Ultrasound assisted magnetic imprinted polymer combined sensor based on carbon black and gold nanoparticles for selective and sensitive electrochemical detection of Bisphenol A

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A B S T R A C T

Sample preparation is considered as one of the most interesting applications of magnetic molecularly imprinted polymer (MagMIP) used as adsorbents for various compounds prior to their determination using the developed analytical techniques. In this context, we present in this paper a developed Ultrasound-assisted magnetic molecularly imprinted polymer (US-MagMIP) combined to an electrochemical sensor modified with a nano-composite of carbon black nanoparticles (CBNPs), and Gold nanoparticles (AuNPs) for highly selective and sensitive detection of Bisphenol A (BPA). The electrochemical characterization of the developed sensor was investigated by electrochemical impedance spectroscopy and cyclic voltammetry. Various parameters were optimized such as the effect of voltammetric mode, the effect of pH, the amount of US-MagMIP and the rebinding time. The electrochemical sensor exhibits a high sensitivity for BPA with a LOD of 8.8 nM with a wide linear range from 0.07 µM to 10 µM. Moreover, this sensor provides a high selectivity towards various likely interferents by combination with US-MagMIP prior to analysis. The developed analytical approach was applied successfully for determination of BPA in Tap and mineral water samples.

1. Introduction

Bisphenol A (BPA) is an important raw material, owing to its wide use as a monomer in the synthesis of polycarbonate (PC) and epoxy resins, along with others applications such a variety of common products including baby and water bottles, dental fillings, and the lining of food cans [1,2]. A large number of researchers have shown that BPA can be considered as an endocrine-disrupting chemical and has been implicated in a wide variety of adverse health outcomes in humans and possible toxic for environment [3,4]. It is also found that BPA could postulate to cause reproductive disorders including, result in neural and behavioural changes in infants and children, diabetes, hyperactivity, obesity and various kinds of cancers, such as breast, prostate and testicular cancer [5,6]. Therefore, the development of an easy, reliable, selective and sensitive analytical methods for the detection of BPA has become an essential issue in environmental monitoring.

A variety of analytical methods used for the determination of BPA have been developed including high performance liquid chromatography (HPLC) [7], fluorimetry [8,9], gas chromatography [10],

enzyme-linked immunosorbent assay (ELISA) [11], flow injection chemiluminescence [12] and HPLC-mass spectrometry (HPLC-MS) [13]. Although, these techniques are highly sensitive and accurate, but some of the factors such as expensive instrumentation, need for trained technicians and extraction steps, have restricted their application. Recently, the electrochemical methods have boomed in convenient and effective detection of trace BPA with high sensitivity, simple operation and portability. It can be noticed in the last decade that developing and applying of electrochemical methods for BPA become very attractive for researchers. The modification of the surface of such sensors with nanomaterials can improve the sensitivity of the electrode [14–16].

Carbon black nanoparticles (CBNPs) gained more attention as a powerful nanomaterial because of their significantly widespread availability, high surface area-to-volume ratios and a large number of defect sites. It is cheaper than other carbon materials, such as carbon nanotubes and graphene, and has opened up new horizons for the development of electrochemical sensors with low-cost and excellent electroanalytical performances [17,18,14]. Besides of the direct use of CBNPs modified electrodes, they can also be used as a support for the

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preparation of other nanostructures. Indeed, Arduini et al [16] described the use of AuNPs onto a CBNPs layer which showed an elctrocatalytic effect on the redox processes of glucose, hydrogen peroxide and ascorbic acid. A similar approach was proposed by Hou et al. [19], using ferroferric oxide nanoparticles deposited on the CBNPs surface which demonstrated a high electrocatalytic activity toward the oxidation of BPA.

Gold nanoparticles (AuNPs) represent a high conductivity, good biological compatibility, catalytic/electrocatalytic properties and high surface-to-volume ratio. It is an excellent nanoplatform for the fabrication of novel (bio) sensors [20–22]. AuNPs has been used for electrode modification for BPA determination: molybdenum disulfide nanoflower-chitosan-AuNPs composites [23], poly(amidomine)-AuNPs-silk fibroin [24] and AuNPs onto the surface of glassy carbon electrode modified multiwalled carbon nanotubes (MWCNTs) [15].

However, the direct determination using electrochemical methods suffer from several problems among them, non-specific-binding and poor regeneration. Fortunately, there is various highly selective sensing materials that can overcome these problems. Molecularly imprinted polymers (MIPs) are one of these ideal sensing materials. Therefore, it is necessary to develop a separation/pre-concentration step.

MIPs are defined as synthetic materials that can mimic the molecular recognition by antibodies, enzymes or other biological receptors. The artificial generated recognition sites provided by MIPs are able to rebind specifically a target molecule with a high affinity compared to other closely related compounds. MIPs based electrochemical sensors have found application including metals ions, amino acids, emerging pollutants such as drugs and food additives, proteins and bacteriophage or microbial cells. MIPs offered various advantages such as their low-cost preparation, great selective recognition ability, high stability and good sensitivity towards the target analyte [25–29].

Various approaches were reported for the synthesis of molecularly imprinted polymers many including suspension polymerization [30,31], emulsion polymerization and precipitation polymerization [32,33]. The use of ultrasound assisted for the synthesis of MIPs offers advantages such as the acceleration of polymerization reaction rate and generate more homogeneous chain growth, greater yields, and milder conditions [34,35]. Based on ultrasonication-assisted polymerization, Xia et al [36] reported a simple synthesis of 17β-Estradiol-imprinted MIPs-encapsulated surfactant-modified magnetic nanoparticles (65 °C, 2 h)

As a novel imprinted polymer, the ultrasound assisted magnetic molecularly imprinted polymers (US-MagMIPs), can be used for a simple and fact separation process by using an external magnetic field and the sample can be easily collected without additional centrifugation or filtration. Moreover, due to their low toxicity, good biocompability as well as their good magnetic properties, they can be used for biomedical and environmental applications [37–39].

Recently, a new mode of adsorption and separation methods using the magnetic molecularly imprinted solid phase extraction (MagMISPE) technique, which utilizes MagMIPs as adsorbent materials in solid-phase extraction, has been applied most as strategy for the quantification of target analytes in samples with complex components [40,41]. This technique is based on the use of magnetic adsorbents, which can make the separation phase between the adsorbent and the aqueous solution easier and rapid, by an external magnetic field.

In this context Herein, we present a developed simple, rapid analytical procedure for sensitive and selective detection of BPA. This novel developed method is based on the use of US-magMIPs as adsorbent in order to capture and bind selectively BPA prior to its determination using the highly sensitive developed electrochemical sensor based on nanocomposite of CBNPs and AuNPs,

2. Experimental

2.1. Reagents and materials

Carbon black nanoparticles N220 (CBNPs) was obtained from Cabot Corporation (Ravenna, Italy). Gold nanoparticles (AuNPs) (5 nm diameter, OD 1, stabilized suspension in 0.1 mM PBS), Bisphenol A, Catechin, Caffeic acid, 17-β-Estradiol, Hydroquinone, Iron (III) chloride hexahydrate ($FeCl_3.6H_2O$), iron (II) chloride tetrahydrate ($FeCl_2.4H_2O$), Ammonium hydroxide solution (NH_4OH), Oleic acid (OA), acetone, methacrylic acid, ethylene glycol dimethacrylate (EGDMA), acetic acid, acetonitrile, Potassium ferricyanide $[K_3Fe(CN)_6]$, potassium ferrocyanide $[K_4Fe(CN)_6]$, potassium phosphate monobasic ($KH2PO4$), potassium phosphate dibasic (K_2HPO_4) and potassium chlorade (KCl) were purchased from Sigma Aldrich. Ammonium persulfate (APS) ≥98% was purchased from Lobachemie (India).

2.2. Apparatus

PalmSens (Pamsens BV Houten, the Netherlands) was used as electrochemical instrument in connection with a PC controlled by software PsTrace 3.0 to perform the electrochemical measurments. Home produced Screen-printed electrodes (SPEs) were received as gift from the University of Rome Tor Vergata (Italy) and were consisted on film of polyester film as substrate, graphite as working and counter electrodes and silver chloride was used as reference electrode. The diameter of the working electrode was 0.3 cm, resulting in a geometric area of 0.07 cm^2 [14].

Regarding the synthesis of US-MagMIP/NIP, Ultrasonic bath equipped with thermostat operating at 37 kHz (Elmasonic S30(H), Germany) was used.

2.3. Solutions

Stock solution (10^{-3} M) of Bisphenol A, Catechin, Caffeic acid, 17-β-Estradiol and Hydroquinone were dissolved in methanol, diluted as required using PBS, and stored in a refrigerator at 4 °C.

Two water samples were used: one was drinking water collected from laboratory in Mohammedia city and one was mineral water purchased from local market in Mohammadia city in Morocco.

2.4. Synthesis of magnetite nanoparticles

The Fe_3O_4 nanoparticles were synthesized as follow: 13.56 g of $FeCl_3.6H_2O$ and 4.96 g of Fe $FeCl_2.4H_2O$ were dissolved in 250 mL of distilled water in a three-necked bottomed flask (500 mL). Then the solution was stirred under nitrogen conditions at 80 °C. Under stirring and N_2 conditions, 20 mL of NH_4OH solution was added into the mixture of Fe(II) and Fe(III) drop by drop. A black product was obtained demonstrating the formation of magnetite particles. The reaction was proceeding for 40 min at 80 °C. At Room temperature, the magnetite was separated using magnet bare and washed several times using distilled water. Then the Fe_3O_4 particles were dried in the oven [42]

2.5. Synthesis of ultrasound assisted magnetic molecularly imprinted polymer

2.5.1. Preparation of aqueous ferrofluid solution

The procedure used is described below:

The aqueous ferrofluid solution was prepared as follow: 200 mg of Fe_3O_4 nanoparticles were dissolved in 20 mL of distilled water and sonicated for 5 min at 60 °C, then 140 μL of oleic acid (OA) was added followed by a sonication for 5 min. A solution containing 134 mg of SDS was introduced into the Fe_3O_4-OA solution. The obtained mixture was sonicated for 10 min at room temperature. The final prepared aqueous ferrofluid solution was of 10 mg/mL.
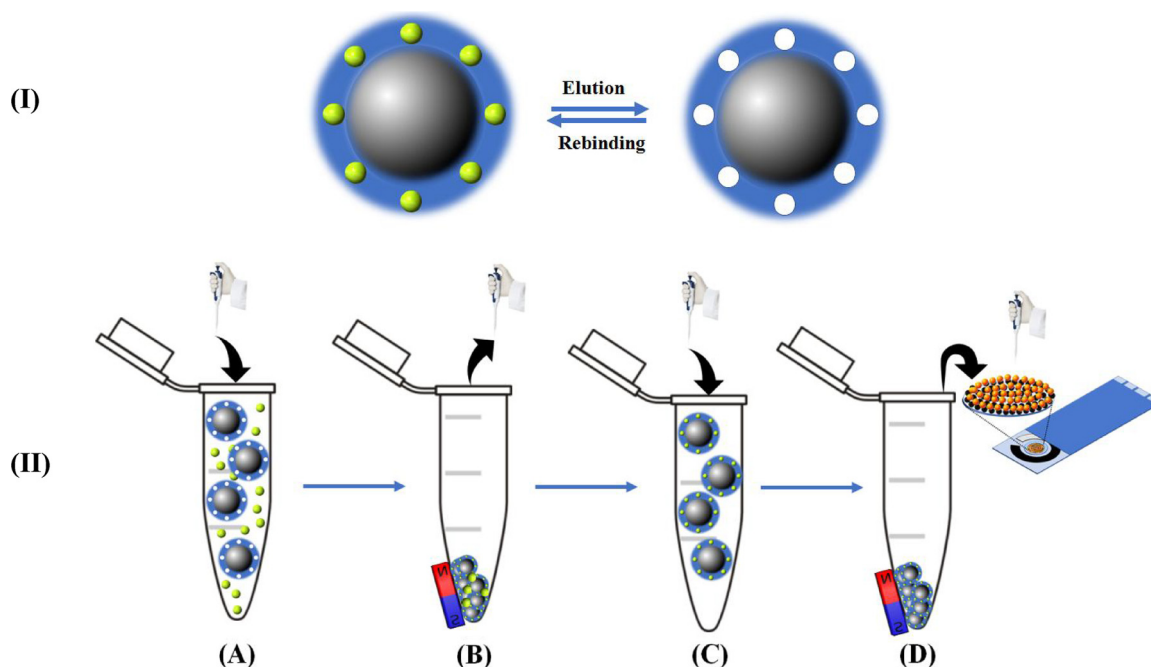
Scheme 1. (I) Synthesis of the ultrasound assisted Magnetic Molecularly Imprinted Polymers (US-MagMIPs), **(II) (A)** Rebinding process between BPA and US-MagMIP **(B)** separation of US-MagMIP from the solution and throw the supernatant **(C)** Elution of BPA using 20% of methanol **(D)** Drop-casting of 60 μL of the residual concentration of BPA on the surface of AuNPs/CBNPs/SPCE. BPA (⬤), Fe$_3$O$_4$ (⬤).

2.5.2. Preparation of prepolymerization solution

51.1 mg of bisphenol A (Template molecule) was added into 10 mL of Acetonitrile:water (3:1). The methacrylic acid (172 μL) (Functional monomer) was added into the solution and well mixed. The mixture was let in dark for 2 h to allow the hydrogen bondi²ng (H-bonding). A volume of 317 μL of EGDMA (Crosslinker) was introduced shortly before final polymerization.

2.5.3. Synthesis of ultrasound assisted magnetic molecularly imprinted polymers

10 mL of aqueous ferrofluid solution was suspended into 10 mL of prepolymerization solution followed by 5 min of Nitrogen degassing under sonication. 16 mg of Ammonium persulfate used as radical initiator of polymerization process was added into the two necked bottomed flask and placed under ultrasonication bath at 65 °C for 2 h.

The resultant particles were separated by an external magnet and followed by an intensive template removal using acetic acid in methanol (1:9). Then the US-MagMIP were washed several times using methanol and distilled water (1:1) and finaly with distilled water. The final US-MagMIP product was dried at oven at 45 °C. Following the same procedure in absence of the template molecule (BPA) the ultrasound assisted magnetic non-imprinted polymer (US-magNIP) was synthesized [36].

2.6. Preparation of carbon black suspension

The carbon black suspension (1 mg/mL) was prepared by sonication for 1 h of 10 mL of a mixture of distilled water/Dimethylformamide (DMF) (1:1) containing 10 mg of Carbon black nanoparticles.

2.7. Preparation of AuNPs /CBNPs/SPCE

Before the modification, Screen Printed Carbon Electrode (SPCE) were pretreated using Amperometry + 1.7 V for 180 s in a solution of Phosphate Buffered Saline (PBS) pH 7.0 (0.1 M).

The CBNPs/SPCE was prepared by casting 6 μL of CBNPs, as reported in previous work [17,43], and then was dispersed onto the surface of the pretreated SPCE and drying at 45 °C for 10 min. To obtain the best response of the modified electrode, the amounts of AuNPs which are used as received whitout dillution was optimized.

AuNPs/CBNPs/SPCE sensor were prepared consisting of 1, 2 and 3 layers of AuNPs solution on the surface of the previously prepared CBNPs/SPCE, for each layer depositing 2 μL of AuNPs suspension and drying at 45 °C for 10 min.

2.8. Electrochemical methods

Cyclic Voltammetric (CV) measurements were recorded over a potential range from −0.5 V to +0.9 V in 5 mM of ferri-ferrocyanide, 0.1 M KCl, and from −0.1 V to +1.0 V for the study of electrochemical behavior of BPA in PBS, at a scan rate of 100 mV s^{-1}, and the potential step was 10 mV.

Electrochemical impedance spectroscopy (EIS) measurements were carried out in the frequency range from 10 kHz to 0.1 Hz at a potential of 200 mV in 5 mM of ferri-ferrocyanide, 0.1 M KCl.

Differential Pulse Voltammetry (DPV) was applied in PBS (0.1 M, pH 7.0) containing a certain amount of BPA by applying a sweep potential from 0.0 V to 1.0 V at pulse amplitude of 100 mV, pulse width 0.2 s and scan rate of 10 mV s^{-1}.

Square-Wave Voltammetry (SWV) measurements were carried out at the pulse amplitude, 10 mV with the frequency 10 Hz. The potential was varied from 0.0 V to 1.0 V.

All electrochemical measurements were performed at laboratory temperature.

2.9. Rebinding experiments

The adsorption experiments of US-MagMIP and US-MagNIP were conducted by varying the initial concentration of BPA from 0.07 to 10 μM, were prepared in PBS (pH 7.0, 0.1 M). 3.5 mg of US-MagMIP/US-MagNIP were suspended in 500 μL of various concentration of BPA. The mixtures were incubated at room temperature for 15 min under continuous stirring (800 rpm) and then the magnetic materials were collected via an external magnetic field from the solution, and the clear
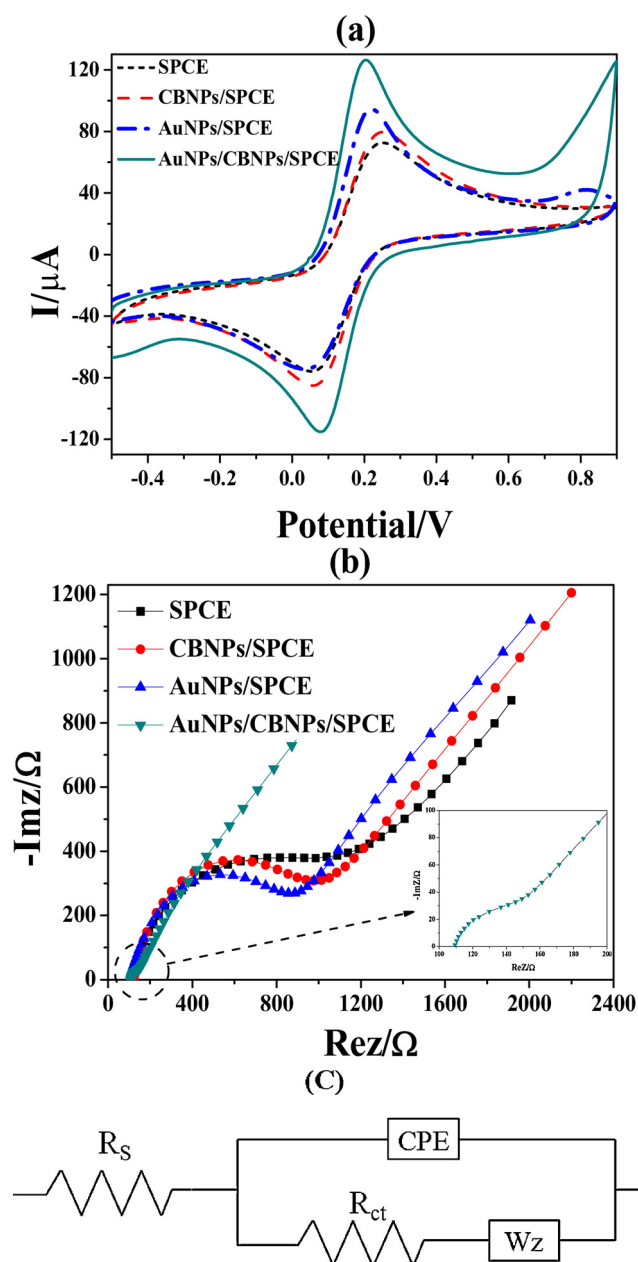
(a)

(b)

(C)

Fig. 1. (a) Cyclic voltammograms and (b) Nyquist plots of bare SPCE, CBNPs/ SPCE, AuNPs/SPCE and AuNPs/CBNPs/SPCE in the solution of 5 mM [Fe (CN)$_6$]$^{3-/4-}$ and 0.1 M KCl with the frequencies swept from 10^3 to 0.1 Hz. Inset: spectra of CBNPs/AuNPs/SPCE (c) Equivalent circuit used to fit the Nyquist spectra.

supernatant was discarded. The BPA was eluted from magnetic materials by 100 μL of methanol and stirring for 15 min for removing the maximum possible amount of the binding BPA from US-MagMIP and US-MagNIP, and then 400 μL of PBS was added. Finally, the mixture was separated using a magnet. This method was used to prepare each concentration from 0.07 to 10 μM. Then 60 μL of the residual concentration of BPA in solution was dropped on the surface of prepared electrode (AuNPs/CBNPs/SPCE) for DPV measurements (see Scheme 1).

3. Results and discussion

3.1. Electrochemical properties of the modified electrode

The electrochemical characterization of the different electrodes were investigated by CV and electrochemical impedance spectroscopy (EIS) using a solution of 5 mM [Fe(CN)$_6$]$^{3-/4-}$, 0.1 M KCl as the electrochemical redox probe. The Fig. 1(a) shows the CVs of bare SPCE, CBNPs/SPCE, AuNPs/SPCE and AuNPs/CBNPs/SPCE in 5 mM [Fe (CN)$_6$]$^{3-/4-}$ solution containing 0.1 M KCl. As indicated in Table 1S, at bare SPCE, a couple of redox peaks of [Fe(CN)$_6$]$^{3-/4-}$ appear with a peak-to-peak separation (ΔE_P) of 197.9 mV. After modifying the electrode with CBNPs, a decrease of ΔE_P to 193.7 mV and an increase of 11% of the oxidation peak current was observed. At AuNPs/SPCE, the peak current increases more, by 32%, and the ΔE_P decreased even further, to 181.7 mV, which can be attributed to the electrocatalytic activity and good conductivity of AuNPs. After modification of the surface of SPCE by AuNPs/CBNPs the redox peak current was greatly increased up to 79% of the value for an unmodified electrode and a pair of well-defined redox peaks with ΔE_P of 124.1 mV was obtained. This can be attributed to the excellent electrocatalytic activity, huge specific active surface area provided by AuNPs and CBNPs.

The EIS method was used to investigate the electron transfer on the interface of the bare and modified SPCE electrodes. This technique has been widely employed for the electrochemical behavior investigation of the reaction dynamics and the membrane/solution structure. The Fig. 1(b) presents Nyquist plots of 5 mM [Fe(CN)$_6$]$^{3-/4-}$ at different electrodes. The spectra were fitted using an appropriate equivalent circuit shown in Fig. 1(c). The charge transfer resistance, R$_{ct}$, is in series with Warburg impedance, W$_z$. Both are in parallel with constant phase element, CPE. The cell resistance R$_s$, was added in series with them. The values obtained from fitting circuit are shown in Table 2S. The results show that with each modification there is a decrease of charge transfer resistance, indicating easier electron exchange. A small decrease of R$_{ct}$ was observed when the SPCE was modified with AuNPs and CBNPs. The R$_{ct}$ value decreases dramatically with AuNPs on top of CBNPs, which indicate that the AuNPs/CBNPs nanocomposite greatly, facilitates the electron transfer between solution and electrode interface. This can be attributed to the synergetic effect of both nanomaterial modifiers.

3.2. Electrochemical behavior of BPA and effect of AuNPs amount

The electrochemical behavior of 1 μM BPA at the bare SPCE and the modified electrodes were measured by DPV. As shown in Fig. 2, an oxidation peak is observed at all tested electrodes within the potential range from 0.3 to 0.6 V. At bare SPCE electrode, the oxidation peak of BPA was the lowest. After surface modification using CBNPs and AuNPs, the oxidation peak of BPA increases by 21% and 60% of the current intensity value obtained by the unmodified electrode respectively, which can be attributed to the large electroactive surface of the CBNPs and AuNPs modified electrode for BPA determination. At AuNPs/CBNPs/SPCE (2 μL), a highest oxidation peak was obtained, which is approximately 90% of the CBNPs/SPCE and 41% of the AuNPs/SPCE current peak values. This result could be attributed to the high enlarged specific surface area of the electrode provided by AuNPs and CBNPs as well as their synergetic electrocatalytic effect. Furthermore, the oxidation peak potential obtained at AuNPs/CBNPs/SPCE showed a negative potential shift indicates the good electrocatalytic ability to the electrochemical reaction of BPA.

The effect of the amount of AuNPs drop-coated onto the surface of CBNPs/SPCE was also studied to optimize the response. As shown in Fig. 2, the response of 1 μM BPA for various amount of AuNPs: 2 μL, 4 μL and 6 μL. The optimum sensor response was obtained using 6 μL of AuNPs. Thus, this volume was chosen for the next experiments.
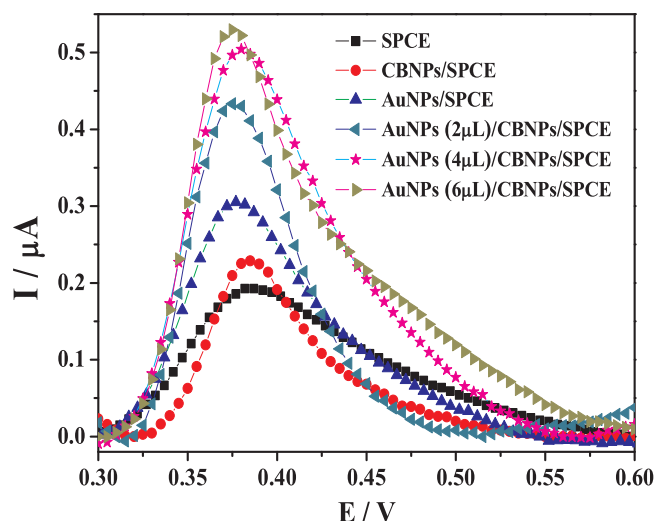
Fig. 2. DPVs of 1 μM BPA in 0.1 M PBS (pH 7.0), at SPCE, CBNPs/SPCE, AuNPs/SPCE and AuNPs/CBNPs/SPCE.

3.3. Effect of pH

The influence of pH on the oxidation of 1μM BPA at AuNPs/CBNPs/SPCE was investigated in the pH range from 5 to 9 by DPV and is illustrated in Fig. 1S. The oxidation peak potential, E_{pa}, shifted to negative potential values with an increasing pH following a linear relationship (Fig. 3(a)), indicating that the protons are directly involved in the oxidation of BPA. The obtained slope was −53 mV per unit of pH which is close to the theoretical value of 59 mV, indicating that the number of electrons and protons involved in BPA oxidation is equal. The current intensity increased gradually from pH 5.0 to 7.0, and then decreases. In this work, pH 7.0 PBS was thus selected as the supporting electrolyte for further studies in order to maximize the sensitivity for the determination of BPA (Fig. 3(b)).

3.4. Influence of scan rate

The effect of scan rate (ν) on the oxidation of BPA at AuNPs/CBNPs/SPCE was studied and illustrated in Fig. 4. Fig. 2S(a) show that the oxidation peak current increases linearly with scan rate in the range of 10 to 100 mV s^{-1}. It indicates that the electrochemical oxidation of BPA at AuNPs/CBNPs/SPCE is an adsorption-controlled process. The relationship between the peak potential (E_{pa}) and the logarithm of scan rate (lnν) is also shown in Fig. 2S(b). As can be seen that the value of E_{pa} shifted positively with increasing of scan rate, and that is obeys the following equation: $E_{pa} = 0.052 \ln\nu + 0.422$ ($R^2 = 0.983$). As for an adsorption-controlled and totally irreversible electrode process, the relationship between E_{pa} and lnν is expressed as fellows by Laviron (1974).

$$Epa = E° + \left(\frac{RT}{\alpha nF}\right)\ln\left(\frac{RTK^0}{\alpha nF}\right) + \left(\frac{RT}{\alpha nF}\right)\ln\nu$$

where E° is formal redox potential, K° is standard rate constant of the reaction, n is electron transfer number, R, T and F have their usual meanings. Thus, the value of αn can be easily calculated from the slope of E_{pa} versus lnν. In this work, the slope is 0.052, therefore, αn is calculated to be 0.49. In general, α is assumed to be 0.5 in a totally irreversible electrode process. Thus, the electron transfer number (n) is calculated to be about 1 (generally taking T = 298 K, R = 8.314 J K^{-1} mol^{-1}, and F = 96,485 C mol^{-1}). The same reaction was also observed in other studies [44,45]. Therefore, the electrochemical oxidation of BPA on the proposed electrode is a one-electron and one-proton process. Hence, the mechanism for the electrocatalytic oxidation
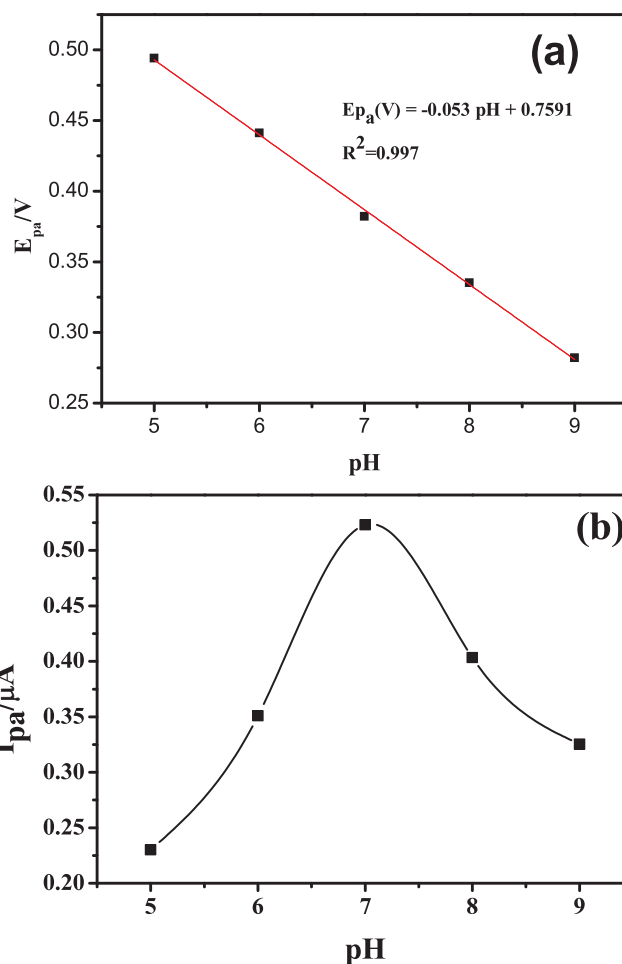

Fig. 3. Variation of (a) peak potential and (b) peak current of DPV of 1 μM BPA at AuNP/CBNPs/SPCE in PBS with different pH values: 5, 6, 7, 8 and 9.
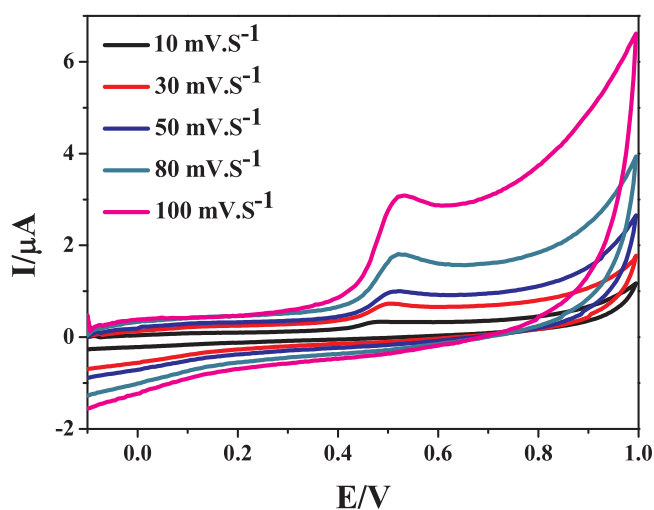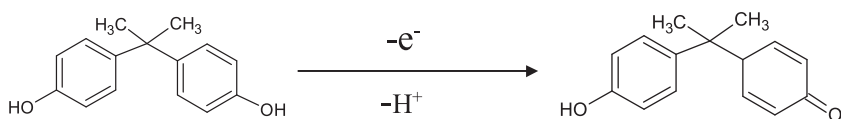

Fig. 4. Cyclic voltammograms at AuNPs/CBNPs/SPCE in PBS (pH = 7) containing 1 μM BPA at 10, 30, 50, 80 and 100 mV s^{-1}.

of BPA on the fabricated sensor was predicted and illustrated in Scheme 2.

3.5. Sensitivity of the AuNPs/CBNPs/SPCE

Under our experimental conditions, Differential pulse voltammetry

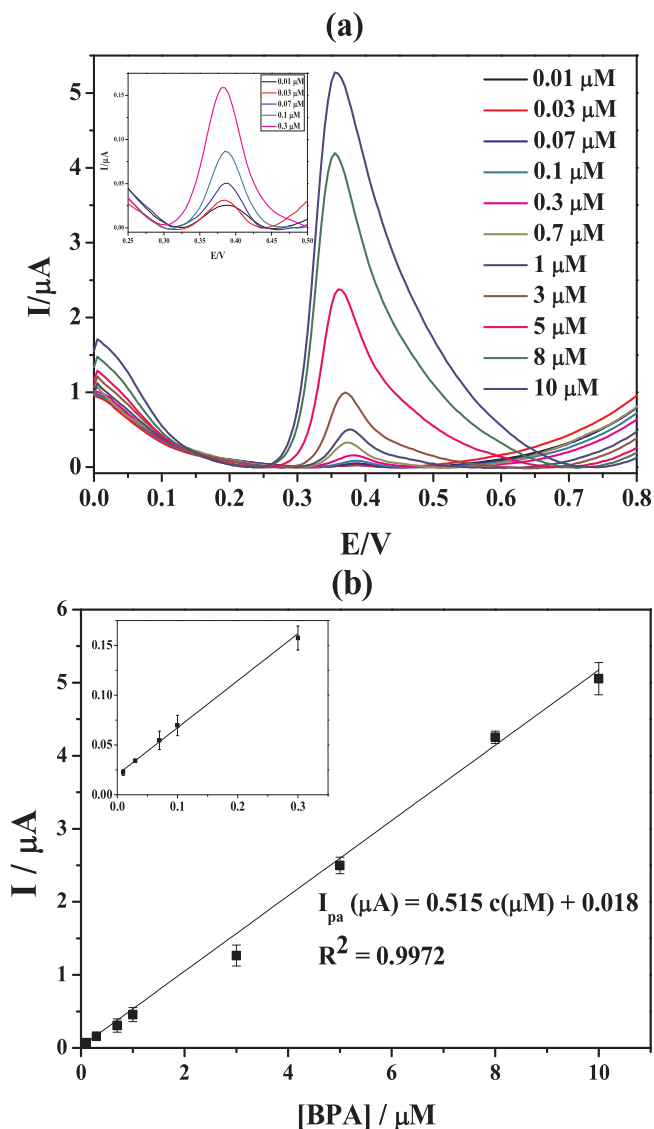**Scheme 2.** Possible oxidation mechanism of BPA at AuNPs/CBNPs/SPCE.

Fig. 5. (a) DPV of different concentration of BPA from 0.01 μM to 10 μM at AuNPs/CBNPs/SPCE in 0.1 M PBS (pH = 7), **(b)** Corresponding calibration curve.

Fig. 6. Effect of amount of US-MagMIP on the recoveries of BPA **(b)**Effect of rebinding time.

(DPV), exhibits a high sensitivity towards BPA detection in comparison with square-wave voltammetry (SWV) (see Fig. 3S), was used to construct calibration curves. Th yjhe electrochemical determination of BPA under the optimized experimental conditions, AuNPs/CBNPs/SPCE, was performed with different concentrations of BPA. The Fig. 5(a) shows the electrochemical responses of BPA oxidation with successive addition of BPA. The corresponding calibration curve presented in Fig.5(b) in the BPA concentration range from 0.01 μM to 10 μM following the equations I_{pa} (μM) = 0.515c (μM) + 0.018 (R^2 = 0.997). The detection limit (LOD) calculated according to $(3 \times SD_{blank})/Slope$ was 3 nM (n = 3).

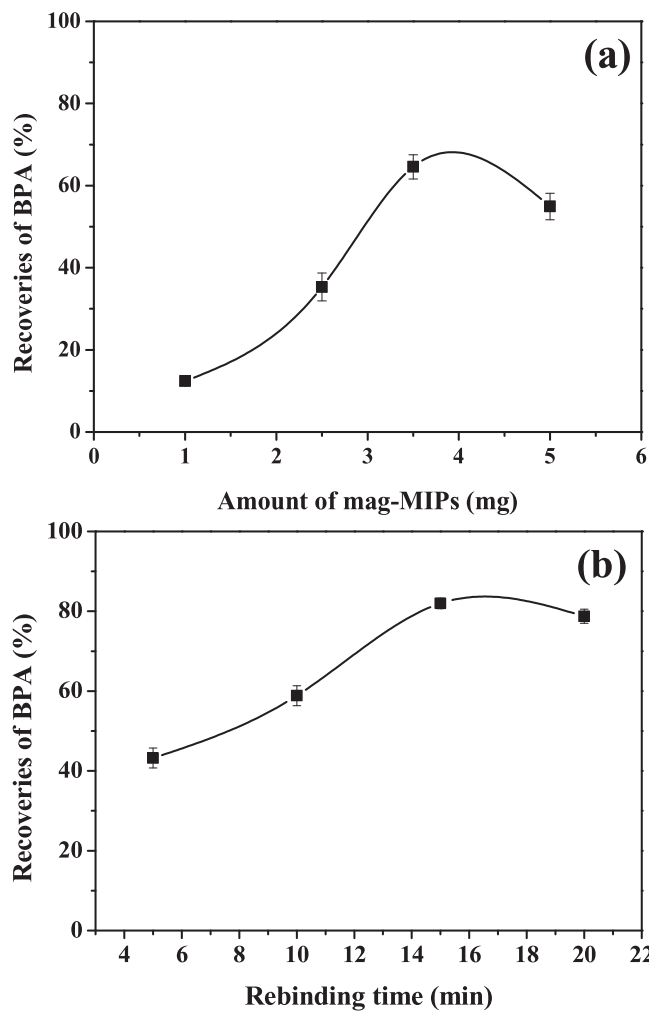## 3.6. Sensitivity of the AuNPs/CBNPs/SPCE using the adsorption properties of US-MagMIP

3.6.1. Effect of US-MagMIP amount

Different amounts of US-MagMIP ranging from 1 to 5 mg were applied to extract the analyte from 500 μL of phosphate buffer containing 1 μM of BPA (10 min). The results (Fig. 6(a)) indicated that 3.5 mg of US-MagMIP reached a maximum recovery of BPA. Therefore, the amount of US-MagMIP was fixed at 3.5 mg in order to maximize the sensitivity of the detection of BPA.

3.6.2. Rebinding time

The efficient time of contact between the analytes and the sorbents surface is an important factor that influences the adsorption yield. This rebinding process between BPA and US-MagMIP was performed using mechanical stirrer, and the response of AuNPs/CBNPs/SPCE was tested using DPV. Therefore, the effect of adsorption time was studied by varying the time range from 5 to 20 min. As shown in Fig. 6(b) that after extraction for 15 min, recoveries of BPA could easily achieve the highest values. Thus, 15 min was selected as optimum adsorption time.
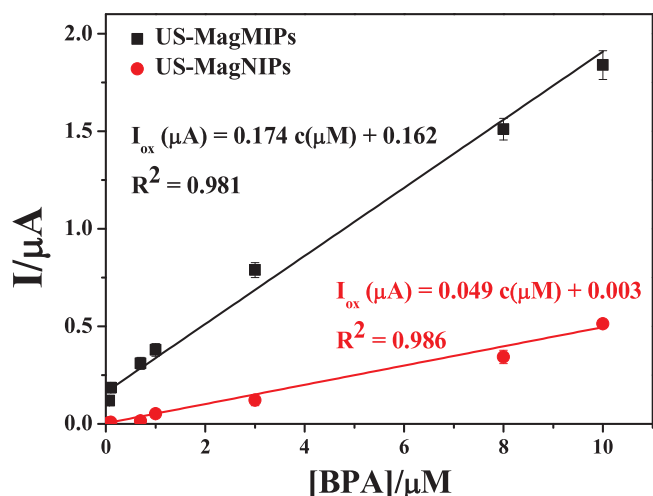
Fig. 7. Calibration curve at AuNPs/CBNPs/SPCE for increasing concentration of BPA in PBS (pH = 7) using US-MagMIP and US-MagNIP.

3.6.3. Sensitivity

Under optimal conditions, the calibration curves of the electrochemical responses of various concentrations of BPA were performed.

The Fig. 4S showed DPV curves with the successive additions of BPA extracted using the US-MagMIP and US-MagNIP at the developed AuNPs/CBNPs/SPCE sensor. Fig. 7 depicts the corresponding calibration curve, the oxidation peak current were proportional to BPA concentration range between 0.07 and 10 μM for the BPA extracted using US-MagMIP and US-MagNIP following the regression equation Ipox (μM) = 0.174c (μM) + 0.162 (R^2 = 0.981) and Ipox (μM) = 0.049c (μM) + 0.003 (R^2 = 0.986), respectively. The calculated detection limit (LOD) for US-MagMIP and US-MagNIP were 8.8 nM and 31.5 nM respectively.

It can be noticed that the LOD using the adsorption properties of US-MagMIP has been increased slightly (8.8 nM) compared to the one obtained case of standard solution of BPA measured directly on AuNPs/CBNPs/SPCE (3 nM). However, the combination of the developed sensor with the synthesized US-magMIP improved significantly the selectivity.

It should be noticed that after several washes of the US-magMIP, some residual traces of BPA still not totally removed and shows a very low signal response in the range of detection limit level.

Despite that, the obtained LOD for BPA is one of the lowest ever achieved until now, as it is clearly indicated from the comparison with previous works, shown in Table 1.

The stability of the developed sensor for a long term was also investigated by keeping the electrode for 4 weeks at 4 °C. After this period, the sensor still maintained 88% of its initial response, which indicates a good storage stability of the AuNPs/CBNPs/SPCE.

3.6.4. Selectivity study

The selectivity of the developed electrochemical sensor towards BPA was investigated using others similar compounds to BPA by exploring the sensing system based on the US-MagMIP and US-MagNIP. Four compounds named included: Caffeic acid, Catechin, Hydroquinone and 17-β-Estradiol were tested in concentarrtion of 1 μM (Fig. 8). The developed sensor showed a much higher sensitivity for BPA than others, indicating that the US-MagMIP had less specific interaction site for the similar compounds, which is attributed to the high affinity of the US-MagMIP toward BPA. In addition, there is a low significant difference of the current peak intensity between the four compounds for US-MagNIP. Therefore, the AuNPs/CBNPs/SPCE sensor using the adsorption capacity of US-MagMIP had high selectivity toward BPA.

Table 1
Comparison of the analytical performance of the proposed sensor for BPA detection with other sensors from literature at similar configurations.

Electrode configuration	Method	Linear range / μM	Detection limit/nM	Ref.
PEDOT/GCE	CV	90–410	55000	[46]
	Amp	40–410	22000	
AuNPs/SGNF/GCE	LSV	0.08–250	35	[47]
Pt/Gr–CNTs	DPV	0.06–10.0	42	[48]
EG	SWV	1.56–50	760	[49]
f-SWCNT/PC4/GCE	CV	0.099–5.794	30	[50]
CTS-GR/CILE	DPV	0.1–800	26	[51]
Laccase-Thionine-CBNPs/SPCE	Amp	0.5–50	200	[52]
Na-doped WO$_3$/CPE	DPV	0.081–22.5	28	[53]
CBPE	SWV	1–16	300	[54]
AuNPs/CBNPs/SPCE	DPV	0.07–10	8.8	This work

PEDOT/GCE: poly(3,4-ethylenedioxythiophene)-modified Glassy Carbon Electrode; SGNF: Stacked graphene nanofibers; EG: exfoliated graphite ;f-SWCNT/PC4/GCE: functionalized single-walled carbon nanotubes (f-SWCNT)/ carboxylic-functionalized poly(3,4-ethylenedioxythiophene) (PC4) complex modified glassy carbon electrode (GCE); CTS-GR/CILE: chitosan (CTS)-graphene (GR)/carbon ionic liquid electrode (CILE); CPE : Carbon paste electrode ; CBPE : Carbon Black Paste Electrode; AuNPs/CBNPs/SPCE: Screen-printed carbon electrode modified with carbon black and gold nanoparticles.
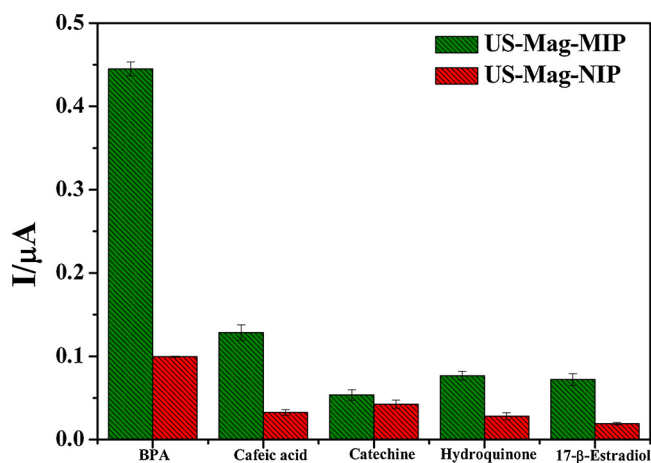

Fig. 8. Response of AuNPs/CBNPs/SPCE sensor toward 1 μM BPA and similar compounds after its binding and elution from US-MagMIP and US-MagNIP.

3.6.5. Sample analysis

In order yto evaluate the performance of AuNPs/CBNPs/SPCE in practical analytical applications, the DPV procedure for the determination of BPA in real water samples was carried out. 5 mL of the sample solution was added to 5 mL PBS buffer (pH 7.0, 0.2 M) and then was analyzed using the optimized experimental conditions using US-MagMIP. No BPA was found in the water sample, then 0.1 μM and 1μM of BPA were added to the sample and analyzed following the procedure described above in 2.8. section. The obtained results (Table 2) showed that the recovery was in the range of 96.4%–104.3% indicating that the

Table 2
Determination of BPA in water samples.

Sample	Added (μM)	Found (μM)	Recovery (%)	[a]RSD (%)
Tap Water	0.1	0.103	103.5	3.18
	1	1.043	104.3	6.17
Mineral Water	0.1	0.096	96.4	3.84
	1	0.984	98.4	8.3

[a] All the measurements were performed in triplicate.

sensor is perfectly adequate for application in water samples.

4. Conclusions

In this work, a novel electroanalytical method combined with highly selective ultrasound assisted magnetic molecularly imprinted polymer was developed to determine BPA in water samples. The developed sensing strategy based on AuNPs/CBNPs/SPCE combined with US-MagMIPs shows clear advantages, such as a very low detection limit, good repeatability and stability, high sensitivity, simple preparation process and short time of analysis as well as a high selectivity towards BPA compared to other likely interferent species.

The developed procedure was applied successfully for determination of BPA in tap and mineral water samples. The developed strategy could be a promising alternative to traditional sample pretreatment using classical cartridges prior to analytical detection and can be used for monitoring water security.

Acknowledgments

Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.snb.2018.08.092.

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