Sustainable GDE based in Sugarcane Bagasse for On-Site H_2O_2 electroeneration: Application for Amoxicillin removal in Flow Reactors for scalable water treatment.

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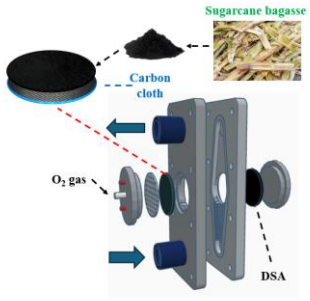

This study investigates using sustainable sugarcane bagasse-based gas diffusion electrodes (GDEs) for H_2O_2 generation and amoxicillin removal. While comparable H_2O_2 production was achieved with traditional GDEs, sugarcane bagasse offered an eco-friendly alternative. The electrochemical advanced oxidation process (EAOP) combinated (UVC-Fe-H_2O_2) effectively degraded amoxicillin (85% in 60 minutes) overcome methods like UVC or H_2O_2 alone. Furthermore, the combined process demonstrated superior removal of total organic carbon (58.5%). Besides, the combination of EAOPs with electrogenerated H_2O_2 and scalable electrochemical flow reactors (EFRs) offers a promising solution. Although, these findings suggest sugarcane bagasse GDEs with UVC-Fe-H_2O_2 hold promise for treating antibiotic-contaminated water.

Introduction

This work explores the use of gas diffusion electrodes (GDE) for a promising environmental application: generating hydrogen peroxide (H_2O_2) on-site to degrade pollutants. GDEs with carbon-based materials are highly efficient for H_2O_2 production, but traditional options often rely on petroleum sources [1,2]. To address this, we present an sustainable alternatives like sugarcane bagasse, a readily available source of carbon. Additionally, the growing presence of antibiotics in the environment, particularly in water sources, necessitates effective treatment methods. Electrochemical advanced oxidation processes (EAOP) using electrogenerated H_2O_2 offer a solution for eliminating these contaminants. Furthermore, the use of electrochemical flow reactors (EFR) enhances the scalability of this technology. Here we present an GDE based in sugarcane bagasse, applied in an flow reactor combinated with EAOP (UVC-FE-H_2O_2), to remove commercial amoxicilin as a contaminant target.

Material and Methods

Chemicals

Commercially available amoxicillin pills were used. Ferrous sulfate heptahydrate ($FeSO_4 \cdot 7H_2O$ ≥ 99%, Vetec) served as the catalyst. Potassium sulfate (K_2SO_4 99%, Vetec) and sulfuric acid (H_2SO_4 95-98%, Vetec) were used for electrolyte preparation and pH adjustment. Ammonium molybdate ($(NH_4)_6Mo_7O_{24}$) solution (2.4×10^{-3} mol L^{-1}) was used for H_2O_2 quantification. Acetonitrile (ACN, Sigma Aldrich) and ultrapure water from a Milli-Q® Direct-Q system (18.2 MΩ cm) (Merck Millipore) were used to prepare the mobile phases for liquid chromatography.

Electrochemical setup

An electrochemical flow reactor (EFR) described elsewhere [3] was used to compare GDEs for H_2O_2 generation. The setup had a 4 mm inter-electrode gap, 2.0 L capacity (semi-batch), and 10 L h^{-1} flow rate controlled by a peristaltic pump. GDEs was fed with O_2 gas (99% purity) at 80 mL min^{-1}. The 0.05 mol L^{-1} electrolyte (pH 3.0) used a DSA®-Cl_2 anode (De Nora do Brazil) and either a commercial carbon GDE (CPL6) or a sugarcane bagasse GDE. Both electrodes had a 20 cm^2 exposed area.

Experiments configurations

H_2O_2 production of both GDEs (CPL6 and cane) was compared at various current densities (25-150 mA cm^{-2}). Current efficiency (CE) and energy consumption (EC) were evaluated using equations **eq. 1** and **eq. 2** for a more comprehensive comparison.

$$\mathrm{CE}(\%) = \frac{2\,\mathrm{F}\,C_1\,\mathrm{V}}{I\,t_1} x\ 100 \qquad \textbf{(eq. 1)}$$

$$\mathrm{EC}(\mathrm{kWh}\ kg^{-1}) = \frac{1000\,\mathrm{E}\,\mathrm{I}\,t_2}{M} \qquad \textbf{(eq. 2)}$$

The terms in both equations can be find in this work [3]. The EAOP tests for degradation of 20 mg L^{-1} amoxilin was performed in the same electrochemical conditions describe before. The UV-C light used was low-pressure Hg lamp (254 nm; Philips). For Fenton reactions 2.5 µmol L^{-1} of $FeSO_4$ was used. Also blank experiments to better evaluation of effect of each EAOP process is performed.

Gas diffusion electrode preparation

We built the electrode following our prior method [3]. Briefly, we mixed 80% carbon mass with 20% PTFE and pressed it onto a ZOLTEK carbon cloth

at 4.5 tons, 290°C for 15 minutes.

Analytical method

Amoxiciln was measured using an HPLC system (Shimadzu, series 20) with a DAD, employing a C18 column and 50% ACN: 50% H_2O U.P. as the mobile phase at a flow rate of 1.0 mL min^{-1}. The mineralization extent was monitored by total organic carbon (TOC) determination using a Shimadzu TOC-VCPN. H_2O_2 was measured at intervals during the 1-hour experiment. Samples were mixed with ammonium molybdate, forming a detectable compound at 350 nm for analysis [4]. Subsequently, UV-1900 spectrophotometer (Shimadzu) was used for analysis.

Results and Discussion

In Figure 1-a is show the current densities tests and de concentration of H_2O_2, for both GDEs (CPL6 and cane), after 60 min of electrolysis.

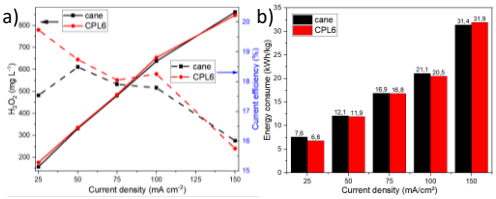

Figure 1. Comparison between GDEs (CPL6 and cane), by variating current densities **a)** Concentration of H_2O_2 and current efficiency, **b)** Energy consumption.

For all current desinties applied (25 to 150 mA cm^{-2}), the concentration of H_2O_2 electrogenerated is almost the same for both GDEs. However, for the lowest current density applied (25 mA cm^{-2}), the efficiency was the most different (17.5 and 19.7 %, for cane and CPL6, respectively). Altough, the analysis of energy consumption (Figure 1-b) show less than 1 kWh kg^{-1} difference between both GDEs, for all current densities.

The degradation of commercial amoxicillin (Amox) in different EAOPs (anodic oxidation (AO), ultraviolet in 254 nm (UVC), H_2O_2 electrogenerated (H_2O_2) and Fenton combination with H_2O_2 and UVC (Fe-H_2O_2 and UVC-Fe-H_2O_2)) conditions is presented in Figure 2.

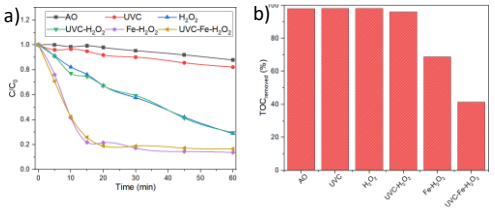

Figure 2. Use of GDE of cane in different EAOP condition applied in Amox degradation, **a)** degradation curve, **b)** TOC removed. Electrochemical condition: 25 mA cm^{-2}, pH 3, 2.0 L at 0.05 mol L^{-1} of K_2SO_4 solution, and 20 mg L^{-1} of amoxicilin.

Figure 2-a shows the degradation curves for amoxicillin removal. Conditions with only AO (anodic oxidation) and UVC (ultraviolet C radiation) have low effectiveness, reaching only 12.0% and 18.0% removal after 60 minutes, respectively. Similarly, the removal of total organic carbon (TOC) for both conditions is close to zero (Figure 2-b). Electrogenerated hydrogen peroxide (H_2O_2) and its combination with UVC show a better, and practically identical, effect on amoxicillin degradation, removing around 30.0% after 60 minutes. However, the H_2O_2 condition alone removes almost no TOC, while UVC-H_2O_2 removes only 4.0%. The best response for amoxicillin degradation is found for the electro-Fenton reaction (Fe-H_2O_2) and its combination with UVC (UVC-Fe-H_2O_2). Both conditions also exhibit very similar degradation curves, reaching 80.0% removal after 15 minutes of reaction, with a slight decrease to 85.0% at 60 minutes (Figure 2-a). However, for TOC removal, the combined process (UVC-Fe-H_2O_2) shows a better effect (58.5%) compared to the electro-Fenton process alone (31.1%).

Conclusions

The results show that GDE made with sugarcane bagasse have praticaly the same efficiency of the well-know commercial carbon printex L6. Also, in application of EAOP process, the combination of UVC-Fe-H_2O_2, show the most effective method for amoxicillin removal from water. It achieved a remarkable 85% degradation, and 58.5% of TOC removed within just 60 minutes, significantly outperforming alternative methods like AO, UVC, and even H_2O_2 alone.

Acknowledgments

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