Electrochemical degradation of benzotriazole by UV/H_2O_2 in a Printex L6 carbon-based gas diffusion electrode modified with of lanthanum oxide
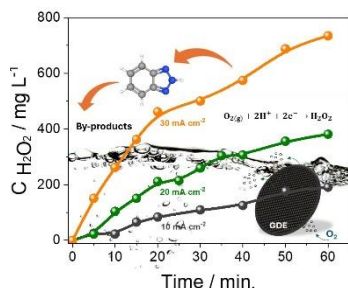
F. Escalona-Durán[1] G.R. Santos[1], C.H.M. Fernandes[1], W.R.P. Barros[1,2], M.R.V. Lanza[1]
[1]São Carlos Institute of Chemistry, University of São Paulo, Avenida João Dagnone, 1100 – Jardim Santa Angelina, São Carlos/SP, 13563-120 , Brazil.
[2]Federal University of Grande Dourados , Rodovia Dourados-Itahum, Km 12, Dourados /MS, 79804-970, Brazil

This study evaluated various La_2O_3/Printex L6 carbon (La/C) ratios (1.0-1.0%) for H_2O_2 electrogeneration applied to Benzotriazole (BTA) degradation. The rotating ring-disk electrode (RRDE) technique identified 5.0% La/C ratio as optimal for H_2O_2 selectivity in acidic media. Using Printex L6 carbon-based gas diffusion electrode (GDE) modified with 5.0% La/C, H_2O_2 concentration of 735 mg L^{-1} was achieved at 30 mA cm^{-2} at pH 5.8 during 1 h. The modified GDE was used to assess the electrogenerated H_2O_2/UVC degradation of 10 mg L^{-1} BTA, being reached 100% and 63% of removal and mineralization, respectively.

Introduction
BTA is a toxic and bioaccumulative heterocyclic compound used extensively as a corrosion inhibitor and stabilizer, causing significant water pollution due to widespread release of wastewater.

Several advanced oxidation processes (AOPs) have been studied for BTA degradation in aqueous solutions. UV/H_2O_2 and UV/TiO_2 methods are effective but incur high costs due to energy use, H_2O_2 dosage, and catalyst requirements.

Electrogerated H_2O_2 (e-H_2O_2) by GDE proves to be a attractive approach for the BTA degradation , being advantageous because, in principle, is a system that is easy to assemble and economically competitive with other technologies [1-2]. This study explores the use of La_2O_3 as metal oxide in GDE to improve the selectivity and activity of oxygen reduction reaction (ORR) via 2e-. The e-H_2O_2/UVC process was evaluated in the modified GDE with low content of La_2O_3/Printex L6 carbon applied for the BTA degradation at acidic condition.

Material and Methods
Synthesis and characterization of La_2O_3
The synthesis of La_2O_3, employed for modifying GDE, was performed using a modified Pechini method with $La(NO_3)_3 \cdot 6H_2O$ as the precursor. Thermogravimetric analysis, X-ray diffraction, Raman spectroscopy, and scanning electron microscopy were used to evaluate its thermal stability, crystalline structure, vibrational modes, and surface morphology, respectively.

Electrochemical characterization
The ORR was assessed using the rotating disk electrode technique with La/C ratios (1.0-10%) supported on Printex L6 carbon. Measurements were conducted on a commercial ring-disk electrode (Pine Instruments, N= 0.37) as the working electrode, a platinum wire as the counter electrode

and an Ag/AgCl (3 M KCl) electrode as the reference. The electrolyte was a 0.05 M K_2SO_4 solution (pH 5.8). The solution was saturated with $O_{2(g)}$, being maintained during the measurements. Experiments were performed with an Autolab PGSTAT 302N potentiostat/galvanostat and a rotator, at a constant scan rate of 5.0 mV s^{-1} and electrode rotation speeds from 300 to 1,500 rpm.

H_2O_2 quantification using La/C-GDE
The optimal metal/carbon ratio (5.0%) identified by the RRDE were used to prepare GDE. GDEs not modified and modified were tested in a non-divided cell to measure H_2O_2 production at various current densities. An Ag/AgCl (3 M KCl) electrode acted as the reference, and a DSA® electrode served as the counter electrode. A 250 mL 0.05 M K_2SO_4 solution, was used as supporting electrolyte. $O_{2(g)}$ was supplied to the GDEs at 80 mL min^{-1}. H_2O_2 concentration was quantified using the peroxymolybdate complex method and analyzed by UV-visible spectrophotometry at 350 nm with a UV-1900 spectrophotometer.

BTA electrochemical degradation
The optimal current density, determined from H_2O_2 production studies, was applied to evaluate the degradation of 250 mL of 10 mg L^{-1} BTA in 0.05 M K_2SO_4 (pH 5.8). The same non-divided cell used for H_2O_2 electrogeneration was employed. BTA degradation and mineralization was performed using the e-H_2O_2/UVC method. A UV-C light source (NUCHONG 9W lamp) was used as irradiation source.

Results and Discussion
Morphological analysis of La_2O_3
Fig. 1a shows the thermal decomposition of La_2O_3 in an oxidizing atmosphere. Analysis indicates the

presence of $La(OH)_3$ and minor oxycarbonate. The decomposition occurs in three stages: loss of adsorbed water, decomposition of $La(OH)_3$ to LaOOH, and dehydration of LaOOH to La_2O_3 at 100, 367 and 514 °C, respectively The final weight loss is attributed to the decomposition of surface carbonates formed from atmospheric CO_2 interaction. Figure 1b shows the X-ray diffraction pattern characteristic of the La_2O_3 structure.
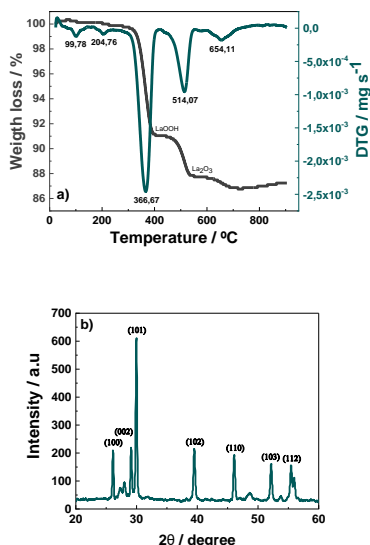

Figure 1. a) Thermogravimetric (TG) and differential thermogravimetric (DTG) curves for La_2O_3 obtained in an oxidizing atmosphere **b)** X-ray diffraction pattern**.**

Electrochemical characterization of La/C ratios

Fig. 2 compares LSV curves in acidic media, for the ORR for 1.0-10% content of La supported on PCL6. The disk LSV curves for 1.0 and 5.0% La/C ratios show similar shapes and currents to PCL6, indicating selective to O_2 reduction by 2e-. 10% La/C modifier exhibited a lower ORR initiation potential and higher disk current, but a lower ring current than PCL6, suggesting reduced H_2O_2 production. These results suggest that higher modifier concentrations may favor the 4-e⁻ pathway, increasing water production.
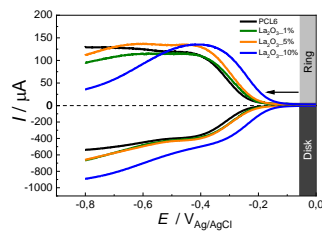

Figure 2. LSV curves for the ORR at 1.0 – 10% content of La/C in a 0.05 M K_2SO_4 solution, saturated with $O_{2(g)}$. Electrode rotation speed: 900 rpm.

H_2O_2 electrogeration

Fig. 3 show electrogenerated H_2O_2 in 0.05 M K_2SO_4 at current densities of 10, 20, and 30 mA cm⁻². Increasing the current density from 10 to 30 mA cm⁻² increases H_2O_2 production. Optimal results at the highest current density studied are obtained, achieved a peak H_2O_2 concentration of 735 mg L⁻¹.
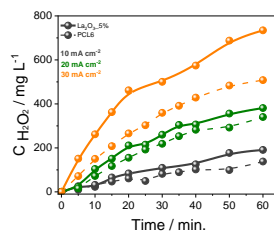

Figure 3. Concentration of H_2O_2 electrogenerated in a 0.05 M K_2SO_4 as a function of the applied current density.

BTA electrochemical degradation by e-H_2O_2/UVC process

Fig. 4 show the degradation of 10 mg L⁻¹ BTA at 30 mA cm⁻² by e-H_2O_2, e-H_2O_2/UVC, anodic oxidation (AO) and AO/UVC process. The e-H_2O_2/UVC treatment show total removal of the contaminant in 20 min of electrolysis and 63% of and mineralization after 1 h.
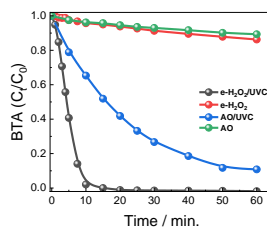

Figure 4. BTA degradation by e-H_2O_2, e-H_2O_2/UVC, AO and AO/UVC process at 30 mA cm⁻².

Conclusions

The La_2O_3 used as a modifier in low proportions demonstrated high performance for the ORR via 2-e- pathway, showing enhanced activity at lower potentials compared to PCL6, at acidic condition.

References
[1] J. Wang, C. Li, M. Rauf, H. Luo, X. Sun, Y. Jiang. Sci. Total Environ. 759 (2021) 143459.
[2] J. Xie, J. Jing, J. Gu, J. Guo, Y. Li, M. Zhou J. Environ. Chem. Eng. 10 (2022) 107882.