# EAAOP 7

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# PROGRESS IN THE COMBINATION OF ADVANCED OXIDATIVE PROCESSES FOR THE DEGRADATION OF EMERGING POLLUTANTS

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The discharge of untreated effluents into water bodies has contributed to the presence of emerging pollutants, originating from domestic, pharmaceutical, and industrial waste. Contaminants such as tetracycline (TC) are concerning due to their harmful effects on health and the environment, including alterations in the endocrine system and impacts on aquatic fauna (Sihlahla and Mngadi, 2024). However, conventional water treatment methods are not effective in degrading low concentrations of contaminants in effluents, leading to the development of other methodologies such as advanced oxidation processes. (AOPs). The importance of these processes lies in their ability to mineralize a wide range of contaminants, including emerging pollutants, transforming them into less toxic or harmless substances, such as $CO_2$ and $H_2O$. Furthermore, the AOPs can be integrated into existing treatment systems, enhancing their effectiveness and contributing to the protection of water resources (Singh et al., 2024; Srivastava and Sachdev, 2023).

The implementation of different AOPs in the degradation of contaminants has shown promising results with high efficiencies in pollutant removal; processes such as ozonisation, photocatalysis, electrochemical oxidation, among others, allow the generation of highly reactive free radicals, capable of degrading a wide range of pollutants. By combining techniques, such as the integration of ozone or electro-oxidation with UV radiation, it is possible to increase the degradation rate and expand the spectrum of treated contaminants. This multifaceted approach not only maximizes process efficiency but also reduces treatment time and the formation of undesirable by-products, resulting in a more effective and sustainable solution for the management of contaminated water (Thind et al., 2024).

In this work, combination of processes such as electro-oxidation, photocatalysis, and ozonisation were implemented to evaluate their efficiency in the degradation of tetracycline. During the electrochemical oxidation, parameters such as supporting electrolyte, ionic strength, and flow were optimized. The system consisted of a filter-press type cell with a commercial DSA anode ($Ti/Ti_{0.7}Ru_{0.3}O_2$) and a stainless steel cathode. The system was maintained in continuous flow throughout each experiment. To evaluate the influence of ionic strength, sulfuric acid was used as a supporting electrolyte. It was observed that using 0.04 mol $L^{-1}$ resulted in a higher percentage of TC degradation, reaching 63.2% removal, while with 0.02, 0.06 and 0.08 mol $L^{-1}$ removals between 53.9% and 61.7% were achieved. The implementation of sodium chloride showed better degradation percentages than when sulfuric acid was used, achieving around 98% removal. The presence of chloride ions in the medium favored the formation of reactive chlorine species such as hypochlorous acid, which has high oxidative power, since the commercial anode used promotes the evolution of these chlorine species, and not species like sulfate radical or persulfate. Alternative solvents such as methanol and ethanol were also evaluated in the degradation of TC from the idea of a prior pre-concentration process with activated carbon. As mentioned by Oliveira et al., (2020), low concentrations hinder the application of electrochemical processes on a large scale, mainly due to energy costs, as a lot of charge is lost in parallel reactions. To improve this technique, preconcentration processes

with activated carbon and desorption with organic solvents have been implemented and have proven efficient in treating aqueous and gaseous pollutants (Oliveira et al., 2020; De Mello et al., 2022).

From this, experiments were conducted in methanol and ethanol media, where methanol proved to be more efficient in TC removal, achieving removal up to 82.1% after 120 minutes of electrolysis. For ethanol, it was possible to remove up to 57.5% of TC after 120 minutes, and 77.5% after 5 hours of electrolysis (Fig. 1a). This percentage of degradation is possibly due to oxygen-centered and/or carbon-centered radicals such as methoxy, hydroxymethyl, ethoxy, or hydroxyethyl formed from the oxidation of the solvent. Electron Paramagnetic Resonance (EPR) Spectroscopy was used to detect the free radicals in solution, and through computational simulations, each of the radical species was separated. (Fig. 1b). Other advanced oxidative processes such as photoelectrocatalysis with UV light and ozonisation showed differences in the percentages of TC degradation in aqueous medium, due to the different radicals formed during each process. The combination of these processes presents itself as a promising methodology to increase the efficiency in the degradation of pollutants in water treatment.

**References**


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# PROGRESS IN THE COMBINATION OF ADVANCED OXIDATIVE PROCESSES FOR THE DEGRADATION OF EMERGING POLLUTANTS (Poster)

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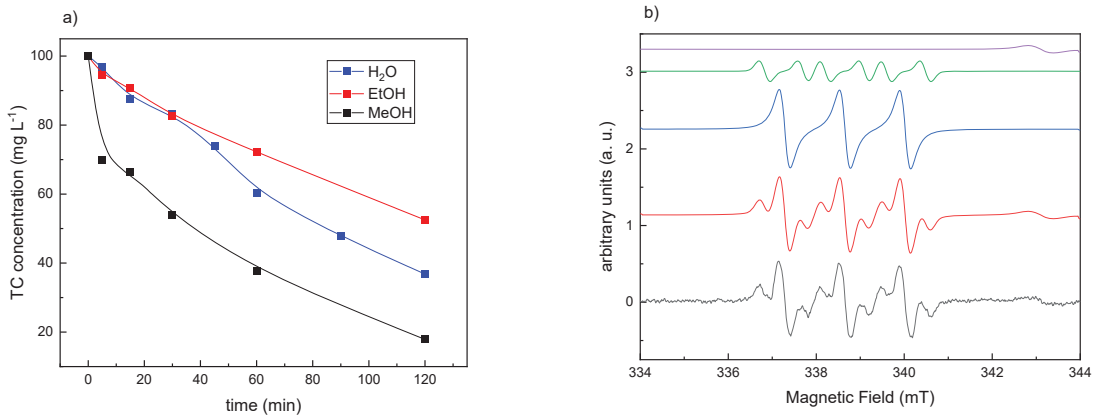


**Figure 1.** a) Electrochemical oxidation of TC in aqueous medium, methanol and ethanol using $H_2SO_4$ 0.04 mol $L^{-1}$ as supporting electrolyte, 10 mA $cm^{-2}$ and 600 mL $min^{-1}$. b) Experimental and simulated spectra of EPR experiments in methanol medium.

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