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Grips

Development of Oxygen-based Cobalt Manganese Oxide Modified Membrane Reactor for Tetracycline Oxidative Degradation

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Introduction

Antibiotics have served an essential function in treating infectious diseases since they were first developed. Tetracyclines (TCs), a broad-spectrum antibiotic, are the one of the most widely used antibiotics in both human and animal medicines.[1] Unfortunately, the abuse, misuse and overuse of antibiotics have resulted in their ubiquitous discovery in the natural environment, resulting in ecological damage and imbalance. TCs are often not found in large concentrations in the environment, but they can be found in high concentrations from pharmaceutical industry effluents. Pharmaceutical waste is frequently dumped untreated straight into wastewater treatment facilities which are not designed for antibiotic removal. Moreover, the stability of TCs contribute to its slow degradation in the human or animal bodies and in the environment.[3] The accumulation of TCs in the environment and drinking water can cause toxicity to the microbial communities, disrupt gut microbiomes and promote antibiotic resistance.

Conventional wastewater treatments are not developed with the intention to remove TCs from wastewater. Adsorption and advanced oxidation processes such as photolysis have been explored for TC treatment. However, they require disposal of sorbents or high energy inputs. Thus, there is a need for environmentally-friendly and efficient methods for TC removal.

Background

Membrane-based reactors (MBR) are an advanced wastewater treatment process that combines membrane filtration with biological or chemical reactions. The membrane is composed of hollow fibers with surface-modified cobalt and manganese oxide. Oxygen is pumped through the hollow fibers to regenerate the oxide species. Previous research has shown an O_2-based membrane MnOx film reactor (O_2-MMnfR) for the effective oxidative degradation of TCs. The Mn leaching from the system can be reduced with the doping of cobalt to produce an O_2-based membrane CoMnOx film reactor (MCoMnfR). Co ions can effectively inhibit the Jahn-Teller effect and promote ion diffusion in the formation of the metal oxide coating.[2] In this manner, the effectivity of the MBR can be enhanced for the degradation of TC.

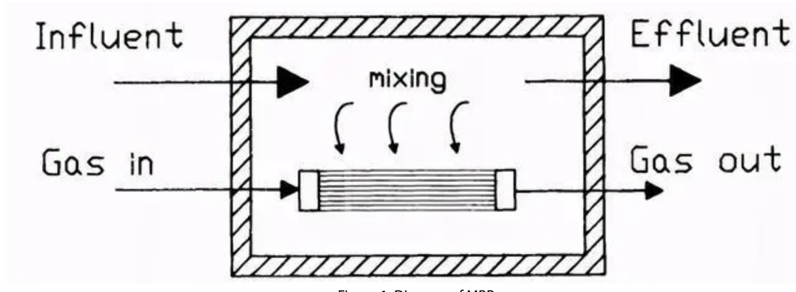

Figure 1. Diagram of MBR

Objectives

The objective of the study is to develop an O_2-based membrane CoMnOx film reactor for the degradation of tetracycline. CoMnOx NPs are synthesized in situ by self-assembly on the exterior of the hollow fiber membranes. The degradation of TC is studied by varying the initial TC concentration, oxygen pressure and pH. Samples are collected every hour analyzed through HPLC to determine the reduction of TC over time. The manganese content is also analyzed through AAS to ascertain the loss rate of manganese. XRD, SEM and ATR-FTIR are applied to characterize the CoMnOx surface deposition on the membrane. Toxicity tests will be performed by observing the growth rate of microbial cultures through turbidity (OD600).

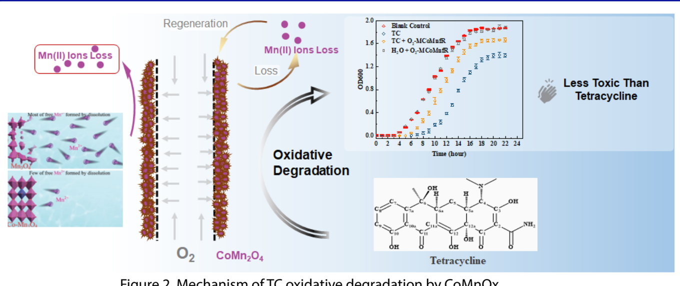

Figure 2. Mechanism of TC oxidative degradation by CoMnOx

Methodology

Reactor Setup

The bench-scale double-tube reactor used in this study followed the configuration of previous studies[1], as depicted in Fig. 3 and Fig. 4. The reactor has a working volume of 70 mL and each tube contains a bundle of 32 identical hollow-fiber membranes. Each membrane has an outer diameter of 260 µm, an inner diameter of 220 µm, and a length of 25 cm, resulting in a total membrane surface area of 0.65 dm².

In situ deposition of CoMnOx NP on the membrane was performed by immersing the hollow fiber membranes in an ethanol solution of 15mg/L $CoSO_4$ and 30 mg/L Mn(AC)₂ in the tubes. A mixed gas of 4% NH_3 and 96% Ar at 3 psi was supplied to the ends of the membrane bundles. After 1 week, the membranes were rinsed with pure water and air-dried until use. Brown colored CoMnOx nanoparticles were deposited on the outer surface of the membranes.

Operating conditions

Reactor parameters were varied in terms of initial TC concentration of the influent, the pH, and the oxygen pressure supplied to the fiber membrane. Initial TC concentration was studied at 15 mg/L, 30 mg/L and 60 mg/L . The pH was adjusted to 5, 7 and 9. The oxygen pressure was varied from 0 MPa (hypoxia), 0.02 MPa, 0.04 MPa, and 0.06 MPa.

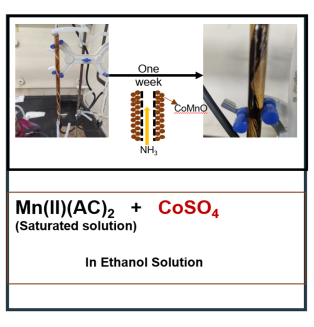

Figure 3. In situ deposition of CoMnOxNP

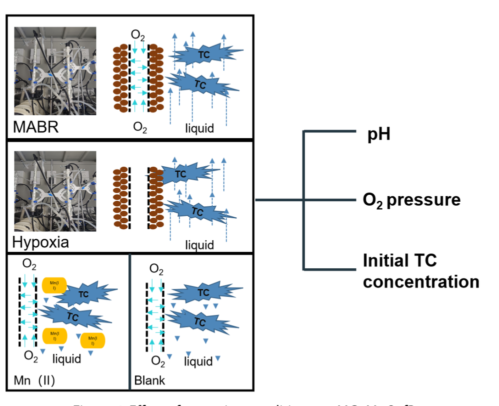

Figure 4. Effect of operating conditions on MCoMnOxfR

Sample Collection and Analysis

Aqueous samples were collected from the reactors every hour for the first 14 hours using 3 mL syringes and immediately filtered through 0.2 µm membrane filters for further use. The content of TC was analyzed by high performance liquid chromatography (HPLC). The concentration of dissolved Mn was detected by atomic absorption spectrometry (AAS) in the filtrate before and after the reaction.

Surface Atomic Composition Characterization

The fiber samples were examined using a scanning electron microscope (SEM) to observe adhesion on the membranes and X-ray diffraction spectroscopy (XRD) to determine crystal structure. Dried membrane filaments under went attenuated total reflection Fourier transform infrared (ATR-FTIR) to determine surface composition.

Results and Discussion

Characterization of CoMnO film

The SEM confirmed the successful coating of CoMnOXNP on the surface of the membrane (Fig. 4a). ATR-FTIR and XRD analysis identified the nanoparticles deposited as $CoMn_2O_4$ (Fig. 4b & 4c).

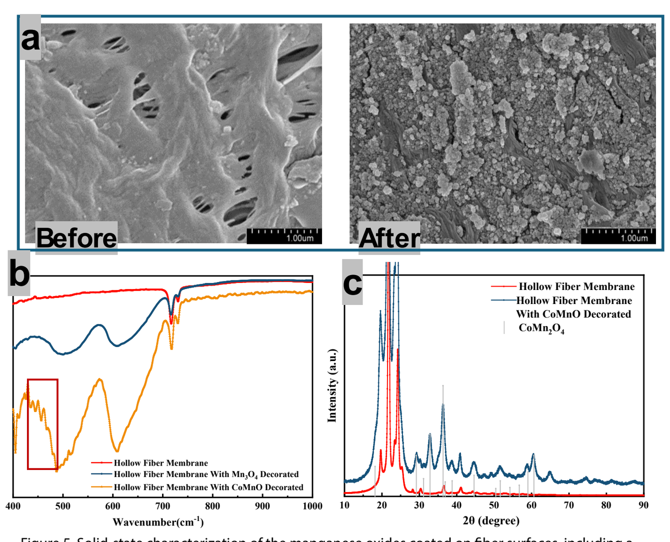

Figure 5. Solid-state characterization of the manganese oxides coated on fiber surfaces, including a (a) representative SEM image, (b) FTIR spectrum and (c) XRD spectrum

Efficacy of TC removal by the O_2-MCoMnfR

Compared with manganese oxide without Co modification, CoMnOx has higher tetracycline degradation efficiency and lower manganese loss. The Co-modified manganese oxide film reactor satisfies EU standards with a divalent manganese loss rate of less than 0.4 mg/L in the absence of tetracycline.[1]

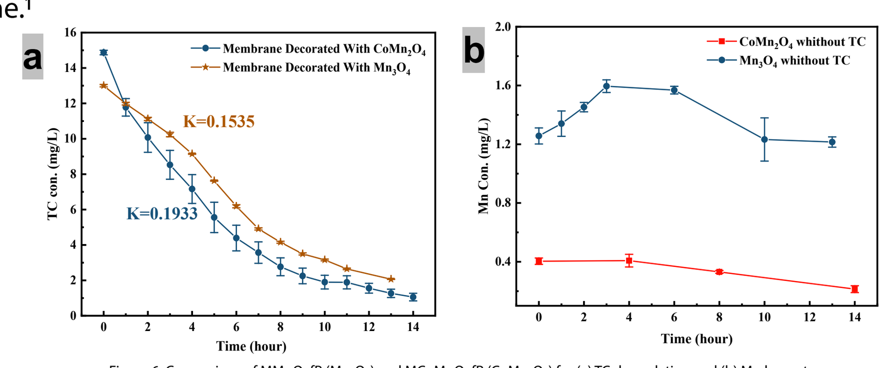

Figure 6. Comparison of MMnOxfR (MnO_x) and MCoMnOxfR ($CoMn_2O_4$) for (a) TC degradation and (b) Mn loss rate

Factors affecting TC degradation and Mn loss rate

Oxygen pressure and TC concentration were shown to significantly affect the rate of degradation. Divalent manganese exhibits a low loss rate in experimental settings at an oxygen pressure of 0.06 MPa. Below this pressure, the oxygen supply is insufficient. Manganese concentration lost to the effluent increases as the reaction progresses and TC degradation efficiency is greatly impacted (Fig. 7b & Fig. 8b).

High initial concentrations of tetracycline cause considerable loss of manganese oxide and irreversible damage to the manganese oxide film (Fig. 8c). This also significantly affects the rate of TC degradation (Fig. 7c).

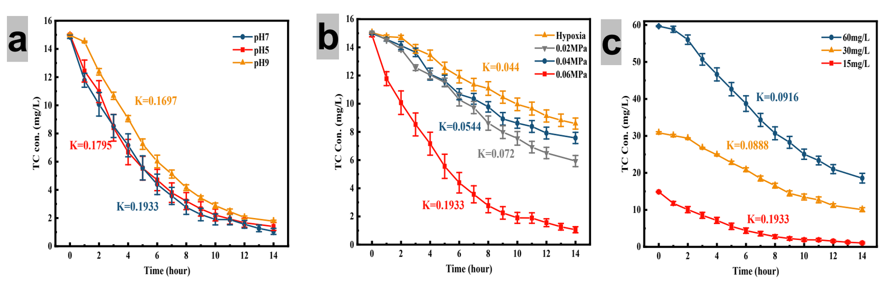

Figure 7. TC degradation curves for (a) change in pH, (b) change in oxygen pressure supply and (c) initial TC concentration

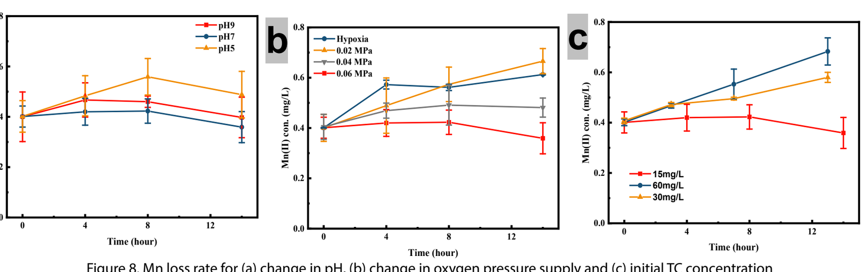

Figure 8. Mn loss rate for (a) change in pH, (b) change in oxygen pressure supply and (c) initial TC concentration

Toxicity Test

The small amount of Mn (0.05 mg/L) flowing out from the membrane is shown to have no toxic effect on microorganisms. The OD values of microbial cultures exposed to the MCoMnfR treated TC showed notably greater growth than that of untreated TC, indicating that the transformation products (TPs) resulting from TC degradation exhibit reduced biotoxicity compared to TC itself.

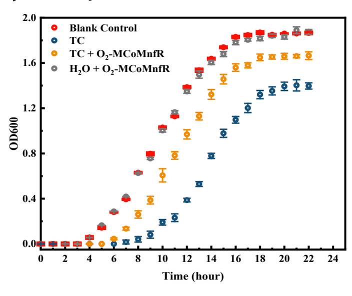

Figure 9. OD600 turbidity values for treated and untreated TC indicating growth of microbial cultures

Conclusion

An O_2-based MCoMnfR demonstrating effective removal of TC was innovatively developed in this study, with a first-order kinetic constant of 0.0.1933 h⁻¹. While various techniques exist for TC removal from wastewater, the O_2-MCoMnfR system offers distinct advantages. First, its oxygen delivery can be meticulously controlled by modulating O_2 pressure, thereby minimizing excess oxygen in bulk water and reducing costs related to air aeration compared to traditional approaches. Furthermore, the hollow fibers provide an extensive surface area for manganese oxide, enhancing oxygen utilization efficiency and accelerating the TC oxidation rate. The resulting optimal conditions were determined to be 15 mg/L initial TC concentration at pH 7 with oxygen pressure of 0.06 MPa. These conditions prove more stringent than existing TC concentrations in wastewater and allow for efficient regeneration of the CoMnOxNP for oxidative degradation. Moreover, solid-state characterization of the membrane demonstrated the successful deposition of $CoMn_2O_4$ nanoparticles. Compared to previous studies, Co doping significantly reduced the Jahn Teller effect, consequently diminishing the loss of Mn and increasing the degradation efficiency. For future recommendations, longer experiments are needed to verify the stability of the reactor system, while exploring the degradation and stability in complex actual wastewater and other multi-antibiotic coexistence systems.

Key References

[1] X.-Y. Li, C.-Y. Lai, and H.-P. Zhao, "A novel oxygen-based manganese oxides modified membrane reactor for TC oxidative degradation," Journal of Water Process Engineering, vol. 59, p. 104978, Mar. 2024. doi:10.1016/j.jwpe.2024.104978
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