor was developed for the quantification of BPA. The development of the electrochemical sensor was carried out by depositing a thin layer of GMC on the GCE surface via a cost-effective, environmental-friendly approach. The electrochemical properties of the GMC-modified GCE revealed a successful deposition of GMC on the surface of GCE as evidenced by increasing the electrochemical active surface area, decreasing the interfacial resistance, and enhancing the electron transfer process. BPA electrochemical sensing processes, based on DPV, CV, and chronoamperometry, revealed satisfactory efficiency of GMC-modified electrochemical sensor, in terms of sensitivity, linearity, selectivity, detection limit, and reproducibility, Under the optimal parameters, the GMC-modified electrochemical sensor was used to highly-selective quantification of BPA in secondary-treated sewage samples with a high recovery of 98.13 – 100.36 %. Therefore, the GMC-modified electrochemical sensor can be efficiently used as an efficient portable device for cost-effective, rapid, and sensitive quantification of BPA content in different environmental samples, such as sewage.

Conflicts of interest

There are no conflicts to declare.

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