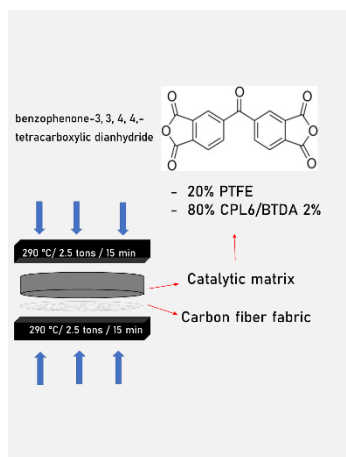


Degradation of Diethyl phthalate by hydrogen peroxide electrogenerated by gas diffusion electrode based on amorphous carbon modified with benzophenone

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Taynara Oliveira Silva^{1,3}, Géssica de Oliveira Santiago Santos^{1,3}, Renata Colombo², Marcos Roberto de Vasconcelos Lanza¹, Manuel Andrés Rodrigo Rodrigo³



In this work, a novel gas diffusion electrode (GDE) made of Printex L6 carbon and 2.0% benzophenone-3,3',4,4'-tetracarboxylic dianhydride (PL6C/BTDA 2%) was employed for the production of hydrogen peroxide and for the removal of diethyl phthalate (DEP). Different advanced oxidation processes that included the mediated electrochemical oxidation with electrogenerated hydrogen peroxide ($e\text{-H}_2\text{O}_2$) and with UVC photolysis ($e\text{-H}_2\text{O}_2/\text{UVC}$) were evaluated. As result, the integrated $e\text{-H}_2\text{O}_2/\text{UVC}$ obtained the best performance, being synergistic respect to the two single technologies integrated, and leading to the total elimination of DEP within 30-minute treatment, reaching the highest kinetic rate constant (0.3 min^{-1}) and exhibiting the lowest electrical energy consumption ($2.17 \text{ kWh m}^3 \text{ order}^{-1}$) among technologies tested. Fifteen by-products, generated through oxidation processes, were identified, enabling the proposal of the degradation mechanism of DEP.

Introduction

Interest in hydrogen peroxide (H_2O_2) production has surged owing to its versatile applications across various industries, notably in textiles and cosmetics, as well as in bacterial and viral disinfection and waste remediation processes. Indeed, it serves as a primary component in numerous advanced oxidation processes (AOPs), encompassing a range of electrochemical advanced oxidation processes (EAOPs), where it is generated electrolytically in situ. In addition to its high reduction potential ($E^\circ = +1.77 \text{ V vs SHE}$), H_2O_2 can be activated in the presence of UVC irradiation to hydroxyl radical ($\bullet\text{OH}$) ($E^\circ = +2.80 \text{ V vs SHE}$) (Lima et al., 2020; Oturan et al., 2014; Y. Song et al., 2016).

This work aims to employ these GDE for the purpose of H_2O_2 electrogeneration in a tangential-flow reactor 3D printed, specifically for the degradation of diethyl phthalate (DEP) using AOP.

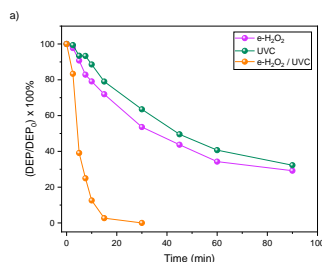
Material and Methods

The evolution of DEP concentration was monitored by high-performance liquid chromatography with a UV-DAD detector using a C18 column (Phenomenex®: 150 mm \times 4.6 mm, 5 μm particle size) as the stationary phase and a mixture of 90% formic acid and acetonitrile (ACN - ratio 30:70) as the mobile phase, in isocratic elution mode (at 0.8 mL min^{-1}). The degradation byproducts and degradation pathway were determined using a liquid chromatograph system (Prominence LC 20AT)

coupled to a triple quadrupole mass spectrometer (LC-MS/MS 8030). The mobile phase was a combination of water with 0.1% formic acid (A) and acetonitrile (B) and the elution was performed in gradient mode: 0-5 min: 10-100% B; 5-8 min: 100% B; 8-10 min: 100-10% B). The analysis was performed with electrospray ionization (ESI) interface in positive ionization mode with a scan range of m/z between 50 and 500. The desolvation gas (N_2) flow rate was set at 1 L min^{-1} , and the temperature of desolvation and ion source block was maintained at 250°C and 400°C, respectively.

Results and Discussion

The DEP degradation experiments were conducted using the GDE PL6C/BTDA 2% and applying the same current density of 50 mA cm^{-2} , recirculating through the cathodic compartment of the electrochemical cell a synthetic wastewater containing this pollutant, shown in Fig 1.



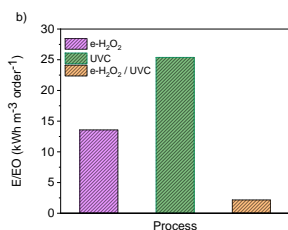


Figure 1. (a) Relative percentage of DEP removed over time based on the application of different treatment processes using GDE PL6C/BTDA 2% at 50 mA cm⁻². and (b) Electrical energy consumed in order to reduce the concentration of DEP by one order of magnitude under the application of different advanced oxidation processes.

Photodegradation exhibits a degradation pattern consistent with the previously discussed processes, resulting in the partial degradation of DEP in 90 minutes duration tests. The oxidation of DEP molecule exhibited remarkable enhancement when the combined approach of e- H₂O₂ and UVC light (e- H₂O₂/UVC) was employed. This hybrid treatment achieved complete DEP elimination within 30 min treatment. The notable improvement observed in this treatment can be predominantly attributed to the •OH, generated through the activation of e-H₂O₂ under UVC irradiation.

Fifteen DEP degradation products (DP1–DP15) were identified in the treatment processes (e-H₂O₂/UVC). Chromatographic and mass spectrometry information for these degradation compounds is displayed in Figure 2.

In Pathway I, the occurrence of self-coupling of phenoxy radicals and successive hydroxylation processes of DEP were suggested, leading to the formation of high-molecular-weight products DP1, DP2, and DP3. Degradation reactions of these high-molecular-weight compounds can also occur through the attack of •OH radicals, with the likely formation process for DP4, DP5, and DP6.

A second mechanism for the formation of intermediates (Pathway II) was proposed by the continuous hydroxylation of the DEP molecule, leading to the formation of DP7, DP8, DP9, DP10, and DP11. Pathway III describes the oxidation of DEP, with DP12 being the only intermediate formed by this route. The attack of the hydroxyl radical on the DEP molecule, causing the breaking of C-C and C-O bonds, is proposed in Pathway IV. The loss of two methyl groups from DEP generated DP13, the removal of a methoxy unit from DP13 gave rise to DP14, and subsequent hydroxylation of DP14 generating DP15.

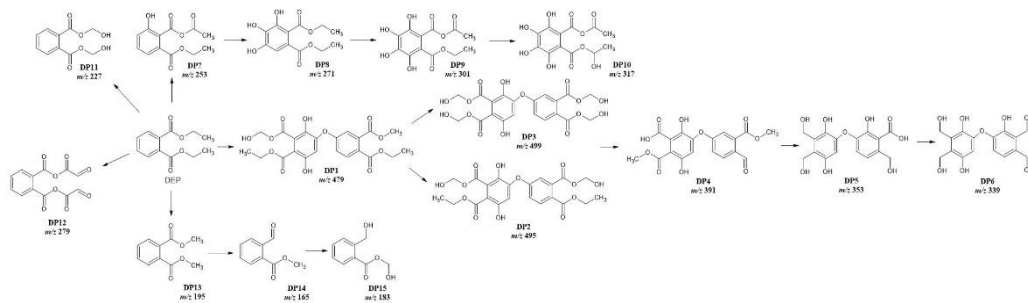


Figure 2. Proposed degradation pathways of DEP using different advanced oxidation processes.

Conclusions

The degradation of DEP was more efficiency using the process combine e- H₂O₂ and UVC, generated •OH that is a strong oxidant agent. Finally, a consistent mechanism that explains the oxidative degradation of DEP in the cathodic compartment of an electrochemical cell by EO/e-H₂O₂/UVC is proposed, explaining the formation of the different intermediates detected by MS.

Acknowledgments

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