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Electrochemical degradation of butyl paraben on platinum and glassy carbon electrodes

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ABSTRACT

In this work, the electro-oxidation of butyl paraben (BuP) in aqueous solutions under different experimental conditions was studied by cyclic voltammetry. For this purpose, platinum and glassy carbon electrodes were employed in different electrolytes such as KCl, H_2SO_4 and $K_4P_2O_7$. The best electrochemical response was observed for glassy carbon electrode in the presence of $K_4P_2O_7$ based on the oxidation peak at 0.7 V vs. Ag/AgCl. Consequently, the glassy carbon electrode was selected to further study the influence on prevention of electrode passivation of three different surfactants, namely sodium dodecyl sulfate (SDS), 4-octylphenol polyethoxylate (Triton X-100) and cetyltrimethylammonium chloride (CTAC). The best results were obtained with CTAC. In order to detect and quantify butyl paraben, differential pulse voltammetry measurements were performed with several paraben concentrations. As optimized in previous experiments, glassy carbon electrodes were employed in $K_4P_2O_7$ (0.1 M) and CTAC (40 μM). The limit of detection was found to be 0.1 μM, but precise quantification could be assured only above 1.0 μM. Real river water samples were analyzed and the typical concentration of butyl paraben was found to be around 0.1 μM. However, selectivity tests are necessary to improve the reliability of this method. Electrolysis technique was employed in order to study the degradation of butyl paraben using the following optimized conditions: $E = 1.5$ V (vs. Ag/AgCl) on a glassy carbon electrode in $K_4P_2O_7$ (0.1 M) and CTAC (40 μM) at pH = 5, 7 or 9. Our result showed that the degradation of butyl paraben was more efficient in acidic media. Analysis by HPLC–MS technique confirmed $C_4H_5O_4^-$; $C_{11}H_{13}O_5^-$; $C_{11}H_{11}O_5^-$ and $C_{11}H_{13}O_4^-$ as the main degradation products.

1. Introduction

Parabens are esters of p-hydroxybenzoic acid that are widely used as chemical preservatives in food, cosmetics, and pharmaceuticals [1,2]. These preservatives are active against fungi, bacteria, and yeast. Furthermore, they are colorless, odorless, inexpensive, and stable in wide ranges of pH and temperature [3,4]. Parabens were first used in pharmaceuticals in the mid 1920s [5] and, since then, the application of paraben preservatives has been expanded and diversified [6]. In 1981, parabens were already used in more than 13,200 pharmaceutical formulations [3]. A study conducted in 1995 analyzed 215 cosmetic products and found that nearly all (99%) of leave-on products and most (77%) rinse-off products contained parabens [7]. In a recent survey conducted in 2013, a total of 282 food samples, representing 13 food categories, (i.e. cereals, meat, fish and seafood, eggs, dairy products, bean products, fruits, vegetables, cookies, beverages, cooking oils, condiments, and others) were all found to contain parabens [8].

Unfortunately, some recent studies have shown that parabens possess estrogenic activity since they can bind to estrogen receptors, causing unwanted effects in the organisms such as changes in hormone concentration. A relationship between breast cancer and application of paraben-containing products on skin is speculated since these compounds were found in breast tumors [9]. In 2005–2006, the analysis of urine samples from 2548 people above the age of six years in the United States showed that 47% of the samples had butyl paraben [10]. Parabens were also found in human urine samples from Spain and Denmark [11,12]. Studies have also shown the presence of parabens in human plasma, serum and milk at concentrations of the order of a few nanograms per milliliter [13,14].

There are different types of parabens categorized according to the alkyl radical. This property affects the solubility and the antimicrobial activity [15]. The most commonly used are methyl paraben (MeP), ethyl paraben (EtP), propyl paraben (PrP) and butyl paraben (BuP); the last one displays the highest estrogenic activity [16].

An assay of estrogenic activity of parabens in yeast showed that butyl paraben was three times stronger than nonylphenol, a strong endocrine deregulator. Tests of butyl paraben in juvenile rainbow

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trout (*Oncorhynchus mykiss*) showed positive results for inducing protein synthesis within the yolk (*vitellogenin*) [17]. Another study also reported that butyl paraben caused DNA damage in male sperm of rats [18]. In 2011, Denmark prohibited the use butyl paraben, its isoforms, and its salts, in products consumed by children under 3 years old [19].

Parabens have also been detected in sewage effluents, surface and ground water, rivers, and even in drinking water [20–23]. A study carried out in Portugal revealed the presence of parabens in treated water, demonstrating that treatment plants are not prepared to eliminate these endocrine disrupting chemicals [24]. Błędzka et al. [15] showed that the removal of endocrine disruptors at low concentrations in conventional sewage treatment plants is a difficult and costly process and that any modern techniques show good enough efficiency in the removal of certain substances. As alternative to conventional wastewater treatments, electrochemical methods are presented as promising techniques in view of their selectivity, efficiency, and environmental compatibility [25]. Szpyrkowicz et al. [26] applied this method for the treatment of tannery wastewater using a Ti/Pt electrode. Kuramitz et al. [27,28] used a carbon fiber electrode to oxidize and remove bisphenol A and noniphenol. Vega et al. [29] studied the electrochemical behavior of phenolic estrogenic compounds at a carbon nanotube-modified electrode aiming towards remediation of wastewater.

Nevertheless, it is known that anodic oxidation of phenolic compounds inactivates the surface of graphite and noble metal electrodes through the formation of polymers that block the electrode surface (passivation). However, the use of surfactants as antifouling agents has been advocated in the literature to avoid this problem [30,31]. Hu et al. [32] successfully applied cetyltrimethylammonium bromide (CTAB) as a surfactant to improve the electrochemical degradation activity of estradiol, estrone, and estriol at a glassy carbon electrode. Brugnera et al. [33] used a screen-printed carbon electrode in CTAB micellar medium to detect the presence of bisphenol A.

In the literature, there are no studies showing the electrochemical behavior of butyl paraben on platinum and glassy carbon electrodes. In addition, there are no studies related to the anodic oxidation of butyl paraben on glassy carbon electrode in the presence of surfactants. Quantification of paraben generally is performed by HPLC [34–36], however, an electrochemical quantification method was not found in the literature up to now. Few studies have reported the use of electrochemical techniques for parabens quantification [37] despite the advantages in relation to cromatographic methods. Electroanalysis requires less time, easier sample preparation and detection limits comparable to other analytical methods. In fact, Gholivand et al. [38] achieved limits of detection as low as 0.3 nM using differential pulse voltammetry for propyl paraben detection.

Thus, in this work, we investigated the electrochemical behavior of butyl paraben using platinum and glassy carbon electrodes under different conditions and in the presence of surfactant, SDS, Triton X-100, and CTAC. Afterwards, a quantification via electrochemical method is suggested. In addition, we performed the electrochemical degradation of butyl paraben using optimized conditions and analyzed the degradation products using HPLC–MS.

2. Experimental

2.1. Reagents

The following high-purity grade chemicals were used without further purification: butyl p-hydroxybenzoate (butyl paraben), purity ≥99.0% (Aldrich, USA), sodium chloride (NaCl), purity ≥99.0% (Aldrich, USA), sulfuric acid (H_2SO_4), purity ≥99.0% (Aldrich, USA), potassium diphosphate ($K_4P_2O_7$), purity ≥99% (Riedel-de Haen, Germany), hydrochloric acid (HCl), purity ≥99.0% (Aldrich, USA), sodium hydroxide (NaOH), purity ≥99.0% (Aldrich, USA), ethanol, purity ≥99.0% (Qhemis, Brazil) and cetyltrimethylammonium chloride (CTAC), sodium dodecyl sulfate (SDS) and 4-octylphenol polyethoxylate (Triton X-100) (all from Aldrich, USA).

2.2. Apparatus and characterization techniques

Electrochemical measurements were carried out using an Autolab® potentiostat model PGSTAT 30 coupled to a microcomputer and managed by GPES 4.9 software. All electrochemical studies were performed in a conventional glass electrochemical cell with a working volume of 25 mL. A three-electrode configuration was employed, with a working electrode of glassy carbon or polycrystalline platinum foil (each electrode with geometric area of 1.0 cm^2). A platinum wire was used as the counter electrode and an Ag/AgCl electrode in 3 M KCl solution was used as the reference electrode, separated by a glass frit. Thus, all potentials mentioned in this work refer to Ag/AgCl/KCl (3 M). The glassy carbon electrode was previously polished with alumina particles up to 0.05 μm size and washed with deionized water. The electrolyte solutions were 0.1 M KCl, H_2SO_4 or $K_4P_2O_7$. Cyclic voltammetric profiles were collected at a scan rate of 20 mV s^{-1}. Differential pulse voltammetry was employed for detection and quantification of butyl paraben, with step potential of 9 mV, modulation amplitude of 0.10 V and scan rate of 20 mV s^{-1}. Chronoamperometric studies (electrolysis) were carried out at a constant potential of 1.5 V.

The detection and quantification of butyl paraben in real water samples were performed without any pretreatment. The water samples were collected from Mogi-Guaçu river, located in the center of São Paulo state in Brazil. Two points of the river 12 km away from each other were chosen: the first one at Rincão city, and the second one at Guatapará city. Even though Guatapará city is smaller, the river crosses its urban area, where domestic sewage is directly discharged into the river. On the other hand, at Rincão city, the river crosses only the countryside.

For differential pulse voltammetry measurements, the samples were used as collected, only adding the electrolyte and surfactant. For analysis by high performance liquid chromatography (HPLC), the samples were extracted and concentrated about 100 times by dispersive liquid–liquid microextraction (DLLME), with acetone as the dispersing agent and 1-octanol as the extractor solvent according to the method of Galinaro and Vieira, 2014 [39]. The HPLC measurements were carried out using a Shimadzu® system equipped with a LC 20AD pump, a DGU-20A5 degasser, a CTO-20A oven kept at 30 °C, and a SPD-20A UV/visible detector. Methanol and water mixture (7:3 v/v) was used as mobile phase with a flow rate of 1 mL min^{-1} in a reverse phase C18 column (4.6 mm × 250 mm × 5 μm model Shim-pack CLC-ODS (M) Shimadzu, Japan).

During the chronoamperometric oxidation measurements, 1.0 mL aliquots of the electrolyte were taken every 2.5 h and analyzed using a V-630 UV/Vis spectrophotometer (Jasco Co., Japan) equipped with a quartz cell of 1 cm pathlength in the spectral range 200–400 nm. The pH solution of the electrolyte was adjusted with HCl and NaOH both at 1 M. The identification of reaction products in these sample aliquots was carried out with a liquid chromatograph LC–ESI-MS (liquid chromatograph electrons spray ionization mass spectrograph) coupled with a LTQ-Orbitrap Velos Thermo Fisher Scientific mass spectrometry system (Bremen, Germany) operating in the negative ion detection mode. A reverse phase column C18 (4.6 mm × 250 mm × 5 μm), model Shim-pack CLC-ODS (M) (Shimadzu, Japan) was used with a mixture of solvents A + B (A = water/formic acid, 99.9/0.01 (v/v %) and B = methanol/formic acid, 99.9/0.01 (v/v %)) as the mobile phase. A flow rate of 1.0 mL min^{-1} was used with the following linear eluting gradient: 0–10 min, 65% B in A; 10–15 min, 100% B; 15–22 min, 65% B in A. All measurements were carried out at room temperature (25 ± 1 °C).

Analysis of the byproducts was performed by comparing the chromatogram of the electrolyte solution prior to the application of 1.5 V as a control sample with the chromatograms of aliquots that were