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Simultaneous degradation of hexazinone and diuron using ZrO_2-nanostructured gas diffusion electrode

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HIGHLIGHTS

- ZrO_2-nanostructured GDE is reported as promising cathode for electrochemical AOPs.
- An increase of 130.3% was attained in the current efficiency of ORR to H_2O_2.
- H_2O_2 electrogeneration on nanostructured GDE was 93% higher than on unmodified GDE.
- Simultaneous removal of hexazinone and diuron was attained by H_2O_2/Fe(II)/UV.

ARTICLE INFO

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Zirconium oxide
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ABSTRACT

Although several authors have reported the treatment of diuron in wastewater by advanced oxidative processes (AOPs), only a handful of investigations reported using commercial herbicides composed of a mixture of active organic molecules· H_2O_2 is a well-known oxidant that is widely employed in AOPs and which can be produced by oxygen reduction reaction (ORR) on gas diffusion electrode (GDE). However, the development of efficient non-noble electrocatalysts that consume less energy for ORR is still a matter of considerable interest. This study reports the electrogeneration of H_2O_2 on both unmodified and ZrO_2-nanostructured GDE. The ZrO_2-nanostructured GDE was applied toward the simultaneous degradation of hexazinone and diuron using the commercial formulation of these herbicides. The ZrO_2-nanostructured and bare GDEs produced 435.6 mg L^{-1} and 225.8 mg L^{-1} of H_2O_2, respectively. Furthermore, an increase of 130.3% was observed in the current efficiency of oxygen reduction to H_2O_2 in the presence of ZrO_2, indicating that less energy was consumed. Indeed, the production of 1 kg of H_2O_2 using ZrO_2-nanostructured GDE consumes 10.2 kWh at 25 mA cm^{-2}, while bare GDE consumes 32.8 kWh at the same current density. Hexazinone and diuron were found to have been completely removed, albeit 28% of the organic carbon remained in solution after 120 min of electrolysis by H_2O_2/Fe(II)/UV. A complete removal of organic load will require longer treatment time. The residual carbon may be associated with other species present in the formulation. The results show that ZrO_2-nanostructured GDE is a promising material suitable for environmental applications.

1. Introduction

Diuron (3-(3,4-dichlorophenyl)-1,1-dimethylurea) is one of the most widely applied herbicides in agricultural activities used for controlling pests. This herbicide has toxic effects on humans and ecosystems due to its resistance toward biological and chemical degradation [1]. Diuron is mainly used in formulations combined with other compounds, such as hexazinone (3-cyclohexyl-6-(dimethylamino)-1-methyl-1,3,5-triazine-2,4(1H,3H)-dione), which has a different mode of action, thereby ensuring better performance for the commercial product. Although several authors have reported the treatment of diuron in wastewater by advanced oxidative processes (AOPs) [2–5], only a handful of investigations reported to have used commercial formulations with a mixture of active organic molecules.

Hydrogen peroxide (H_2O_2) is one of the most widely employed oxidants in AOPs. Notwithstanding the popularity of H_2O_2, little effort

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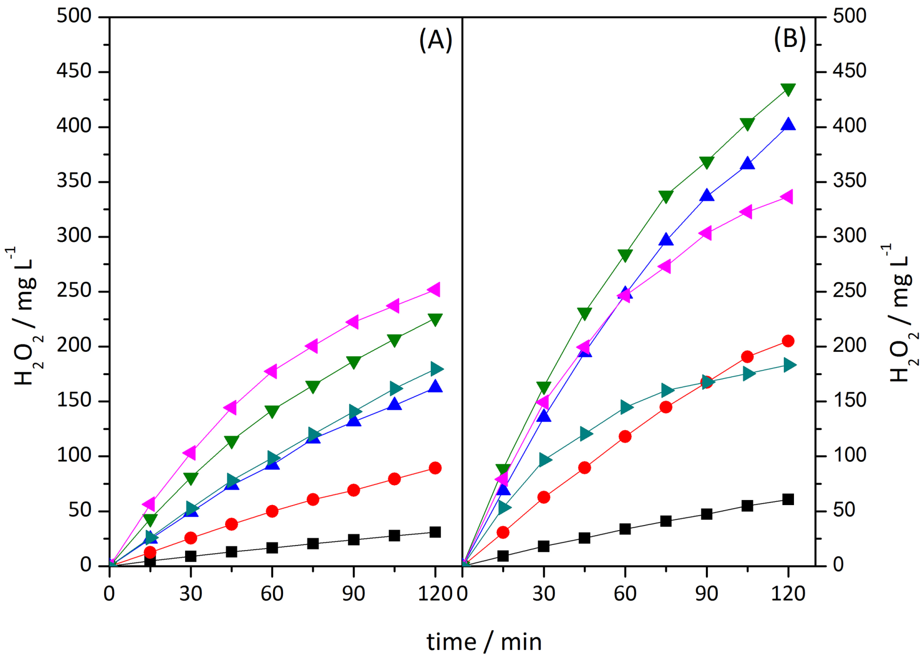

Fig. 1. H_2O_2 electrogeneration in 0.1 mol L^{-1} K_2SO_4 (pH = 2, adjusted by H_2SO_4) and at a fixed current density of (■) 10, (●) 25, (▲) 50, (▼) 75, (◀) 100 and (▶) 150 mA cm^{-2} using (A) unmodified and (B) ZrO_2-nanostructured GDE as function of electrolysis time.

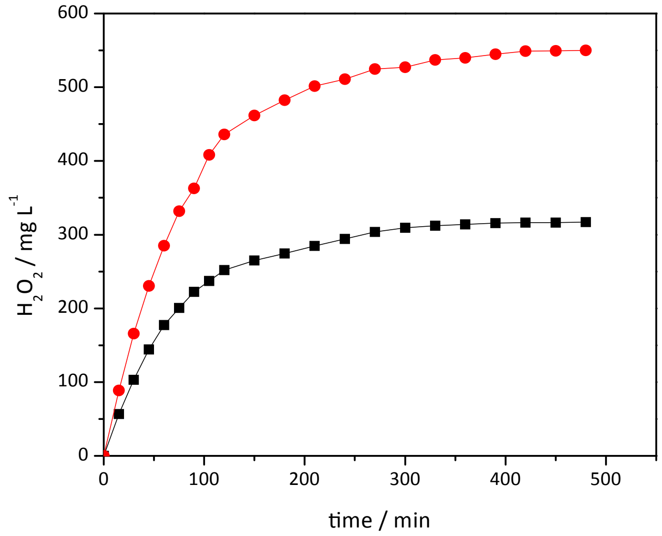

Fig. 2. H_2O_2 electrogeneration on (■) unmodified and (●) ZrO_2-nanostructured GDE at 100 mA cm^{-2} and 75 mA cm^{-2}, respectively, as function of exhaustive electrolysis time. Electrolyte solution: 0.1 mol L^{-1} K_2SO_4 at pH = 2, adjusted by H_2SO_4.

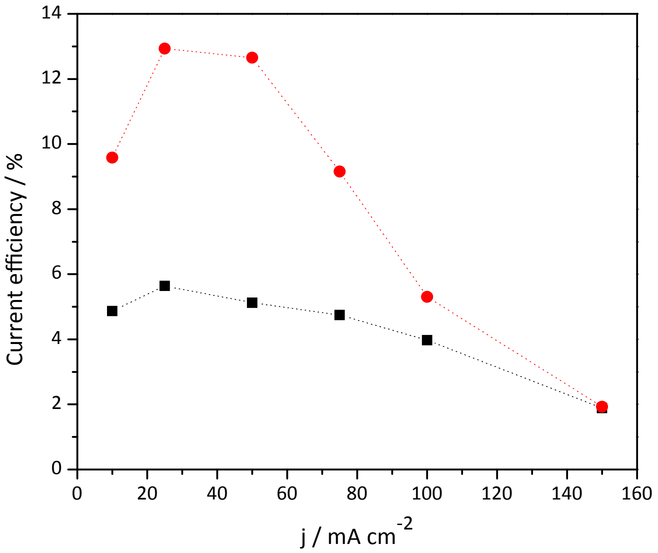

Fig. 3. Current efficiency for the H_2O_2 electrogeneration on (■) unmodified and (●) ZrO_2-nanostructured GDE as function of the applied current after 120 min of electrolysis. Electrolyte solution: 0.1 mol L^{-1} K_2SO_4 at pH = 2, adjusted by H_2SO_4.

has been devoted toward modernizing its way of production as the conventionally expensive way of producing H_2O_2 seems to be predominant to date. The H_2O_2 used in wastewater treatment units is still produced by anthraquinone auto-oxidation [6], which involves high costs of production, transport and storage; these high costs, undoubtedly, contribute to the substantial rise in the final price of H_2O_2 [7]. In this context, in situ electrogeneration of H_2O_2 via oxygen reduction reaction (ORR) using gas diffusion electrode (GDE) has been reported as a promising alternative [8]. Oxygen can be reduced on the electrode surface through two or four-electron transfer, i.e., H_2O_2 or H_2O production, respectively (Eqs. (I), (II)). The electrogenerated H_2O_2 can be further reduced on the cathode surface (Eq. (III)) or made to undergo disproportionation into H_2O and O_2 in the bulk of electrolyte solution (Eq. (IV)) [9,10].

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \qquad \text{(I)}$$

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \qquad \text{(II)}$$

$$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O \qquad \text{(III)}$$

$$2H_2O_2 \rightarrow O_2 + 2H_2O \qquad \text{(IV)}$$

To attain high activity and selectivity for H_2O_2 production, one needs to maximize the contact or interaction between oxygen, electrode and electrolyte solution [11]. In this sense, the porous structure of the GDE allows the oxygen to permeate through its structure to the solution by pressure difference. Several authors have reported the use of GDE as an efficient cathode for H_2O_2 electrogeneration [12–15] and its application in AOPs [15–19]. Nonetheless, the selectivity of H_2O_2 production on this electrode can be increased by catalysts such as quinones [12,20,21], metal-phthalocyanines [22,23], transition metal oxides [16,24–29] and others [30–35] supported on diverse materials. Gold [36,37] and palladium [38,39] are by far the most employed metals,