



Removal of phthalic acid from aqueous solution using a photo-assisted electrochemical method



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ABSTRACT

Phthalic acid esters, along with their degradation byproduct phthalic acid (PhA), can enter surface water systems through water leaching and remain in the environment for protracted periods causing serious problems to aquatic and human lives. Thus, the aim of the present study was to assess the possible application of photo-assisted electrochemical technology (PAE) in the removal of PhA and total organic carbon (TOC) from aqueous solutions using a DSA[®] electrode. Examination of system parameters, including type and concentration of supporting electrolyte, applied current density, pH and temperature, revealed that highest removals of PhA and TOC could be attained at 30 °C with an applied current density of 20 mA cm⁻² using acidic electrolytes containing 50 mmol L⁻¹ NaCl. Under these conditions, the photolysis of electrogenerated HOCl produced highly reactive oxidizing agents, including HO[•], which promoted the complete removal of PhA and 60% removal of TOC within 3 h; however, the system requires further optimization since the mineralization current efficiency was low (20%) and the energy consumption was high (100 kW h g⁻¹).

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Introduction

The contamination of surface waters by synthetic organic compounds, such as those present in pharmaceuticals, cosmetics, personal healthcare products, packaging materials *etc.*, is an issue of considerable concern owing to the increasing scarcity of potable water worldwide. Although pollutants of this type are usually present only at low concentrations, their removal by conventional municipal treatment plants is typically inefficient and incomplete [1,2]. Moreover, since these compounds are xenobiotics, they may remain in the food chain for considerable periods causing serious problems to aquatic organisms and, potentially, to animal and human health [2].

The phthalic acid esters (PAE) form a group of synthetic chemicals that are used as additives in a wide range of industrial processes, most especially to impart flexibility to plastics. The compounds are bound to the structure of the plastic through polar interactions but may enter the environment through leaching by water [3]. Consequently, effluents contaminated with PAEs need to be treated before disposal into water bodies. A significant number

of reports are available concerning the breakdown of PAEs, and various technologies for the treatment of effluents containing these esters have been published [4–6]. On the other hand, few studies have focused on the degradation of phthalic acid (PhA; benzene-1,2-dicarboxylic acid) [7,8], a compound formed by the total hydrolysis of PAEs and frequently found as a byproduct of PAE oxidation [9].

Although many methods are available for the treatment of effluents containing synthetic organic compounds at low concentrations (with a certain amount of dissolved electrolytes), those involving electrochemical oxidation offer a number of distinct advantages in that they are easy to implement and control, are generally very powerful, but do not necessitate the handling of dangerous reagents. Electrochemical degradation of an organic pollutant can occur either directly on the anode surface or through an indirect process mediated by oxidizing species electrogenerated *in situ* [10]. In most electrochemical processes, the electro-generated oxidants comprise highly reactive hydroxyl radicals [HO[•]], but other species, such as Cl₂, HClO and OCl⁻, may also be present when chloride-containing solutions are electrolyzed [11].

A key factor in the development of an efficient electrochemical process is the choice of appropriate electrode material. In this context, boron-doped diamond (BDD) film anodes have been employed extensively in the electrodegradation of various types of organic pollutants, including many synthetic compounds, in

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processes that can also be photo- or Fenton-assisted [12–14]. However, a number of concerns have been raised regarding the use of BDD film anodes, particularly in respect of cost and film stability. A dimensionally stable anode (DSA[®]) might represent an alternative electrode material by virtue of its electrochemical stability and commercial availability [15]. Application of a DSA[®] electrode for the efficient removal of an organic pollutant is typically accomplished with the use of NaCl as an inorganic additive or as supporting electrolyte [16,17]. The main disadvantage of this technique is that degradative oxidation is accompanied by the production of undesirable organochlorine compounds, the concentrations of which depend on the amount of NaCl employed [18]. One method by which this problem can be avoided is to perform the electrodegradation in the presence of UV radiation. The resulting photo-assisted electrochemical process is able to generate HO[•] *in situ* from the active chlorine species, thereby yielding high rates of organic removal [17,19,20] and producing treated solutions that are non-toxic, as demonstrated by Malpass et al. [21].

The aim of the present work was, therefore, to investigate the influence of various operational variables, including composition of supporting electrolyte, applied current density, pH and temperature, on the photo-assisted electrochemical degradation of PhA. The electrochemical experiments, which were carried out using a commercially available DSA[®] anode under UV radiation, were designed to assess the performance, with respect to a purely mass-transfer controlled process, and possible application of the technology in the removal of PhA and total organic carbon (TOC) from dilute aqueous solution.

Experimental

Materials

Analytical reagents (a.r.) Na₂SO₄, Na₂CO₃, NaNO₃ and NaOH (all of Qhemis[®]) were purchased from Hexis Científica (Jundiaí, SP, Brazil), a.r. NaCl was from Synth (São Paulo, SP, Brazil), a.r. PhA was from Sigma–Aldrich (St. Louis, MO, USA), a.r. 2-propanol was from Merck Brazil (São Paulo, SP, Brazil), and methanol (HPLC grade), H₂SO₄ (98% pure) and H₃PO₄ (85% pure) were from Mallinckrodt Baker (Avantor Performance Materials, Ecatepec Estado de Mexico, Mexico). All reagents were used as received. Deionized water (resistivity $\geq 18.2 \text{ M}\Omega \text{ cm}$ at 25 °C), obtained using a Milli-Q[®] system (Merck Millipore Brazil, Barueri, SP, Brazil), was used for the preparation of all solutions.

Experimental setup

Photo-assisted electrochemical experiments were performed in a one-compartment filter-press flow cell comprising a DSA[®] anode (nominal composition: Ru_{0.3}Ti_{0.7}O₂) on a Ti substrate and a Ti-mesh cathode, both from De Nora do Brasil Ltda. (Sorocaba, SP, Brazil). The exposed geometric areas of both electrodes were 15 cm². The Ti-mesh was sandblasted with 60–70 μm glass microspheres and cleaned with 2-propanol for 30 min in an ultrasonic bath prior to location in the flow cell. The electrodes were maintained approximately 1.0 cm apart by insertion of Viton[®] and Teflon[®] spacers of thicknesses 1 and 2 mm, respectively. A quartz window, held between two silicon spacers (thickness 2 mm) with central openings, was positioned just after the Ti-mesh to allow the passage of UV light to the DSA[®] surface. UV radiation was supplied by a Philips 250 W high pressure Hg lamp ($\lambda_{\text{max.intensity}} \sim 254 \text{ nm}$; irradiance 0.417 W cm^{-2}) located 7 cm from the DSA[®], producing irradiance at the anode of 0.113 W cm^{-2} . A standard hydrogen electrode (SHE; $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$), serving as the reference electrode, was placed outside the flow cell. Electrical contact with the SHE was

maintained through an IONAC cationic membrane strip, one end of which was mounted between the Viton[®] spacers and the other immersed in an electrolytic solution ($0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$) positioned just below the cell. The flow cell was connected to a reservoir via silicone tubing and a peristaltic pump. In order to avoid direct contact with the UV radiation, the flow cell setup was assembled inside a closed box equipped with an exhaust system. Further details of the cell reactor and a schematic representation of the photo-assisted electrochemical system are available in previous publications from our group [19,20,22].

Cyclic voltammetry

Prior to voltammetric analysis, the DSA[®] was subjected to an anodic pre-treatment for 15 min at 20 mA cm^{-2} in $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ solution with constant circulation. Cyclic voltammetry (CV) measurements (5 cycles at 20 mV s^{-1}) were recorded, without recirculation of electrolyte, using a potentiostat/galvanostat coupled to a SPGSTAT30 booster (amplifier), both from Autolab (Eco Chemie, Utrecht, The Netherlands).

Photo-assisted electrodegradation experiments

The UV-assisted electrochemical degradation of PhA was carried out under galvanostatic conditions for 60 min with 0.5 L of an aqueous solution containing 150 mg L^{-1} of analyte recirculated at a flow rate of 28 L h^{-1} (0.025 m s^{-1}). In order to assess the performance of the system, the following variables were investigated: (i) addition of NaCl, Na₂SO₄, Na₂CO₃ and NaNO₃ to the supporting electrolyte at 100 mmol L^{-1} ionic strength, (ii) concentration (25, 50 and 100 mmol L^{-1}) of NaCl in the supporting electrolyte, (iii) applied current density (10, 20 and 40 mA cm^{-2}), (iv) pH (3, 7 and 11) of electrolyte solution, and (v) temperature (15, 30 and 45 °C) of electrolysis.

Analysis of process performance

The performance of the UV-assisted electrochemical degradation of PhA was assessed from determinations of the decay in the concentrations of analyte and TOC. PhA was analyzed quantitatively by high performance liquid chromatography using a Shimadzu (Kyoto, Japan) model LC-10ADVP instrument equipped with a model SPD-10AVP detector and a reversed phase C18 column ($150 \times 4.6 \text{ mm}$ i.d.; $5 \mu\text{m}$). Isocratic elution was performed with a mobile phase comprising a 1:3 (v/v) mixture of methanol and H₃PO₄ (20 mmol L^{-1}) delivered at a flow rate of 0.5 mL min^{-1} . The oven temperature was maintained at 40 °C and detection was at 278 nm. The concentration of PhA was estimated from the chromatographic peak area by reference to a calibration curve constructed with a.r. grade analyte (the limit of quantification and detection were 1.0 ppm and 0.5 ppm, respectively). TOC was monitored using a high-temperature combustion method (Shimadzu model VCPH TOC analyzer) by sampling 10 mL aliquots of the electrolyte every 15 min. TOC was taken to be the difference between the values for total carbon and inorganic carbon (the limit of quantification and detection were 0.5 ppm and 0.1 ppm, respectively).

The mineralization current efficiency (MCE) was calculated according to [23]:

$$\text{MCE} = \frac{\Delta(\text{TOC})_t \cdot nFV}{4.32 \times 10^7 \text{ mlt}} \times 100 \quad (1)$$

where $\Delta(\text{TOC})_t$ is the change in TOC (mg carbon L^{-1}) after time t (h), n is the number of electrons exchanged assuming that the total electric charge applied was consumed in the mineralization process (complete oxidation by HO[•] from H₂O discharge) according

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