Continuous Degradation of Antibiotics Using Sequential DBD Plasma with 3-Electrode Fenton Electrolysis

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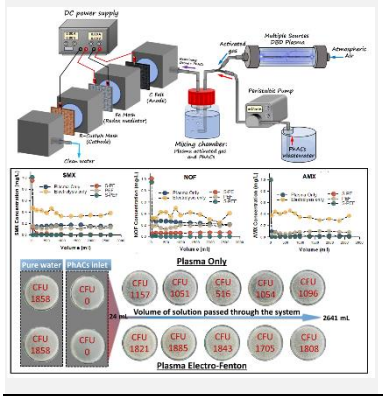

This study investigated a two-step system (DBD plasma and electrocatalysis) for removing antibiotics, sulfamethoxazole (SMX), norfloxacin (NOF) and, amoxicilin (AMX) from wastewater. The combined approach (S-PEF) effectively degraded all antibiotics, even at colder temperatures, while sole plasma treatment struggled. S-PEF's efficiency stems from hydroxyl radical (•OH) generation and efficient O_3 dissociation. S-PEF also reduced predicted toxicity of antibiotics and potentially deactivated their antibacterial properties, hindering antibiotic resistance development. This method offers a promising solution for wastewater treatment.

Introduction

Antibiotic usage has surged by 30% in recent decades, leading to increased environmental presence through wastewater. This contributes to antimicrobial resistance, a global concern fueled by resistant bacteria and genes found in environmental samples. Conventional wastewater treatments struggle to eliminate these elements effectively. Advanced oxidation processes (AOPs) like atmospheric air dielectric barrier discharge (DBD) plasma offer promise but face limitations, such as low ozone (O_3) solubility and the formation of harmful by-products. Most research on plasma-based treatment methods has been in lab settings, posing challenges for practical applications.

Addressing these concerns, a continuous flow water treatment system integrating DBD plasma with electrocatalysis has been developed. This system, called sequential plasma electro-Fenton (S-PEF), focuses on degrading antibiotics' active functional groups to prevent antimicrobial resistance. It comprises a sequential setup with quadruple-source DBD plasma followed by electrocatalysis using carbon felt, Fe mesh, and reduced copper oxide nanowires. S-PEF optimizes parameters like wastewater flow rate and system setups, achieving efficient degradation of antibiotics and denitrification of nitrogen oxide species, with promising selectivity and O_3 removal.

Material and Methods

The homemade multi-source DBD plasma setup includes four small quartz tubes (165 mm length, 2 mm diameter, 1 mm thickness) securing solid-brass electrodes. For degradation, solutions containing each of these three pharmaceutical compounds (SMX, NOF, and AMX) at 1 mg L^{-1}. These solutions were bubbled with DBD plasma activated gas in a mixing bottle. Then, the solution flowed through at rates with 7 mL min^{-1} into the electrocatalysis system with three electrodes: carbon felt and Fe mesh in the anodic chamber, and reduced copper nanowires (rCuNWs) in the cathodic chamber. The S-PEF system combining plasma with electrocatalysis was compared with other setups: sequential plasma electrocatalytic system without Fenton (S-PE), plasma electro-Fenton (PEF) without sequencing, and a 2-electrode setup (S-PE_2F) using Fe mesh instead of carbon felt.

Results and Discussion

This study investigated a two-step system for effectively removing antibiotics (SMX, NOF, and AMX) from wastewater. DBD plasma generates O_3 which degrades some antibiotics (SMX and AMX) effectively. However, NOF removal is limited due to lower susceptibility and potential competition for reactive species with other antibiotics. The system produces nitrogen-containing byproducts (NO_2-N and NO_3-N) as a result of PhACs degradation or plasma dischage through atmoshperic air. This step utilizes electrocatalysis to further degrade remaining antibiotics and O_3 from the first step.

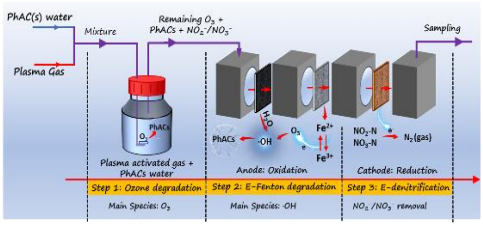

Figure 1. Setup of S-PEF indicated by the role of each step through the sequential treatment.

S-PEF efficiently removes all three antibiotics, particularly NOF, which was challenging for DBD plasma alone. The effectiveness relies on, (i) Dissociation of O_3 into highly reactive •OH through the iron mesh catalyst (Fe mesh) and the applied voltage and (ii) Fenton reaction involving Fe ions and H_2O_2, further generating •OH. The DBD plasma pretreatment allows for initial O_3 degradation of some antibiotics before encountering scavenging effects from common wastewater components like carbonate (CO_3^{2-}) and humic acid. Compared to PEF, non-sequential setup, the PhACs degradation is greatly retarded by the presence of CO_3^{2-} and humic acid. S-PEF demonstrates minimal impact from nitrate (NO_3-N) present in wastewater but can achieve significant NO_3-N removal through cathodic reduction.

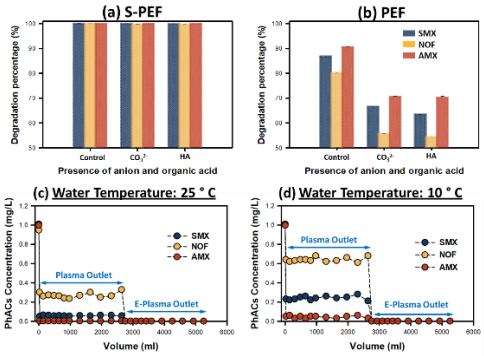

Figure 1. Degradation retardation by presence of anions and humic acid for (a) S-PEF and (b) PEF setup, S-PEF conducted at different temperatures (c) 25 °C and (d) 10 °C for the degradation of PhACs

For temperature effect, colder temperatures (10°C) enhance O_3 solubility but hinder degradation, while warmer temperatures (25°C) promote O_3 decomposition and degradation despite lower O_3 solubility. S-PEF effectively removes O3 regardless of temperature and demonstrates superior energy efficiency. The S-PEF system offers lower treatment costs compared to sole plasma for both temperature conditions.

The study used the ECOSAR program to predict the lethal concentration (LC_{50}) of the SMX, NOF, AMX on various organisms. SMX exhibited the highest predicted toxicity for all tested organisms (fish, daphnia, green algae. However, the S-PEF treatment significantly reduced the predicted toxicity of all three PhACs compared to their parent compounds.

Conclusions

The study found that SMX and AMX were effectively oxidized by sole plasma within 30 minutes, while the degradation of NOF was unexpectedly low (21%). The use of air discharge plasma at a flow rate of 2 L min^{-1} resulted in the highest degradation efficiency for all three PhACs due to a chain reaction between ROS and RNS, leading to a higher concentration of •OH. S-PEF setup not only improved PhAC degradation but also facilitated denitrification, fully converting NO_2^-/NO_3^- to N_2 to prevent eutrophication. electrical energy required (EEO) and treatment cost were significantly reduced to 0.04 kWh L^{-1} and 0.003 USD L^{-1}, respectively.

Acknowledgments

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References

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