



Electrochemical study for the simultaneous determination of phenolic compounds and emerging pollutant using an electroanalytical sensing system based on carbon nanotubes/surfactant and multivariate approach in the optimization



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ABSTRACT

A voltammetric method for the simultaneous determination of phenolic compounds hydroquinone (HQ), catechol (CT), 4-nitrophenol (p-NP), and the emerging pollutant acetaminophen (AC) using a multi-walled carbon nanotubes (MWCNT) paste electrode in the presence of surfactant has been described. The relationship of oxidation potential and pH levels a Nernstian system for all compounds and the calculated diffusion coefficients were found to be 5.45×10^{-6} , 3.35×10^{-5} , 1.17×10^{-5} , and $2.60 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ for HQ, CT, AC, and p-NP, respectively. The best analytical condition for the simultaneous determination of phenolic compounds has been achieved by using a multi-response optimization approach. Under the optimum condition—Britton–Robinson buffer at 0.1 mol L^{-1} pH 8, CPB at $450 \mu\text{mol L}^{-1}$, and differential pulse voltammetry (pulse amplitude of 117 mV, pulse time of 23.98 ms, and scan rate of 8.61 mV s^{-1}), limits of detection of 0.07, 0.49, 0.29, and $0.32 \mu\text{mol L}^{-1}$ for HQ, CT, AC, and p-NP were obtained, respectively. The method permits the simultaneous analysis in the presence of some pesticides and other phenolic compounds. The developed method was applied in water (tap and domestic wastewater) and dermatological creams, whose accuracy has been attested through addition and recovery assays and comparing with HPLC–DAD as a reference method.

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1. Introduction

The increase of world population and agricultural and industrial practices has led to increases of levels of pollutants in surface waters and potable worldwide, especially the mostly polar ones that can be dissolved in water and transported through the water cycle [1]. Some of them are regulated by environmental protection agencies worldwide, and others are not regulated yet. The presence of pollutants has raised concerns for environmental quality and human health. For instance, 4-nitrophenol (p-NP) is a toxic compound that causes irritation to the skin, eyes, and respiratory tract and in the bloodstream interacts with hemoglobin forming metahemoglobin, which may cause cyanosis, confusion, and loss of consciousness [2]. This compound is also a toxic degradation product of insecticides ethyl and methyl parathion, and due to its toxicity and persistence in the environment, the U.S. EPA

(U.S. Environmental Protection Agency) has classified this compound as a priority pollutant and a dangerous substance, and according to this agency, the maximum allowed level of this compound in waters is $20 \mu\text{g L}^{-1}$ [3,4]. Other phenolic compounds have not been regulated by environmental protection agencies, such as the structural isomers catechol (CT) and hydroquinone (HQ), but in similar way to p-NP, these compounds have received a singular interest, due to their toxicity and persistence in the environment. Catechol has been widely used as antioxidant, antiseptic, and antifungal [5]. In the human body, CT is absorbed from the gastrointestinal tract, causing side effects such as hypertension, renal tubule degeneration, impaired liver function, cancer, neurodegenerative diseases [6,7]. Hydroquinone is a phenolic compound naturally found in wood, tobacco smoke, coal tar, crude oil, and other materials. Due to its ability to inhibit the tyrosinase (melanin production participant) and facilitate degradation of melanosomes (intracellular corpuscles of melanin store), HQ is widely used as active principle in creams used for skin bleaching [8], but some studies have reported the cancerous alteration in mouse bone after administration of doses of hydroquinone [9]. As mentioned, these compounds have ambiguous behavior, and therefore, their (eco)toxicological effect on

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the environment and human health is still not clearly elucidated. Moreover, the monitoring of CT in water samples can still be justified taking into account that this compound is a transformation product of the pharmaceutical carbamazepine, a very well-known emerging pollutant. Therefore, the occurrence of CT in drinking water and domestic waste water may indicate the presence of emerging pollutants from pharmaceutical sources. Emerging pollutants constitute a new class of several compounds which are increasingly released into the environmental compartments (water, soil, and air) at low levels and have not been regulated [10].

The great concern on the monitoring of these compounds and mainly their transformation products relies upon the lack of information regarding their occurrence and real toxicity on human health. Acetaminophen (AC) is a pharmaceutical product and has been considered an emerging pollutant, which is widely used through the world as an analgesic to relieve pain associated with arthralgia, neuralgia, headache, back pain, and postoperative pain [11]. In the human body, it acts as an inhibitor of prostaglandin synthesis in the central nervous system and as a sedative in the center of the heat setting hypothalamus [12]. This pharmaceutical compound and their transformation products have been detected in sewage treatment plant and environmental samples [13,14] and surface water [15].

According to the aforementioned, the phenolic compounds investigated in the present study can be found together in different kinds of water samples as original source or originated from the degradation of pharmaceutical products or insecticides. Thus, there exists a real need in developing analytical methods for the multi-residues analysis of organic pollutants due to their different properties. The multi-residues determination of pollutants has been widely carried out by high-performance liquid chromatography (HPLC) and gas chromatography (GC) [16]. However, these techniques suffer from some disadvantages, such as high acquisition and maintenance costs, time-consuming analysis; make use of toxic solvent as mobile phase in the case of HPLC; and need previous sample pretreatment [17]. In contrast, voltammetric techniques are particularly attractive because they are fast, sensitive, and amenable to portability and generally have low instrumental cost. On the other hand, in general, complicated strategies for designing/modification of electrochemical sensor must be usually performed to avoid peaks overlapping and, thus, enabling the multi-residues analysis [18–21]. In this sense, a good design to produce a simple electrochemical sensing system for simultaneous analysis determination of organic pollutants with high sensibility, selectivity, and robustness has been based on the application of carbon nanotubes as electrodic material associated with surfactants [22–25].

Even though there are some analytical methodologies developed for this purpose, the multi-residues analysis by voltammetry is still an exciting goal, and at the best of our knowledge, the simultaneous determination of four organic pollutants herein studied has not been reported yet. It is worth to emphasize that the optimum voltammetric conditions for the multi-residues analysis of HQ, CT, AC, and p-NP using the electrochemical sensing based on carbon nanotubes/cationic surfactant system were herein obtained through multi-response assays [26]. This chemometric tool makes it possible to reduce the number of experiments and allows evaluating interaction effects between factors studied when more than one analytical response is studied. Therefore, the uniqueness of the present study not only lies in the development of a new easy, sensitive, and selective voltammetric method for the simultaneous determination of four phenolic compounds but also in exploiting of chemometrics tools which has rarely been reported in the literature for simultaneous electrochemical analysis. The electrochemical oxidation of compounds has been studied by cyclic voltammetry at the carbon nanotubes/surfactant interface, and the differential pulse voltammetric method has been applied in water samples (tap and domestic wastewater) and dermatological creams and validated regarding selectivity, linearity, precision, and accuracy by comparing with HPLC-DAD as a reference method.

2. Materials and methods

2.1. Apparatus

Electrochemical experiments were performed in a three-electrode single-compartment glass cell, containing a platinum wire as auxiliary electrode, an Ag/AgCl ($\text{KCl } 3.0 \text{ mol L}^{-1}$) as reference electrode and a carbon nanotubes paste electrode (CNTPE, geometric area = 0.071 cm^2 and active area = 0.047 cm^2) as working electrode. For the voltammetric measurements, a potentiostat/galvanostat PalmSens (Palm Instruments BV, Houten, Netherlands) controlled by PSTrace 3.0.4 software (Palm Instruments BV) was employed. For comparison studies, a glassy carbon electrode (GCE—geometric area = 0.071 cm^2) was used. Prior to use of the electrode, it was polished with alumina 1.0 and $0.3 \mu\text{m}$ and rinsed with ultrapure Milli-Q® water (Millipore, Bedford, MA, USA). For chromatographic experiments, a Shimadzu liquid chromatograph equipped with a LC-20AT (Shimadzu, Kyoto, Japan) coupled with a diode array detector (DAD) at 280 nm and sample loop of $20 \mu\text{L}$ was employed. The separation of phenolic compounds was accomplished on a Shimadzu CLC-ODS (M) column (column size: $250 \times 4.6 \text{ mm i.d.}$, particle size: $5 \mu\text{m}$) at $25 \text{ }^\circ\text{C}$ at a flow rate of 0.9 mL min^{-1} using a methanol:water mixture (30:70 V/V) as mobile phase.

2.2. Reagents

Hydroquinone (HQ) (99%), catechol (CT) (99%), acetaminophen (AC) (99%), and cetylpyridinium bromide (CPB, 98%) were purchased from Sigma–Aldrich (St. Louis, MO, USA), while 4-nitrophenol (p-NP) (99%) and cetyltrimethylammonium bromide (CTAB 99%) were obtained from Acros Organics (Morris Plains, NJ, USA). Multi-walled carbon nanotubes (MWCNTs; of 10–40 nm in diameter and 5–20 μm in length; purity: 93%) were obtained from CNT Co. Ltd., Korea. Mineral oil (Nujol®) was acquired in local drugstores. Phosphate buffer solution was prepared by its respective salt dissolution (NaH_2PO_4 99–102%, Merk, Darmstadt, Germany). Britton–Robison (BR) buffer solution was prepared by mixing acetic, orthophosphoric, and boric acids at 0.5 mol L^{-1} , with pH adjusted with a 2.0 mol L^{-1} NaOH solution. All chemicals were analytical grade, and the solutions were prepared using ultra-purified water (resistivity > $18 \text{ M}\Omega \text{ cm}$) supplied by a Milli-Q system (Millipore®). Domestic wastewater discharged in lake and tap samples were collected, respectively, in the Igapó Lake and State University of Londrina, both located in the city of Londrina, Paraná, Brazil. The dermatological creams ($2 \text{ g } 100 \text{ g}^{-1}$ and $4 \text{ g } 100 \text{ g}^{-1}$) were acquired in local drugstores.

2.3. Carbon nanotubes paste sensor preparation

The carbon nanotubes paste electrode (CNTPE) was prepared by mixing 10.0 mg of multi-walled carbon nanotubes (MWCNT) with 23.3 mg of mineral oil (Nujol®) in a Petri dish, resulting in a paste with composition of 30:70% w/w (MWCNT/Nujol®). The paste was carefully inserted into a cavity (3.0 mm of diameter and 1.0 mm of depth) at the end of a Teflon® tube having a graphite disc as electrical contact within the tube cavity. The paste electrode surface was smoothed and carefully rinsed with Milli-Q® water. The paste was conditioned by cyclic voltammetry in the potential range from -1.0 up to 1.0 V with scan rate of 75 mV s^{-1} during 30 min.

2.4. Experimental procedure

The electrochemical characterization of oxidation process of phenolic compounds by cyclic voltammetry (scan rate at 30 mV s^{-1} and potential step of 5 mV) was carried out at an electrochemical cell 15.0 mL capacity using 0.1 mol L^{-1} phosphate buffer at pH 7 as supporting electrolyte, without previous removal of oxygen. The records

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