Enhanced UVC/H_2O_2 applied for the degradation of benzotriazole in real aquatic matrices using Printex L6 carbon-based gas diffusion electrode

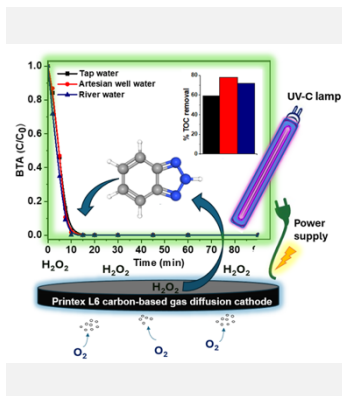F. Escalona-Durán[1] , C.H. M. Fernandes[1], A. R. Doria[1], G.O.S. Santos[1], W.R.P. Barros[1,2], M.R.V. Lanza[1]*

[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

Benzotriazole (BTA) is a recalcitrant compound characterized by its high toxicity to aquatic organisms. In this work, the effect of UVC/electrogenerated H_2O_2 was investigated for the BTA degradation. The studies were caried out by analyzing the influence of the current densities applied, pH, initial BTA concentration, and reaction time. Under the optimal conditions (50.0 mA cm^{-2}, pH 6.0 and, [BTA]=10 mg L^{-1}) obtained in K_2SO_4 0.05 mol L^{-1}, the BTA degradation in tap water, river water and artesian well water samples was evaluated. In all cases, 100% elimination of the pollutant in the first 20 min. of treatment was reached, with TOC removal of ~60, 72, and 78%, respectively, after 90 min. of electrolysis. The post-treatment river water sample was evaluated using the *Lactuca sativa L* method, showing the absence of toxicity of the by-products formed. An exhaustive BTA degradation during 5 h, allowed a mineralization rate of 70%.

Introduction

Benzotriazol (BTA) is found in a wide variety of matrices, such as industrial fluids, antifreeze, additives for the protection of metal surfaces, UV stabilizers, anticorrosives [1] and pesticides.

Due to its ability to destroy organic compounds in aqueous media, photocatalytic oxidation has received increasing attention for BTA degradation [2–3], but the high cost of catalysts limits its application in real aqueous systems. Indirect electrochemical processes also appears to be a promising alternative to increasing the degradation efficiency of BTA, mainly with use of hydrogen peroxide (H_2O_2) as oxidant. In this sense, the use of gas diffusion electrodes (GDE) [4] is shown to be a novel and attractive approach for the degradation of BTA, being advantageous because, in principle, it can be operated without the presence of a catalyst. In addition, the GDE allows the generation of important oxidizing species, in a system that is easy to assemble and economically competitive with other technologies.

Thus, this study explored the effectiveness of Printex L6 carbon-based GDE (PCL6-GDE) as an alternative route for the electrochemical degradation of BTA at different pH scale in tap water, river water and artesian well water samples, using a flow-by electrochemical reactor assisted by a UVC lamp.

Material and Methods

250 mL of a BTA aqueous solution was placed in a flow-by electrochemical reactor, assisted by a light source (UVC lamp, NUCHONG 9W). A three-electrode system was used, with an GDE as the working electrode, a DSA® eletrode as the counter electrode, and an Ag/AgCl (3M KCl) electrode as reference. The H_2O_2 generated at the working electrode (O_2(g) flow rate 30 mL min^{-1}) was quantified with UV-vis spectrophotometry, using the peroxymolybdate method. For the BTA quantification, a HPLC (SHIMADZU 20A), equipped with a C-18 Phenomenex® column, and a UV detector were used (λ= 256 nm). The mobile phase was 50% acetonitrile/50% water at a flow rate of 0.6 mL min^{-1}. For toxicity evaluation, the the experiments were conducted using seeds of *Lactuca sativa L*. Quantification tests for inorganic ions were also carried out in real aquatic matrices using ion chromatography (Metrohm CH-9101 Herisau Ionic Chromatograph).

Results and Discussion
Using PCL6-GDE for H_2O_2 electrogeneration

Fig. 1 shows the H_2O_2 electrogenerated in K_2SO_4 (0.05 mol L^{-1}), at different current densities (12.5, 25, and 50 mA cm^{-2}) and different pHs values (3.0, 6.0 and 9.0). The effect of UVC radiation on the H_2O_2 electrogeneration at the highest current density studied is also shown. The increase in current density from 12.5 to 50 mA cm^{-2}, records an increase in H_2O_2 production, obtaining the best results at pH 6.0 for low current densities. However, for the highest current density studied, the pH of the system does not lead to a significant change in the H_2O_2 electrogeneration, registering in all cases an average maximum concentration of ~912 mg L^{-1}.
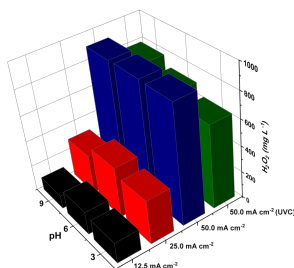
Figure 1. Concentration of H_2O_2 electrogenerated as a function of the applied current density and the pH.

As expected, when UVC radiation is placed in the system, a decrease in the H_2O_2 concentration is observed as a consequence of its photocatalytic decomposition, reaching ~714 mg L^{-1}.

BTA degradation under UVC/H_2O_2 by using PCL6-GDE

Fig. 2 shows the BTA degradation for different initial contaminant concentrations (10, 25, and 50 mg L^{-1} in K_2SO_4 0.05 mol L^{-1} at pH 6.0), applying a current density of 50 mA cm^{-2}. Inset of Fig. 2 shows the TOC removal at the end of electrolysis.
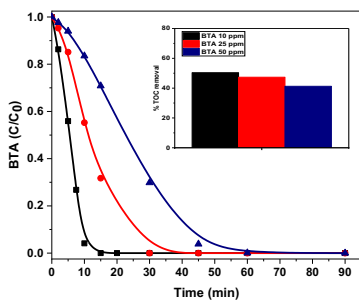

Figure 2. BTA degradation for different initial contaminant concentrations and TOC removal percentage (*inset*).

The kinetics of BTA removal change considerably depending on the initial concentration of the contaminant, going from requiring 15 min. to degrade 100% of 10 mg L^{-1} BTA to requiring 30 min. to degrade ~70% of 50 mg L^{-1} BTA (Fig. 2). However, the TOC removal does not vary significantly with a lower initial concentration of BTA 41.3% < 47.3% < 50.4% (Inset Fig. 2).

BTA degradation in real aquatic matrices under UVC/H_2O_2 by using PCL6-GDE

Fig. 3 shows the degradation of 10 mg L^{-1} BTA in tap water, river water, and artesian well water samples when applied a current density of 50 mA cm^{-2}.
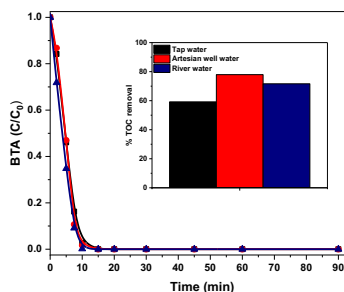

Figure 3. BTA degradation in different real aquatic matrices and TOC removal percentage (*inset*).

In all conditions, only 20 min. were enough to eliminate 100% of the contaminant. However, it was found that for river water and artesian well water, there was a greater TOC removal (72 and 78%, respectively), while in the case of tap water, the percentage was 60%, remaining closer to the values obtained in the studies with deionized water. The considerable increase in TOC removal is probably due to the contribuition of inorganic ions throughout degradation, mainly influenced by chloride and sulfate ions.

Conclusions

The fabricated Printex L6 carbon-based GDE led to the production of high concentrations of H_2O_2, favored by the increase in current density. The UVC/H_2O_2 treatment of river water and artesian well water, contaminated with BTA, allowed the degradation of 100% of the contaminant with up to 70% mineralization in a short period of time, evidencing the efficiency of the treatment and suggesting being an economical technology for the remediation of real aqueous environments.

References
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