



Ceramic polyaniline-carbon composite obtained by ultrasound-assisted sol-gel route: Electrochemical performance towards environmental pollutants



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ABSTRACT

A new ceramic carbon polyaniline electrode material, namely Sonogel-Carbon-polyaniline (SNG-C-PANI), was synthesized using high-power ultrasound. The synthesis conditions were optimized by means of a full factorial design. The electroactivity of polyaniline, previously characterized by means of Raman spectroscopy, is retained into the sonogel matrix. After the synthesis and the subsequent characterization, the electrode material was applied in the electrochemical determination of a benchmark analyte, 4-chloro-3-methylphenol (PCMC), providing excellent figures of merit, e.g. high sensitivity ($5.19 \times 10^3 \pm 110 \mu\text{A}/\text{mM}\cdot\text{cm}^2$) and low limit of detection (0.36 μM), as well as suitable selectivity and reproducibility (%RSD < 4%). Besides the electroactive surface can be restored by performing a cyclic electrochemical treatment or simple mechanical polishing, minimizing fouling phenomena commonly found in conducting polymer layer-based sensors. The electrochemical detection of other chlorophenols of interest was also performed, obtaining remarkable analytical results. Finally, the electrochemical sensor was successfully applied in spiked tap water analyses.

1. Introduction

The investigations concerning conducting polymers started in the 20th century, with the discovery of a conducting film of polyacetylene obtained by doping with iodine [1]. Since then, several pieces of research focused on diverse properties of conducting polymers, including high electrical conductivity, stability and low cost, have been published [2,3], demonstrating their usefulness for electrochemical sensing purposes [4]. Particularly, polyaniline (PANI) has been deeply studied due to its high conductivity, among other electrochemical properties. It is constituted by three ideal oxidation states: non-oxidized (leucoemeraldine, pale yellow), half oxidized (emeraldine base, blue, or emeraldine salt, green) and fully-oxidized (pernigraniline, violet) [5]. The redox conversion from emeraldine base, insulating nature, to emeraldine salt, conducting nature, has been already exploited in gas sensors [6,7] and other electrochromic devices [8].

The application of this conducting polymer in electrochemical sensors, mainly constituted by conductive thickness-controlled films deposited over supporting electrodes [9,10], should be also addressed. Their nanostructured morphology can be tailored by controlling several factors, such as monomer concentration, instrumental parameters and solvent, among others. In this sense, several polyaniline nanostructures, like nanorods, nanospheres and nanofibers, were characterized by electron microscopy [11].

Their analytical application has been also reported. Polyaniline films undergo deprotonation processes at neutral and alkaline media, decreasing their electroactivity; therefore, their use for electrochemical sensing purposes is limited in biological matrices [12]. The copolymerization of aniline with aniline derivatives can be used to solve out this drawback, avoiding the deprotonation of the polymeric chain and hence, retaining its electroactivity even at physiological pH values [13–16]. The electrochemical evaluation of polyaniline films modified

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with several redox mediators in neutral media has been recently reported in the literature. In this regard, non-enzymatic sensors based on self-doped polyaniline were employed for electrochemical sensing prospects [17–19]. Self-doped enzymatic sensors were also reported. In this regard, self-doped polyaniline/prussian blue was employed as glucose biosensor in human serum, displaying short response time, selectivity and excellent operational stability [20]. Other enzymatic sensors constituted by polyaniline with embedded glucose oxidase and gold nanoparticles were synthesized and evaluated as well [21,22].

In spite of the great electrochemical performance provided by these devices, their lifetime is limited due to the degradation of the film upon the use, as it was reported in bibliography [23,24]. Several strategies to restore the electroactivity of the surface and hence, to overcome fouling effects were investigated. Carbon paste materials modified with polyaniline are promising alternatives to conform electrochemical devices based on their remarkable electrochemical properties and renewable surface. In this sense, silicon dioxide-polyaniline core shell decorated with gold nanoparticles [25], carbon nanofibers decorated with polyaniline and platinum nanoparticles [26] and polyaniline/carbon nanotubes/starch [27] materials have been developed for the determination of several analytes of interest in aqueous electrolytic media. Nonetheless, their low stability in several solvents can be noticed. The inclusion of conducting polymers within a silicon oxide matrix was studied years ago as another alternative to minimize degradation phenomena as well. The silicon oxide network was obtained by high-power ultrasound assisted-sol–gel technology, avoiding the use of any organic solvent. A polythiophene derivative powder synthesized by chemical method was incorporated into the matrix using this procedure. Its electrochemical stability at high potential was demonstrated, suggesting the minimization of overoxidation processes [28]. The entrapment of tyrosinase onto a Sonogel-Carbon surface with a conducting polymer layer obtained by sinusoidal current procedure and its employment in analyzing different wine and beer samples were also reported in literature [29].

We have recently reported the inclusion of a conducting polymer into a silicon oxide network by high-power ultrasound-assisted polymerization of the monomer in the presence of a silane precursor. This novel material, based on Sonogel-Carbon formulation, has been successfully employed on the determination of ascorbic acid in biological and pharmaceutical matrices and cannabinoids in organic/buffer media. The electrode surface was rapidly renewed by a simple polishing method, increasing the usage time of the electrochemical device [30,31].

In this work, the high-power ultrasound synthesis of novel polyaniline-carbon electrode material embedded in a silicon oxide network is developed. With the aim of obtaining a rigid material with optimum electrochemical and mechanical features, a factorial design was used. The electrochemical performance of the SNG-C-PANI device towards 4-chloro-3-methylphenol, a hazard pollutant employed as model organic analyte [32], was evaluated. Although the electrochemical determination of this compound was previously reported with Sonogel-Carbon formulation (without PANI), giving adequate voltammetric responses, a time-consuming preconcentration step was required before performing each analytical measurement [33]. Here the measuring methodology has been simplified further. Besides, several electrochemical studies, including pH, repeatability and reproducibility were assayed with the developed material. Lastly, the developed sensor was applied in the analysis of spiked tap water samples collected from different locations of Andalusia (Spain).

2. Experimental

2.1. Reagents

Aniline was purchased from Riedel-De Haen. Hydrochloric acid was from Panreac. Ammonium persulfate was from Sigma-Aldrich. Methyltrimethoxysilane was from Merck and graphite powder was

from Alfa Aesar. Several salts were used to prepare buffer solutions: sodium formate and formic acid from Merck to prepare formic/formate buffer, acetic acid from Panreac and sodium acetate from ACS reagents to prepare acetic/acetate buffer, and dipotassium phosphate from Merck and potassium diphosphate from Panreac to prepare phosphate buffer solution. To adjust the pH of the buffer solutions, potassium hydroxide from Panreac was employed. Potassium hexacyanoferrate from Sigma Aldrich was used in the electrochemical characterization of the electrochemical device. 4-chloro-3-methylphenol, used as benchmark analyte, was purchased from Merck. Ethanol absolute was obtained from ACS reagents. Several ionic salts were used in the interference study: sodium, potassium and cadmium chloride from Panreac, copper chloride from ACS reagents, mercury chloride from Sigma-Aldrich, potassium chloride, sodium carbonate and sodium sulfate from Merck and sodium nitrate from D’Hemio. Tap water samples were collected from different locations of Andalusia (Spain): the University of Cadiz (Puerto Real – Cadiz), Igualajeja (Malaga) and Granada.

2.2. Instrumentation

The synthesis of SNG-C-PANI and Sonogel-PANI composites was carried out using an ultrasonic generator MISONIX 4000 equipped with a 13 mm titanium tip. Raman spectra were recorded through an *i*-Raman spectrometer B&W Tek, setting the irradiated laser at 785 nm. Acquisition time of spectra was around 8 s, with an average spectral resolution of 4 cm⁻¹. The power of the laser was controlled to avoid the degradation of the samples. Scanning electron microscopy analysis was done with a Nova Nanosem 450 instrument operating at 10 kV. Electrochemical measurements were performed with a Potentiostat/galvanostat PGSTAT20 coupled with a Metrohm unit 663 VA stand. A three-electrode electrochemical cell with the following composition was used: platinum wire as the counter electrode, Ag/AgCl, 3 M KCl as the reference electrode and SNG-C-PANI composite as the working electrode. Sonogel-Carbon-based material was also used as the working electrode for some electrochemical measurements.

2.3. Synthesis of SNG-C-PANI and SNG-C (HCl 1 M; 600 mg C) materials and the corresponding working electrodes

A two-step synthesis of SNG-C-PANI (geometric area: 1.04×10^{-2} cm²) was performed. In the first step, 982 µL of 0.25 M ammonium persulfate in 1 M HCl solution and 18 µL of commercial aniline (0.2 M) were sonicated by means of high-power ultrasound for 60 s at 40% of amplitude (average power of 16 W). After the sonication process, a black green dispersion was observed. In the second step, a mixture containing 480 µL of methyltrimethoxysilane (MTMOS) and 120 µL of the green dispersion previously obtained was sonicated at 40% of amplitude (average power of 10 W). After that, the corresponding amount of graphite powder was added and homogeneously dispersed. The sonication time and amount of graphite powder values tested are shown in Table 1.

The synthesis of Sonogel-Carbon without polyaniline, namely SNG-C (HCl 1 M; 600 mg C) (geometric area: 1.04×10^{-2} cm²) was performed as follows: a mixture containing 480 µL of MTMOS and 120 µL of 1 M HCl solution was sonicated for 40 s at 40% of amplitude (average power of 10 W). After that, 600 mg of graphite powder was added and mixed homogeneously.

The fabrication of the working electrodes was carried out by following the methodology previously reported in literature [34]. In brief, glass capillary tubes (1.15 mm, *i.d.*) were filled with the carbon-based material and compacted. Electrodes were left to dry for one day, and subsequently, they were polished by using a silicon carbide paper (#P1200 from Struers – Germany). The electrodes were ready to use after establishing an electrical contact with a copper wire.

Table 1

Factors and levels established in the design.

Factors	Levels		
	-1	0	+1
Amount of graphite (mg)	500	550	600
Sonication time (s)	40	50	60

-1: low level; +1: high level; 0: central level.

2.4. Experimental design approach

The parameters of the second synthesis step for obtaining the SNG-C-PANI material were studied by means of a 2^2 full factorial design. The amount of graphite powder and the sonication time were selected as factors. Their levels were established according to the mechanical requirements of the electrode materials, as shown in Table 1. Two central points were also included in the design to assure the reproducibility of the synthesis. The response variable in the experimental design was the anodic intensity obtained from the ferrocyanide ion redox process by means of cyclic voltammetry. Electrochemical measurements in presence of 1 mM $K_4[Fe(CN)_6]$ were performed in 0.1 M PBS at pH 7 with 0.5 M potassium chloride as the supporting electrolyte. All the experiments were made by duplicate (two electrodes were used for each formulation) and randomly to avoid bias in the process [35]. Statgraphics software was used for data analysis.

2.5. Electrochemical studies

The general electrochemical procedure was carried out in 25 mL buffer solution with 0.5 M KCl. Before measuring, the buffer solution was purged by passing nitrogen for 10 min and then, eight cyclic voltammetric sweeps ranging from -0.2 V to 0.9 V at 50 mV/s were done in the free-analyte working buffer solution. Electrochemical measurements were performed after adding the corresponding aliquot of stock solution to the electrochemical cell, homogenizing the solution with a magnetic stirrer. The electrochemical characterization of SNG-C-PANI was performed by means of cyclic voltammetry at 50 mV/s in 1 M HCl solution to characterize polyaniline redox processes. Sonogel material was characterized under the same instrumental conditions for comparison purposes. Electrochemical window of the SNG-C-PANI sensor was also studied in different electrolytic media with pH ranging from 4 to 10. Ferrocyanide process was also tested as electrochemical probe with SNG-C-PANI device at different scan rate values. Electrochemical measurements in presence of 10 μ M PCMC were performed in several electrolytic media with pH ranging from 3 to 7: Formic/formate buffer ($HCOOH/HCOO^-$) for pH 3, acetic/acetate buffer (CH_3COOH/CH_3COO^-) for pH 4–5 and phosphate buffer ($H_2PO_4^-/HPO_4^{2-}$) for pH 6–7. In any case, 0.5 M KCl was included as supporting electrolyte. The following DPV conditions were employed: 50 mV modulation amplitude; 8 mV step potential; 0.4 s interval time; 0.05 s modulation time. Differential pulse voltammograms in presence of PCMC ranging from 0.7 to 10 μ M were recorded with the SNG-C-PANI electrochemical device under the same instrumental conditions previously described. Firstly, the background current was recorded in 25 mL of the working buffer solution. After then, the corresponding volume of the 1 mM PCMC solution was added in the electrochemical cell. After the addition and the subsequent magnetic stirring of the solution for 20 s, three successive DPV signals were recorded. The electrochemical renewal of the electrode was applied after the analysis of each concentration by performing fifteen cyclic voltammetric sweeps, ranging from -0.2 V to 0.9 V in 17 mM of potassium hydroxide and 0.1 M lithium perchlorate solution at 50 mV/s. Mechanical polishing of the electrode surface was also performed to restore its electroactivity and increase its usability.

2.6. Water sample analysis

The water samples were analyzed by following a similar methodology reported in bibliography [36]. Firstly, tap water was spiked with 30 μ M of PCMC by adding the corresponding aliquot of 1 mM PCMC stock solution. Afterwards, spiked tap water was diluted 10 times with the working buffer solution in a 25 mL volumetric flask. The electrochemical renewal of the electrode, previously explained in Section 2.5, was applied after performing the corresponding set of analytical measurements for each concentration value tested. The electrochemical analyses were done by triplicate.

2.7. Preparation of SNG-PANI, SNG and polyaniline samples for structural characterization

Sonogel-polyaniline, namely SNG-PANI, was prepared as follows. Firstly, the sonosol was synthesized according to the procedure given in the section 2.3. The as-prepared sample was placed in a cylindrical holder and dried at room temperature for one day. Sonogel, namely SNG, was prepared following the same procedure but replacing the polyaniline dispersion by 1 M HCl solution. After the drying step, the resulting samples were grounded separately with an agate mortar to obtain fine powders. On the other hand, the polyaniline powder was prepared following the first step of the process detailed in subsection 2.3. Afterwards, dispersion was centrifuged for 5 min at 4000 rpm. The supernatant was removed and the resulting powder, namely PANI-US, was dried in an oven for 16 h at 60 °C.

3. Results and discussion

3.1. Sonochemical synthesis of polyaniline-based electrode materials: screening parameters

3.1.1. Polymerization of aniline: UV–Vis monitoring

The polymerization of aniline with ammonium persulfate (APS), in 1 M HCl using aniline: APS molar ratio at 1:1.25 [37–39], was monitored by UV–Vis spectroscopy. Several sonication time values ranging from 15 to 90 s were assayed. After sonication, UV–Vis spectra corresponding to each diluted dispersion were recorded (Fig. 1).

A broad signal around 560 nm was observed in the UV–Vis spectrum recorded at 15 s, attributed to the $\pi-\pi^*$ transition of quinoid groups. Two broad bands around 350 and 680 nm are distinguishable at 30 s, attributed to $\pi-\pi^*$ transitions of benzenoid and quinoid groups, respectively. After 60 and 90 s of polymerization, two main bands located at 440 and 780 nm can be noticed, ascribed to polaronic bands of polyaniline emeraldine salt [40]. Based on the above study, polyaniline emeraldine salt was obtained in 1 min under the instrumental conditions previously mentioned; thus, this sonication time will be employed in further studies.

3.1.2. Fabrication of SNG-C-PANI electrodes: study of polymer/alkoxide ratio and proportion of graphite powder

The synthesis conditions of the preliminary polyaniline-ceramic carbon composites were based on the SNG-C formulation reported in a previous work [34]. The hydrochloric acid, used as catalyst solution in the SNG-C fabrication was replaced by the PANI dispersion obtained in the first synthesis step reported in the experimental section. Polymer/alkoxide volume ratio was evaluated, ranging from 1:7 (v/v) to 1:1 (v/v). Remaining conditions, sonication time and amount of graphite powder were fixed at 10 s and 500 mg, respectively. Worse mechanical characteristics in terms of low adherence between the material and the capillary tube were evidenced for formulations with high polymer/alkoxide volume ratio values, 1:1, 1:2 and 1:3 (v/v). Concerning the remaining formulations synthesized, ranging from

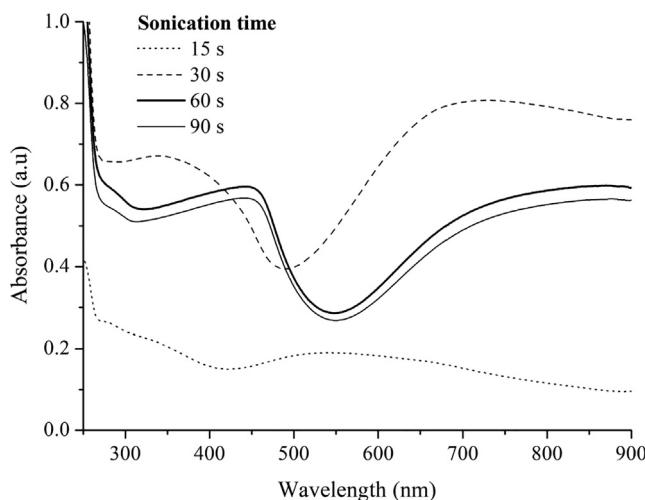


Fig. 1. UV-Vis spectra recorded with diluted dispersions of polyaniline obtained at different sonication times.

1:7 to 1:4 (v/v), good adherence material/capillary tube was observed after the drying step.

Electrode materials with lower polymer/alkoxide volume ratio ranging from 1:7 and 1:4 were electrochemically evaluated using the ferrocyanide probe. Fig. 2 shows the voltammograms recorded in a neutral electrolytic medium in presence of 1 mM $K_4[Fe(CN)_6]$.

As observed in the previous figure, the oxidation peak current seems to be increased with the polymer/alkoxide volume ratio. This behavior can be attributed to the higher proportion of emeraldine salt, the conducting form of polyaniline. Based on these results, polyaniline/alkoxide volume ratio with 1:4 (v/v) will be selected for future studies.

The proportion of graphite powder included in the material was also studied to obtain conducting materials with suitable mechanical features. In this regard, values ranging from 400 to 700 mg were investigated. Graphite amounts ranging from 500 mg to 600 mg led to SNG-based materials with suitable mechanical characteristics.

3.2. Sonochemical synthesis of polyaniline-based electrode materials: experimental design

Experimental design was performed to study the effect of the factors and their interactions in the electrochemical response of the

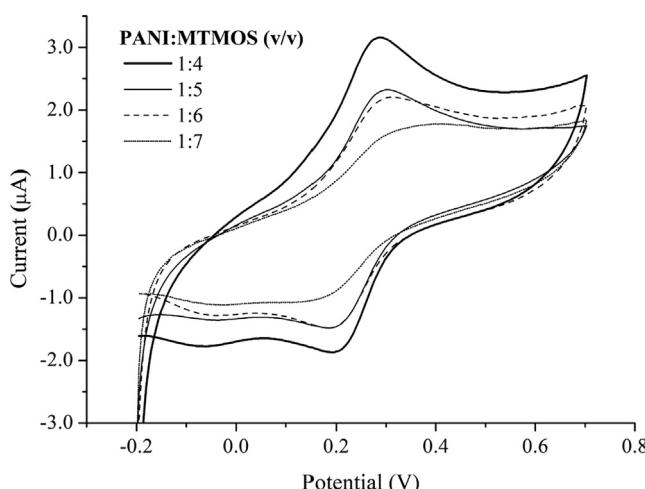


Fig. 2. Cyclic voltammograms recorded with SNG-C-PANI devices with different silane/polyaniline volume ratio in presence of 1 mM of potassium hexacyanoferrate (II) at 50 mV/s, in 0.1 M phosphate buffer at pH 7. 0.5 M KCl was used as supporting electrolyte.

device. Cyclic voltammograms with remarkable shapes displayed two redox peaks, ascribed to the oxidation/reduction of potassium hexacyanoferrate. As illustrative examples, the cyclic voltammogram corresponding to the formulation which provides the best electrochemical response in terms of peak current and reversibility, and another cyclic voltammogram derived from the central point are shown in the supplementary material (see Fig. S1).

The experimental results derived from the experimental design, in terms of anodic peak intensity and differences between anodic and cathodic potentials, are summarized in Table 2.

From the previous table, higher anodic intensities were observed when sonication time takes the lowest value. Regarding the amount of graphite, no trend on the response was observed. The variability of the measurements, expressed as the variation coefficient, is lower than 5% for all the experiments, indicating a good repeatability. Furthermore, high electrochemical reversibility can be pointed out based on the differences between anodic and cathodic peak potentials, E_a-E_c , closed to 59 mV in all cases.

The effect of factors and their interactions on the response was statistically analyzed by the analysis of variance at a significance level of 95%. The vertical line in Pareto diagram (see Fig. 3A) determined that sonication time is the only significant factor with a negative effect, which means that lower sonication times led to higher peak intensities. The interaction between both factors was also found significant. From the interaction plot (see Fig. 3B), high influence of the interaction on the response can be ascribed: electrochemical intensity is maximized with the amount of graphite when sonication time takes the lowest level, while analytical current is reduced with the amount of graphite when sonication time takes the highest one. The presence of the center point allows estimating that a curvature is present on the response surface, as shown in Fig. 3C; the interaction between both factors, previously discussed in Pareto diagram and interaction plot, determines the inclination of the response surface. Based on above, the anodic intensity seems to be maximized at higher amount of graphite and at lower sonication time.

From the experimental design, the following synthesis conditions were established for the second step: $V_{MTMOS} = 480 \mu L$; $V_{PANI} = 120 \mu L$; $A = 40\%$; $t = 40$ s; $C_{graphite} = 600$ mg.

3.3. Electrochemical characterization of SNG-C-PANI device

3.3.1. Electrochemical study of the electroactivity of polyaniline

The new synthesized material was electrochemically characterized by cyclic voltammetry in an acid medium, 1 M HCl. For the sake of comparison, the cyclic voltammogram recorded with Sonogel-Carbon synthesized under the same conditions but replacing the PANI dispersion by 1 M HCl aqueous solution, namely SNG-C (HCl 1 M; 600 mg C), was also shown (see Fig. 4A). Two oxidation peaks located around 0.2 and 0.9 V, attributed to the leucoemeraldine-emeraldine and emeraldine-pernigraniline oxidation processes, respectively, are noticeable for SNG-C-PANI sensor. Their corresponding cathodic counterparts can be evidenced in the reverse scan. Two central peaks related to the shrinkage of the polymeric chains are also remarkable [41,42]. No relevant peaks were found in the cyclic voltammogram recorded with the sonogel material without polyaniline. Thus, the electroactivity of polyaniline in the SNG-C-PANI sensor was confirmed.

The SNG-C-PANI material was electrochemically tested in several buffer media reported in the experimental section. Different voltammetric shapes were observed depending on pH value (see Fig. 4B), which may be explained considering the dependence of the electroactivity of polyaniline with the pH, previously discussed in the literature [43,44].

3.3.2. Electrochemical evaluation of developed material: Electrochemical study of the ferrocyanide probe

The electrochemical behavior of the SNG-C-PANI material was studied using ferrocyanide ion as electrochemical probe. Two well-

Table 2
Experimental results derived from the experimental design.

Experiments	Experimental conditions		Anodic intensity \pm $^1\text{SD}(\mu\text{A})$	E_a-E_c (mV)	$^{2\text{CV}}$ (%)
	C_{graphite} (mg)	$t_{\text{sonication}}$ (s)			
1,5	500	40	1.35 \pm 0.03	78.0	2.22
2,6	600	40	1.44 \pm 0.01	78.0	0.69
3,7	600	60	1.17 \pm 0.04	108	3.42
4,8	500	60	1.33 \pm 0.01	88.0	0.75
9,10*	550	50	1.23 \pm 0.03	83.0	2.44
11,12*	550	50	1.24 \pm 0.03	88.0	2.42

^1SD = Standard Deviation.

$^{2\text{CV}}$ = Percentage of variation coefficient.

*Central points.

defined peaks located at 0.28 and 0.2 V, ascribed to the redox processes of the ferrocyanide ion, were observed at all scan rate values studied (see Fig. 4C). The anodic and cathodic peak current ratio values were close to 1 for all scan rates tested, which indicates the quasi-reversible nature of the redox process [45]. The relationship between the peak height and the square root of the scan rate is linear, with a correlation coefficient around 0.999 (inset of Fig. 4C), indicating that the mechanism which takes place on the electrode surface is preferably diffusion controlled.

3.4. Electrochemical performance of SNG-C-PANI device for the determination of 4-chloro-3-methylphenol, used as organic analyte

3.4.1. Preliminary detection of PCMC by means of cyclic voltammetry

The electrochemical performance of the SNG-C-PANI device towards PCMC was investigated by means of cyclic voltammetry. Electrode material namely SNG-C (HCl 1 M; 600 mg C), previously electrochemically characterized, was used for comparison purposes. A substantially increase of the background current was recorded for SNG-C-PANI (see Fig. 5), attributed to the presence of the polymer. Additionally, higher peak intensity can be evidenced with the conducting polymer-based device, ascribed to the conducting role of the PANI within the material.

3.4.2. pH study

Electrolytic media with different pH values were studied, as previously detailed in Section 2.5. The oxidation peak is shifted with the pH of the electrolytic medium (see Fig. 6A), suggesting the participation of the protons in the electrochemical process [46]. The relationship between the peak potential and the pH is linear, with a slope of 58 mV (see Fig. 6B), indicating the involvement of the same number of electrons and protons in the electrode reaction (see Scheme 1). This result is in consonance with other works focused on the electrochemical determination of PCMC and similar redox compounds [47,48].

In order to obtain voltammetric peaks with remarkable shapes and sensitivities, the peak current and width ratio ($I_p/\omega^{1/2}$) was considered in this study. Based on the experimental results shown in Fig. 6B, acetic/acetate buffer at pH 4 led to the best $I_p/\omega^{1/2}$ value.

The repeatability of the electrochemical measurements should also be considered, since the electrochemical oxidation of phenol and substituted phenols is very complex [47,49]. Similar oxidation peak heights were obtained in acid buffer (see Fig. S2), suggesting that the formation of non-conducting layers due to the adsorption of intermediate products on the electrode surface plays a minor role in this medium. Based on above, acetic/acetate at pH 4 was chosen in this work as the best option for the electroanalysis of the target chlorophenol.

3.4.3. Renewal surface and reproducibility study

Preliminary electrochemical assays of PCMC using the developed material pointed out a decreasing trend on the peak height with the

number of electrochemical measurements (see Fig. S3); thus, the renewal of the electrode surface was attempted to improve the repeatability of the electrochemical measurements provided with the sensor.

Several cyclic voltammetric sweeps in acetic/acetate buffer at pH 4, highly acid (hydrochloric acid) or highly basic solutions (potassium hydroxide) [50] were applied after performing each analysis, following the procedure detailed in the experimental section. Decreasing trends on the peak height after performing the renewal procedure in buffer and acid media, around 56% and 53% of the initial measurement (see Fig. S4A), respectively, can be noticed. On the contrary, similar oxidation peak heights after performing successive renewals in basic solution were evidenced. Based on this study, the repeatability of the electrochemical measurements using basic renewal procedure is remarkable.

Even though the electrochemical renewal provides meaningful improvement in the variability of the response, the mechanical polishing of the electrode surface was also evaluated, based on reproducible results displayed with other similar electrode materials in previous works [30,31]. The DPV voltammogram recorded after performing the mechanical renewal and the subsequent electrochemical treatment resulted perfectly overlapped with the initial one (Fig. S4B). Thus, it is possible to state that the electroactivity of the electrode surface is totally restored by using the mechanical polishing and voltammetric treatment tandem.

The reproducibility of the electrochemical responses using five SNG-C-PANI sensors was also assessed. Similar peak heights were obtained (see Fig. S5), with a variation coefficient lower than 4%, demonstrating the excellent reproducibility of the analytical measurements.

3.4.4. Effect of concentration of PCMC

Several concentrations of PCMC ranging from 0.7 μM to 10 μM were evaluated with the sensor developed in this work under the instrumental DPV conditions given in the Experimental section. Fig. 7 depicts the voltammograms recorded for each concentration of PCMC together with the corresponding calibration curve.

Well-defined DPV signals can be evidenced for all concentration values tested, with a linear relationship between peak height and concentration of PCMC ($R^2 = 0.999$). The error bars for each concentration are greatly reduced, showing a mean value lower than 4% in all cases (considering three independent assays for each concentration). On the basis of these results, an outstanding variability of the measurements was revealed and hence, their repeatability can be stated.

The sensitivity was determined as the slope of the regression line. The value obtained was $5.19 \times 10^3 \pm 110 \mu\text{A}/\text{mM}\cdot\text{cm}^2$. The sensitivity displayed with the SNG-C-PANI sensor is higher than the one displayed with the ceramic material without polyaniline, exposing the relevant conducting role of the polyaniline. The limit of detection (LD), calculated as three times the standard deviation of the intercept divided by the slope of the regression line, was 0.36 μM . Importantly,

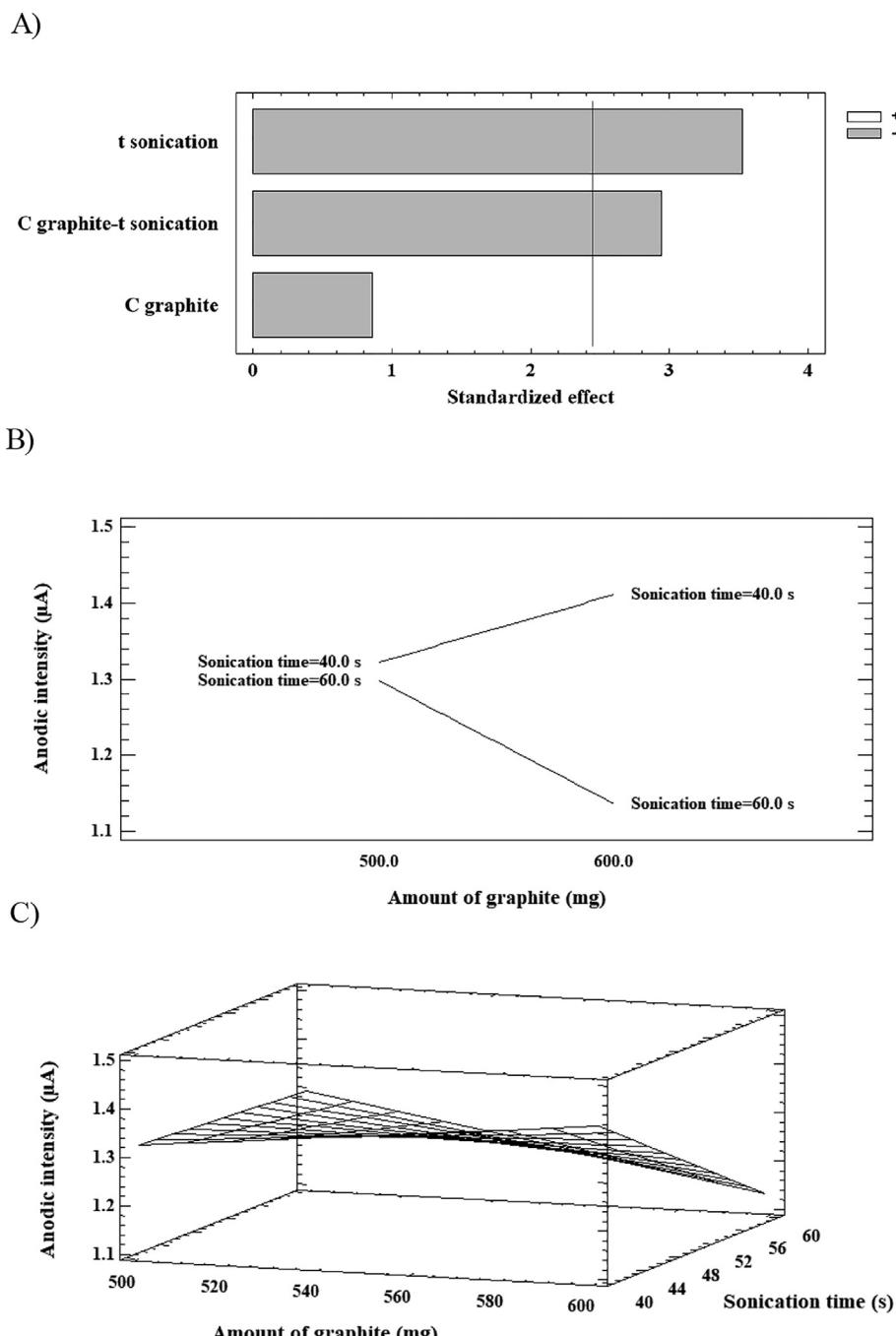


Fig. 3. (A) Pareto diagram with standardized effects derived from the experimental design. (B) Interaction plot between the amount of graphite powder and sonication time. (C) Response surface derived from the design.

the figures of merit calculated are comparable with other electrochemical devices reported in literature (see Table 3).

Besides, the sensitivity of the device developed in this work is higher than almost all cases reported in the literature, according to Table 3, indicating better electrochemical behavior for PCMC detection. Furthermore, low detection limit was reached, similar than those shown in the previous table. It is noteworthy to mention that the limit of detection calculated is lower than the maximum concentration of PCMC allowed for water organisms, following the ambient water quality criteria established by the environmental agency [51]. Moreover, its surface can be renewed easily using an electrochemical treatment and/or by simple mechanical polishing. Additionally, the easy, low cost and low-time consuming fabrication method of the working electrodes should be also highlighted. For all these reasons, the sensor

developed in this work is very promising for the electroanalytical determination of chlorophenols.

3.4.5. Influence of salts on the analytical performance of the device

Several inorganic salts present in water samples were tested in presence of 7 μM of PCMC. In this sense, sodium, potassium and calcium salts were analyzed at 100-fold higher than PCMC. Regarding chloride compounds constituted with metals commonly found in water, 10-fold higher than PCMC was tested. The percentage of the electrochemical current was calculated by using the following equation:

$$\text{Response}(\%) = \frac{I_{\text{PCMC+ionic salt}}}{I_{\text{PCMC}}} \times 100$$

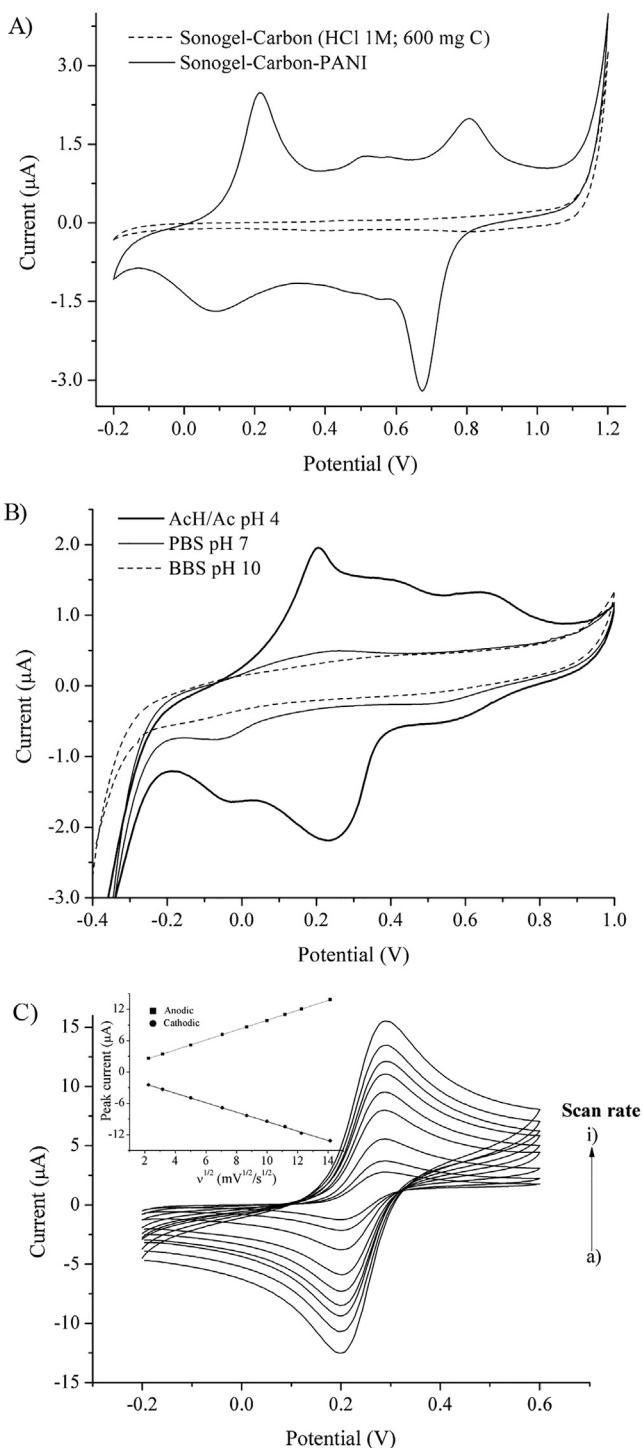


Fig. 4. (A) Cyclic voltammograms recorded with SNG-C (HCl 1 M; 600 mg C) and SNG-C-PANI in 1 M HCl solution (free-analyte), at 50 mV/s. (B) Cyclic voltammograms recorded with SNG-C-PANI in several buffer media with different pH, at 50 mV/s. (C) Cyclic voltammograms recorded with SNG-C-PANI sensor in presence of 5 mM of potassium hexacyanoferrate (II) at different scan rate values, in 0.5 M KCl.

Where $I_{PCMC+ionic\ salt}$ is the peak current corresponding to the mixture of PCMC and the ionic salt tested and I_{PCMC} is the peak current corresponding to the PCMC oxidation without any compound. Experimental results are shown in Fig. 8.

The percentage values were ranging from 95 to 110% in all cases tested, revealing the low influence of inorganic salts on the electroox-

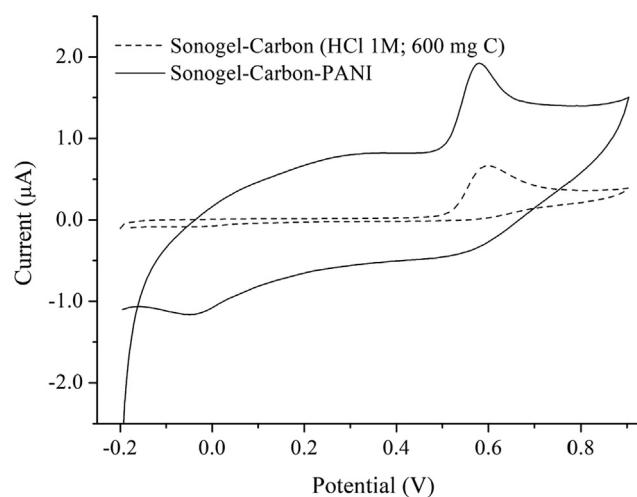


Fig. 5. Cyclic voltammograms recorded with SNG-C-PANI and SNG-C (HCl 1 M; 600 mg C) sensors in presence of 100 μM PCMC in 0.1 M PBS, pH 7, with 0.5 M KCl at 50 mV/s.

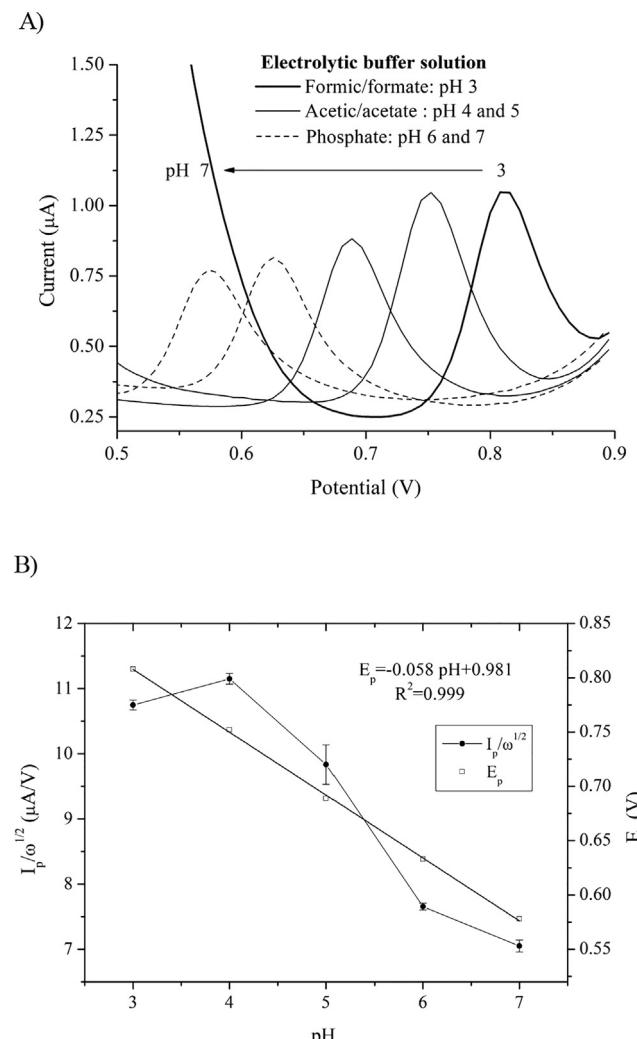
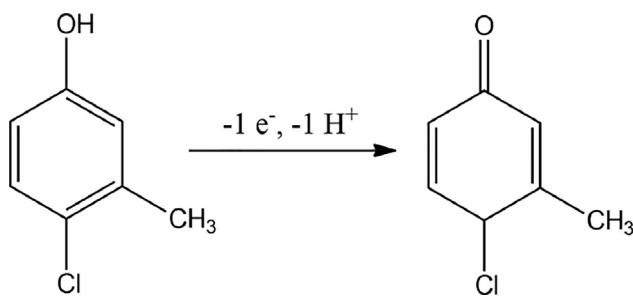
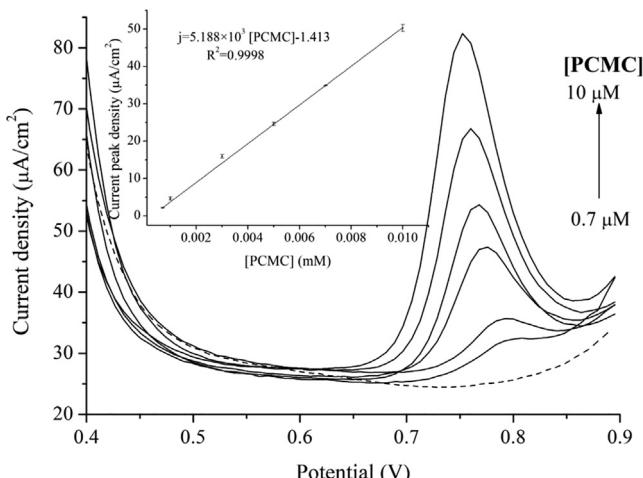


Fig. 6. (A) DPV signals recorded with SNG-C-PANI sensor in presence of 10 μM PCMC in different electrolytic media. 0.5 M KCl was used as supporting electrolyte in any case. (B) Dependence of peak current/width ratio and peak potential in presence of 10 μM PCMC with the pH.

**Scheme 1.** Electrochemical oxidation mechanism of PCMC.**Fig. 7.** DPV signals in presence of several concentration of PCMC ranging from 0.7 μM to 10.0 μM : 0.7 μM ; 1.0 μM ; 3.0 μM ; 5.0 μM ; 7.0 μM and 10.0 μM . The dashed line corresponds to the background. The inset reports the calibration curve with the regression line.

idation of PCMC. Therefore, the suitable electrochemical sensing of PCMC with the developed sensor in presence of several salts was demonstrated. Thus, it was feasible to propose the sensor for further studies concerning real water sample analysis.

3.4.6. Tap water analysis

The determination of PCMC in spiked tap water samples was carried out with the developed device by standard addition method. The recovery was calculated by using the following expression:

Table 3
Analytical parameters of PCMC obtained by using different electrochemical sensors.

Electrode material	Analytical parameters			Reference
	Sensitivity ($\mu\text{A}/\text{mM}\cdot\text{cm}^2$)	LD (μM)	LR (μM)	
GP-CCE	2.80×10^2	2.71	9.00–29.0	[36]
CNT-CCE	1.40×10^3	0.71	3.00–32.0	[36]
BDDE	2.65×10^2	0.36	0.50–10.0	[54]
UiO-66-NH ₂ -@PEDOT/GA/GCE	1.87×10^0	0.20	0.60–18.0	[48]
MWCNT/GC	5.91×10^3	8.80	14.0–137.5	[55]
SNG-C (HCl 1 M; 600 mg C)	3.96×10^3	0.52	0.70–7.00	This work
SNG-C-PANI	5.19×10^3	0.36	0.70–10.0	This work

GP-CCE: Graphite-Carbon Ceramic Electrode; CNT-CCE: Multi-walled Carbon Nanotubes-Carbon Ceramic Electrode; BDDE: Boron-doped Diamond Electrode; UiO-66-NH₂-@PEDOT/GA/GCE: UiO-66-NH₂-metal organic framework modified with PEDOT and graphene aerogel; SNG-C (HCl 1 M; 600 mg C): Sonogel-based material without polyaniline (synthesized with 1 M HCl solution); SNG-C-PANI: Sonogel-Carbon-Polyaniline; LD: Limit of Detection; LR: Linear Range.

$$\text{Recovery}(\%) = \frac{C_{\text{det}}}{C_{\text{spiked}}} \times 100$$

Where C_{det} is the concentration of PCMC determined in the tap water using proposed methodology and C_{spiked} is the concentration of PCMC added to tap water sample.

The recovery values obtained, ranging from 95% to 105% (see Table 4), are very satisfactory according to analytical standards. The coefficient of variation, considering three independent assays, is lower than 5% for all samples analyzed, proving the adequate repeatability of the electrochemical measurements.

From the above-mentioned results, the successful application of the SNG-C-PANI sensor in the electrochemical analysis of spiked tap water samples collected from different locations of Andalusia (Spain) was clearly established.

3.5. Electrochemical performance of SNG-C-PANI device for the detection of other chlorophenols: 2,4-dichlorophenol (DCP) and 2,4,6-trichlorophenol (TCP)

Based on the promising electrochemical features of the developed material for PCMC determination, the electrochemical performance towards 2,4-dichlorophenol (DCP) and 2,4,6-trichlorophenol (TCP) was also tested. SNG-C (HCl 1 M; 600 mg C) was employed for comparison.

As it can be seen in Fig. 9A and B, the oxidation peaks obtained with SNG-C-PANI are higher than those corresponding to SNG-C (HCl 1 M; 600 mg C); thus, the SNG-C-PANI material displays better electrochemical performance towards both analytes. Therefore, the sensor developed in this work seems to be promising for the electrochemical detection of different chlorophenols.

3.6. Structural characterization of Sonogel-PANI based materials

3.6.1. Characterization of Sonogel-PANI by Raman spectroscopy

Sonogel-polyaniline material (SNG-PANI) was characterized by means of Raman spectroscopy. The sonogel material synthesized under the same conditions but replacing the PANI dispersion by 1 M HCl solution (SNG-1 M HCl) and polyaniline powder obtained by using the preparation route described in the experimental section (PANI-US), were also characterized for comparison purposes. Fig. 10 shows Raman spectra recorded for all samples.

The main bands of polyaniline can be observed in the Raman spectrum recorded with SNG-PANI sample, all of them absent in sonogel-based spectrum and present in the one recorded with polyaniline powder: 1170 cm^{-1} , ascribed to C–H vibrations of aromatic rings; 1250 cm^{-1} , attributed to C–N stretching; 1330 and 1375 cm^{-1} , ascribed to C–N^{•+} stretching of polaronic units; 1500 cm^{-1} , ascribed to N–H deformation; and 1600 cm^{-1} , attributed to C–C stretching of

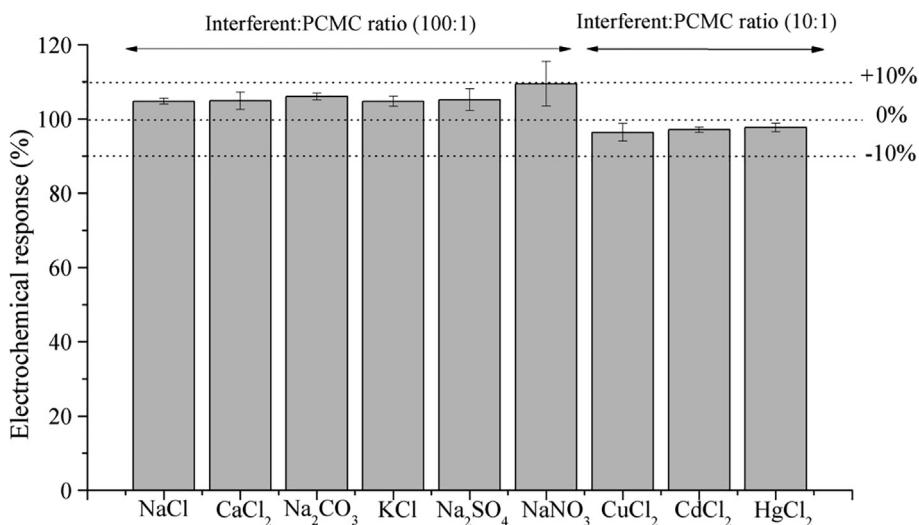


Fig. 8. Electrochemical responses provided by SNG-C-PANI sensor in presence of 7 μM of PCMC and several ionic salts.

Table 4

Experimental results derived from the analysis of PCMC in spiked tap water.

Tap water samples	C_{spiked} (μM)	$C_{\text{det}} \pm {}^1\text{SD}$ (μM)	Recovery \pm SD (%)
Cadiz	3.00	3.05 ± 0.04	102 ± 1.39
Granada	3.00	3.11 ± 0.01	104 ± 0.40
Malaga	3.00	2.93 ± 0.12	97.7 ± 3.88

¹ SD = Standard Deviation.

benzene rings [52,53]. Therefore, the presence of polyaniline in the sonogel network was confirmed.

3.6.2. Surface characterization of SNG-C-PANI electrodes by scanning electron microscopy and elemental analysis by X-ray energy dispersive spectroscopy (EDS)

Alternatively, the surface of SNG-C-PANI sensor was characterized through scanning electron microscopy (SEM). No separation between material and capillary tube was appreciated in the micrograph corresponding to a non-used electrode (see Fig. S6A), attributed to no volume contraction after drying step. After performing several analytical measurements, separation capillary tube/material does not seem to increase, which can be ascribed to low effect of erosion phenomena (see Fig. S6B). More specific surface analysis can be done by recording SEM micrographs at higher magnifications (see Fig.s S6C y S6D). Fissures and holes can be evidenced in both micrographs, although a cracking surface was evidenced after using the electrode and hence, the effects of the analytical measurements and the subsequent electrochemical treatment on the surface characteristics should be addressed. Nevertheless, great number of fissures were not observed after use, indicating the usability of the sensor after long time of analysis.

Elemental analysis was done by using EDS technique. The presence of silicon and oxygen, ascribed to silicon oxide network and carbon, attributed to graphite powder and the polymeric backbone was confirmed (see Fig. S6E). Chloride and sulfur can be explained considering the employment of hydrochloride and ammonium persulfate solution for the polymerization of polyaniline.

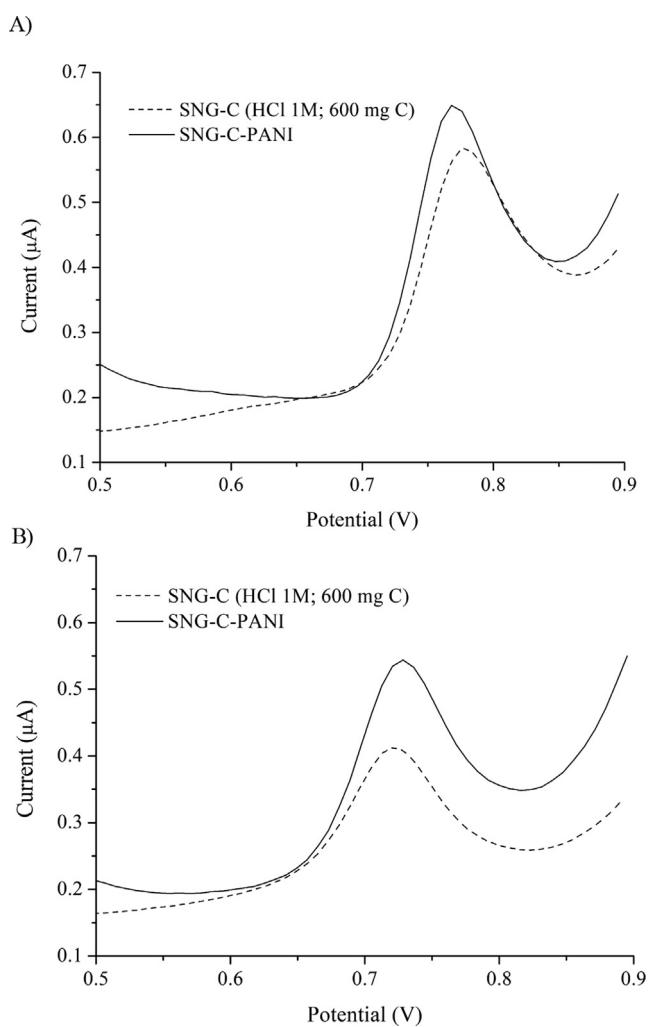


Fig. 9. (A) Differential Pulse voltammograms recorded with SNG-C-PANI and SNG-C (HCl 1 M; 600 mg C) in presence of 10 μM dichlorophenol (DCP). (B) Differential Pulse voltammograms recorded with SNG-C-PANI and SNG-C (HCl 1 M; 600 mg C) in presence of 10 μM trichlorophenol (TCP).

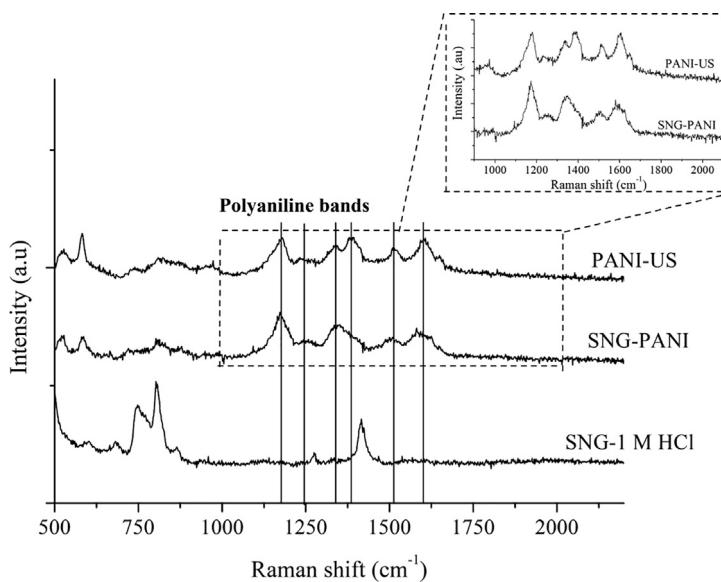


Fig. 10. Raman spectra recorded for PANI-US, SNG-1 M HCl and SNG-PANI samples.

4. Conclusions

New polyaniline-carbon ceramic composite was successfully synthesized by using the high-power ultrasound-assisted sol-gel technology. The preservation of the polymer electroactivity into the sonogel matrix was corroborated by cyclic voltammetry studies. SNG-C-PANI showed satisfactory analytical features towards the determination of 4-chloro-3-methylphenol, used as model organic analyte: excellent figures of merit, high reproducibility and low influence of several ionic compounds on the electrochemical response. Furthermore, the electroactivity of the surface was restored by performing simple and fast renewal procedures after routine analysis, minimizing fouling and degradation phenomena. Moreover, the electrode material displayed remarkable results for the electrochemical sensing of other chlorophenols of interest.

Based on the promising analytical performance exposed in this work, SNG-C-PANI can be considered as an excellent alternative to electrochemical conducting polymer layer-based devices and other carbon-based materials for the electrochemical analyses of electroactive analytes as in buffer as in tap water samples.

CRediT authorship contribution statement

David López-Iglesias: Investigation, Methodology, Formal analysis, Writing – original draft. **Francesca Fanelli:** Formal analysis, Writing – review & editing. **Lorenzo Marchi:** Formal analysis, Writing – review & editing. **Rodrigo Alcántara:** Supervision, Writing – review & editing. **Marina Cocchi:** Conceptualization, Supervision, Writing – review & editing. **Laura Cubillana-Aguilera:** Conceptualization, Funding acquisition, Resources, Writing – review & editing. **José María Palacios-Santander:** Conceptualization, Funding acquisition, Resources, Writing – review & editing. **Juan José García-Guzmán:** Formal analysis, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jelechem.2021.115971>.

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