Tetracycline Removal in Aqueous Solutions via Electro-Fenton-like Process with Aluminum Electrodes

POSTER
Ph.D. Student: Y
Journal: XXX

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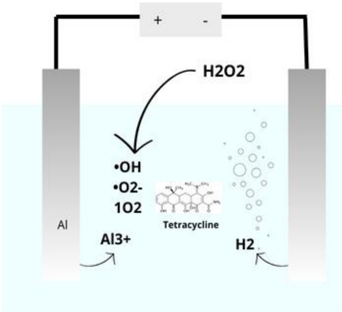

In this study, a electro-Fenton like reaction for in-situ H_2O_2 decomposition to generate active oxidation species by aluminum electrodes was investigated for tetracycline degradation. Oxidative processes utilizing hydrogen peroxide combined with electrochemical methods such as electrocoagulation have shown promising results in the degradation of complex molecules like antibiotics. The present research aimed to assess the removal of the antibiotic tetracycline from aqueous media using an electrocoagulation system with aluminum electrodes and the addition of H_2O_2. The findings indicated a 90% removal rate in the process without H_2O_2 at a potential of 10 V and an electrolysis time of 45 minutes. Conversely, under the same conditions with the addition of 50 mg/L of hydrogen peroxide, a 100% efficiency rate was achieved, demonstrating the high oxidizing potential of hydrogen peroxide on the tetracycline molecule.

Introduction

Tetracycline is an antibiotic widely used for human and animal treatment, which has been detected in surface waters and effluent treatment plants at concentrations of µg/L and ng/L [1,2]. Therefore, adopting effective processes for removing antibiotics from aqueous media is essential.

Electrocoagulation coupled with the electro-Fenton system has demonstrated a removal efficiency of 97% for the antibiotic tetracycline [3]. However, the conventional electro-Fenton process necessitates acidic conditions to prevent iron precipitation, which is often a drawback [4]. Consequently, technologies involving Fenton-like processes have emerged with the aim of establishing oxidative processes based on the Fenton reaction but free of iron [5].

Therefore, the present study aims to utilize aluminum electrodes for the removal of tetracycline in aqueous solution using the electro-Fenton-like process.

Material and Methods

The electrochemical tests utilized two aluminum electrodes with a working area of 1 cm² and a distance of 1 cm between electrodes, along with a Calomel electrode serving as a reference electrode. The volume of the Tetracycline solution was 200 mL with a concentration of 50 mg/L, and the conductivity was adjusted to 500 mS with a 01 M KCl solution.

A 2^2 Full Factorial Design with triplicate at the central point was conducted to assess the impact of electrical potential (6, 8 and 10 V) and electrolysis time (15, 30 and 45 min) on tetracycline removal.

Subsequently, the influence of adding hydrogen peroxide (30% P.A.) during electrolysis was evaluated from the optimal conditions, using concentrations of 50, 75 and 100 mg/L.

Tetracycline concentrations were measured using a UV-Vis spectrophotometer at a wavelength of 357 nm [6].

Results and Discussion

The results demonstrate that the electrocoagulation process removed up to 90% of tetracycline under various conditions of time and electrical potential. Figure 1 illustrates that test 4, conducted at a potential of 10 V and a duration of 45 minutes, exhibited the highest removal percentage, reaching 90%.

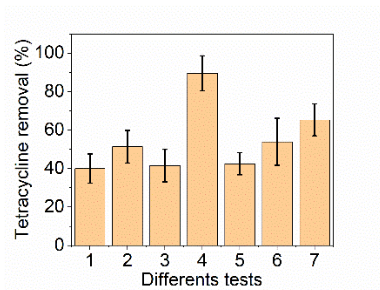

Figure 1. Tetracycline removal for differents tests.

The statistical analysis predicts, through the Pareto Chart of Standardized Effects presented in Figure 2, that the variables electrolysis time, electrical potential, and the interaction of both variables significantly influence the tetracycline removal process.

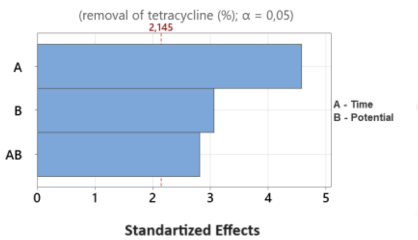

Figure 2. Pareto chart of Standardized Effects

Furthermore, the analysis of variance reveals that altering the electrical potential from 6 V to 10 V and the time from 15 minutes to 45 minutes, along with the interaction of these variables, yields removal percentages with a statistically significant difference, with $p < 0.05$, considering a 95% confidence interval. Although the results obtained from the electrocoagulation tests are promising, the technology merely transfers tetracycline from the aqueous phase to the solid phase through the in-situ generation of coagulant/flocculant, without degradation [3]. Therefore, we aimed to assess the impact of H_2O_2 concentration using an electrical potential of 10 V and an electrolysis time of 45 minutes.

In Figure 3, the effect of adding various concentrations of H_2O_2 on the percentage of tetracycline removal is depicted. It is evident that the addition of peroxide enhances the system's efficiency by removing a higher concentration of tetracycline, with a removal percentage approaching 90% within the first 15 minutes of electrolysis for all peroxide concentrations.

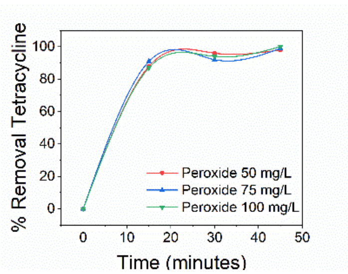

Figure 3. Removal of tetracycline in the face of differents concentrations of hydrogen peroxide.

However, with a 95% confidence level, statistical analysis reveals that increasing the peroxide concentration from 50 mg/L to 75 mg/L and 100 mg/L does not have a statistically significant impact on the removal percentage, as indicated by the analysis of variance resulting in $p > 0.05$. Hence, a concentration of 50 mg/L of peroxide is sufficient to oxidize the tetracycline present in the solution.

Figure 4 illustrates the kinetics of the electrolytic reactions occurring in the system both without peroxide and with the addition of 50 mg/L of peroxide. It is evident that the addition of H_2O_2 enhances the system's efficiency, as evidenced by a much lower tetracycline concentration within the same time interval compared to tests without peroxide. This enhancement enables the removal of 100% of the tetracycline within 45 minutes of electrolysis.

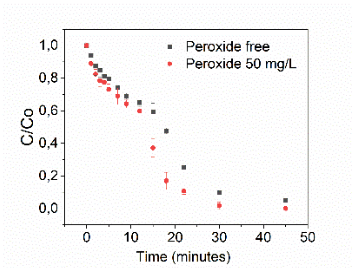

Figure 4. Tetracycline removal for differents tests.

The remarkable efficiency exhibited by the system arises from the addition of hydrogen peroxide, which facilitates the generation of hydroxyl radicals. These radicals serve as highly potent oxidants, reacting with and oxidizing the organic constituents within the effluent [5]. Furthermore, aluminum electrodes, utilized in the current study as a source of electrons, have been shown to be thermodynamically more efficient. They provide a significantly stronger driving force for electron transfer to H_2O_2 compared to Fe^0, thereby promoting Fenton-like reactions [4].

Conclusions

The electrochemical process reached 90% efficiency, increasing to 100% with the addition of H2O2, demonstrating that the incorporation of H2O2 facilitates the generation of hydroxyl radicals, promoting Fenton-type reactions. This oxidative process promoted the degradation of the antibiotic tetracycline, further highlighting the effectiveness of the electro-Fenton approach in wastewater treatment.

Acknowledgments

The authors gratefully appreciate the Unochapecó, the FAPESC (Grant Number 2023TR001470) and the CAPES for their financial and technological support.

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