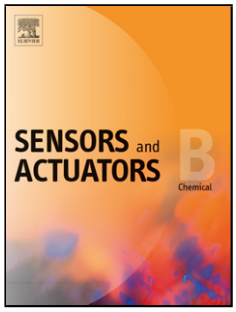

Title: An ordered mesoporous carbon modified electrochemical sensor for solid-phase microextraction and determination of triclosan in environmental samples

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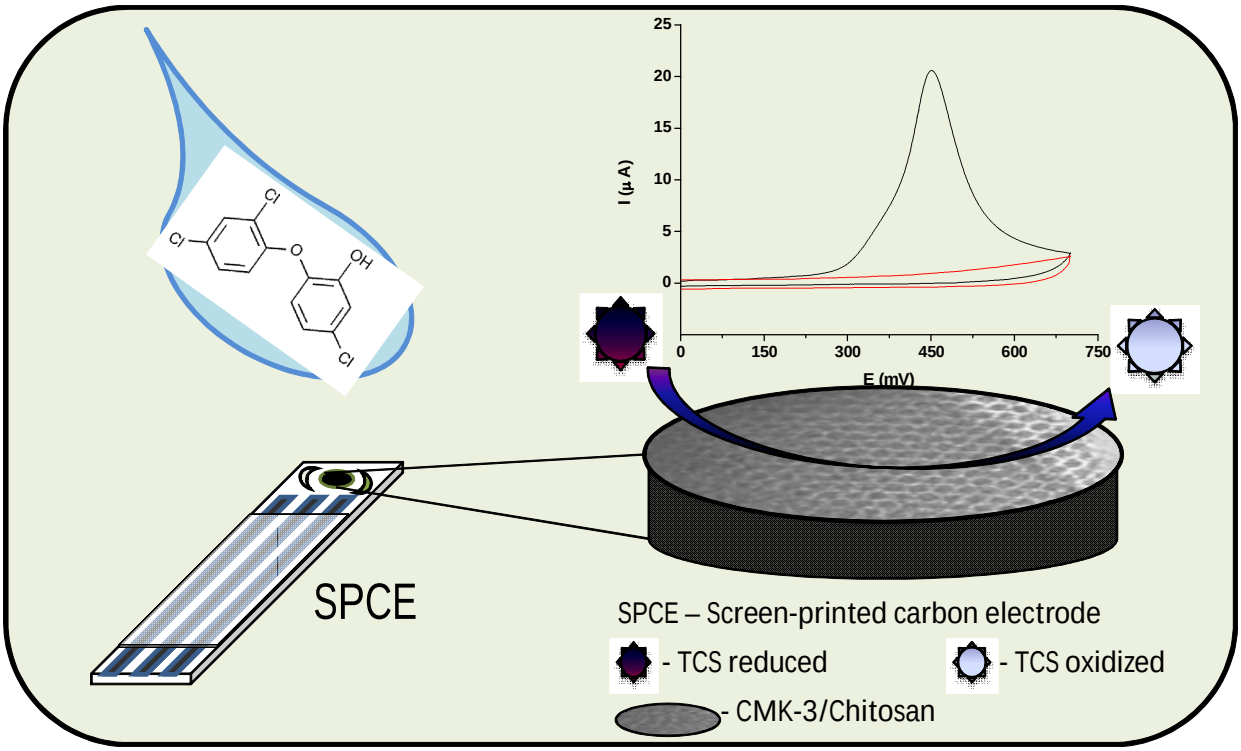
Highlights

- We developed a simple electrochemical sensor with an ordered mesoporous carbon modified screen-printed carbon electrode to detect triclosan.
- CMK-3 was used for solid-phase microextraction, since it has an excellent extraction selectivity towards triclosan in water samples.
- The proposed sensor presented high sensitivity, low detection limit, excellent stability and reproducibility.
- This electrochemical platform offered a useful tool for on-site triclosan determination in environmental samples.

Graphical Abstract



An ordered mesoporous carbon modified electrochemical sensor for solid-phase microextraction and determination of triclosan in environmental samples

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ABSTRACT

A simple and sensitive electrochemical sensor was performed with an ordered mesoporous carbon modified screen-printed carbon electrode (SPCE) to detect triclosan (TCS) in river water samples. A nanostructured mesoporous carbon CMK-3 type was successfully obtained from ordered mesoporous silica SBA-15 type used as hard-templated and sucrose as carbon precursor. Due to its high specific surface area (1125 m^2 g^{-1}), large pore volume (1.16 cm^3 g^{-1}), uniform mesostructure (4.4 nm), good conductivity and excellent electrochemical activity, this porous carbon material provides selectivity and sensitivity for the electrochemical determination. CMK-3 was immobilized onto a SPCE using chitosan (CH) as a binder. CMK-3/CH/SPCE was characterized by cyclic voltammetry, transmission electron microscopy, scanning electron microscopy, X-ray diffraction, energy dispersive spectrometry and N_2 adsorption-desorption isotherms.

CMK-3/CH was used for solid-phase microextraction, since it has an excellent extraction selectivity towards organic aromatic compounds. The electrochemical behavior of TCS showed an irreversible oxidation peak measured by square wave voltammetry. The detection limit of this electrochemical sensor was 0.24 ng mL^{-1} with a wide linear range from 0.8 ng mL^{-1} to 40 ng mL^{-1}, the intra- and inter-assay coefficients of variation were below 4%. This electrochemical platform offered a useful tool for on-site TCS determination in environmental samples.

KEYWORDS: Electrochemical sensor, Solid-phase microextraction, Ordered mesoporous carbon, Triclosan, Environmental monitoring

1. INTRODUCTION

Triclosan, (ether 2,4,4-trichloro-2-hydroxydiphenyl or TCS) is a non-ionic, broad-spectrum antimicrobial agent, and has been extensively used in personal care products, such as shampoo, liquid soap, and toothpaste [1,2]. Due to it is a stable and lipophilic compound, the high consumption has caused great concern over its environmental fate. TCS has been widely found in river water, lake water, sediments, fish, and even in human milk at ng L^{-1} levels [3,4]. The TCS toxicity on humans has been investigated for many years. The adverse effects include only mild itching and allergy on sensitive skins. Therefore, TCS is generally regarded as a low toxicity chemical [5]. However, under certain conditions TCS photodegradation can lead to the formation of dioxin-type derivatives, chloroform and chlorophenols [6,7], which were classified by the United States Environmental Protection Agency as probable human carcinogens [8]. Moreover, some researches also indicated that these compounds are extremely toxic and highly potent endocrine disruptors. As a consequence the use of TCS in personal care products has been restricted [9]. In accordance with the European Economic Community Council Directive 76/768 (Annex VI and subsequent amendments), its use is restricted to a maximum concentration of 0.3% (w/w) [10]. Therefore, analytical methods should be able to determine TCS selectively and sensitively in environmental samples at trace levels.

Due to the effects mentioned above several analytical methods have been developed for TCS determination in many samples, including high performance liquid chromatography-mass spectrometry (HPLC-MS) [11,12], ultra high performance liquid chromatography-mass spectrometry (UHPLC-MS) [13,14], high performance liquid chromatography-UV (HPLC-UV) [15,16], gas chromatography-mass spectrometry (GC-MS) [17,18], liquid chromatography-mass spectrometry (LC-MS) [19] and capillary electrophoresis-UV (CE-

UV) [20]. Although the TCS determination by these methods has been widely used in different sample matrices, because of their high selectivity and sensitivity, most of them are associated with several shortcomings, including high cost of equipment, complicated sample pretreatment and long analysis time. In contrast, the electrochemical sensor has remarkable advantages, it is a simple, sensitive and portable instrument which enables real time detection, for this reason it has been extensively used in the detection of environmental contaminants. Among electrochemical techniques, square wave voltammetry (SWV) combined with the use of a screen-printed carbon electrode (SPCE) as detection system represents an interesting alternative. SPCE offers many advantages such as simplicity, versatility, reduced cost and minimum sample volume required (20-40 μL drop) [21].

Since the discovery of ordered mesoporous carbons (OMCs), the attention has been focused in different applications due to the periodically mesoporous structure, high specific surface area, large pore volume, and tunable pore size distribution. OMCs have been considered as suitable nanomaterials for the development of electrochemical sensors and biosensors [22-24]. These materials have been widely used in electrocatalytic applications, largely because of their fast electron transfer, avoiding surface fouling and excellent electrocatalytic activity. The excellent electrocatalytic properties of modified electrodes with OMCs have been reported [25-27].

Solid-phase microextraction (SPME) has been widely applied to the extraction of analytes in biological, food, environmental, forensic and pharmaceutical samples. Other kind of carbon materials, such as nanotubes and nanofibers have been used in SPME, usually as an extractant phase for organic compounds [28-30]. The π–π stacking structure, hydrophobic surface, ordered porous structure and high specific area of the OMCs allow to adsorb

effectively organic molecules, especially aromatic compounds from water and gas samples [31-33], and therefore have a promising application in the preconcentration and determination of TCS.

In this work, a simple, fast and practical method for the determination of TCS in environmental samples has been developed. The characterization and application of CMK-3/CH/SPCE as a platform for preconcentration and electrochemical detection of TCS has not yet been reported.

2. EXPERIMENTAL

2.1. Reagents and solutions

All reagents used were of analytical reagent grade. TCS and CH (from crab shells, medium molecular, 85% deacetylated) were obtained from Sigma Aldrich (St. Louis, MO, USA). Dichloromethane and tetraethyl orthosilicate (TEOS 98%) were purchased from Merck (Darmstadt, Germany). Sucrose was obtained from Biopack. Hydrochloric acid, sulfuric acid and hydrofluoric acid were acquired from Fluka (Buchs, Schweiz). All the other employed reagents were of analytical grade and they were used without further purification. Aqueous solutions were prepared by using deionized water from a Milli-Q system.

2.2. Instruments

Electrochemical experiments were performed in unstirred solutions by using a BAS 100 B/W electrochemical analyzer (Bioanalytical System, West Lafayette, IN), employing positive feedback routine to compensate the ohmic resistance. Cyclic and square wave voltammograms were obtained by employing a SPCE, composed by a graphite circular working electrode (Ø = 3 mm), silver (Ag) as the pseudo-reference electrode and graphite

as the auxiliary electrode (SPCE), and modified SPCE. All the potentials in the text are referred to the Ag. All the experiments were conducted at room temperature (25 ± 1°C).

The structural characteristics of the nanostructured carbon material were obtained from small angle X-ray diffraction (XRD) measurements in a Panalytical-Empyrean diffractometer using Cu Kα radiation from 1 to 5° of 2θ. Scanning electron microscopy (SEM) images were taken on a LEO 1450VP, equipped with an Energy Dispersive Spectrometer (EDS) analyzer, Genesis 2000. Transmission electron microscopy (TEM) images were obtained using a FEI Tecnai G2-20 (Super-Twin) electron microscope.

Textural characterization was carried out by N_2 adsorption-desorption isotherms at 77 K using a manometric adsorption equipment (ASAP 2000, Micromeritics), where the samples were previously degassed at 150°C for 12 h, up to a residual pressure smaller than 1.5 Pa.

2.3. Synthesis of CMK-3

CMK-3 was synthesized using the ordered mesoporous material SBA-15 as inorganic template and sucrose as carbon source by means of a nanocasting technique based on the procedure reported by Barrera et al. [34]. SBA-15 was obtained under non-hydrothermal conditions with a molar ratio 0.017P123:1TEOS:6HCl:140H_2O following the procedure reported elsewhere [35]. SBA-15 was suspended in an aqueous solution of sucrose and H_2SO_4 in a mass ratio of 1:1.3:0.14:5 (SBA-15:sucrose:H_2SO_4:H_2O). This mixture was stirred at room temperature for an hour followed by a polymerization step drying at 100°C for 6 h and subsequently the temperature was raised to 160°C for 6 h. In order to ensure the complete filled of the SBA-15 porous structure the resultant dark brown composite was impregnated a second time with a solution of 0.8, 0.09 and 5 g of sucrose, H_2SO_4 and H_2O, respectively, sucrose, per gram of SBA-15 initial. Then, the second polymerization step

was at same conditions that the first impregnation. The carbonization step was performed at 900°C for 6 h with a heating rate of 3°C min^{-1} in N_2 atmosphere (180 mL min^{-1}). The resulting silica/carbon composite was leaching with hydrofluoric solution (5 wt.%) at room temperature during 24 h in order to remove the inorganic template. The CMK-3 was filtered several times with a mixture of deionized water and ethanol (50:50 v/v) up to a conductivity value smaller than 10 μS cm^{-1} and finally it was dried at 80°C for 12 h.

2.4. Preparation of the CMK-3/CH/SPCE

In order to improve the sensitivity and reproducibility of the results an electrode pretreatment before each voltammetric experiment was performed. This treatment generates the oxidation of the graphite impurities and provides a more hydrophilic surface [36]. CH solution was obtained by adding 0.1 g of CH to 10 mL of ethanol:H_2O (1:2) under stirring conditions and maintaining at pH 3.00 through the addition of 0.1 mol L^{-1} HCl solution. The undissolved material was filtered. Then, the pH value was gradually adjusted to pH 8.00 using 0.1 mol L^{-1} NaOH solution. Finally, the obtained filtrate was appropriately diluted with ethanol:H_2O (1:2) to a 0.5% CH solution and stored at 4ºC.

With the aim to obtain the CMK-3/CH preparation, 1.1 mg of CMK-3 was dispersed in 1 mL of CH (0.5% in etanol:H_2O (1:2) solution) with the aid of ultrasonic stirring for 45 min. CMK-3/CH dispersion was kept at 4ºC which is stable for at least 5 months. Finally, 10 μL of the CMK-3/CH previously obtained were dropped on the SPCE working electrode and the solvent was evaporated under the action of an infrared heat lamp.

2.5. Samples pretreatment

Environmental water samples were collected from five different rivers in San Luis, Argentina, using pre-cleaned amber glass bottles of 500 mL. Samples bottles were filled without headspace and immediately placed in coolers filled with ice packs and transferred to the laboratory for refrigerated storage at 4ºC until analysis, which was done within 1 week after collection in all instances. Before each analysis, the samples were passed through a Millipore mixed cellulose ester membrane filters of 0.45 μm pore size and adjusted to pH 9.50. Control samples were also passed through the same filters. TCS is highly lipophilic and significantly soluble in water only as anion at sufficiently alkaline pH [37].

2.6. Triclosan determination in river water samples

The procedure for the TCS quantification in river water samples involves the following stages. Firstly, 50 mL of the preconditioned sample was placed in a beaker at 37°C. The CMK-3/CH/SPCE was put in contact with the sample under stirring for 10 min. In this step, the TCS anion present in the sample was electrostatically attracted by the positively charged amino groups of chitosan [38], and was adsorbed on the CMK-3 immobilized onto the SPCE. It has been reported that mesoporous carbon materials with large mesopore size could be beneficial for efficient diffusion and transport of reactants and products in solution [39]. After, the modified electrode was removed of the sample, it was washed several times with deionized water and carefully dried with N_2 flow. Finally, the sensor was introduced into 0.1 mol L^{-1} PBS buffer pH 9.50, and the electrochemical measurement was performed using SWV with the following general parameters: step E = 4 mV, S.W. amplitude = 25 mV, S.W. frequency = 15 Hz, samples per point = 256, studied potential range = 0-700 mV and sensitivity = 1×10^{-5} A V^{-1}.

The obtained current response was directly proportional to the TCS concentration in the river water samples. The blank solution was prepared in the same way except that instead of sample 50 mL of deionized water was employed. For the next analysis, the modified electrode was conditioned with 0.01 mol L^{-1} HCl and dichloromethane for 5 min at 37°C. Then, the electrochemical sensor was washed several times with deionized water and carefully dried with N_2 flow. With this treatment the remaining TCS adsorbed on CMK-3 was desorbed and the hydrophobic oxidation products were removed; thereby the sensor is available to perform a new determination.

3. RESULTS AND DISCUSSION

3.1. Electrochemical behavior of TCS

The electrochemical behavior of TCS at CMK-3/CH/SPCE was examined using cyclic voltammetry (CV). Figure 1(A) shows the CV of 5 mmol L^{-1} TCS in 0.1 mol L^{-1} PBS buffer pH 9.50 at CMK-3/CH/SPCE (scan rate = 75 mV s^{-1}). During the anodic sweep from 0 to 700 mV, an oxidation peak at 450 mV was observed. On the reverse scan from 700 to 0 mV, no reduction peak appears, indicating that the oxidation of TCS was an irreversible process. During the following cyclic sweeps, the oxidation peak current decreased significantly, caused by the fact that the TCS oxidation product was adsorbed onto the electrode and thereby blocking the CMK-3/CH/SPCE surface (data not shown). On the other hand, the CV response of CMK-3/CH/SPCE in 0.1 mol L^{-1} PBS buffer pH 9.50 without TCS was also studied. The CV curve was smooth and no peaks were observed, suggesting that the oxidation peak at 450 mV corresponds to TCS.

The electrochemical response of TCS under different scan rates (v) was studied using CV at CMK-3/CH/SPCE (Figure 1(B)). When v was gradually increased from 25 to 175 mV s^{-1},

only an oxidation peak was observed and the oxidation peak current (I_p) increased linearly with the square root of v. The linear relationship between I_p and $v^{1/2}$ suggests that the TCS oxidation was controlled by diffusion (Figure A1 (A), Supporting information). In addition, the oxidation peak potential (E_p) of TCS gradually shifts to more positive potentials when v was increased, also revealing that the TCS oxidation was an irreversible process. The linear relationship between E_p and natural logarithm of ν followed the Laviron equation [40].

Generally in the irreversible electrochemical reaction, the value of $\alpha \cdot n$ can be easily calculated from the slope of E_p vs ln v plot. In this case, the slope was 0.035 mV. Therefore, the value of $\alpha \cdot n$ is 0.73. According to the above investigation, n was confirmed as 1, thus α is 0.73. Thereby the calculated α is in the range of 0.4 to 0.8, indicating that the electrochemical reaction is an irreversible process (Figure A1 (B), Supporting information) [41].

3.2. Characterization of CMK-3

The specific surface area (S_{BET}) of CMK-3 sample was obtained with the Brunauer, Emmet and Teller (BET) method [42], using the adsorption data in the range of relative pressures from 0.05 to 0.22. The total pore volume (V_{TP}) was obtained by the Gurvich's rule at a relative pressure of 0.98 [43]. The micropore volume ($V_{\mu P}$) and primary mesopore volume (V_{PMP}) were determined by the α_S-plot method [44, 45] using the GCB-I [46] as the reference adsorbent. The pore size distribution (PSD) of the CMK-3 was obtained by the VBS macroscopic method [47, 48] using the adsorption branch data.

CMK-3 material exhibits micrometer rod-like particles in the morphology as is shown in Figure 2 (A), and it is in concordance with other ones previously reported [34]. Analysis by EDS showed that all the siliceous inorganic material was successfully removed from the

carbon structure by means of the acid treatment. Figure 2 (B) shows the TEM micrographs where an ordered mesoporous carbon (hexagonal symmetry) with uniform pore size is observed.

Figure 3 (A) shows three well-resolved peaks, [100], [110] and [200], of the CMK-3 hexagonal structure, which are associated to *p6mm* space group. These peaks are characteristic of these kinds of ordered mesoporous carbons, and they are in agreement with the results showed in TEM micrograph. In Figure 3 (B) N_2 adsorption-desorption isotherm at 77 K of the CMK-3 is shown. This material presents a Type IV isotherm and has a hysteresis loop H_2 types which are typical of mesoporous materials. The textural properties of CMK-3, obtained from adsorption data, were S_{BET}: 1125 m^2 g^{-1}, $V_{\mu P}$: 0.12 cm^3 g^{-1}, V_{MPP}: 0.53 cm^3 g^{-1} and V_{TP}: 1.16 cm^3 g^{-1}. Figure 3 (B) (insetted) shows a narrow pore size distribution of CMK-3 with a mesopore width around of 4.4 nm.

3.3. Electrochemical characterization of the CMK-3/CH/SPCE

CV of $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$ couple is a convenient and valuable tool to monitor the surface properties of the electrode during different modifying steps. Figure 4 (A) shows the CV for: (a) blank/SPCE, (b) bare SPCE and (c) CMK-3/CH/SPCE, which were recorded in 1 mmol L^{-1} $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$ in 0.1 mol L^{-1} KCl (Scan rate = 75 mV s^{-1}). Well defined cyclic voltammograms and characteristics of a diffusion-controlled redox process were observed at the bare SPCE surface. Due to the electrostatic attraction between the

positive charge surface of CMK-3/CH/SPCE electrochemical platform and the negative $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$ system, the redox response was amplified significantly more than the bare SPCE. When CMK-3 was immobilized on the SPCE, the redox peak current and background current at this modified electrode were both enlarged, which demonstrated the increase of faradaic and non-faradaic residual currents. These phenomena may be attributed to two factors: firstly, the excellent electrical conductivity of CMK-3, secondly, the increase of the electroactive surface area and more electrocatalytic sites of this detection platform. Moreover, the integration of CMK-3 and CH produce a synergistic effect, leading to increased adsorption, electrochemically active sites and the effective electrode area.

As shown in Figure 4 (B), when the *v* was gradually increased from 25 to 200 mV s^{-1}, the currents of redox peak and the square roots of *v* had good linear relationship, indicating that this electrochemical reaction process on the sensing platform was diffusion controlled. The apparent electroactive surface area of this modified electrode could be described by Randles-Sevcik equation [49]. Thus, the electrochemistry surface area for CMK-3/CH/SPCE was 0.275 cm^2.

3.4. Study of variables

In order to carry out the TCS voltammetric determinations in river water samples, many variables that affect the electrochemical response and therefore the obtained results should be analyzed. The fixed electrochemical parameters to perform the optimization of these relevant variables were: step E = 4 mV, S.W. amplitude = 25 mV, S.W. frequency = 15 Hz, samples per point = 256, studied potential range = 0-700 mV, sensitivity = 1×10^{-5} A V^{-1} using SWV with CMK-3/CH/SPCE as working electrode. Regarding to the TCS

concentration, a standard solution of 20 ng mL^{-1} in 0.1 mol L^{-1} PBS buffer was employed in all studies.

The pH employed for the TCS determination procedure is a relevant parameter which affects the sensitivity of the technique, because the TCS solubility depends on the pH value. For this reason, the pH was evaluated in a range from 6.50 to 10.50. The response rate increased when the pH is raised from 8.00 to 9.50, insignificant differences with higher pH values were observed. Therefore, a pH of 9.50 was selected as optimum (Figure 5 (A)).

The CMK-3 concentration employed for the electrode surface modification was also optimized. This study was carried out in the range of 0.3-1.3 mg mL^{-1}. An important increase of the signal was observed from 0.3 to 1.1 mg mL^{-1}. However, at higher concentrations insignificant differences were obtained. Then 1.1 mg mL^{-1} of CMK-3 was used for the modification process (Figure 5 (B)).

3.5. Analytical performance

Linearity and range of the developed method were studied by analyzing different concentrations (n=5) of standard solution containing 0.1-50 ng mL^{-1} TCS in 50 mL of river water sample (previously conditioned). A linear relation was observed between the concentration range of 0.8-40 ng mL^{-1}. The calibration graph was described according to the following equation: ΔI (nA) = 68.0 + 5.3 C_{TCS} (ng mL^{-1}) with a correlation coefficient (R^2) of 0.992, where ΔI is the difference between current of the blank and sample (Figure A2, Supporting information). The detection (LOD) and quantification (LOQ) limits were determined according to the IUPAC recommendations [50], achieving values of 0.24 and 0.8 ng mL^{-1}, respectively.

The repeatability of the TCS determination was carried out in 20 ng mL^{-1} TCS in 0.1 mol L^{-1} PBS buffer pH 9.50 by SWV using the CMK-3/CH/SPCE. The relative standard deviation (R.S.D.) for n=5 was 3.2%. Additionally, we evaluated the reproducibility of the sensor once a week during one month, under the same conditions described above, showing a R.S.D. of 3.9%. The stability of CMK-3/CH/SPCE was evaluated by 35 days and no significant change was observed in the voltammetric responses. In order to evaluate the analytical applicability, the proposed sensor was applied to TCS determination in five river water samples under the conditions previously described. The TCS concentrations were obtained using the standard addition method and the results were confirmed by HPLC. The results demonstrated that both methods were statistically equal at a confidence level of 95% (Table 1).

It is well known that the selectivity of the platform is a vital factor for the implementation of SPME in the analysis of a real sample. Normally, the organic contaminants are one of the most common impurities in real water samples and therefore the possible interferences were evaluated. To evaluate the extraction selectivity of CMK-3/CH, the sensor was applied to 20 ng mL^{-1} TCS determination in a 10-fold concentration solution of potential environmental pollutants including non-polar and polar organic compounds, such as hydroquinone, 2,4-dichlorophenol, n-hexane, benzopirene, toluene, chloroform and tetrachlorethylene. It was observed that due to pH 9.50, the TCS charged negatively was attracted electrostatically by the CH positively charged and then was retained by the CMK-3 mesoporous structure [38,39]. Only a slight interference was obtained with hydroquinone and 2,4-dichlorophenol, which may be explained by the fact that these compounds can be negatively charged. However, the interferences were below 3 and 5% respectively compared to the measure of TCS. The platform showed an excellent TCS extraction due to

the large specific surface area and pore volume, uniform mesopores, and π-π structure of CMK-3. In addition, 25-fold concentration of K^+, Na^+, Mg^{2+}, Ca^{2+}, Zn^{2+}, Cu^{2+}, Fe^{3+}, Al^{3+}, Cl^-, NO_3^-, SO_4^{2-} and PO_4^{3-} had no influence on the TCS determination.

Table 2 summarized and compared the most relevant articles related to modified electrodes with different electrochemical techniques for TCS determination. Our detection system also used a very sensitive electroanalytical technique such as SWV, combined with the CMK-3/CH that provides a high selectivity to the electrochemical sensor. Moreover, in this method we measure the oxidation peak current of TCS, and the current response was proportional with the concentration in the sample. Finally, the electrochemical method showed an appropriate linear range and LOD for sensing of TCS in environmental samples.

4. CONCLUSIONS

The aim of this work was to develop an electrochemical sensor for TCS determination in river water samples that can be used as a method for on-site environmental monitoring. The proposed sensor used the high specific surface area, large pore volume, fast electron transfer and excellent electrocatalytic activity of the CMK-3. This mesoporous carbon enabled us to achieve an increased active area, an improved sensibility and a low detection limit. Another relevant feature of this electrochemical sensor is the selectivity, which was provided by the CMK-3/CH platform; the TCS was attracted electrostatically by the positively charged amino groups of CH, and was adsorbed on the mesoporous carbon immobilized onto the SPCE. In addition, the detection limit in this report was lower than previous studies employing an electrochemical method, and allowed us to perform the analysis in a short time, requiring only 15 min, much less than the time normally used for a

screening method. These features make of it an adequate and significant tool for TCS determination in environmental samples.

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Vitae

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Figure captions

Figure 1. (A) Cyclic voltammograms of blank (red line), and 5 mmol L^{-1} TCS (black line) in 0.1 mol L^{-1} PBS buffer pH 9.50 at CMK-3/CH/SPCE (Scan rate = 75 mV s^{-1}). (B) Cyclic voltammograms of 5 mmol L^{-1} TCS in 0.1 mol L^{-1} PBS buffer pH 9.50 at CMK-3/CH/SPCE. Scan rate (from a-g): 25, 50, 75 100, 125, 150, 175 mV s^{-1}.

Figure 2. (A) SEM and (B) TEM micrographs of CMK-3.

Figure 3. (A) X-ray Diffraction pattern and (B) N_2 adsorption-desorption isotherm at 77 K and PSD (insetted) of CMK-3.

Figure 4. (A) Cyclic voltammograms of 1 mmol L^{-1} $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$ in 0.1 mol L^{-1} KCl at (a) Blank/SPCE, (b) bare SPCE and (c) CMK-3/CH/SPCE (Scan rate = 75 mV s^{-1}). (B) Cyclic voltammograms of 1 mmol L^{-1} $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$ in 0.1 mol L^{-1} KCl at CMK-3/CH/SPCE. Scan rate (from a-h): 25, 50, 75 100, 125, 150, 175, 200 mV s^{-1}. Linear relationship between the peak currents (I_p) and the square root of the scan rates ($v^{1/2}$) was insetted.

Figure 5. (A) Study of pH employed for the TCS determination procedure. (B) Study of the CMK-3 concentration employed for the electrode surface modification.

Table 1
Comparison of triclosan concentration in river water samples by voltammetric sensor and high performance liquid chromatography.

Samples[d]	Triclosan concentration[a]	
	VS[b]	HPLC[c]
RW 1	0.89 ± 0.02[e]	0.93 ± 0.03
RW 2	1.35 ± 0.01	1.33 ± 0.04
RW 3	5.14 ± 0.04	5.18 ± 0.06
RW 4	9.19 ± 0.03	9.23 ± 0.05
RW 5	18.53 ± 0.05	18.37 ± 0.02

[a] ng mL^{-1}
[b] Voltammetric sensor
[c] High performance liquid chromatography
[d] River water samples
[e] Mean of three determinations ± S.D.

Table 2
Comparison with other papers involving modified electrodes with different electrochemical techniques for TCS determination.

Modification	**Electrode**	**Technique**	**Linear range** ($ng\ mL^{-1}$)	**LOD** ($ng\ mL^{-1}$)
Electropolymerized molecularly imprinted polymer (MIP) [1]	GCE[a]	CV	57.9-868.6	23.1
Tosyl-functionalized carbon nanoparticles [5]	GCE	CV	2895.4-28954	2895.4
Multiwall carbon nanotube (MWCNT) [7]	GCE	DPV[c]	50-1750	16.5
Screen printed carbon electrode [21]	SPCE	DPV	347.4-289540	347.4
Carbon nanoparticles-poly (diallyldimethylammonium chloride) [37]	ITO[b]	CV	144.7-14477	144.7
Carbon nanodots-chitosan [38]	GCE	LSV[d]	2.89-289540	2.66
CMK-3/CH [this work]	SPCE	SWV	0.8-40	0.24

[a] Glassy carbon electrode
[b] Tin-doped indium oxide (ITO) coated glass
[c] Diferential pulse voltammetry
[d] Linear sweep voltammetry

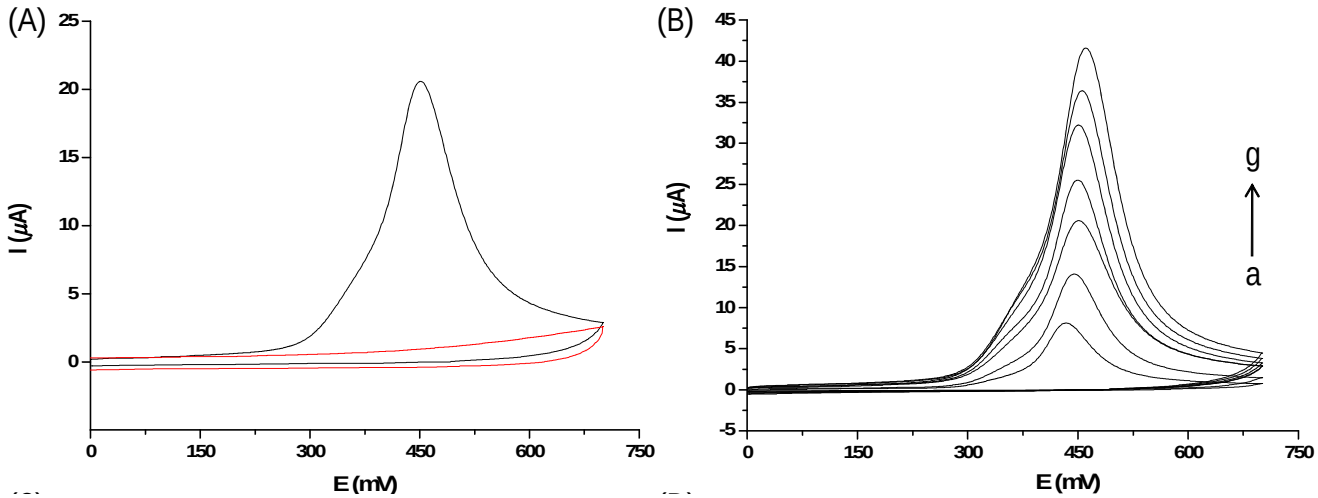

Figure 1

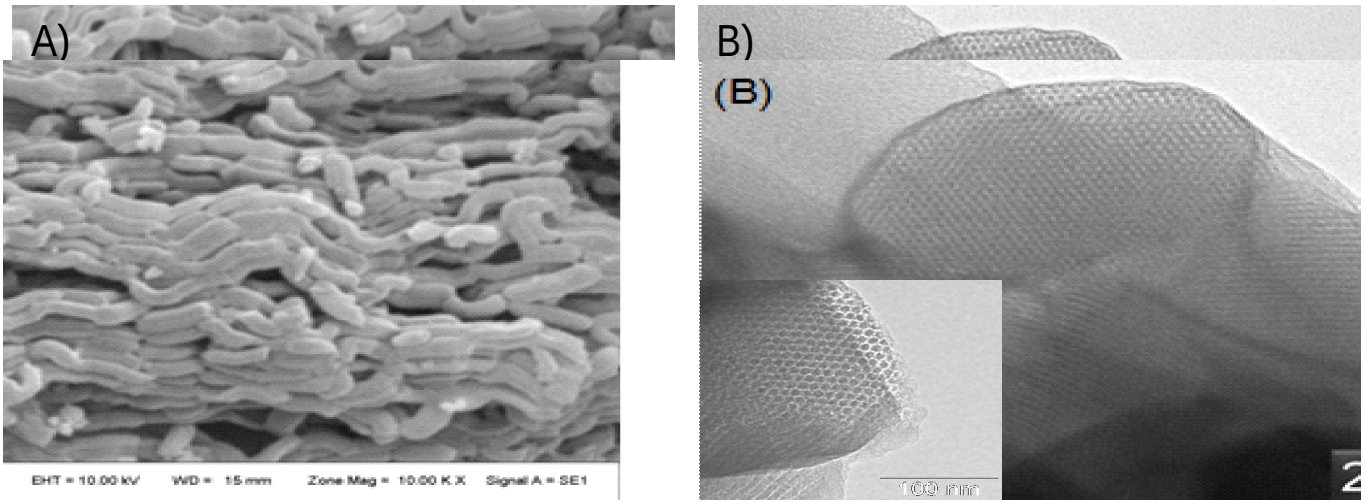

Figure 2

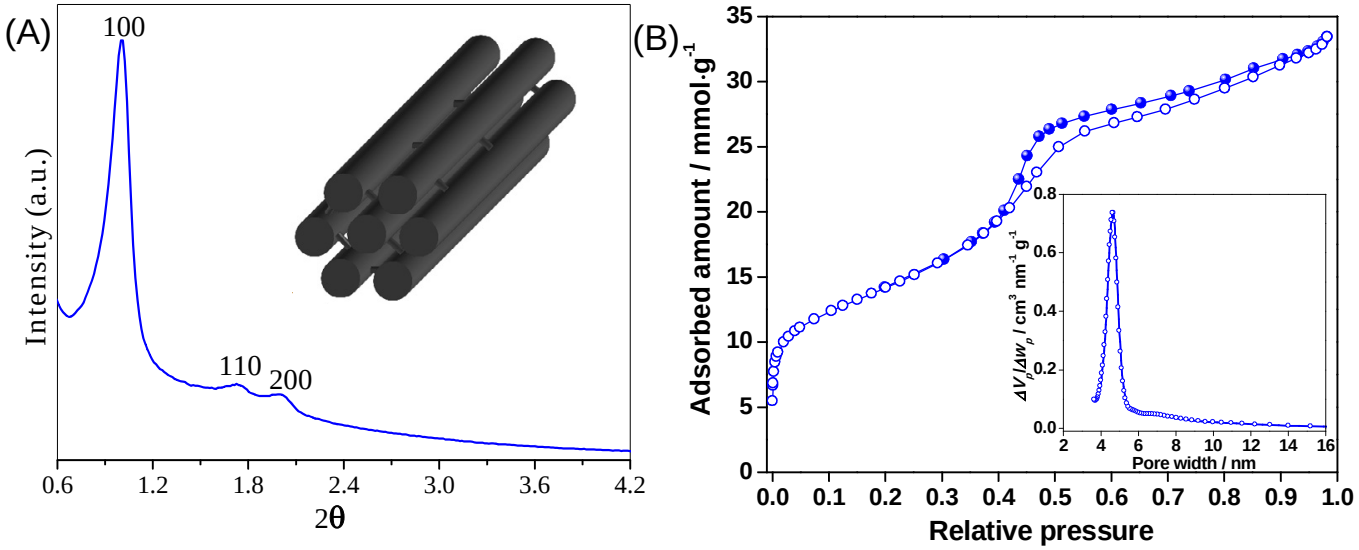

Figure 3

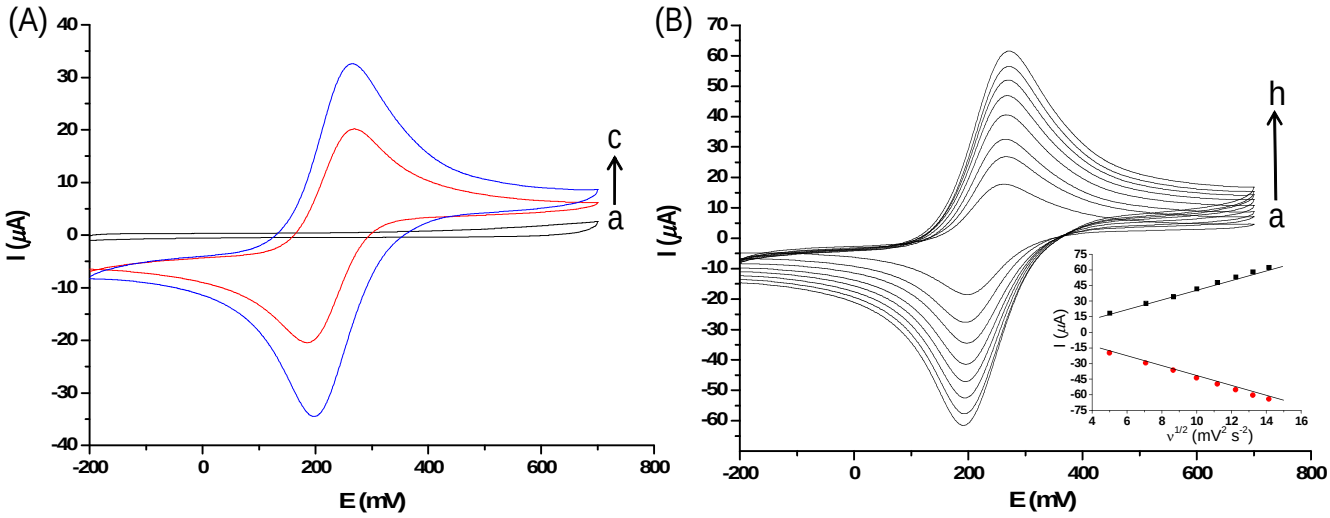

Figure 4

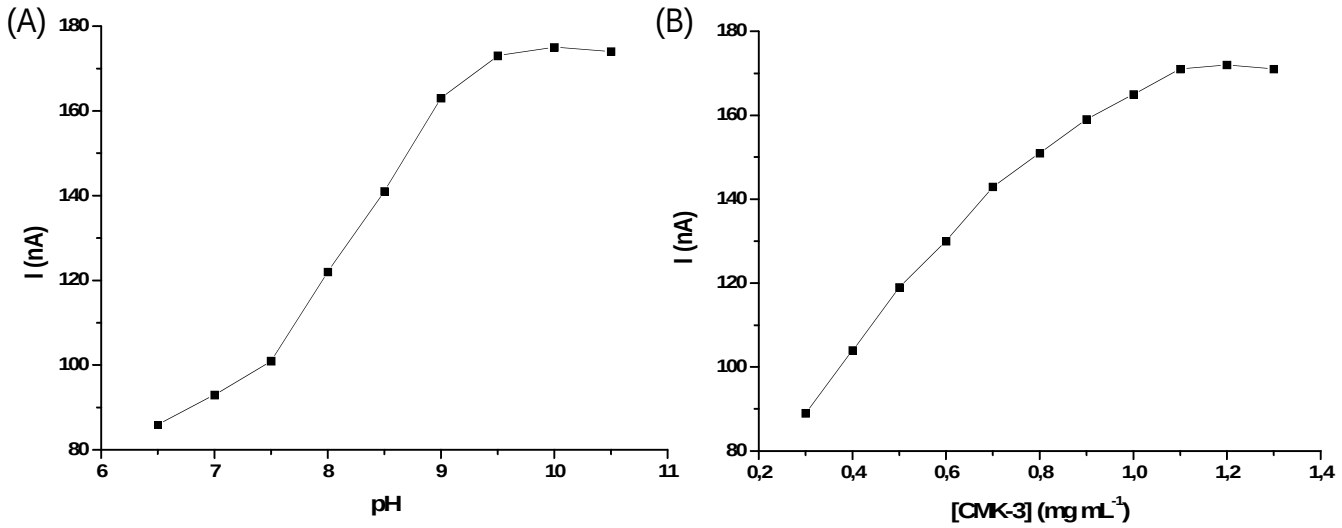

Figure 5