

## Article

# Bulk Modification of Sonogel–Carbon with Polyaniline: A Suitable Redox Mediator for Chlorophenols Detection

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**Abstract:** In this work, the development and characterization of a new ceramic material modified with polyaniline powder obtained by a high-power ultrasound sol-gel route is presented. A preliminary screening of the conducting polymer electroactivity was performed by means of cyclic voltammetry in free analyte solution. Remarkable figures of merit for 4-chloro-3-methylphenol (PCMC) determination, selected as the model organic analyte, was obtained with the developed material: the sensitivity and the limit of detection were  $2.40 \mu\text{A}/\mu\text{M}\cdot\text{cm}^2$  and  $0.69 \mu\text{M}$ , respectively. The developed device was also successfully applied in the electrochemical determination of PCMC in water samples collected from different sources, obtaining recovery values ranging from 92% to 105%. The electrochemical performance of the device for the detection of other chlorophenols of interest was better in comparison with the bare electrode in all cases, due to the presence of the bulk modifier in the material. Therefore, the electrode material can be promoted for electrochemical assays of different chlorophenols in buffer and real water media for environmental monitoring.



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**Keywords:** Sonogel–Carbon; polyaniline; bulk modifier; 4-chloro-3-methylphenol; spiked water

## 1. Introduction

Presently, conducting polymers are widely investigated due to their high electrical conductivity and tailored nanostructures. Particularly, polyaniline (PANI) emerged as a suitable option for several applications, such as supercapacitors, batteries and electrochemical devices [1,2]. The electrodeposition of polyaniline films onto gold, carbon or indium tin oxide (ITO) electrode surfaces is widely employed for the determination of diverse analytes [3–5]. Regarding the analytical application, the conducting form of polyaniline (emeraldine salt) possesses an insulating form (emeraldine base) when suffering deprotonation processes at high pH values [6]. In some pieces of research, self-doped polyaniline composites, obtained by copolymerization of polyaniline derivatives, can retard the deprotonation at high pH values, obtaining remarkable results in neutral buffer solutions [7–10].

Despite their excellent electrochemical behavior, surface fouling and the degradation of the deposited film upon use are common drawbacks for analyses [11]. With the aim of minimizing fouling phenomena, carbon paste materials modified with bulk polyaniline were developed. In this sense, silicon dioxide capped with gold nanoparticles ( $\text{SiO}_2\text{@AuNPs}$ ) [12], carbon nanofibers coated with polyaniline and platinum [13], carbon nanofibers coated with gold nanoparticles and polyaniline and modified with butyl-3-methylimidazolium hexafluorophosphate [14], graphene nanosheets with multi-walled carbon nanotubes (MWCNT) and polyaniline [15], copper oxide/graphene oxide/polyaniline [16], polyaniline/starch/MWCNT [17] and Prussian blue/polyaniline [18] nanocomposites were employed for electrochemical purposes.

Our group is devoted to the development of electroactive bulk materials with interesting mechanical and electrical properties using sol-gel technology assisted by high-power

ultrasound. In this regard, their employment for the electrochemical sensing of different metals and compounds is reported in a review published in the previous decade [19]. The modification of Sonogel–Carbon (SNG–C) surfaces by drop casting was reported in this work, leading to significant improvements in the sensitivity and selectivity of electrochemical oxidation processes of target analytes. The entrapment of tyrosinase within the conducting polymer layer electrodeposited on the SNG–C surface using a sinusoidal current procedure was also reported in this work, allowing the quantitation of the polyphenol indices of several alcoholic beverages and minimizing the influence of sugars in the electrochemical response.

The inclusion of bulk modifiers into the SNG–C matrix constitutes another feasible modification route. The modifier can play a conducting role in the material, leading to higher sensitivities for the determination of diverse analytes. Furthermore, the electroactivity of the surface can be restored mechanically after performing each electrochemical assay, minimizing the surface fouling phenomena and, hence, increasing the lifetime of the device. In this sense,  $\beta$ -cyclodextrin, furoylthioureas, cysteine and carbon nanopowder-modified materials were developed, obtaining remarkable electrochemical features in the electrochemical determination of benchmark analytes in buffer and real matrices [20–22].

The development of bare sol-gel materials based on conducting polymers, poly-(3,4-ethylenedioxythiophene) (PEDOT) and polyaniline, were also synthesized and subsequently applied in electrochemical analyses, providing excellent analytical results [23,24]. Among these works, the manufacturing of a ceramic polyaniline sol-gel composite by using a two-step procedure is noteworthy to mention. The first step involves the sonication of aniline with ammonium persulfate in acid medium, leading to polyaniline dispersion. Subsequently, the formation of the silicon oxide network was promoted through the sonication of the silane/graphite mixture. After synthesis, the composite provided excellent results for 4-chloro-3-methylphenol (PCMC) determination. Thus, the analytical utility of bare and bulk-modified sonogel-based materials for the electrochemical determination of diverse analytes is fully demonstrated in several pieces of research.

In the present work, the bulk modification of Sonogel–Carbon with polyaniline powder is reported. The hybrid composite preserves the electroactivity of the conducting polyaniline embedded in the silicon oxide network, leading to remarkable electrochemical results for model organic pollutant detection, namely of 4-chloro-3-methylphenol. The developed sensor was employed in the quantitation of PCMC in spiked water samples, obtaining suitable recovery values. Furthermore, the antifouling capability of the modified composite could be pointed out based on repeatability studies. With the aim of evaluating further applicability of the modified composite in the detection of different hazardous pollutants, the electrochemical sensing towards other chlorophenols is also investigated.

## 2. Materials and Methods

### 2.1. Reagents

All the reagents used were received without further purification. 4-Chloro-3-methylphenol, 2,4-dimethylphenol, pentachlorophenol and 2-chlorophenol were obtained from Merck (Germany, Darmstadt). 2,4,6-Trichlorophenol was purchased from Fluka (Spain, Barcelona). To synthesize Sonogel–Carbon–PANI electrodes, graphite powder from Alfa Aesar (Germany, Johnson Matthey GmbH), methyltrimethoxysilane (MTMOS) from Merck (Germany, Darmstadt), HCl from Panreac (Spain, Barcelona), aniline from Riedel-De-Haën (Germany, Seelze) and ammonium persulfate from Sigma-Aldrich (USA) were used. For the preparation of the buffer solutions, potassium chloride, boric acid and sodium chloride were purchased from Merck (Germany, Darmstadt) and glacial acetic acid, potassium hydroxide, ethanol and disodium tetraborate decahydrate were from Panreac (Spain, Barcelona). Lastly, potassium hexacyanoferrate (II) from Sigma-Aldrich (USA, St Louis, MO) was used to characterize the electrode material.

## 2.2. Instrumentation

The high-power ultrasound-assisted synthesis of the electrode materials was performed using a MISONIX S-4000 ultrasonic generator (USA, ME, Farmingdale) coupled with a 13 mm diameter titanium tip. The infrared spectra of the developed materials in powder form were recorded with an IRAffinity-1S infrared spectrophotometer from Shimadzu (Japan, Shimadzu) coupled with an attenuated total reflectance (ATR) unit. The electrochemical measurements were made using a PGTSTAT12 potentiostat/galvanostat autolab coupled to a 663 VA stand from Metrohm (The Netherlands, Utrecht). A three-electrode cell with the following composition was employed: a platinum wire as a counter electrode, Ag/AgCl (3 M KCl) as the reference electrode and the Sonogel–Carbon-based composites as the working electrodes.

## 2.3. Synthesis of Polyaniline Powder and Graphite/Polyaniline Composites

To synthesize the polyaniline powder, the following procedure was applied: Firstly, polyaniline dispersion was obtained using a procedure described in a previous work [24]. In brief, a precursor mixture containing 982  $\mu\text{L}$  of a 0.25 M of ammonium persulfate in 1 M HCl solution and 18  $\mu\text{L}$  of commercial aniline was sonicated under high-power ultrasound for 60 s. The as-synthesized black–green dispersion was centrifuged for 5 min at 4000 rpm (centrifugal acceleration = 1790 g). Subsequently, the supernatant was removed and the powder was dried in an oven for 16 h.

The graphite/polyaniline composites, ranging from 1 to 20% of PANI, were prepared by adding the corresponding amount of graphite and polyaniline powder. Afterwards, the mixture was stirred in the vortex for 30 s.

## 2.4. Synthesis and Elaboration of Sonogel–Carbon–Polyaniline Electrodes

The synthesis of the Sonogel–Carbon modified with polyaniline was carried out using the high-power ultrasound-assisted sol-gel technology procedure. Briefly, 500  $\mu\text{L}$  of MTMOS and 100  $\mu\text{L}$  of 0.2 M HCl solution were sonicated under high-power ultrasound for 10 s. Afterwards, 500 mg of the graphite powder/polyaniline mixture was added to the sonosol. After preparation of the material, the elaboration of the working electrodes was carried out following the procedure reported for Sonogel–Carbon electrodes [25]. The glass capillary tubes, i.d. 1.15 mm (geometric area:  $1.04 \times 10^{-2} \text{ cm}^2$ ), were filled with the carbon/polyaniline material and, subsequently, were left to dry for one day. After that, the capillary tubes were polished mechanically with P1200 silicon carbide paper (Struers, Germany).

## 2.5. Measuring Procedure

The electrochemical measurements were carried out as follows: Firstly, 25 mL of buffer solution was added to an electrochemical cell. The electrode surface was previously conditioned by means of cyclic voltammetry in free analyte buffer solution by recording eight cyclic sweeps from  $-0.2 \text{ V}$  to  $0.9 \text{ V}$  and vice versa at  $50 \text{ mV/s}$ . After performing the conditioning step, the background was recorded using the differential pulse voltammetry (DPV) technique in free analyte solution. Afterwards, an aliquot of the stock solution was added to the electrochemical cell and the system was stirred for 30 s and, subsequently, the corresponding voltammogram was recorded. The bare electrode, Sonogel–Carbon without PANI (SNG–C), was also employed as the working electrode for some comparative electrochemical measurements.

## 2.6. Real Sample Analysis

The analysis of several water samples collected from different sources was performed following a similar procedure reported in other works [26]. In brief, the water samples were spiked with  $25 \mu\text{M}$  of PCMC and diluted 10 times with the buffer solution to reach  $2.5 \mu\text{M}$ . The analytical quantitation was performed using the standard addition method. The PCMC concentration added to the electrochemical cell ranged from  $2.0$  to  $6.0 \mu\text{M}$ .

### 3. Results

#### 3.1. Effect of the Modifier on the Mechanical/Electrochemical Features of the Conducting Composite

First of all, the effect of the graphite powder/polyaniline proportion on the final properties of the material was studied. For this purpose, Sonogel–Carbon electrodes modified with different proportions of graphite powder and polyaniline (PANI) mixtures, ranging from 1% to 20% of PANI, were prepared following the synthesis procedure reported in Section 2. After preparation, formulations higher than 4% of PANI offered liquid consistencies, leading to difficulties in the manufacturing of the electrodes, such as problems in the filling and compactness steps. Furthermore, no adherence between the glass capillary tube and the material was noticed after the drying step, suggesting high volume contraction. On the contrary, formulations with low PANI content showed a consistency similar to that of the original Sonogel–Carbon material, with better mechanical features for the manufacturing of electrochemical sensors. Thus, ceramic formulations with low polyaniline proportions were selected for further studies.

The electrochemical evaluation of Sonogel–Carbon-modified composites was made by means of DPV using a model chlorophenol, namely 4-chloro-3-methylphenol (PCMC). Figure 1A shows the differential pulse voltammograms recorded with carbon–ceramic composites at different proportions of PANI ranging from 1% to 4%. The corresponding differential pulse voltammograms displayed remarkable symmetric oxidation peaks, ascribed to their suitable electrochemical features. Regarding the electrochemical response, the best peak height was achieved at 2% PANI (see Figure 1B) and, hence, this material presents the greatest electrochemical performance for PCMC detection. The low variability of the electrochemical responses provided with this formulation are also noteworthy, and can be directly related to exceptional reproducibility. Therefore, this ceramic–polyaniline formulation, namely SNG–C–2% PANI, was selected for further studies.

#### 3.2. Electrochemical Characterization

##### 3.2.1. Characterization of the Redox Process of Polyaniline

The redox process of polyaniline in the material was studied by means of cyclic voltammetry in 1 M HCl free analyte solution to assess the proper modification of the Sonogel–Carbon electrode. The cyclic voltammograms recorded with the modified electrode displayed the main waves ascribed to polyaniline, all of them absent in the voltammogram recorded with the unmodified Sonogel–Carbon electrode (see Figure S1 and the inset): two anodic peaks around 0.2 V and 0.9 V, corresponding to leucoemeraldine–emeraldine and emeraldine–pernigraniline oxidation, respectively, and two cathodic peaks located at 0.05 V and 0.7 V, corresponding to the reduction counterparts [27]. Therefore, the presence of conducting-form polyaniline within the Sonogel–Carbon matrix was confirmed.

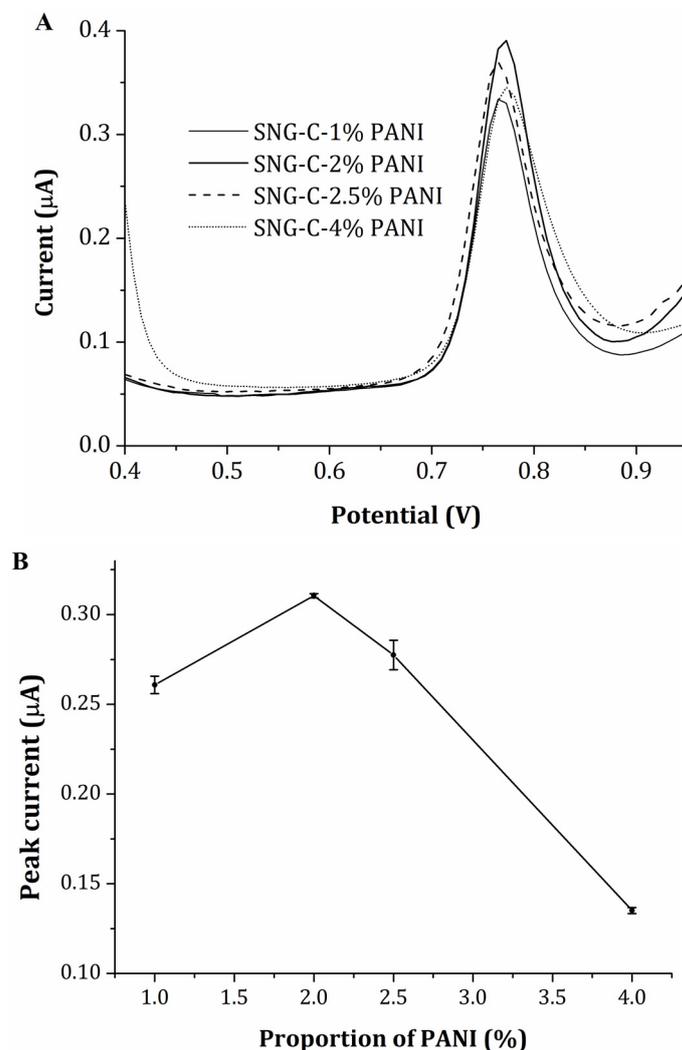
##### 3.2.2. Electrochemical Behavior Using Ferrocyanide System

The electrochemical behavior of the ferrocyanide ion process was subsequently studied with the SNG–C–2% PANI electrodes. Figure S2 shows the cyclic voltammograms recorded at different scan rates in the presence of 5 mM potassium hexacyanoferrate (II) in 0.5 M KCl, showing high electrochemical reversibility. The relationship between the peak current and the square root of the scan rate is linear, with a regression coefficient of 0.999 (see Figure S2A), indicating a preferably diffusion-controlled process. The unmodified material was also characterized using a ferrocyanide probe for comparison.

The quasi-reversible behavior of the ferrocyanide probe could be monitored through the Randles–Sevcik equation (Equation (1)), as shown in the research work cited below [28].

$$I_p = 0.436 nFA_{\text{electroactive}} C \sqrt{\frac{nFDv}{RT}} \quad (1)$$

where  $I_p$  is the current peak,  $n$  is the number of electrons involved in the electrochemical reaction,  $A$  is the electroactive area,  $C$  is the concentration of the redox probe,  $D$  is the diffusion coefficient,  $v$  is the scan rate,  $F$  is the Faraday constant and  $T$  is the temperature.



**Figure 1.** (A) Differential pulse voltammograms recorded with formulations with different proportions of polyaniline ranging from 1% to 4%, in presence of a 10 μM 4-chloro-3-methylphenol solution. (B) Peak heights recorded using different proportions of polyaniline in a 10 μM 4-chloro-3-methylphenol solution. A buffer solution containing 0.1 M acetic/acetate at pH 4 with 0.5 M KCl was used as electrolytic medium.

According to the previous equation, the electroactive area can be calculated. As can be explained in a previous article, only the voltammetric peaks corresponding to the forward scan were considered.

$$A_{\text{electroactive}} = \frac{I_p / v^{1/2}}{0.436 nFC \sqrt{\frac{nFD}{RT}}} \quad (2)$$

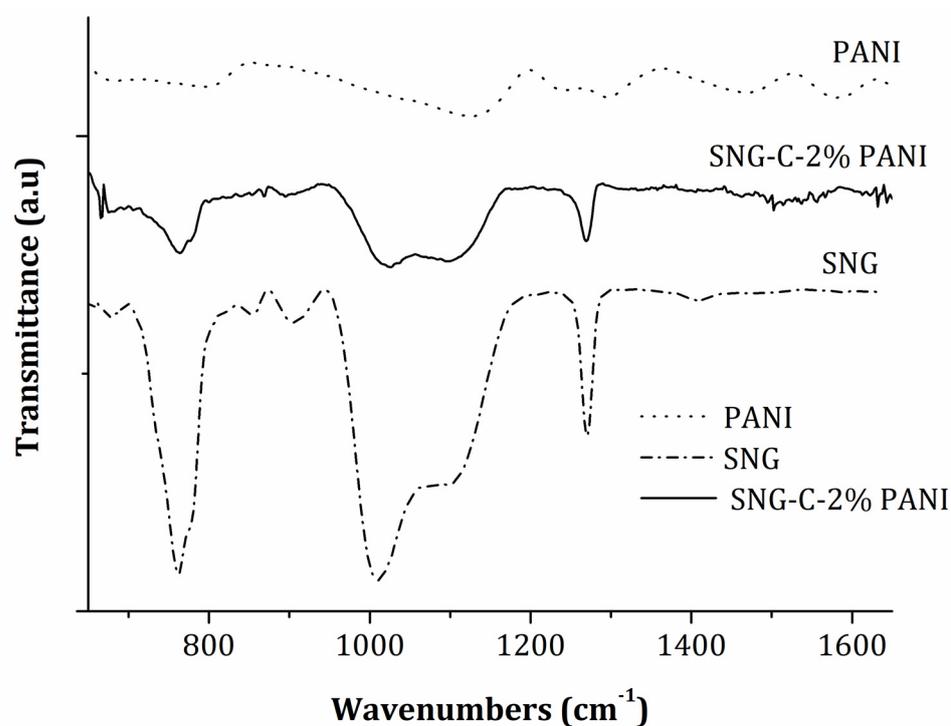
The slopes between the current peak and the square root of the scan rate for both materials ( $I_p / v^{1/2}$ ) were determined at low scan rates, from 25 mV/s to 125 mV/s, using the corresponding linear regression equations (see Figure S2B). Regarding the diffusion coefficient,  $6.5 \times 10^{-6}$  cm<sup>2</sup>/s was reported in the literature for a similar ferrocyanide/potassium chloride electrochemical system [29,30]. Based on this information, the electroactive area estimated for the modified material is  $7.2 \times 10^{-3}$  cm<sup>2</sup>, while the one corresponding for the unmodified device is  $6.9 \times 10^{-3}$  cm<sup>2</sup>. No substantial increase in the electroactive surface

area was observed after the modification of the material, which is in consonance with results previously reported with a similar bulk-modified composite [22].

### 3.3. Structural Characterization by Fourier Transformed Infrared Spectroscopy (FTIR)

The developed modified material was structurally characterized by means of Fourier transform infrared spectroscopy. The polyaniline powder and the unmodified Sonogel composite were also characterized for comparison purposes.

The IR spectra recorded with both Sonogel–Carbon-based materials show the presence of bands corresponding to Si–CH<sub>3</sub> and Si–O vibrations, ascribed to the silicon oxide network and non-hydrolysable methyl groups from the silane precursor (see Figure 2): 770 cm<sup>-1</sup>, attributed to Si–CH<sub>3</sub> stretching, 1025 cm<sup>-1</sup> and 1125 cm<sup>-1</sup>, attributed to Si–O–Si stretching and 1275 cm<sup>-1</sup>, ascribed to Si–CH<sub>3</sub> deformation. These assignments are in consonance with those recorded for carbon–ceramic oxide materials reported in the literature [25,31]. Although no polyaniline bands were appreciated in the SNG–C-modified spectrum, the electroactivity of this conducting polymer is confirmed by cyclic voltammetry.



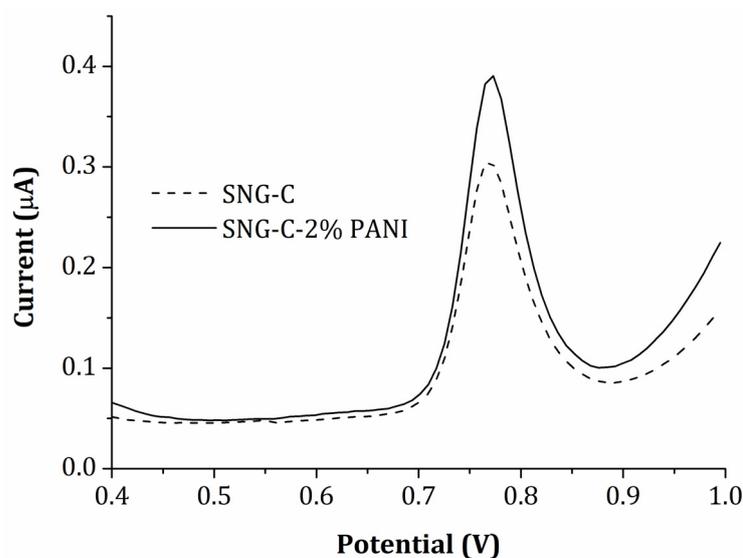
**Figure 2.** FTIR spectra recorded with different conducting materials: (dotted line) PANI, (dashed line) SNG–C–2% PANI and (solid line) SNG.

Thus, the absence of polyaniline bands in this formulation can be ascribed to its low proportion in the material.

### 3.4. Electrochemical Assessment of PCMC Using SNG–C-Modified Material

#### 3.4.1. Preliminary Electrochemical Detection

The detection of PCMC, used as a benchmark chlorophenol, was investigated with SNG–C–2% PANI by means of DPV. In order to study the role of the conducting polymer in electrochemical detection, the unmodified electrode (SNG–C) was also used. Figure 3 shows the DPV recorded with both materials in the presence of 10 μM of PCMC in 0.1 M acetic/acetate buffer (ABS) at pH 4 with 0.5 M KCl. The peak height provided with the SNG–C–2% PANI is higher than the one recorded with the bare material, around 25% of the electrochemical response, addressing the superior sensitivity of the modified composite for PCMC detection. This enhancement on the electrochemical response provided by the modified composite may be ascribed to a favorable polymer–analyte interaction.

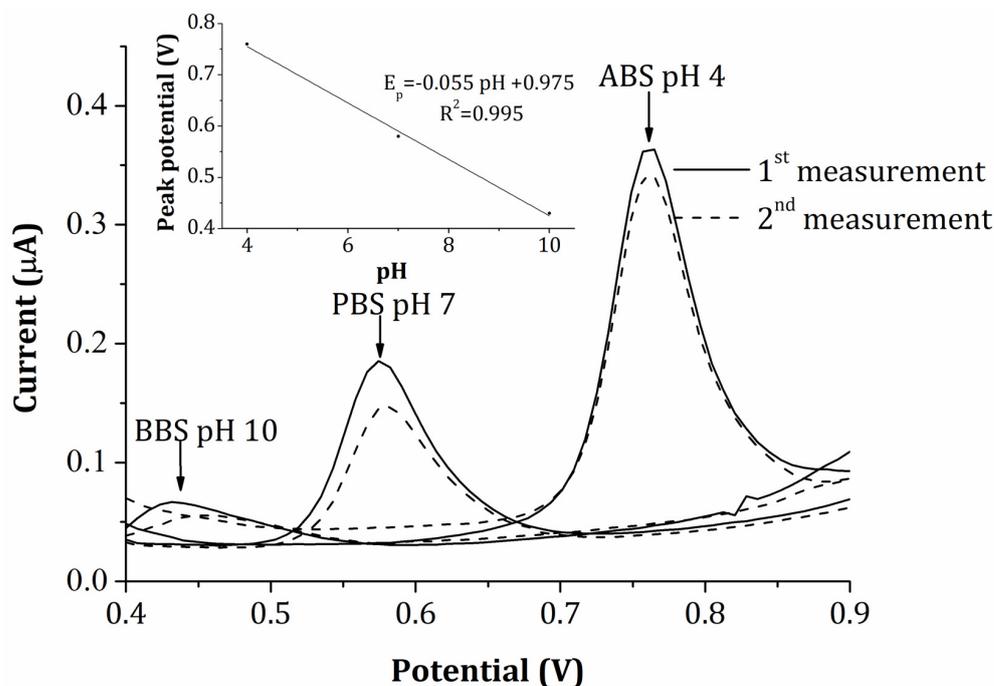


**Figure 3.** Differential pulse voltammograms recorded with SNG-C-2% PANI and SNG-C in presence of 10  $\mu\text{M}$  of PCMC in 0.1 M acetic/acetate buffer (ABS) at pH 4 with 0.5 M KCl.

According to these results, we can assume that electroactivity of polyaniline is retained within the conducting polymer composite material.

#### 3.4.2. Effect of pH on PCMC Electro-Oxidation

A preliminary screening of the buffer solution employed for electroanalytical purposes was performed. Figure 4 shows differential pulse voltammograms recorded with SNG-C-2% PANI in the presence of the same concentration of 4-chloro-3-methylphenol diluted in three buffer solutions at different pH values. In all cases, 0.5 M KCl solution was used as the supporting electrolyte.



**Figure 4.** Differential pulse voltammograms recorded with SNG-C-2% PANI in presence of the same concentration of 4-chloro-3-methylphenol using three different buffer solutions at different pH: acetic/acetate buffer (ABS) at pH 4, phosphate buffer (PBS) at pH 7 and borate buffer (BBS) at pH 10. The inset reports the linear relationship between the peak potential and pH.

The peak potential shifts with the pH, attributed to the participation of the protons in the redox reaction. The slope between the peak potential and the pH is 55 mV, close to 59 mV (see inset, Figure 4) ascribed to one-proton–one-electron processes [32]. Concerning the electrochemical response, the buffer solution at pH 4 led to the best peak height for PCMC detection. Additionally, no major change in the peak current was observed after performing the second measurement in acid solution. Thus, this medium is selected for electrochemical assays of the target chlorophenol.

### 3.4.3. Effect of PCMC Concentration

The developed material was employed in the voltammetric determination of PCMC ranging from 0.7 to 7.0  $\mu\text{M}$  using DPV under the instrumental conditions detailed in Section 2. The current densities at different PCMC concentrations (calculated using the geometrical area of the electrode) recorded with the SNG–C–2% PANI composite are plotted as a function of the PCMC concentration (see Figure 5A). The calibration curve considering three measurements at each PCMC concentration value is shown in the corresponding inset. The relationship between the peak current density and the concentration of PCMC can be described by the following equation:  $j = 2.40 [\text{PCMC}] - 0.78$  ( $R^2 = 0.991$ ), where  $j$  is the current density (expressed in  $\mu\text{A}/\text{cm}^2$ ) and  $[\text{PCMC}]$  is the concentration of the studied analyte (expressed in  $\mu\text{M}$ ). The sensitivity was determined as the slope of the calibration curve, obtaining  $2.40 \pm 0.18 \mu\text{A}/\text{cm}^2$ . The detection limit (LOD) was calculated by  $\text{LOD} = 3 \times S_q/m$ , where  $S_q$  is the standard deviation of the intercept and  $m$  is the slope of the linear equation. The value obtained was 0.69  $\mu\text{M}$ .

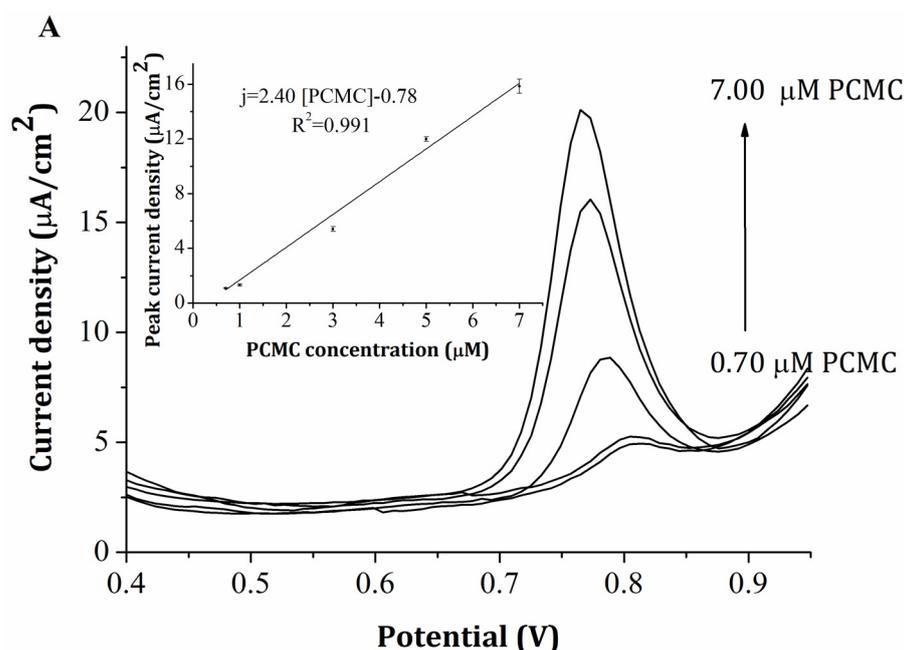
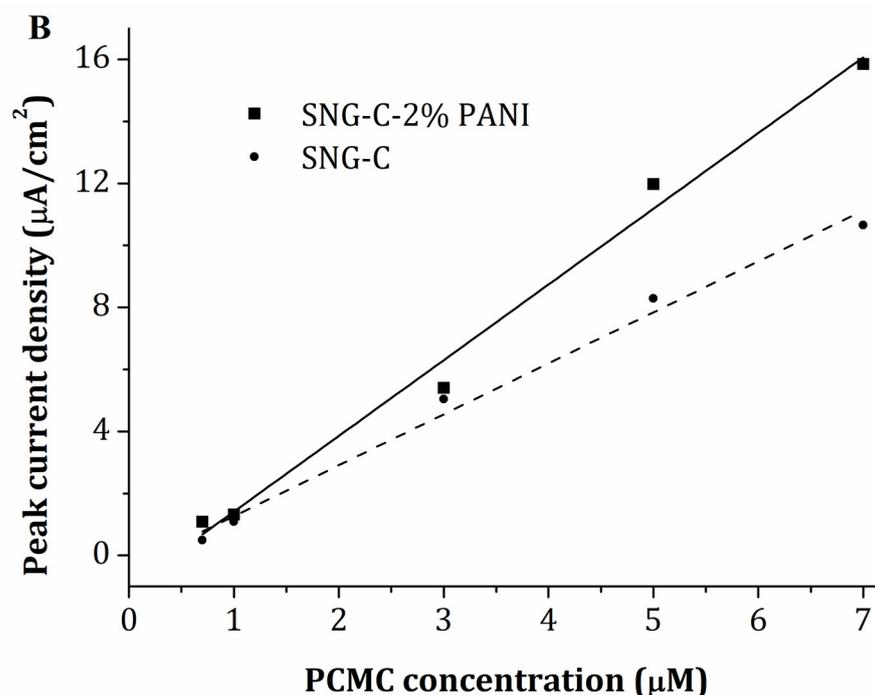


Figure 5. Cont.



**Figure 5.** (A) Differential pulse voltammograms recorded with SNG-C-2% PANI in presence of different concentrations of PCMC. The inset reports the relevant calibration plots. (B) Calibration curve recorded with SNG-C-2% PANI and SNG-C in presence of different concentrations of 4-chloro-3-methylphenol in 0.1 M acetic/acetate with 0.5 M KCl at pH 4.

The electrochemical performance for PCMC determination provided with the modified material was compared with the unmodified one to demonstrate the usefulness of the modification process. Figure 5B exposes the average calibration curve obtained with both electrode materials (considering three measurements for each point) under the same instrumental conditions. As can be seen from the figure, the sensitivity provided with SNG-C-2% PANI is greater than the one obtained with SNG-C, which can be ascribed to the presence of the polymer. This finding is in consonance with what was observed in the preliminary test with PCMC (Section 3.4.1). The detection limit of SNG-C was also calculated, obtaining 0.71 µM, which is slightly higher than the one associated with the modified device.

A comparison of the analytical parameters for PCMC determination with other electrode materials was carried out. The sensitivity obtained with the developed device is comparable to those reported with other sensors (see Table 1), which can be attributed to high electron transfer capability.

**Table 1.** Figures of merits for the determination of 4-chloro-3-methylphenol obtained using several electrochemical sensors.

	Sensitivity [ $\mu\text{A}/\mu\text{M}\cdot\text{cm}^2$ ]	LOD [ $\mu\text{M}$ ]	Reference
SNG-C-2% PANI	2.40	0.69	This work
MWCNT-GCE	1.48	8.8	[33]
GP-CCE	0.28	2.71	[26]
MWCNT-CCE	1.41	0.71	[26]
BDD	0.08	0.46	[34]
UiO-66-NH <sub>2</sub> @PEDOT/GA/GCE	$1.87 \times 10^{-3}$	0.20	[32]

GP-CCE: Graphite-carbon ceramic electrode; BDD: Boron-doped diamond electrode; MWCNT-GCE: Multiwalled carbon nanotubes-glassy carbon electrode; UiO-66-NH<sub>2</sub>@PEDOT/GA/GCE: PEDOT-modified electrode with UiO-66-NH<sub>2</sub> and graphene aerogel; MWCNT-CCE: Multiwalled carbon nanotubes-carbon ceramic electrode.

On the other hand, LOD is lower than the concentration value permitted in aquatic environments established by the United States Environmental Protection Agency (US-EPA), around  $3.5 \mu\text{M}$  [35]. In this way, it can be deduced that the material may be used for PCMC environmental monitoring in aquatic matrices. Additionally, no organic solvent consumption in the manufacturing process should be highlighted. For all these reasons, the bulk modification of Sonogel–Carbon with polyaniline seems to be promising for the electrochemical sensing of PCMC.

#### 3.4.4. Reproducibility and Repeatability Studies

The reproducibility of the electrochemical measurements in the same PCMC solution using seven different SNG–C–2% PANI electrodes was studied. The coefficient of variation was 4%, indicating that the fabrication process provides electrode materials with similar electrochemical performance.

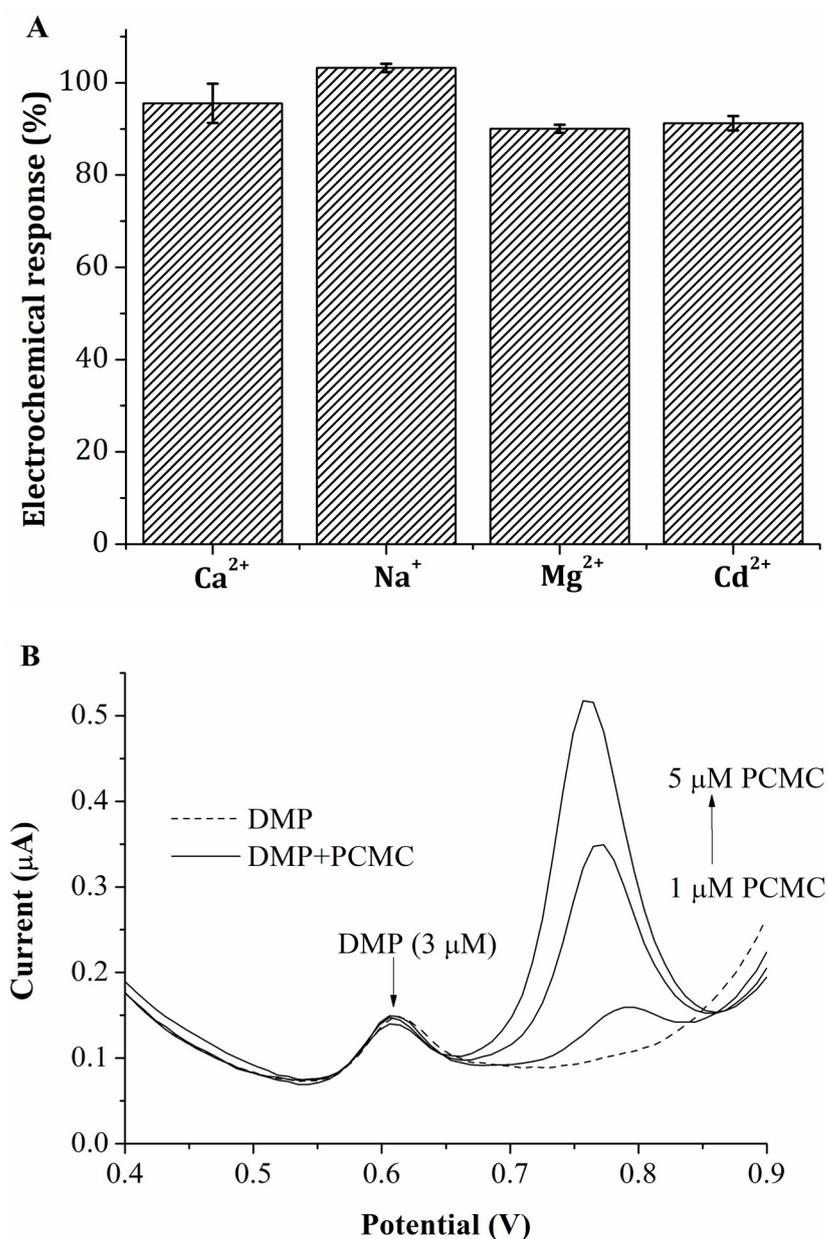
The repeatability of the electrochemical measurements was also evaluated by performing nine successive measurements in the same PCMC solution. The coefficient of variation between the peak heights was 3.9%. Based on these results, an excellent repeatability can be concluded, which can be ascribed to the resistance of fouling by oxidation products of PCMC. Hence, no surface cleaning beyond the initial polishing is required.

#### 3.4.5. Effect of Salts and Phenols on PCMC Detection

The influence of some typical ion species, i.e., calcium, sodium, magnesium and cadmium salts, on the electrochemical response was examined. Measurements in the presence of  $7 \mu\text{M}$  of PCMC and higher concentration of these salts (100-fold of calcium and sodium salts and 10-fold of cadmium and magnesium ones) were performed by triplicate. The electrochemical response of the device is remarkably similar in presence of the analyte and different salts (see Figure 6A), suggesting a low influence of these compounds in the determination of 4-chloro-3-methylphenol. Moreover, the variation coefficient values are lower than 6% in all electrochemical assays, confirming the repeatability of the electrochemical measurements discussed in the previous subsection and the absence of fouling on the electrode surface. Therefore, no influence of diverse salts on PCMC detection was achieved.

The electrochemical analysis of the target chlorophenol (PCMC) was performed in the presence of another substituted phenol, 2,4-dimethylphenol (DMP). Voltammetric assays were carried out in the presence of different PCMC concentrations and a fixed concentration of 2,4-DMP. As derived from the voltammograms shown in Figure 6B, peaks corresponding to PCMC and DMP oxidation are located at different potentials. The oxidation peak of PCMC increased with the PCMC concentration, while DMP oxidation peak remained invariable in all the experiments. These results suggest a negligible adsorption of DMP at the micromolar concentration level, similar to the findings derived from the electrochemical PCMC assays shown in Section 3.4.4.

Hence, the minimization of fouling phenomena provided with the developed device for PCMC determination could be extended to other substituted phenols. Furthermore, no interference on the electrochemical detection of the target chlorophenol in the presence of DMP could be concluded. This finding opens the door to studying the possible simultaneous determination of both phenols.



**Figure 6.** (A) Electrochemical responses obtained with SNG-C-2% PANI in presence of 7  $\mu\text{M}$  of 4-chloro-3-methylphenol and 700  $\mu\text{M}$  of calcium and sodium salts and 70  $\mu\text{M}$  of magnesium and cadmium salts. (B) Differential Pulse voltammograms recorded with the developed material in presence of different concentrations of PCMC and 3  $\mu\text{M}$  of DMP. A buffer solution containing 0.1 M acetic/acetate at pH 4 with 0.5 M KCl was used as electrolytic medium.

#### 3.4.6. Spiked Water Analysis

The electrochemical determination of PCMC in water collected from different sources in Spain was conducted using DPV. The experimental results derived from this study in terms of recovery percentages are shown in Table 2.

**Table 2.** Electrochemical determination of PCMC in spiked water samples collected from different areas of Andalusia (Spain).

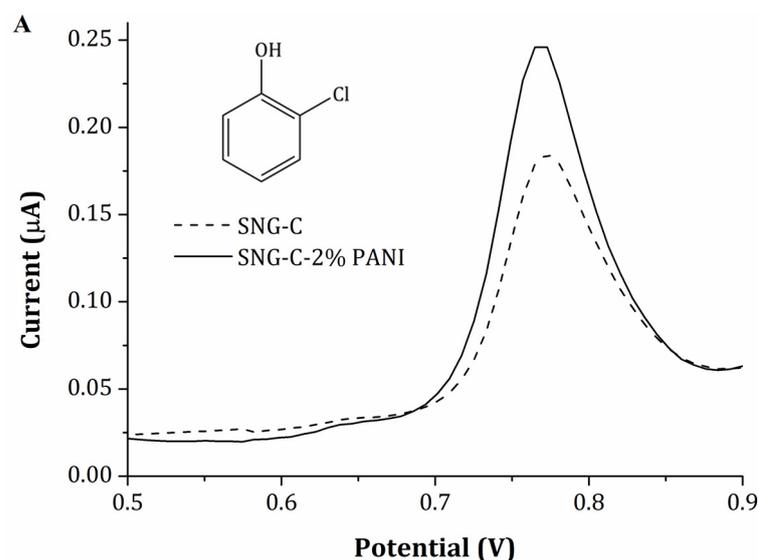
Water from Diverse Sources	C <sub>Added</sub> (μM)	C <sub>Determined</sub> (μM)	Recovery (%)
Fountain water (Ubeda, Jaén)	2.50	2.49	99.6
Well water (Chiclana de la Frontera, Cádiz)	2.50	2.32	92.3
Tap water (Puerto Real, Cádiz)	2.50	2.47	98.8
Mineral water	2.50	2.62	105

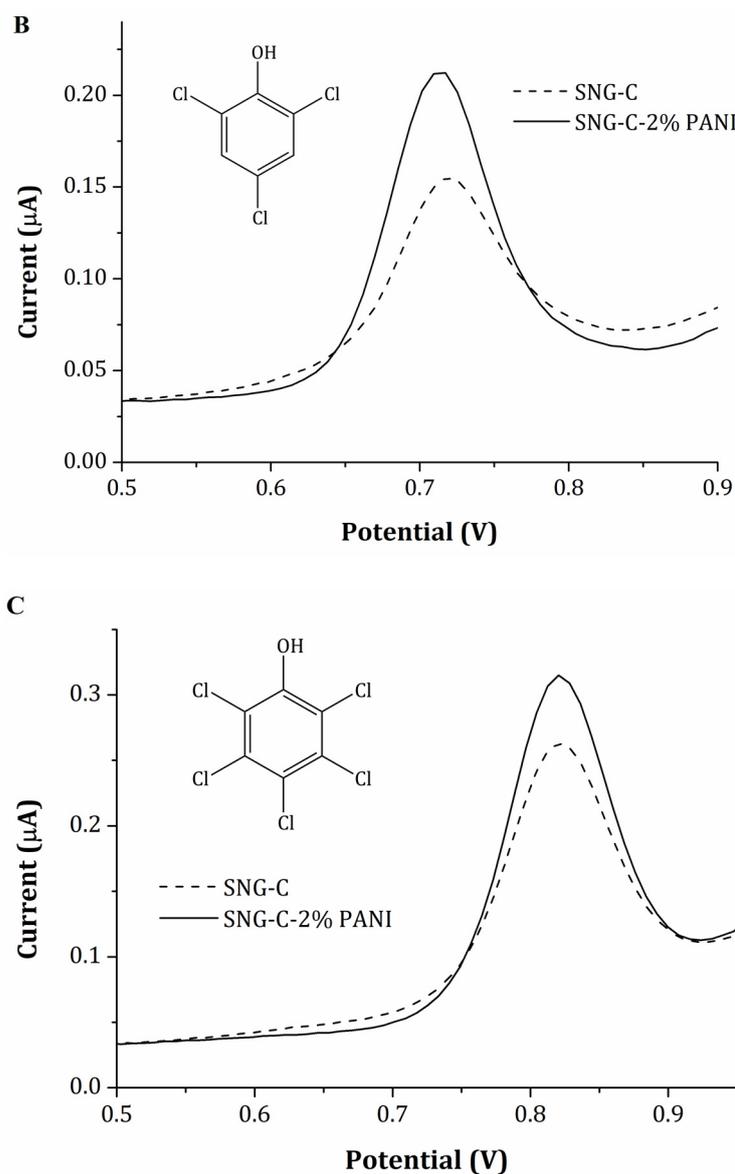
The recovery values for all water samples analyzed in this study range from 92% to 105%, which are suitable according to analytical standards. Hence, the electrode material developed in this work is promising for the quantitation of PCMC in different spiked water samples and, hence, it is suitable for environmental monitoring.

### 3.5. Electrochemical Detection of Other Chlorophenols of Interest

The applicability of detection other chlorophenols of interest with the developed ceramic composite was examined. The electrochemical detection of 2-chlorophenol (2-CP), 2,4,6-trichlorophenol (TCP) and pentachlorophenol (PCP), was assessed in this work. The bare material, Sonogel–Carbon, was also employed under the same instrumental conditions for comparison.

Figure 7 shows the differential pulse voltammograms recorded with the developed material and the unmodified material in the presence of 7 μM of target chlorophenols in 0.1 M ABS with 0.5 M KCl at pH 4. Higher oxidation peak heights in comparison with those obtained with the bare material are noticed, which can be ascribed to the presence of the conducting form of the polymer within the matrix. Based on this study, the developed material is promising for the detection of diverse chlorophenols in the electrochemical frame.

**Figure 7.** Cont.



**Figure 7.** Differential pulse voltammograms recorded with SNG-C-2% PANI in presence of 7 μM of different chlorophenols: (A) 2-chlorophenol (2-CP), (B) 2,4,6-trichlorophenol (TCP) and (C) pentachlorophenol (PCP). A buffer solution containing 0.1 M acetic/acetate with 0.5 M KCl at pH 4 was used as electrolytic medium.

#### 4. Conclusions

The development of a Sonogel-Carbon material modified with a conducting polymer (PANI) was carried out using an environmentally friendly route based on high-power ultrasound. The polyaniline powder was embedded in the silicon oxide matrix, maintaining its electroactivity within the material. Better figures of merit for PCMC determination were obtained with the modified composite in comparison with those obtained with the bare material, which can be attributed to a favorable polymer-analyte interaction. Analytical results were also very satisfactory in comparison with other sensors reported in the literature. Furthermore, no surface fouling in PCMC analysis can be evidenced, making this sensor suitable for successive electrochemical analyses. The electrochemical detection of PCMC in the presence of different salts and one substituted phenolic compound can be also stated with the developed device. Moreover, the Sonogel-Carbon and polyaniline modification approach could be employed in the manufacturing of other modified devices, such as screen-printed electrodes. On the basis of these results, polyaniline could be

proposed as an adequate bulk modifier of the sol-gel carbon matrix for the environmental monitoring of chlorophenols.

**Supplementary Materials:** The following supporting information can be downloaded at <https://www.mdpi.com/article/10.3390/chemosensors11010063/s1>. Figure S1. Cyclic voltammograms recorded with SNG-C and SNG-C-2% PANI in free analyte 1 M HCl solution; Figure S2: (A) Cyclic voltammograms recorded with SNG-C-2% PANI in presence of 5 mM of potassium hexacyanoferrate (II) in 0.5 M KCl at different scan rates. The inset reports the relationship between the peak intensity and the square root of the scan rate; (B) relationship between the anodic peak intensity and the square root of the scan rate in presence of ferrocyanide recorded from 25 mV/s to 125 mV/s with SNG-C and SNG-C-2% PANI composites.

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