



A Simple and Sensitive Portable System for a Rapid Evaluation of Bisphenol A Contamination in Potable and Environmental Waters Using a Mesoporous Silica-Modified Carbon Paste Electrode

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**A Simple and Sensitive Portable System for a Rapid Evaluation of
Bisphenol A Contamination in Potable and Environmental Waters
Using a Mesoporous Silica-Modified Carbon Paste Electrode**

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Abstract

In this work, two ordered mesoporous silicas (HMS and SBA-15) were prepared and incorporated into carbon paste electrodes (CPEs) to obtain mesostructured sensors for a rapid determination of bisphenol A (BPA) in waters by voltammetric techniques. The materials were characterized by nitrogen adsorption-desorption measurements, transmission electron microscopy and scanning electron microscopy. The electrochemical properties of the modified carbon paste electrodes were studied by differential pulse voltammetry (DPV) and cyclic voltammetry (CV). Results showed that the sensor modified with HMS (HMS-CPE) exhibited strong adsorption activity toward the oxidation of BPA, with a well-defined voltammetric peak at + 0.6 V. Moreover, the HMS-CPE exhibited a wider linearity range, from 0.25 to 4.4 μM BPA, with a detection limit of 61 nM (S/N = 3) and good reproducibility by DPV. The enhanced performance of the HMS-CPE could be attributed to its high surface area, with a 3 D wormhole-like channel structure that favored an excellent accessibility, high adsorption capacity and faster adsorption rate of BPA. This novel sensor was coupled to a portable system and successfully applied for a rapid determination of BPA in tap, mineral, well and river water samples with good recovery, ranging from 98 to 103%.

Keywords: Bisphenol A; mesostructured sensor; potable water; environmental water

1. Introduction

Bisphenol A (BPA) is an endocrine disruptor that mimics endogenous estrogens [1] widely used in the production of polycarbonates plastic and epoxy resins that are used in many food containers and packing materials. BPA present a problem of migration into the environment and food attributed to the leakage of residual monomers from polycarbonate plastic and epoxy resins, by process of heating or exposure to acid or basic conditions. Recent toxicological studies revealed that the exposure to BPA has increased through food and waters and this is potentially harmful to human health, even at very low concentration [2]. For these reasons, it is essential to develop simple, selective and sensitive methods for a rapid monitoring of BPA in environmental water samples.

For BPA determination in environmental samples liquid and gas chromatography coupled to mass spectrometry detection have been currently employed [3, 4]. These analytical techniques can achieve high sensitivity, selectivity and good precision, but they are expensive techniques that require a laborious sample pre-treatment, making them unsuitable for onsite rapid monitoring. In comparison, electrochemical techniques are less expensive and present fast response speed, simple operation, high sensitivity, selectivity and the possibility to perform analysis *in-situ* [5]. Additionally, nanomaterials offer unique chemical, physical, optical, catalytic and electronics properties and present an excellent alternative for sensors research [6]. In the field of environmental monitoring, nanomaterials-based sensors showed a great potential in the determination of trace contaminant [7]. Some examples of nanomaterials-based sensors for monitoring BPA and other endocrine disruptor compounds in environmental samples include, mesoporous silicas [8, 9], carbon nanotubes [10, 11], gold nanoparticles, silk fibroin and dendrimers [12, 13]. Nanomaterials, with large surface area, high surface reactivity and strong

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3 adsorption capacity, favor the efficient capture of the target analytes or amplify the signal
4 associated with detection.
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8 In this sense, ordered mesoporous silicas (OMS) can be effectively exploited to develop
9 modified carbon paste electrodes (OMS-CPEs) for voltammetric detection. They possess
10 unique properties such as large BET surface area, high porosity, controllable and
11 narrowly distributed pore size, and ordered pore arrangement that display a high
12 sensitivity attributed to a better preconcentration efficiency, a better accessibility to the
13 binding sites and faster diffusion processes of the target analyte relative to OMS [14, 15].
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15 Additionally, these types of electrodes have other advantages such as non-toxicity,
16 surface renewal, very low background currents and easy fabrication. For all these reasons,
17 these modified electrodes represent an excellent alternative for environmental monitoring
18 of organic and heavy metal pollutants. For example, different OMS have been used to
19 develop OMS-CPEs in order to improve the sensitive detection of BPA [8],
20 diethylstilbestrol [9], *o*-nitrophenol [16], aminophenol isomers [17], copper [18], lead
21 [19, 20] and mercury [21, 22] in environmental water samples, among others.
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26 In the present work, firstly two ordered mesoporous silicas including HMS and SBA-15
27 type were evaluated and compared to develop OMS-CPEs. The effect of different
28 morphology, surface area, pore volume and diameter of these materials was studied for
29 voltammetric detection of BPA in aqueous medium by differential pulse voltammetry
30 (DPV) and cyclic voltammetry (CV). Secondly, factors affecting the detection of BPA
31 were investigated employing HMS-CPE and, in the optimal operating parameters, the
32 electrode performance was evaluated (linearity, detection and quantification limits,
33 precision and selectivity). The HMS-CPE was used for BPA determination in tap,
34 mineral, well and river waters with very good recoveries.
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2. Materials and Methods

2.1 Chemicals and Reagents

For ordered mesoporous silicas preparation (SBA-15 and HMS), tetraethylorthosilicate (TEOS, 98%, $M = 208.33 \text{ g/mol}$, $d = 0.934 \text{ Kg/m}^3$), poly(ethylene glycol)-block-poly(propylene glycol)-blockpolyethylene glycol Pluronic 123 ($M_{av} = 5800 \text{ g/mol}$, $d = 1.019 \text{ Kg/m}^3$) and dodecylamine (DDA) 98% ($M = 185.36 \text{ g/mol}$) were purchased from Sigma–Aldrich (Spain). Chlorhydric acid 37% ($M = 35.45 \text{ g/mol}$, $d = 1.19 \cdot 10^{-3} \text{ g/mL}$) and ethanol absolute ($M = 46.07 \text{ g/mol}$, $d = 0.79 \text{ g/mL}$) were purchased from Panreac (Spain). Water (resistivity $18.2 \text{ M}\Omega \text{ cm}$) used in the preparation of solutions was obtained from a Millipore Milli-Q-System (Waters, USA).

For OMS-CPEs and electrochemical studies, BPA (+99% purity), glacial acetic acid (99.99% purity) and mineral oil were obtained from Sigma-Aldrich Química SL (Madrid). KH_2PO_4 of analytical grade (99.5% purity) and ethanol were obtained from Scharlau (Sentmenat, Barcelona). NaCl (99% purity), $\text{NaH}_2\text{PO}_4 \cdot 12\text{H}_2\text{O}$ (99-102% purity), $\text{CH}_3\text{-COONa} \cdot 3\text{H}_2\text{O}$ (99-101% purity) and H_3PO_4 of analytical grade were obtained from Panreac (Madrid). Graphite powder was obtained from Sugelabor (Metrohm, Madrid, No 6.2801.000). The solvent used for all electrochemical studies was ultrapure water ($18.2 \text{ M}\Omega \cdot \text{cm}$) obtained from a Millipore Milli-Q-System (Merck, Madrid).

BPA was dissolved in ethanol to prepare a 0.01 M standard solution and stored at $4 \text{ }^\circ\text{C}$.

For electrochemical studies a working solution of BPA ($10 \text{ }\mu\text{M}$) was prepared daily by diluting the standard solutions with the corresponding electrolyte. For linearity determination, working solutions of BPA from 0.4 to $4.4 \text{ }\mu\text{M}$ were prepared directly in the electrochemical cell by adding successive aliquots of BPA 0.01 M .

2.2 Real water samples

A drinking water sample was collected from a running water tap in Madrid (Canal de Isabel II) and used immediately. Mineral water (Lanjarón, Sierra Nevada, Granada), river water (Jarama river, Madrid) and well water (collected in Fuente del Fresno, San Sebastián de los Reyes, Madrid) were filtered through a 0.45 μm membrane filter (Millipore Membrane filters, 0.45 μm HA) to remove suspended particles and stored, in polyethylene bottles, at $-20\text{ }^{\circ}\text{C}$ prior to use. Only, for mineral and river water, the pH was adjusted at 8 with NaOH (0.1 M) prior to voltammetric determination of BPA.

2.3 Instruments

For electrochemical studies with CPEs, differential pulse voltammetry (DPV) and cyclic voltammetry (CV) measurements were performed on a hand-held, battery-powered Bipotentiostat model $\mu\text{STAT200}$ (Dropsens, Spain) using a conventional voltammetry cell equipped with three electrodes: a OMS-CPE as working electrode, a saturated Ag/AgCl as reference electrode and a platinum wire (Metrohm) as auxiliary electrode. A PC with DropView software for Windows was used to control the instrument, plot the measurements and perform the analysis of results. All measurements were made at room temperature. A pH-Meter model Basic 20 (Crison Instruments) was used to adjust the pH of electrolyte supporting.

2.4 Synthesis of ordered mesoporous silicas

HMS mesoporous silica was synthesized following the method described by Pérez-Quintanilla *et al.* [23] Briefly, 3 g of DDA were dissolved in 13 mL of Milli-Q water and 7.6 mL of ethanol. The solution was stirred until its homogenization, and subsequently 4.2 g of TEOS were added drop by drop. The solution was stirred for 18 h, yielding a

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3 thick white suspension that was filtered and dried at 80 °C for 1 h. The amine was removed
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5 by heating the solid at reflux in ethanol with a Soxhlet for 8 h. Finally, the rests of
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7 surfactant were removed by calcination at 550 °C for 18 h. SBA-15 mesoporous silica
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9 was prepared according to the method of Zhao *et al.* [24] as follows: 2.42 g of Pluronic
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11 123 were dissolved in 72 g of 2 M HCl solution and 18 mL of Milli-Q water with stirring
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13 at 35 °C. Then, 5.1 g of TEOS were slowly added, and the resulting mixture was stirred
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15 at the same temperature for 20 h. After this reaction time, the stirring was stopped and the
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17 temperature was increased to 80 °C and maintained for 24 h. The solid product was
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19 recovered by filtration and washed with water. Then, it was calcined at 500 °C for 18 h.
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21 Table 1 shows the main characterization data for the prepared materials.
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30 **2.5 Characterization of mesoporous silicas**

31 Nitrogen gas adsorption-desorption isotherms were performed using a Micromeritics
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33 ASAP 2020 analyzer. Elemental analysis (% H, % C and % N) were performed using a
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35 microanalyser model LECO CHNS-932. The thermal stability of the modified
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37 nanostructured silicas was studied using a Setsys 18 A (Setaram) thermogravimetric
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39 analyzer with a 100 µL platinum crucible. A synthetic air atmosphere was used and the
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41 temperature increased from 25 °C to 800 °C at a speed of 10 °C per minute. Conventional
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43 transmission electron microscopy (TEM) was carried out on a TECNAI 20 Philips
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45 microscope operating at 200 kV, with a resolution of 0.27 nm and $\pm 70^\circ$ of sample
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47 inclination, using a BeO sample holder. Scanning electron micrographs (SEM) and
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49 morphological analysis were carried out on a XL30 ESEM Philips with an energy-
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51 dispersive spectrometry system (EDS). The samples were treated with a sputtering
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53 method with the following parameters: sputter time 100 s, sputter current 30 mA, and film
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55 thickness 20 nm using sputter coater BAL-TEC SCD 005.
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2.6 Preparation of ordered mesoporous silica modified CPEs

OMS-CPEs were prepared according to a previous work [20] by mixing 0.100 g (20% w/w) of the OMS (HMS or SBA-15) with 0.300 g (60% w/w) of carbon paste. Then, 0.100 g (20% w/w) of mineral oil were added to the mixture and mixed until obtain a uniform paste (HMS-CPE or SBA-15-CPE). The so obtained materials were packed into the end of a 5.0 cm long polyethylene tube (i.d. 3 mm), with a metallic wire as inner electrical contact. Appropriate packing was achieved by pushing the electrodes surfaces against a sheet of paper (this procedure also helps to eliminate the excess of mineral oil). Smoothing of the electrode surface was made by hand-polishing on a filter paper. When necessary, new electrode surface was obtained by replacing the wetted paste by freshly prepared uniform paste and polishing them again on a filter paper. For comparative purpose, an unmodified CPE was prepared according to the same procedure. All freshly-made electrodes were activated by performing 2–3 cycles of DPV until the background was stable. This activation process was realized all days prior to use them.

2.7 Voltammetric measurements

All electrochemical studies with OMS-CPEs were accomplished by DPV and CV. Unless otherwise stated, a 0.1 M acetate buffer (pH 8.0) was used as electrolyte support for BPA determination. After open-circuit accumulation of BPA for 3 min with stirring at 300 rpm, DPV were recorded from 0.0 to +0.8 V and the oxidation peak of BPA around + 0.6 V was measured. The pulse amplitude was 50 mV with a potential step height of 5 mV, the pulse width was 40 ms and the scan rate was 100 mV/s. Cyclic voltamperograms were recorded from 0.0 to +0.8 V at different scan rates. After each measurement, to ensure that BPA was not present on the electrode surface, regeneration of the electrode was

performed by 2–3 cycles of DPV. Each measurement was performed in triplicate and the average value was reported.

3. Results and Discussion

3.1 Characterization of mesostructured silicas

The physicochemical properties of the mesostructured silicas such as the Brunauer-Emmett-Teller surface area (S_{BET}), the total pore volume, and the Barrett, Joyner and Halenda (BJH) average pore diameter are shown in Table 1. Both HMS and SBA-15 materials possessed very high S_{BET} , with typical pore volume and average BJH pore diameter values for surfactant-assembled mesostructures. HMS was the material with the highest S_{BET} , but with a small pore diameter ($962 \text{ m}^2 \text{ g}^{-1}$ and 32 \AA , respectively), while SBA-15 was the material with the lowest S_{BET} and the highest pore diameter ($764 \text{ m}^2 \text{ g}^{-1}$ and 49 \AA , respectively).

The nitrogen adsorption-desorption isotherms for mesostructured silicas are shown in Fig. 1 (A and B). For both HMS and SBA-15 materials the isotherms were type IV according to the I.U.P.A.C. classification and had a narrow hysteresis loop representative of mesoporous solids (pore width between 2 and 50 nm). SBA-15 showed a H1 hysteresis loop, which is indicative of uniform cylindrical pores, while HMS showed a H2 hysteresis loop, which is indicative of wormhole-like pores. The volume adsorbed for both isotherms increased sharply at a relative pressure (P/P_0) at 0.4 for HMS and 0.5 for SBA-15, what represents capillary condensation of nitrogen within the mesopore structure. As it can be seen in Fig. 1 (C and D), narrow pore size distribution was found for SBA-15, what provides evidence for uniform framework mesoporosity while as in HMS, the capillary condensation/evaporation step was not very sharp, and therefore the pore size was not too uniform, with more than one maximum in the pore sized distribution.

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3 Evidence for disordered structure of HMS was confirmed by TEM. These micrographs
4 (Fig. 2 A) showed irregularly aligned mesopores throughout the materials with relatively
5 uniform pore sizes (wormhole-like pore arrangement). On the other hand, TEM images
6 of SBA-15 (Fig. 2 B and C) demonstrated a clear arrangement of ordered hexagonal pores
7 with uniform size throughout the structure. SEM pictures demonstrated the spherical
8 morphology of HMS particles (Fig. 2 D) with mean diameters around 1.7 μm while for
9 SBA-15 (Fig. 2 E) the particle morphology was rod-like (1 x 0.4 μm).
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22 ***3.2 Electrochemical performance of BPA on ordered mesoporous silica modified CPEs***

23 The electrochemical behaviour of OMS-CPEs and unmodified CPE was investigated for
24 BPA determination (10 μM) by DPV at different accumulation time (0, 2 and 5 min) in
25 0.1 M phosphate buffer (pH 7). Table 2 shows the peak current and potential obtained in
26 all tested conditions. As it can be seen, with unmodified CPE any oxidation peak for BPA
27 was obtained in the experimental conditions assayed (Fig. 3A), whereas with OMS-CPEs
28 a well-defined oxidation peak was obtained, around + 0.6 V, for BPA. This fact can be
29 attributed to the large surface area, specific porous networks and narrow pore size
30 distribution of the OMS, which ensure numerous adsorption sites for BPA and a fast mass
31 transport process. As it can be seen in Table 2, the peak high obtained with SBA-15-CPE
32 was very low, suggesting that the adsorption process of BPA on this material was very
33 poor, whereas with HMS-CPE a very high peak was obtained, indicating that with this
34 OMS the adsorption process of BPA on the electrode surface was more effective. With
35 both OMS-CPEs, the oxidation peak of BPA increased by increasing the accumulation
36 time, demonstrating an efficient accumulation of BPA into the silica structure that greatly
37 enhances the oxidation signal. In addition, Fig. 3B shows the DPVs obtained with HMS-
38 CPE in the absence and presence of BPA at different accumulation time. Without BPA,
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3 no oxidation peak was observed that confirmed that the oxidation peak obtained was due
4 to the oxidation of BPA. In addition, the neutral and extensively cross-linked character of
5 the HMS framework allows the efficient and environmentally benign recovery of the cost-
6 intensive template by simple solvent extraction. Therefore, HMS is a promising material
7 to develop CPE for the determination of BPA in waters and was considered a best
8 alternative to other mesoporous silicas such as SBA-15. This fact was confirmed in the
9 present work since with HMS-CPE the accumulation of BPA was most effective,
10 improving the sensitivity in the determination of BPA. Thus, in comparison with SBA-
11 15, the wormhole-like structure of HMS with a higher surface area and spherical
12 morphology (Table 1) favoured the adsorption and mass transport process of BPA toward
13 the electrode.

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15 HMS was reported for the first time by Tanev and Pinnavaia [25] as a neutral templating
16 route to prepare mesoporous silica, based on hydrogen bonding and self-assembly
17 between neutral primary amine micelles and neutral inorganic precursors. This templating
18 route produces mesostructures with thicker pore walls, which improve the stability of the
19 mesopore framework. In HMS, a substantial fraction of $(\text{SiO})_3\text{Si-OH}$ groups are
20 incorporated in the thicker pore walls, instead of being located exclusively at channel
21 surfaces [26]. Moreover, the smaller particle sizes with spherical morphology provide
22 better access to the wormlike-framework-confined mesopores in adsorption processes
23 [27]. The influence of the scan rate on BPA oxidation in the CPE modified with HMS
24 was investigated by CV. Fig. 4 shows the CVs obtained for HMS-CPE in 0.1 M phosphate
25 buffer (pH 7) containing BPA 10 μM with a scan rate ranging from 0.05 to 0.2 V/s. Only
26 an oxidation peak was observed, indicating that the oxidation process of BPA was totally
27 irreversible. In addition, the oxidation peak current of BPA increased by increasing the
28 scan rate. As it can be seen in Fig. 4 (inset), the oxidation peak current (μA) was linearly
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3 proportional to the scan rate (V/s). The regression equation was $I_p = 116.0 v + 4.0$ ($R^2 =$
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5 0.9836). This equation indicated that the electro-oxidation of BPA on the surface of the
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7 modified CPE was an adsorption-controlled process.
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10 11 12 **3.3 Optimization of detection of BPA on HMS modified CPE**

13 14 15 **3.3.1 Effect of pH**

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17 The voltammetric response of BPA (10 μ M) detection (two minutes of accumulation
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19 time) was studied in different media as electrolyte support phosphate buffer and acetate
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21 buffer 0.1 M, at pH ranging from 5 to 8. Fig. 5 shows the effect of electrolyte support and
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23 pH on the oxidation peak current obtained for BPA. When the pH value increased from
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25 5 to 6, the oxidation peak current of BPA increased in phosphate buffer whereas decreased
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27 in acetate buffer. From pH 6 to 8, the oxidation peak current of BPA also improved
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29 gradually with acetate buffer, whereas with phosphate buffer the peak current was similar.
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31 Higher values of pH were not tested since at these values the stability of the OMS and
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33 activity of the electrodes decreased. As it can be seen in Fig. 5, the highest sensitivity in
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35 the determination of BPA was obtained employing acetate buffer as electrolyte support
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37 (pH 8) with the lower signal noise. The background current was relatively low and the
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39 oxidation peak was well shaped. In consequence, acetate buffer at pH 8 was selected as
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41 electrolyte support for BPA determination. In addition, the oxidation peak potential of
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43 BPA shifts negatively with increasing pH value, indicating that the proton takes part in
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45 the oxidation process of BPA, so when pH value increases, the electrochemical oxidation
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47 of BPA becomes easy and the peak current increases.
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3 The effect of the accumulation time on the voltammetric response of BPA was studied
4 using 0.1 M acetate buffer at pH 8 as electrolyte support. Fig. 6 shows the variation of
5 oxidation peak current of BPA with the accumulation time at two concentration values.
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7 Accumulation of the analyte in the electrode surface is a widely used and efficiency way
8 to improve the sensitivity of the detection step. As it can be seen in Fig. 6, peak currents
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10 (μA) increased proportionally with accumulation time (min), from 1 to 6 min at 1 μM
11 concentration ($R^2 = 0.988$) and from 1 to 3 min at 10 μM concentration ($R^2 = 0.945$). These
12 results confirmed that the accumulation time improved the surface amount of BPA and
13 then enhanced the oxidation peak. At low concentration level of BPA, the HMS-CPE
14 surface it is not easily saturated, whereas at high concentration level, the saturation of the
15 electrode surface was obtained at 3 min of accumulation time. For a rapid analysis of
16 BPA, a 3 min accumulation time was found to be sufficient for the BPA determination,
17 but longer time (6 min) may be required in samples with very low BPA concentration.
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3.4 Analytical performance of HMS modified CPE

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36 Under optimized conditions, different concentrations (M) of BPA are measured by DPV
37 after 3 min accumulation time. It was found that the oxidation peak current (μA) of BPA
38 was proportional to its concentration over the range from 0.25 to 4.4 μM with the
39 following equation: $I_p = 77665 C + 0.0282$ ($R^2 = 0.9958$).
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47 The limit of detection (LOD) and limit of quantification (LOQ) were determinate as the
48 concentration of BPA that would give a signal 3 or 10 times the background noise,
49 respectively. The background noise was measured under the optimized conditions. After
50 3 min of accumulation time the LOD and LOQ were 0.061 μM and 0.22 μM , respectively.
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52 It is well known that in CPE modified with silica materials the LOD improves
53 significantly when the preconcentration time increases. It is interesting to note that very
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3 low LOD was obtained with a relatively low accumulation time (3 min). At low
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5 concentration level of BPA, LOD can be improved increasing the accumulation time.
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7 Thus, after 6 min the LOD was 0.042 μM .
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10 The developed HMS-CPE showed very good reproducibility for BPA detection. For a
11
12 single electrode surface (six consecutive determinations) the RSD for the detection of 0.2
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14 μM of BPA solution after 3 min accumulation time was less than 5%. For a ten different
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16 electrode surfaces, used in different days, the RSD was less than 8% (three determinations
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18 for each electrode surface). In addition, the stability of the HMS-CPE was studied by
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20 measuring the electrode response of BPA for 3 months using the electrode every day (3-
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22 4 h per day). When the peak current signal decreased to 90%, the electrode surface was
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24 polished and a new electrode, which maintains the initial oxidation peak current, was
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26 used. The good stability and reproducibility of the HMS-CPE could be attributed to the
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28 mesoporous framework stability of the HMS material.
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33 Finally, a systematic study was carried out to evaluate the interference of other endocrine
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35 disruptors on the determination of BPA. The oxidation peak of 0.2 μM BPA solution in
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37 the absence and in the presence of different interferences was measured. It was found that
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39 10 μM of β -estradiol, 10 μM of estriol and 10 μM of testosterone did not influence on the
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41 BPA determination (the peak current reduction was lower than 10%). On the other hand,
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43 10 μM of progesterone and 10 μM of dienestrol produced an important reduction in the
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45 BPA peak current (near to 50%), interfering BPA analysis.
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51 ***3.5 Analytical application of HMS modified CPE for BPA determination in waters***

52 To evaluate the performance of the developed HMS-CPE, by practical analytical
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54 applications, it was coupled to a portable system by a rapid determination of BPA in tap,
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56 mineral, river and groundwater samples, without any pre-treatment. The BPA
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3 concentration was determined by the standard addition method to compensate the matrix
4 effect from real waters. Accuracy was assessed by recovery test and BPA was added to
5 the water samples to achieve a final concentration of 0.88 μM (three times lower than the
6 specific migration limit marked by the European Commission, 0.6 mg/Kg). As it can be
7 seen in Table 3, the average recovery was $98 \pm 12\%$ for tap water, $103 \pm 7\%$ for river
8 water, $103 \pm 7\%$ for underground water and $102 \pm 6\%$ for mineral water, suggesting that
9 the HMS-CPE developed can be used for practical, rapid and simple analysis of BPA in
10 potable and environmental waters.
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13 Table 4 show other electrochemical methods previously published for the determination
14 of BPA in waters using different modifiers to prepare the CPEs (by mixing). The modified
15 CPE prepared by Yu *et al.* [28] using β -cyclodextrin modified with ionic liquid as
16 modifier presented a lower sensitivity (LOD = 0.083 μM , 5 min accumulation time). On
17 the other hand, compared with the CPE modified with MCM-41 mesoporous silica
18 developed by Wang, Yang and Wu [8], the HMS-CPE possesses a similar sensitivity and
19 precision between different sensors but a better recovery for all waters analysed. In
20 addition, another advantage of HMS versus MCM-41 is that the neutral and extensively
21 cross-linked character of the HMS framework allows the efficient and environmentally
22 benign recovery of the cost-intensive template by simple solvent extraction. Furthermore,
23 the HMS-CPE development in this work has been used in portable analysers for *in situ*
24 monitorization of BPA in environmental waters. Finally, a recent work published by
25 Ghanam *et al.* [29] present a comparative study of several electrochemical carbonaceous
26 CPEs based on graphite, carbon black, multiwall carbon nanotubes and glassy carbon to
27 quantify BPA. The LODs values obtained were comprised between 0.12 and 0.8 μM , for
28 all tested electrodes, so the LOD value obtained with the HMS-CPE developed in this
29 work (0.061 μM after 3 min accumulation time) was lower.
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4. Conclusions

Ordered mesoporous silicas are an intelligent solution to prepare electrochemical sensors because, its high surface area, high porosity, controllable and narrowly distributed pore size and ordered pore arrangement. In this study, we have demonstrated that a carbon paste electrode modified with HMS is a excellent option to determine BPA in potable and environmental waters. The electrode prepared has as main advantages: an adequate LOD (0.061 μM after 3 min accumulation time) that can be increased increasing the accumulation time, a very good stability during 3 months using the electrode every day, reproducibility and a better recovery for tap, mineral, river and groundwater samples. Thus the electrode developed in this work has a great potential to be used in portable analysers for monitoring BPA in water samples.

Conflict of interest

The authors have no conflict of interest to declare

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Table 1. Characterization data for two ordered mesoporous silicas.

Silica	Channel structure	Particle morphology (size, μm)	BET surface area (m^2/g)	BJH pore diameter (\AA)	Pore volume (cm^3/g)
HMS	3 D Wormhole-like	Spherical (1.7)	962	32	0.88
SBA-15	2D hexagonal array	Rope-like (1 x 0.4)	764	49	0.74

Table 2. Peak current and potential obtained for BPA determination using unmodified CPE and OMS-CPEs at different accumulation times.

	Peak current (μA) \pm SD ^a	Potential (V)
Without accumulation time		
Unmodified-CPE	-	-
SBA-15-CPE	-	-
HMS-CPE	0.021 ± 0.006	0.63
2 min accumulation time		
Unmodified-CPE	-	-
SBA-15-CPE	0.050 ± 0.008	0.61
HMS-CPE	0.26 ± 0.05	0.58
5 min accumulation time		
Unmodified-CPE	-	-
SBA-15-CPE	0.17 ± 0.07	0.61
HMS-CPE	0.38 ± 0.09	0.59

^aSD standard deviation (n=3); - not peak detection

DPV recorded from 0.0 to +0.8 V in 0.1 M phosphate buffer (pH 7). Pulse amplitude: 50 mV, potential step height: 5 mV, pulse width: 40 ms, scan rate: 100 mV/s. BPA 10 μM .

Table 3. Recoveries obtained for BPA determination on a HMS-CPE in water samples.

Sample ^a	Found (μM)	Spiked (μM)	Total found (μM)	Recovery (%)	RSD ($n = 3$)
Tap water	0.0	0.0	0.0		
	0.0	0.88	0.85	98	12
Mineral water	0.0	0.0	0.0		
	0.0	0.88	0.90	103	7
Well water	0.0	0.0	0.0		
	0.0	0.88	0.90	103	7
River water	0.0	0.0	0.0		
	0.0	0.88	0.89	102	6

^aTap water: Canal Isabel II, Madrid, mineral water: Lanjarón, Sierra Nevada, river water: Jarama river and well water: collected in Fuente del Fresno, San Sebastián de los Reyes. Experimental conditions: 0.1 M acetate buffer (pH 8) and three minutes of accumulation time. Other experimental conditions in are shown in Table 2.

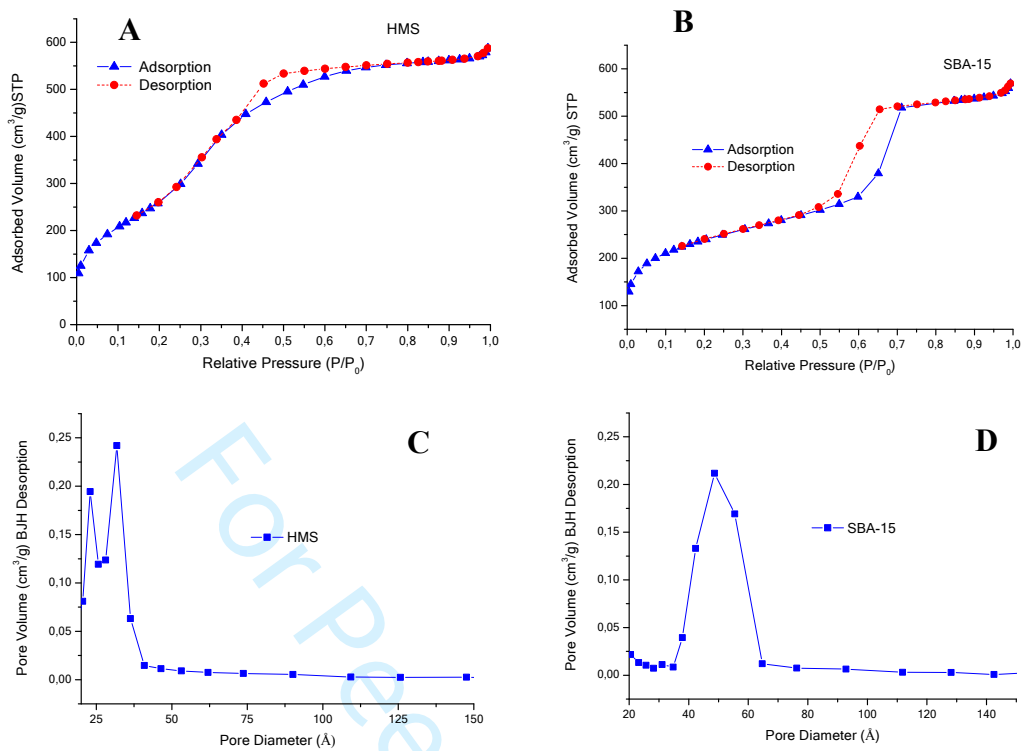
Table 4. Comparison of CPE modified with HMS with others modified CPEs for BPA determination in waters.

Sample	Electrode modifier	Linear range [BPA, μM]	Detection limit (μM)	Accumulation time (min)	Precision ^a (RSD, %)	% Recovery	Reference
Tap, mineral, river and well water	HMS ^b	0.25 to 4.4	0.061	3	8 (n=10)	98 to 103	This work
Tap and river waters and packing materials	β -CD/IL ^b	0.1 to 11.0	0.083	5	5.1 (n=5)	96 to 103	25
Lake water	MCM-41 ^b	0.22 to 8.8	0.038	3	6.4 (n=10)	91 to 107	8

^aPrecision determinate between different sensors.

^bWorking electrode prepared by mixing.

HMS: Hexagonal mesoporous silica; β -CD/IL: β -cyclodextrin modified ionic liquid; MCM-41: ordered mesoporous silica.

**Figure 1.**

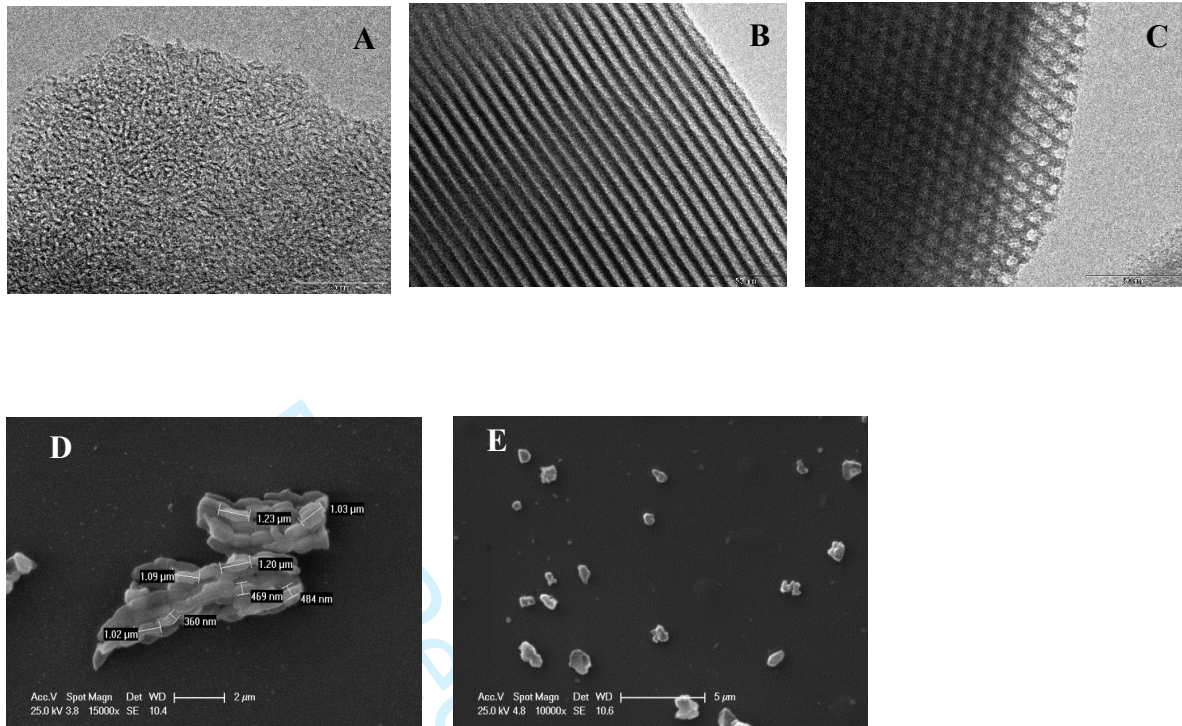


Figure 2.

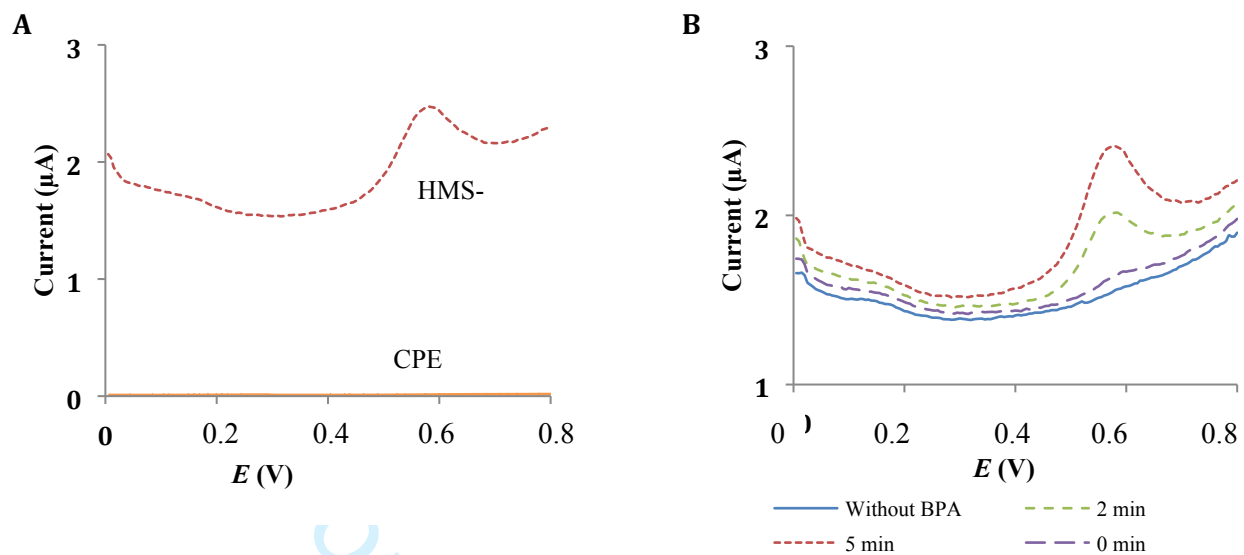


Figure 3.

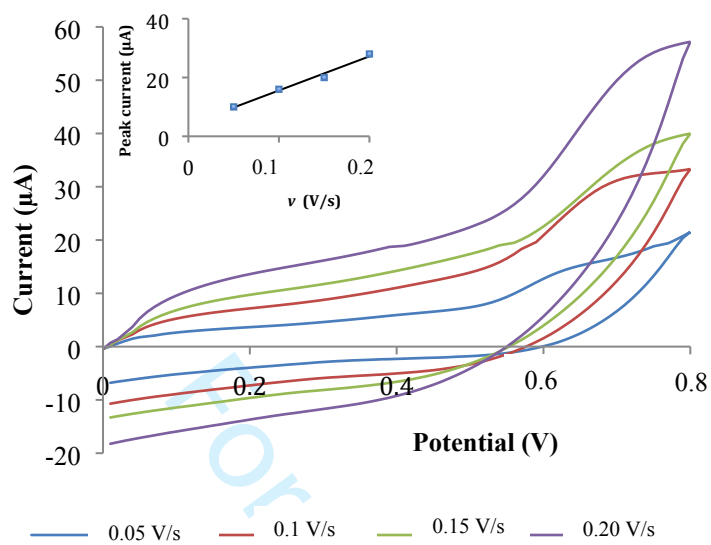


Figure 4.

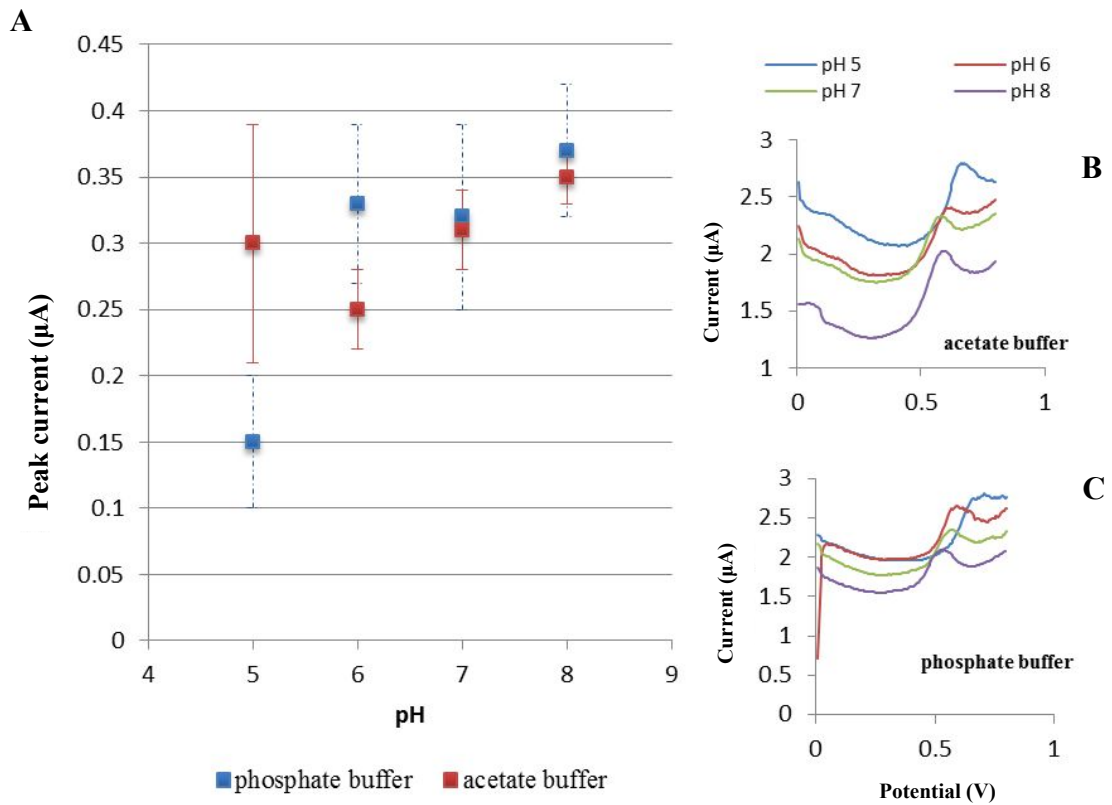


Figure 5.

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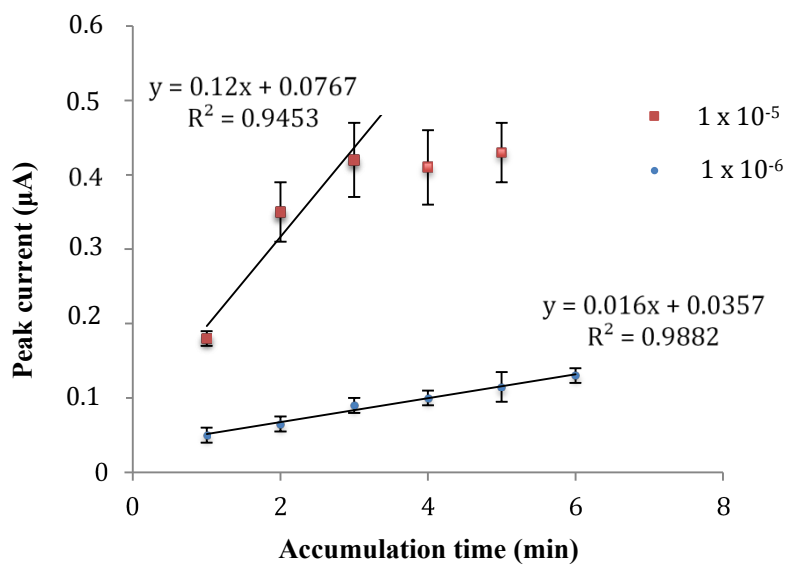


Figure 6.

FIGURE CAPTIONS

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3 **Figure 1.** N₂ adsorption-desorption isotherms of HMS (A) and SBA-15 (B) and pore size
4 distribution of HMS (C) and SBA-15 (D).
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10 **Figure 2.** TEM images of HMS (A) and SBA-15 (B and C) mesoporous silicas and SEM
11 images of HMS (D) and SBA-15 (E) mesoporous silicas.
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17 **Figure 3.** (A) DPV of unmodified CPE and HMS-CPE for BPA (10 μM) at 5 min of
18 accumulation time. (B) DPV of HMS-CPE without BPA and with BPA (10 μM) at
19 different accumulation time. Other experimental conditions used are shown in Table 2.
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26 **Figure 4.** CV obtained for BPA (10 μM) in 0.1 M phosphate buffer (pH 7) with HMS-
27 CPE at different scan ratios. Inset shows the linear relationship of oxidation peak current
28 versus scan rate. Pulse amplitude: 50 mV, potential step height: 5 mV, pulse width: 40 ms.
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35 **Figure 5.** (A) Effect of electrolyte support and pH value on the peak current of BPA 10
36 μM at HMS-CPE. (B) DPV of BPA in acetate buffer at different pH values. (C) DPV of
37 BPA in phosphate buffer at different pH values. Other experimental conditions used are
38 shown in Table 2.
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47 **Figure 6.** Effect of accumulation time on the peak current of BPA at HMS-CPE. DPV in
48 0.1 M acetate buffer at pH 8. Other experimental conditions used are shown in Table 2.
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