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Real-time electrochemical determination of phenolic compounds after benzene oxidation

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ABSTRACT

A sensitive electrochemical sensor was successfully developed on multi-walled carbon nanotubes (MWCNT) and cobalt phthalocyanine (CoPc) modified glassy carbon electrode (GC), and used to detect byproducts formed after the electrolysis of benzene. The GC/MWCNT/CoPc electrode was applied in the detection of phenolic compounds using square wave voltammetry (SWV). The proposed sensor exhibited a sequence in the sensitivity of the tested phenols: catechol > hydroquinone > resorcinol > phenol and 1,4-benzoquinone. The detection limits for individual phenols were also calculated: catechol (15.62 $\mu g\,L^{-1}$), hydroquinone (17.91 $\mu g\,L^{-1}$), resorcinol (46.12 $\mu g\,L^{-1}$), phenol (58.83 $\mu g\,L^{-1}$) and 1,4-benzoquinone (13.75 $\mu g\,L^{-1}$). The proposed sensor was successfully applied in the determination of the total amount of phenols formed after the benzene oxidation, and the obtained results were in full agreement with those from the HPLC procedure.

1. Introduction

One of the major problems associated with groundwater contamination can be attributed to petroleum hydrocarbons, in particular the special aromatic hydrocarbons such as benzene, toluene, ethylbenzene, and xylene (BTEX). In countries of the European Union, Brazil, and the United States of America, the major source of BTEX contamination in soils and groundwater is due to leakage from underground storage tanks for gasoline and diesel [1]. Owing to a growing demand for the supply of water, the contamination of natural water is becoming an increasingly important concern. Therefore, most of the research studies currently available are related to water treatment technologies and remediation of wastewaters BTEX [2–5].

According to the USEPA (United States Environmental Protection Agency) and GWRTAC (Ground-Water Remediation Technologies Analysis Center) [6,7] the most commonly used methods for remediation of groundwater are: air-stripping, air-sparging, soil vapor extraction, reactive barrier, pump-and-treat, bioremediation, chemical oxidation, in situ flushing, and in situ heat treatment [8–10]. In general, these physical processes enable efficient removal of volatile hydrocarbons. However, their non-destructive properties imply the need for auxiliary processes, oriented to adsorb and degrade the previously extracted hydrocarbons.

The electrochemical remediation of effluent promotes the removal or destruction of pollutant species through redox processes. In this treatment, the pollutant species can be removed from gases, liquids or solids in the final stage of an industrial process. This alternative treatment of waste and effluents is unique as it offers advantages such as versatility, energy efficiency, ease of automation, cost effectiveness, chemical stability, and an increase in electrode longevity [11].

It has been shown that some electrochemical methods used for benzene remediation cannot completely oxidize the benzene molecule, though the EAOPs methods have been successfully used for complete benzenic moieties degradation [12,13]. In some cases, additional toxic byproducts may develop, such as phenols [14–18]. According to Oliveira et al., five different byproducts form after the electrolysis of benzene at +2.4 V vs. Ag/AgCl, using a boron-doped diamond (BDD) electrode. These byproducts have been attributed to hydroquinone, resorcinol, catechol, phenol, and p-benzoquinone [19].

Among the organic waste, phenolic compounds present a high potential for the contamination of natural water. This contamination is due to intrinsic characteristics of the phenolic compounds such as solubility, acidity, toxicity, and their bactericide effect. In drinking water, concentrations of phenols up to 1.0 $\mu g\,L^{-1}$ can cause problems related to taste and odor. In addition, it can induce serious harm to human health, even leading to death [20]. Thus, the remediation of groundwater containing benzene and determination of the phenolic byproducts formed has become very important.

Electroanalytical methods used in the determination of phenolic compounds are based on the oxidation reaction of the phenol or catechol groups to form ketone or quinone, respectively [21].

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However, the major challenge in electroanalysis is to develop sensors fabricated with materials that allow an increase in sensitivity and electrocatalysis.

In this sense, carbon nanotubes (CNTs) have been extensively investigated for electroanalytical applications due to their unique structure and physical properties [22,23]. The development of sensors based on CNTs has been driven by their potential use in a large variety of applications, particularly for solid-state chemical and biological sensors [24,25]. It has been observed that phthalocyanine–CNT complexes have the excellent catalytic properties of phthalocyanines without losing any of the electronic properties of carbon nanotubes [26].

Considering that which has been described above, this study focuses on the real-time analysis of phenolic byproducts (hydroquinone, catechol, resorcinol, and phenol) and 1,4-benzoquinone formed from the degradation of benzene using glassy carbon electrodes (GC) modified with multi-walled carbon nanotubes (MWCNT)/cobalt phthalocyanine (CoPc).

2. Experimental

2.1. Instrumentation and methods

Cyclic voltammetry (CV) and square-wave voltammetry (SWV) experiments were performed using a model PGSTAT 30 Autolab electrochemical system (Eco Chemie, Utrecht, the Netherlands) equipped with GPES software (Eco Chemie, Utrecht, the Netherlands). The cell was assembled with a conventional three-electrode electrochemical system: a bare glassy carbon (GC) electrode or a GC electrode modified with MWCNT/CoPc as working electrode, an Ag/AgCl/KCl (3.0 mol L^{-1}) as reference electrode and a Pt plate as auxiliary electrode. All experiments were carried out at a controlled temperature (25 °C). CV was carried out in a 0.5 mol L^{-1} H_2SO_4 solution, over a relevant potential range, with a scan rate of 50 mV s^{-1}. SWV measurements were obtained with a frequency of 10 Hz, a pulse amplitude of 100 mV, and a step potential of 2 mV, in a 0.2 mol L^{-1} acetate buffer solution (pH 5.0) for hydroquinone, resorcinol, p-benzoquinone, catechol and phenol calibration curves.

Electrochemical impedance spectroscopy (EIS) data were obtained using a model PGSTAT 30 Autolab electrochemical system (Eco Chemie, Utrecht, the Netherlands) equipped with FRA2 software (Eco Chemie, Utrecht, the Netherlands). The EIS experiments scanned in a frequency range from 100 kHz to 40 mHz with an amplitude of 10 mV, with 10 data points per frequency decade. Measurements were carried out in 0.5 mol L^{-1} H_2SO_4 containing 1.0 mmol L^{-1} of the redox couple potassium ferricyanide.

Hydroquinone, resorcinol, p-benzoquinone, catechol, phenol, and benzene were determined quantitatively by HPLC using a Shimadzu (Kyoto, Japan) Prominence LC-20AT modular system comprising two CBM-20A pumps, a CTO-10AS oven, a SIL-20A auto sampler, a SPD-20A variable wavelength detector and an LC-10 Workstation Class data processor. Separations were carried out on a Phenomenex Luna C-18 column (250 × 4.6 mm i.d.; 5 μm), protected by a Supelcosil C-18 guard column (4 × 3.0 mm i.d.; 5 μm), eluted with mixtures of water (solvent A) and acetonitrile (solvent B) according to the program: 0–14 min, 15% B (isocratic); 14–23 min, 60–100% B (linear gradient); 23–40 min, 15% B (isocratic). The chromatographic conditions were: oven temperature 35 °C; flow rate 0.8 mL min^{-1}; injection volume 20 μL (Rheodyne loop); and UV detection at 270 nm.

2.2. Chemicals and solutions

All solutions were prepared with water purified in a Millipore Milli-Q system (resistivity ⩾18 MΩ cm). All chemicals were of analytical grade and were used without further purification. Hydroquinone, resorcinol, p-benzoquinone, catechol, phenol, benzene, potassium ferricyanide, and cobalt phthalocyanine were purchased from Sigma–Aldrich. Solutions of buffer supporting electrolyte such as acetic acid/sodium acetate (pH 4.0 and 5.0) and sodium phosphate buffer (pH 6.0, 7.0 and 8.0) of ionic strength 0.1 mol L^{-1} were used in all experiments. Methanol and acetonitrile were obtained from Mallinckrodt (Xalostoc, Edomex., Mexico).

An amount of approximately 1.0 g of MWCNT (90% purity, Sigma–Aldrich, Germany), synthesized by thermal chemical vapor deposition, was mixed with 500 mL of a 1:3 mixture of HNO_3/H_2SO_4 for 12 h, in order to promote its functionalization [27]. This was then filtered through a 0.45 μm Millipore nylon filter membrane. The resulting MWCNT was continuously washed using distilled water until the pH of the filtrate was neutral, and then dried overnight in a vacuum oven at 120 °C.

2.3. Preparation of the electrodes

Prior to modification, the GC electrode surface was polished with 0.05 μm alumina slurries, rinsed thoroughly with double-distilled water, sonicated 5 min in ethanol, 5 min in water, and dried in air. 1.0 mg of functionalized MWCNT and 1.0 mg of CoPc were suspended in ethanol containing 0.5% of Nafion®. The suspension was dispersed using ultrasonic stirring for 30 min. An aliquot of 10 μL of this dispersion was dropped on the GC electrode surface.

3. Results and discussion

3.1. Electrochemical oxidation of benzene

The study of benzene electro-oxidation was carried out by SWV, scanning the potential from +0.8 to +2.2 V, using a frequency of 10 Hz, an amplitude 100 mV, and a step potential of 2 mV. The SWV experiments were performed in 0.5 mol L^{-1} H_2SO_4 containing 2.5×10^{-4} mol L^{-1} of benzene.

Fig. 1 shows SWV voltammograms at all three types of electrode: bare GC (curve a), GC/MWCNT (curve b), and GC/MWCNT/CoPc (curve c). The voltammograms demonstrate that, in the potential range studied, there is only one oxidation process. On the GC/MWCNT film electrode, benzene oxidation occurred at +1.85 V, which is 0.30 V less positive than on a bare GC electrode, showing the electrocatalytic effect of the CNTs. Moreover, the oxidation on such a catalytic surface showed an increase by a factor of 3.5 in the peak current compared with the bare GC electrode, which can be related to the high surface area of the carbon nanotubes.

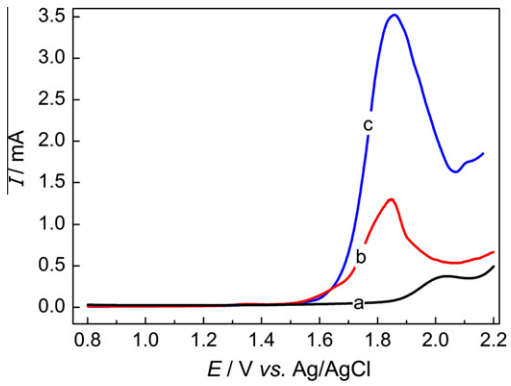

Fig. 1. Square-wave voltammograms in 0.5 mol L^{-1} H_2SO_4 containing 2.5×10^{-4} mol L^{-1} of benzene for the electrodes: (a) bare GC, (b) GC/MWCNT and (c) GC/MWCNT/CoPc.

On the GC/MWCNT/CoPc film electrode, the benzene oxidation potential peak appears at +1.85 V. Another observation was the increase by a factor of 2.5 in peak current compared with the GC/MWCNT electrode in the absence of CoPc. This increase can be associated with the properties of cobalt phthalocyanine, such as more efficient adsorption and electron mediator power. Thus, the electrocatalytic properties of carbon nanotubes are added to the excellent electron mediator power of cobalt phthalocyanine to make the synergistic system GC/MWCNT/CoPc in the electro-oxidation of benzene.

3.2. Electrochemical characterization of the GC/MWCNT/CoPc electrode

The electrochemical response of the GC/MWCNT/CoPc electrode was carried out by CV in 0.5 mol L^{-1} H_2SO_4 solution in the absence and presence of 2.5×10^{-4} mol L^{-1} of benzene, as shown in Fig. 2. No redox process was observed in the potential range of 0.0 to +2.0 V vs. Ag/AgCl at the GC/MWCNT/CoPc electrode in the absence of benzene (blue line). However, when 2.5×10^{-4} mol L^{-1} of benzene is added to 0.5 mol L^{-1} H_2SO_4 solution (red line), one anodic peak at +1.85 V was observed and this process corresponds to the electro-oxidation of benzene. A cathodic peak was also observed at +0.15 V due to the byproducts of benzene generated by reacting with hydroxyl radicals (·OH) produced from water electrolysis on the GC/MWCNT/CoPc electrode. From the second cycle (black line) it is possible to observe the appearance of an anodic peak at +0.60 V, attributed to the byproducts of benzene, which were previously reduced. This anodic peak corresponding to the oxidation of phenols in ketone or quinone, such as the 1,4-benzoquinone. Another observation is a noticeable decrease in the peak of benzene at +1.85 V. This occurs due to the irreversible adsorption of reduced species on the electrode active sites competing with the benzene adsorption step. After subsequent cycles (black line) the anodic peak currents of benzene decreased and the current peak of phenolic compounds formed from the electrochemical degradation of benzene increased.

3.3. Study of the effect of Nafion®

The effect of the amount of Nafion® in the electrode composition was characterized using electrochemical impedance spectroscopy (EIS). The EIS experiments were carried out in 0.5 mol L^{-1} H_2SO_4 containing 1.0 mmol L^{-1} of the redox couple potassium ferricyanide. The spectra were recorded at open-circuit potential (OCP) for the electrodes containing: 0.5%, 1.0%, and 2.0% by weight of Nafion®. Fig. 3 presents impedance spectra as complex plane plots for the GC/MWCNT/CoPc electrode in these three situations. An equivalent electrical circuit with a cell resistance, R_s, in series with a parallel combination of a constant phase element, *CPE*, and a charge transfer resistance, R_{ct}, was used to fit the spectra. The *CPE* was found to be necessary because of the heterogeneous nature of the electrode surface, expressed through the exponent *alpha*, where α represents a perfectly smooth and uniform surface.

In the electrode that contains 2.0% of Nafion® (open square), no semicircle was observed at high to medium frequencies, characteristic of a charge-transfer reaction. Only a straight line was observed, which can be considered as a non-ideal capacitor. This behavior is due to the high resistance of Nafion® in the film. In the spectrum of the electrode containing 1.0% of Nafion® (open circle), the high resistance of the film continues to be observed. However, a significant difference was observed in the spectrum and the R_{ct} could be calculated at 2150 Ω.

As expected, the resistance of the film decreased when the amount of Nafion® in the electrode composition also decreased. In the spectrum of the electrode that contains 0.5% of Nafion® (triangle), a semicircle was observed at high to medium frequencies, characteristic of a charge-transfer reaction, and a straight line at low frequencies, corresponding to diffusion control. The R_{ct} could be calculated at 785 Ω for this electrode. Thus the GC/MWCNT/CoPc electrode with 0.5% of Nafion® exhibited a faster charge-transfer process towards potassium ferricyanide oxidation compared to the other electrodes investigated, and was thus chosen for subsequent measurements.

3.4. Optimization studies of hydroquinone, resorcinol, p-benzoquinone, catechol and phenol on the GC/MWCNT/CoPc electrode

To maximize the SWV analytical signal, the effects of the experimental parameters such as: pre-treatment cleaning potential and time, pH, pulse amplitude, frequency and potential step height were studied at the GC/MWCNT/CoPc electrode.

3.4.1. Effect of pH

The dependence of the electrochemical oxidation of catechol, hydroquinone, resorcinol, phenol and 1,4-benzoquinone on the pH was studied by SWV in the pH range from 4.0 to 8.0 containing 1.0×10^{-4} mol L^{-1} of each phenolic compound and 1,4 benzoquinone. The increase in pH led to a shift in the peak potential towards

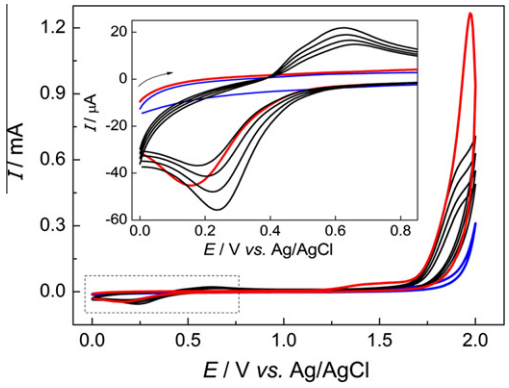

Fig. 2. Cyclic voltammograms for the GC/MWCNT/CoPc electrode: (blue line) 0.5 mol L^{-1} H_2SO_4 in absence of benzene, (red line) first cycle in 0.5 mol L^{-1} H_2SO_4 containing 2.5×10^{-4} mol L^{-1} of benzene and (black line) subsequent cycles in the electrolyte containing benzene. Inset: The oxidation and the reduction of the phenolic byproducts formed. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

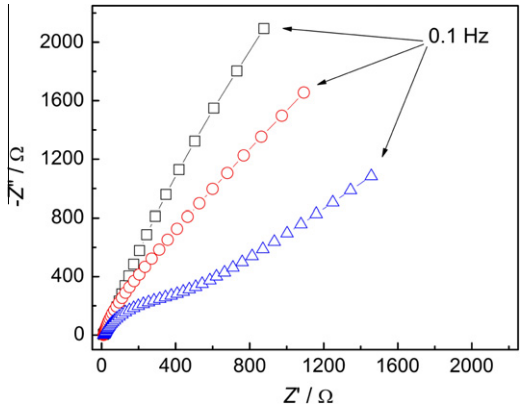

Fig. 3. Complex plane impedance spectra at a GC/MWCNT/CoPc in 0.5 mol L^{-1} H_2SO_4 containing 1.0 mmol L^{-1} of potassium ferricyanide in different amount of Nafion® in the electrode composition: (triangle) 0.5%, (circle) 1.0% and (square) 2.0%.

less positive values. The slope of E_{pa} vs. pH being 62.8; 57.6; 64.1; 52.3 and 61.9 mV per pH unit for catechol, hydroquinone, resorcinol, phenol and 1,4-benzoquinone, respectively. These results are in accordance with the work developed by Hawley et al. [28], which explains that the electro-oxidation of phenols is accompanied by the transfer of equal numbers of electrons and protons.

The plot of I_{pa} vs. pH in Fig. 4 showed that the peak current has a maximum value at pH 5.0 decreasing for both higher and lower pH values. It must be remembered that the catechol or phenol groups should interact with the active phthalocyanine site on the electrode surface. As the phthalocyanine molecule also protonates itself at low pH values, the overall effect agrees with the result observed here, i.e. diminishing the peak current. As to the dopamine/phthalocyanine system, this behavior has already been seen [29]. Based on the I_{pa} vs. pH plot information, pH 5.0 was selected for subsequent experiments using the GC/MWCNT/CoPc electrode.

3.4.2. Study of pre-treatment potential and time for cleaning the electrode surface

In general, the electrochemical detection of phenols is accompanied by adsorption of the oxidation products. Thus, there is a poisoning of the electrode surface and consequent decrease of the analytical signal. The influence of applied potential pre-treatment was investigated for each phenolic compound and 1,4-benzoquinone, in order to clean the surface of the electrode. The following pre-treatment potential values: −1.0, −0.75, −0.50, −0.25 and 0.0 V, were investigated. Complete recoveries of the original responses for the phenols were obtained by applying −1.0 V. This cathodic potential value is sufficient to reduce the adsorbed species on the electrode surface. Thus, −1.0 V was chosen as the pre-treatment cleaning potential in further studies. The influence of pre-treatment time was also evaluated, in the range of 10–60 s, and in this interval no difference was seen. Hence 20 s was chosen as the time of pre-treatment for cleaning the electrode surface.

3.4.3. Optimization of SWV conditions

The influence of square-wave voltammetry parameters was investigated. The frequency was varied in the range of 10–100 Hz, fixing the amplitude at 50 mV and the step potential at 2 mV. The I_{pa} for all phenolic compounds decreased when the frequency was increased. For frequency values up to 10 Hz, a deformation in the voltammetric shape of the phenolic compounds occurred. Thus, a frequency of 10 Hz was chosen. By fixing the frequency at 10 Hz, the effect of potential step increment was studied, in the range of 1–10 mV. For potential steps greater than 2 mV, deformation of the voltammetric profile was observed and the current peak decreased in height. Hence a frequency of 10 Hz and a 2 mV potential step increment were chosen, corresponding to an effective scan rate of 20 mV s^{-1}. The amplitude was varied in the range of 10–100 mV and I_{pa} increased with increasing amplitude in this range for all phenols and 1,4-benzoquinone. No deformation of the peak was observed nor any significant increase in peak width, even for amplitudes greater than 50 mV. Hence, 100 mV was chosen as the square-wave amplitude.

3.5. Analytical parameters for catechol, hydroquinone, resorcinol, phenol and 1,4-benzoquinone studies

SWV experiments were carried out in triplicate using the optimized experimental parameters to obtain the analytical response shown in Fig. 5. The figures of merit for the determination of an individual phenol and 1,4-benzoquinone with the GC/MWCNT/CoPc are summarized in Table 1.

In Table 1 it can be seen that there are no differences in the linear range. However a decreasing sequence in the sensitivity was observed: 1.4-benzoquinone > catechol > hydroquinone > resorcinol > phenol. The detection limits for individual byproducts were also calculated: 1.4-benzoquinone (13.75 μg L^{-1}), catechol (15.62 μg L^{-1}), hydroquinone (17.91 μg L^{-1}), resorcinol (46.12 μg L^{-1}), and phenol (58.83 μg L^{-1}). Such values of the LOD are adequate to monitor contaminations with such moieties according to the European Economic Community directive 80/778 EEC [30,31], which has set a maximum allowable concentration for all types of phenols in aqueous solution as the value of 0.5 mg L^{-1} and 0.1 mg L^{-1} for individual phenols.

3.6. The benzene electrolysis study

The benzene electrolysis experiment was performed using chronoamperometry at a fixed potential of +2.0 V for 1 h. The electrolyte was 0.1 mol L^{-1} of acetate buffer solution pH 5.0 containing 2.5×10^{-6} mol L^{-1} (0.20 mg L^{-1}) of benzene. This value is below its maximum solubility in water at 25 °C [32]. The byproducts formed during electrolysis were analyzed by HPLC and the results are shown in Fig. 6. All products obtained after electrolysis were analyzed comparing their retention times with those obtained experimentally for the standard reagents. According to Kim et al. [33], the electrochemical degradation of benzene produces hydroquinone and benzoquinone on GC electrodes. However, in the HPLC experiments after electrolysis, four phenolic compounds and 1,4-benzoquinone were detected. The analysis of the solution before

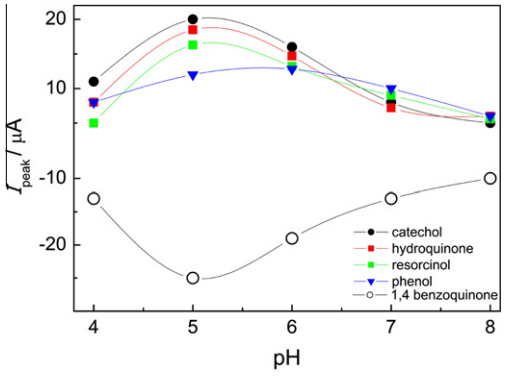

Fig. 4. Effect of pH on the peak current for catechol, hydroquinone, resorcinol, phenol and 1,4-benzoquinone on the GC/MWCNT/CoPc electrode using acetate buffer supporting electrolyte of ionic strength 0.1 mol L^{-1}, containing 1.0×10^{-4} mol L^{-4} of each phenol.

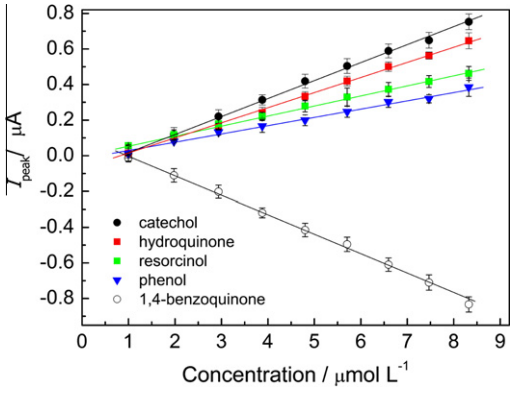

Fig. 5. Linear dependence of the SWV peak current and the concentration of the catechol, hydroquinone, resorcinol, phenol and 1,4-benzoquinone. The concentrations of mixture of phenols in μmol L^{-1} were: 0.99; 1.98; 2.94; 3.86; 4.80; 5.70; 7.46 and 8.32.

Table 1
Figures of merit for the byproducts using the GC/MWCNT/CoPc electrode.

	Linear range (μmol L^{-1})	Slope (μA/μmol L^{-1})	Intercept (μA)	Detection limit (μg L^{-1})
1,4-Benzoquinone	0.99–8.30	−110.21	−0.23	13.75
Catechol	0.99–8.30	71.38	0.02	15.62
Hydroquinone	0.99–8.30	36.10	0.07	17.91
Resorcinol	0.99–8.30	17.15	0.01	46.12
Phenol	0.99–8.30	8.15	0.03	58.83

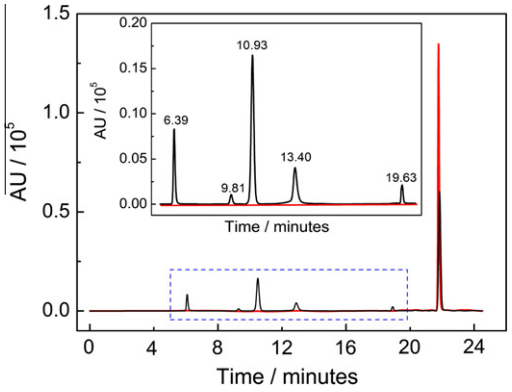

Fig. 6. Chromatograms for 2.5×10^{-6} mol L^{-1} (0.20 mg L^{-1}) of benzene (red line) and after the electrolysis procedure (black line). Inset: The phenolic byproducts formed and the respective retention time. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

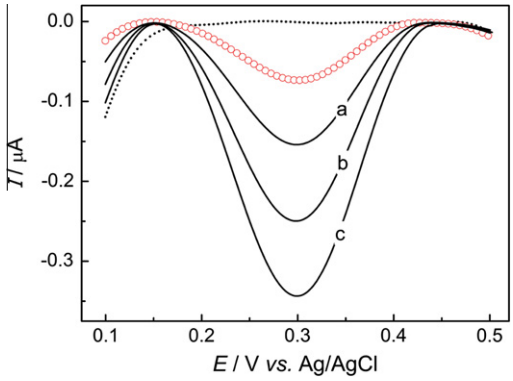

Fig. 7. SWV voltammograms for GC/MWCNT/CoPc electrode for: (dotted line) the sample before the electrolysis, (circle) samples after the electrolysis and (solid line) consecutive additions of a mixture of phenolic compounds (hydroquinone, catechol, resorcinol, phenol and 1,4-benzoquinone) were made in the following concentrations: 0.15, 0.20, and 0.25.0 mg L^{-1}.

electrolysis revealed only one peak due to benzene (red line), recorded at the retention time close to 22.7 min. After electrolysis, a decrease in the benzene peak was observed, as were the appearance of phenolic compound peaks (black line), such as: hydroquinone at 6.39 min; resorcinol at 9.81 min; catechol at 13.40 min; phenol at 19.63 min, and the another byproduct formed at 10.93 min attributed to 1,4-benzoquinone.

3.7. Analysis of total amount of phenolic compounds

Using the standard addition method, the proposed GC/MWCNT/CoPc electrode was applied to the analysis of the phenolic compounds and 1,4-benzoquinone after benzene electrolysis. For this purpose, an initial solution containing 0.20 mg L^{-1} of benzene was electrolyzed for 1 h. After the electrolysis procedure, the total phenols were analyzed using SWV with the optimized conditions, as shown in Fig. 7.

In the electrochemical response of the GC/MWCNT/CoPc electrode for the sample before electrolysis (dotted line), no process was observed. After electrolysis (open circle), the square-wave voltammogram presented a reduction process at +0.3 V. This electrochemical process was attributed to the reduction of quinones formed from benzene oxidation. Sequentially, three additions of a mixture of phenolic compounds (hydroquinone, catechol, resorcinol, phenol) and 1,4-benzoquinone were made in the following concentrations: 0.15, 0.20, and 0.25 mg L^{-1}. In the voltammograms (solid line), a linear increase in the peak at +0.3 V was observed.

Three different electrolysis experiments were performed and the average results obtained using the standard addition method, for three determinations, for each sample, were: 0.099, 0.105 and 0.113 in mg L^{-1} of total phenols. Recoveries between 95.0% and 102.2% of phenolic compounds ($n = 3$) were obtained.

The reproducibility of the GC/MWCNT/CoPc electrode was measured in 10 different experiments ($n = 10$) and on different days. Prior to each experiment, the electrode surface was rinsed thoroughly with double-distilled water. Thus, seven SWV voltammograms in 0.1 mol L^{-1} of acetate buffer solution pH 5.0 containing 0.20 mg L^{-1} of a mixture of phenolic compounds were collected. The relative standard deviation (RSD) was calculated as 3.1%. The repeatability tests were performed in ten different SWV voltammograms with the same concentration of phenolic compounds, and the RSD was found to be 2.2%.

In order to compare the results obtained with the proposed method, HPLC experiments were performed to analyze the total amount of phenolic compounds after benzene electrolysis. The same conditions described for the proposed method were used (initial concentration of benzene, time of electrolysis, three additions of a mixture of phenolic compounds). The results were summarized in Table 2. According to the Student's *t*-test, there were no significant differences between the HPLC and the electrochemical method at a 95% confidence level.

Comparing the results at the GC/MWCNT/CoPc electrode with an electroanalytical method [34], the glassy carbon electrode for direct determination of total phenol presented a higher detection limit of 0.53 mg L^{-1}. An ultrasound-assisted hydrolysis and gas chromatography–mass spectrometric method [35] showed higher detection limits of 60–700 μg L^{-1}, when compared with the GC/MWCNT/CoPc electrode. A method that used a flow injection analysis of volatile phenols in environmental water samples using CdTe/ZnSe nanocrystals as a fluorescent probe [36] archived a low detection limit of 2.7 ng L^{-1}. An immobilized horseradish peroxidase bioreactor with UV/vis spectroscopy [37] yielded detection limits varying of 1.38–1.68 μg L^{-1} of total phenols. However, for

Table 2
Determination of total amount of phenolic compound after benzene electrolysis (each value is the mean of three determinations).

	GC/MWCNT/CoPc		HPLC	
	Found (mg L^{-1})	Recovery (%)	Found (mg L^{-1})	E_r[a] (%)
Sample 1	0.099	95	0.109	−9.17
Sample 2	0.105	98	0.107	−1.87
Sample 5	0.113	102	0.109	+3.67

[a] E_r = Detected proposed GC/MWCNT/CoPc electrode vs. Detected HPLC.

the GC/MWCNT/CoPc film electrode, the good values observed in the recovery procedure show that the proposed method is suitable and efficient for the quantitative determination of the total amount of phenolic compounds in river water samples.

4. Conclusion

An alternative analytical procedure has been proposed in this paper, which allows real time monitoring of phenolic byproducts formed from electrolysis of benzene. The electrocatalytic properties of the carbon nanotubes add to the excellent redox mediator power of the cobalt phthalocyanine decreased the benzene oxidation potential compared with bare GC electrode. The cyclic voltammetry experiments demonstrated that a decrease in the benzene oxidation peak after the first cycle. In subsequent cycles it was observed a progressive increase in the cathodic and anodic peaks at +0.15 and +0.6 V respectively. These electrochemical processes are attributed both reduction and oxidation of the phenolic byproducts formed.

Due to the special characteristics of multi-walled carbon nanotubes and cobalt phthalocyanine as catalytic surfaces, the method yielded values for the LOD lower than those required for environmental control for phenols in natural waters. The study of benzene electrolysis monitored with HPLC confirmed the formation of phenolic products. The proposed GC/MWCNT/CoPc electrode was applied to the analysis of the phenolic compounds after benzene electrolysis and the obtained results were in full agreement with those from the HPLC procedure. The good values observed in the recovery procedure indicate that the proposed method could be suitable to be used in environmental analysis.

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