Application of advanced oxidative processes and ecotoxicological studies in effluents contaminated with malachite green

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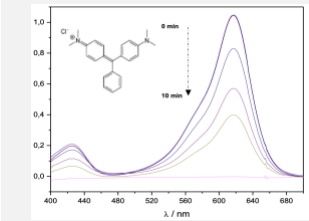
J. M. Pérez [1,2], *J. Tonholo*[1], *C. L. P. S. Zanta*[1] *J.S. Bravo*[2] *(1) Institute of Chemistry and Biotechnology of Federal University of Alagoas, Tabuleiro do Martins, CEP 57072-970, Maceió, Brazil. juan.ramos@iqb.ufal.br (2) Manuela Beltran University, Carrera 1 #No. 60-00, Bogotá , Colombia*



In fish farming, chemicals like Malachite Green are used to combat diseases and parasites, posing challenges for conventional effluent treatments and potentially harming ecosystems. This study assessed the effectiveness of the Fenton reaction, electrochemical treatment, and associated technologies. Results showed over 87% removal of color and COD (chemical oxygen demand) in each process. Toxicity tests conducted over time with various organisms (*Lactuca Sativa* and *Artemia sp*.) demonstrated promising results depending on the biota and environment.

Introduction

Malachite Green, commonly used in textiles and as a fish antiseptic, poses significant health risks including irritation, tumor promotion, and fertility issues through ingestion and inhalation. Effective degradation methods like Advanced Oxidative Processes (AOPs) are crucial for treating wastewater contaminated with malachite green, reducing traditional treatment time. This study explores AOPs' application and ecotoxicological tests in treating fishing industry effluents containing malachite green as a model substrate.

Material and Methods

The Fenton reaction and electrochemical process were conducted separately, both aiming for effluent degradation within specified parameters. The Fenton reaction, carried out in a batch reactor with 250 mL of simulated effluent, adjusted pH and varied concentrations of ferrous sulfate and hydrogen peroxide for 30 minutes. Similarly, the electrochemical process, in continuous flow, utilized ADE electrodes in a jacketed reactor with NaCl solution. Both processes aimed to comply with Brazilian legislation on effluent disposal. Toxicity testing, following Sobrero and Ronco's method, assessed phytotoxicity using lettuce seeds, with samples diluted for evaluation. The *Artemia Sp.* biological test followed ABNT guidelines, hatching microcrustacean cysts in seawater and exposing them to MG solution after 24 hours for testing.

Results and Discussion

The spectrum shows a band at approximately 617 nm, indicating the presence of the chromophore group. This absorption band diminishes within the first 10 minutes, indicating degradation of the aromatic achromophilic group. Additionally, COD analysis reveals a reduction of over 87% during this process. In electrochemical treatment, dye degradation efficiency increases with higher current densities due to enhanced generation of oxidizing species. However, at lower dye concentrations, the oxidation reaction becomes less favorable, leading to parallel reactions like chlorine and oxygen release, as indicated by the response surface.

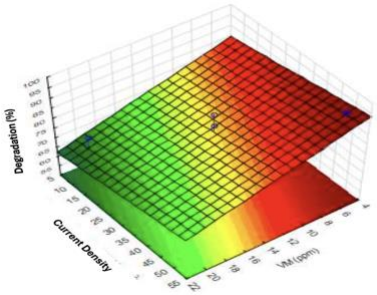


Figure 1 - Response surface for the percentage of color removal as a function of current density and MG concentration.

The Pareto chart from the experimental planning reveals the significance of the analyzed variables regarding color reduction efficiency. All variables and their interactions in the treatment showed statistical significance at a 95% confidence level. Particularly, the concentration of MG (variable of interest) notably impacts color reduction negatively, followed by an increase in current density, then temperature. This indicates that higher dye concentrations lead to lower color reduction. The combination of processes yielded promising results in color and COD removal, achieving rates of 88.6% and 88.5% respectively. This degradation is attributed to the formation of an in-situ oxidizing agent, generated at the electrode surface, and reacting within the solution, particularly through hydroxyl radicals (•OH) in the electrochemically assisted Fenton reaction. Brillas and colleagues (2015) note that Electro-Fenton processes typically exhibit higher removal efficiencies due to overcoming issues like mass transfer limitations and electrode surface poisoning. However, it's noteworthy that the electrochemical process followed by Fenton displayed greater COD reduction compared to Fenton alone or electro-Fenton, achieving rates of 93.3%, 90.8%, and 88.5% respectively. The bioassays assessed the impact of malachite green-containing effluent, treated with

Fenton reaction and untreated, on lettuce seed germination index (GI) and relative growth index (ICR) at various time intervals (24, 48, 72, and 96 hours).

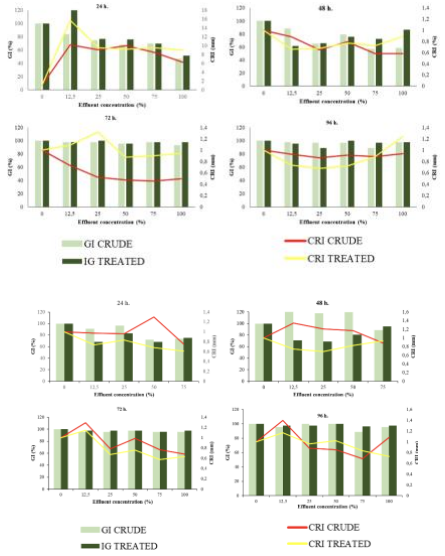


Figure 2 - Relative growth index (ICR) and germination index (GI) of *Lactuca sativa* seeds as a function of effluent concentration (%) treated with Fenton and electrochemical reaction and without treatment, at different times: 24, 48, 72 and 96 hours in ecotoxicity test.

In the initial 48 hours, the germination index (GI) ranged between 60% and 70%, affecting the relative growth index (ICR), possibly due to the formation of toxic chlorinated by-products with high free chlorine concentration, hindering radicle growth. After 96 hours, GI approached 100%, but ICR remained below 1.2mm, suggesting that effluent salinity influences both germination and growth. In the acute toxicity test with *Artemia sp.,* effluent treated with the Fenton reaction exhibited low mortality rates, with the highest concentration showing less than or equal to 22.5% mortality at 24 hours. Similar results were found at 48, 72, and 96 hours, making it difficult to determine the lethal concentration (LC_{50}). These findings align with Lumbaque et al. (2017), who observed reduced ecotoxicity of a dye solution treated with Fenton, as demonstrated in a bioassay with *Daphnia magna* microcrustaceans.

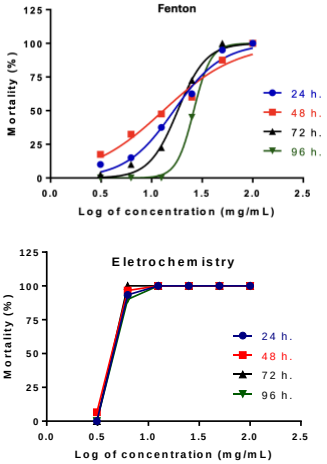


Figure 3 - Percentage of mortality of Artemia sp. larvae. exposed to different concentrations of effluent containing malachite green post treatment.

Conclusions

The Fenton and electrochemical processes are highly effective in oxidizing various organic compounds in effluent treatment. Factors such as the contaminant's chemical structure, pH, reagent concentration, organic load, current density, and electrode type can influence degradation rates. The efficiency of malachite green-containing effluent treatment via the Fenton reaction strongly relies on Fenton reagent concentration. Kinetic assessment indicates an affinity between pollutant concentration and H_2O_2 and Fe^{2+} concentrations, with lower malachite green concentrations correlating to faster oxidation rates.

Acknowledgments

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