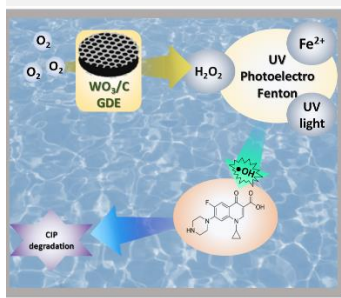


Ciprofloxacin degradation using WO₃ modifying carbon GDEs under Photoelectro-Fenton process

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Pharmaceuticals, including ciprofloxacin (CIP), pose significant environmental threats due to their persistence and adverse effects on ecosystems and human health. In light of this, the electrochemical advanced oxidation process has emerged as a promising method for degrading pharmaceuticals in wastewater. Herein, it was investigated the use of novel WO₃/C gas diffusion electrodes (GDEs) and their application in the PEOAs processes for CIP removal. The results demonstrated enhanced H₂O₂ accumulation and efficient CIP degradation, achieving complete removal within 90 minutes with 90 % of TOC removal under UV-photoelectron-Fenton. These findings underscore the potential of electrochemical advanced oxidation processes for the remediation of pharmaceutical pollutants from water systems.

Introduction

Pharmaceuticals have emerged as significant environmental pollutants due to their persistence and potential detrimental effects on both ecosystems and human health. The improper disposal of pharmaceuticals can lead to a range of adverse impacts, including toxicity and disruptions to endocrine functions.

Among these pharmaceuticals, ciprofloxacin (CIP) stands out as a prominent example. CIP is a fluoroquinolone antibiotic renowned for its broad-spectrum efficacy and extensively prescribed in human and veterinary medicine. The presence of CIP in wastewater poses significant health risks, including the development of antibiotic resistance, disturbances to hormonal balance, and toxicity to aquatic organisms at elevated levels. These risks, in turn, have the potential to inflict adverse effects on entire ecosystems, underscoring the urgent need for effective remediation strategies.[1]

In response to this pressing environmental challenge, the electro-Fenton (EF) process has emerged as a promising approach for the degradation of CIP contaminants. The EF process offers a sustainable and efficient solution for removing CIP from water systems by harnessing the synergistic effects of electrochemistry and Fenton chemistry. This work aims to provide an overview of WO₃/C GDEs for H₂O₂ electrogeneration and the application of the photoelectro-Fenton process in the CIP degradation.

Material and Methods

The H₂O₂ electrogeneration and CIP degradation experiments were accomplished using a gas diffusion electrode (GDE) cathode prepared by a hot-pressing procedure using 3% WO₃ flower-like nanostructure in Vulcan XC-72 containing 20% (w/w)

of PTFE dispersion. The essays were carried out in an undivided 350 mL electrochemical cell using a reference Ag/AgCl electrode, a Pt counter electrode (5 cm²), and the fabricated GDE with continuous O₂ supplying at 0.2 bar. The electrolyte comprised 0.1 mol L⁻¹ K₂SO₄ (pH = 3). The electrolytic processes were performed by the chronopotentiometry technique. The photoelectro-Fenton was carried out using a mercury UV lamp of λ_{max} = 254 nm immersed in the solution. The [CIP]₀ was 25 mg L⁻¹. The CIP degradation was followed by liquid chromatography-tandem mass spectrometry and TOC measurement.

Results and Discussion

Firstly, the GDEs' H₂O₂ electrogeneration efficiency was assessed. Fig. 1 shows the process's H₂O₂ accumulation, current efficiency, and Energy consumption after 120 min of electrolysis at different density currents applied. The WO₃/C GDE shows an accumulation of 920 mg L⁻¹, an increase of 44% in front of unmodified Vulcan GDE at 100 mA cm⁻², and an improvement of current efficiency 2-fold around. The influence of WO₃ nanostructures in the O₂-to-H₂O₂ ORR was stressed out in a previous work.[2]

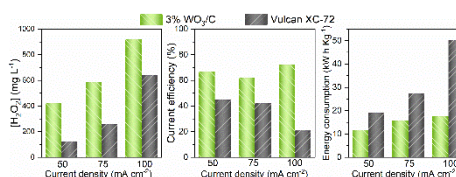


Figure 1. (a) H₂O₂ accumulation, (b) current efficiency, and (c) Energy consumption as a function of electrolysis time at different applied density currents using WO₃/C GDE at 120 min of electrolysis.

The great activity of WO₃/C GDE for H₂O₂ accumulation is used for CIP degradation essays on

different EAOPs-based processes, as shown in Fig 2. The complete CIP removal was achieved in 90 minutes of the UV-photoelectro-Fenton process. The UV-PEF exhibited a superior activity, which was also supported by the pseudo-first-order kinetic analysis displayed in Fig 2b; the obtained results reveal apparent rate constants (k_1) $3.7 \times 10^{-2} \text{ min}^{-1}$ approximately 3-fold bigger than the k_1 -EF process. The UV-PEF improved activity can be related for extra OH radicals formed indirectly by UV light. [3]

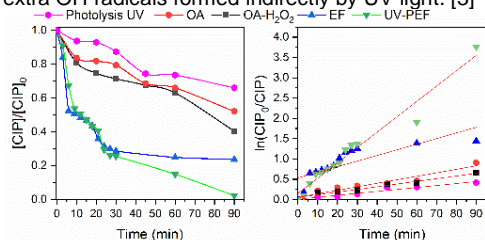


Figure 2. CIP degradation performance and kinetic profile using WO₃/C GDE under different EAOPs applying 100 mA cm⁻² current density at 90 min..

A high mineralization rate accompanied the degradation. TOC was reduced by 90% after 90 min of UV-PEF. Fig. 3(b) illustrates the mineralization efficiency current and energy consumption per TOC mass. The UV-PEF process exhibits great MCE of around 60% and EC of 1.2 kWh per g_{TOC}. These were optimal values in comparison with recent reports using GDEs EAOPs.[4]

Chemical-quantum calculations were also carried out to propose a possible CIP degradation mechanism. From the results, it was possible to suggest more susceptible atoms to radical attack, leading to CIP degradation byproducts and proposed via experimental techniques.

Conclusions

Incorporating WO₃ flower-like nanostructured onto Vulcan XC72 carbon led to a notable improvement in H₂O₂ electrogeneration compared to pure Vulcan. Utilizing the fabricated WO₃/C GDEs in the UV-Photoelectro-Fenton process resulted in complete CIP removal and 90% TOC removal, indicating a trend toward complete mineralization. Moreover, it exhibited excellent energy consumption values and current efficiency for mineralization. A degradation mechanism has been proposed, aligning closely with existing literature. Ultimately, the GDEs catalyst holds significant promise for the remediation of antibiotics from water through EAOPs-based processes.

Acknowledgments

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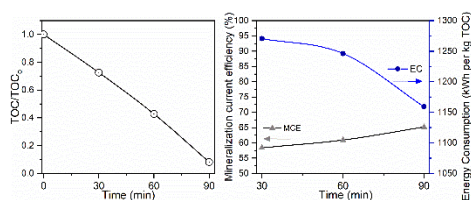


Figure 3. (a) CIP mineralization performance and (b) using WO₃/C GDE under UV-PEF applying 100 mA cm⁻² current density at 90 min.

The results of the LC-ESI-MS/MS analysis indicated that the degradation of CIP was promoted by two degradation pathways, resulting in twelve degradation products (Fig. 4). In pathway 1, the •OH radical attacked the piperazine ring, leading to ring opening or complete degradation. This route was associated with or without the defluorination process of CIP. Pathway 2 was characterized by the attack on the quinolone group, with the cleavage of the C-C bond and transformation of the ring. Additionally, some intermediates suggest that both mentioned pathways occurred simultaneously through the cleavage of the piperazine and quinolone rings.

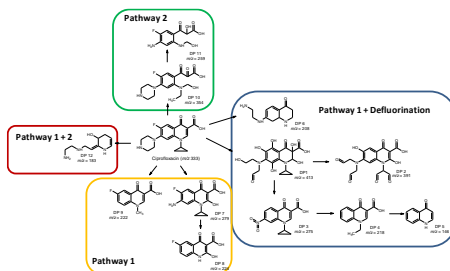


Figure 4. Main reaction pathway proposed for the degradation of ciprofloxacin by electrochemical process.