Executive Summary

Transport of Micropollutants During Electrodialysis Treatment of Anaerobic Effluent

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Background

The presence of micropollutants such as pharmaceuticals, personal care products, and pesticides in anaerobic effluents poses significant environmental and public health concerns. These contaminants are typically not effectively removed by conventional wastewater treatment methods, leading to their persistence in aquatic ecosystems and potential for bioaccumulation. This study focuses on the transport behavior of specific antibiotic micropollutants Tetracycline, Ciprofloxacin, Tylosin Tartrate, Rimsulfuron, and Sulfadiazine during the electrodialysis treatment of anaerobic wastewater effluent. Electrodialysis, an electrochemical separation process utilizing ion-exchange membranes and electric current, has shown promise for the removal of ionic species from aqueous solutions. The primary objective of this research was to elucidate the mechanisms governing the transport and removal efficiency of these antibiotic micropollutants during electrodialysis treatment. This study was conducted at both the Agricultural & Life Sciences department under the supervision of Assistant Professor Manuel Garcia-Jaramillo and the Chemical, Biological, and Environmental Engineering department under the supervision of Assistant Professor Xue Jin at Oregon State University. The findings from this research are expected to contribute to the development of more effective wastewater treatment strategies, thereby mitigating the environmental and public health risks associated with micropollutant contamination.

Purpose

The primary objective of this research was to investigate the transport behavior and removal efficiency of specific antibiotic micropollutants during the electrodialysis treatment of anaerobic wastewater effluent. This study aimed to address the significant environmental and public health concerns posed by the presence of micropollutants, such as pharmaceuticals, personal care products, and pesticides, in anaerobic effluents. These contaminants are known for their persistence in aquatic ecosystems due to their inadequate removal by conventional wastewater treatment methods, leading to potential bioaccumulation and adverse ecological impacts.

Electrodialysis, an innovative electrochemical separation process that utilizes ion-exchange membranes and electric current, was explored as a promising solution for the removal of ionic species from aqueous solutions. The research focused on elucidating the mechanisms governing the transport of antibiotic micropollutants, including Tetracycline, Ciprofloxacin, Tylosin Tartrate, Rimsulfuron, and Sulfadiazine, under controlled electrodialysis conditions. By optimizing parameters such as pH and voltage, the study sought to enhance the understanding of factors influencing the transport and removal efficiency of these micropollutants.

The ultimate goal was to contribute to the development of more effective wastewater treatment strategies, thereby mitigating the environmental and public health risks associated with micropollutant contamination. This research not only aimed to advance scientific knowledge in the field of wastewater treatment but also to provide actionable insights for environmental policy and practice, ensuring safer water resources for future generations.

Methodology

The methodology of this research involved a comprehensive approach to investigate the transport behavior and removal efficiency of antibiotic micropollutants during the electrodialysis treatment of anaerobic wastewater effluent. The study was conducted in a controlled laboratory setting at the Agricultural & Life Sciences department and the Chemical, Biological, and Environmental Engineering department at Oregon State University. The key steps in the methodology included the preparation of synthetic nutrient solutions, spiking these solutions with target antibiotics, and conducting electrodialysis experiments under various conditions.

The antibiotics Tetracycline, Ciprofloxacin, Tylosin Tartrate, Rimsulfuron, and Sulfadiazine were purchased from Sigma-Aldrich. Internal standards, including ciprofloxacin hydrochloride-d8 and sulfadiazine-d4, were supplied by HPC Standards Inc. Methanol and ultrapure water, both LC-MS grade, were used as solvents.

An ultra-high-performance liquid chromatography mass spectrometry (UHPLC-HRMS) system was employed to quantify the antibiotics and identify potential transformation products. The system included a mass spectrometer equipped with a Turbo V Ion Source electrospray ionization (ESI) accessory. Chromatographic separation was performed using a Waters XBridge C18 column.

The electrodialysis setup involved the use of ion-exchange membranes and an electric current to facilitate the separation process. Synthetic nutrient solutions were prepared by dissolving diammonium phosphate in deionized water and adjusting the pH as necessary. The solutions were then spiked with antibiotic stock solutions to achieve the desired concentrations. Electrodialysis experiments were conducted at three different voltages (10 V, 20 V, and 30 V) and at pH levels of 4, 7, and 10. The experiments were run in cycles, with electrodialysis reversal (EDR) mode incorporated to prevent fouling and scaling.

Ultra-performance liquid chromatography coupled with high-resolution mass spectrometry (UPLC-HRMS) was used to determine the initial concentrations of antibiotics, quantify their removal, and identify any transformation products. Linearity and sensitivity of the method were established to ensure accurate quantification.

This methodological framework provided a robust basis for assessing the transport and removal efficiency of antibiotic micropollutants during electrodialysis treatment, contributing valuable insights into optimizing wastewater treatment processes.

Key Findings

The experimental results demonstrated a significant influence of pH and applied voltage on the transport and removal efficiency of antibiotic micropollutants during electrodialysis (ED) treatment.

The pH of the solution played a crucial role in determining the ionization state of the micropollutants, thereby affecting their interactions with the ion-exchange membranes. At lower pH (4), acidic micropollutants existed in their ionized form, enhancing their affinity for cation-exchange membranes. Conversely, at higher pH (10), basic micropollutants became deprotonated and existed as anions, favoring their transport through anion-exchange membranes. This pH dependence significantly impacted the removal efficiencies achieved for the target antibiotics.

The applied voltage across the ion-exchange membranes also influenced micropollutant transport. Higher voltages increased the electromigration of charged micropollutants, leading to enhanced removal rates. However, excessively high voltages risked membrane fouling and scaling, potentially reducing the overall process efficiency.

Notably, the optimal combination of pH and voltage was found to be crucial for achieving high removal efficiencies of the antibiotic micropollutants during ED treatment. The results aligned with previous studies, which reported that the transport mechanisms of organic micropollutants through ion-exchange membranes are complex phenomena, significantly impacted by pH variations and applied voltage.

These findings highlight the importance of carefully controlling operational parameters like pH and voltage to optimize the removal of micropollutants during electrodialysis treatment, while minimizing potential drawbacks such as membrane fouling and scaling.

Conclusions/Recommendations

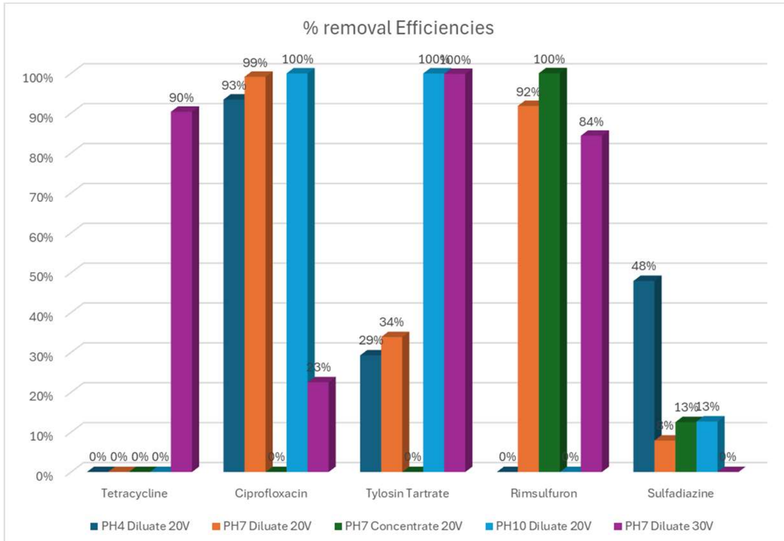

Figure 1. Percentage removal with different conditions

The findings from this internship project contribute significantly to the understanding of micropollutant transport during electrodialysis treatment of wastewater. The experimental results demonstrated the crucial influence of operational parameters, particularly pH and applied voltage, on the removal efficiency of antibiotic micropollutants like Tetracycline, Ciprofloxacin, Tylosin Tartrate, Rimsulfuron, and Sulfadiazine.

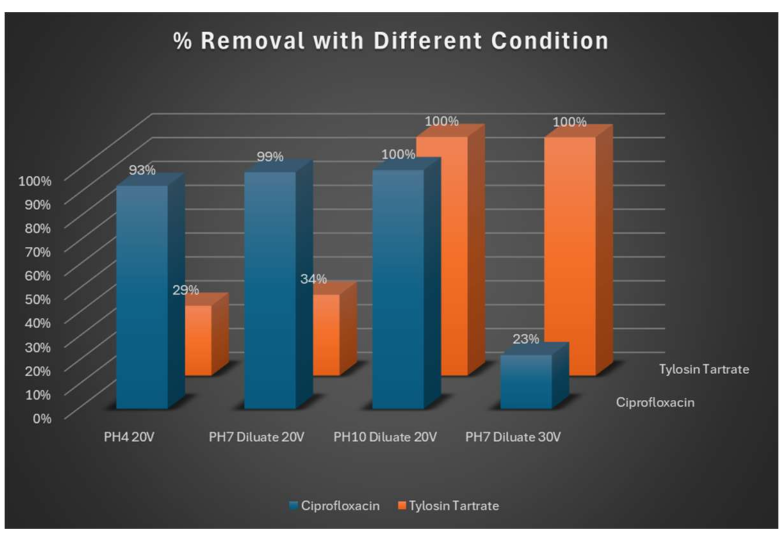

Figure 2. Removal comparison of Ciprofloxacin and Tylosin Tartrate

The observed differences in removal efficiencies of Ciprofloxacin and Tylosin Tartrate during the electrodialysis experiments can be attributed to the interplay of various factors, including pH conditions, physicochemical properties, and operational parameters. At pH 4 and 20V, Ciprofloxacin exhibited a high removal efficiency of 93%, while Tylosin Tartrate showed a lower efficiency of 29%. This can be explained by the zwitterionic nature of Ciprofloxacin, which allows it to exist in an ionized form over a broad pH range, facilitating its migration through the ion-exchange membranes. In contrast, Tylosin Tartrate may not be fully ionized at lower pH values, hindering its transport. As the pH increased to 7 and 10, the removal efficiencies improved for both compounds, with Ciprofloxacin achieving 99% and 100% removal, respectively, and tylosin tartrate reaching 34% at pH 7 and 100% at pH 10. The higher pH values likely optimized the ionization states of these compounds, enhancing their migration through the membranes. These findings highlight the importance of carefully controlling pH and voltage conditions to maximize the removal efficiency of specific micropollutants during electrodialysis treatment.

The observed trends align with previous studies, which reported incomplete retention of micropollutants by ion-exchange membranes due to factors such as electromigration, diffusion, and membrane affinity. The molecular properties of the micropollutants, including charge, size, and hydrophobicity, significantly influenced their transport behavior.

While the experiments focused on selected antibiotics and synthetic solutions, further investigations using complex matrices and a broader range of micropollutants are recommended to validate the applicability of electrodialysis for real wastewater treatment scenarios. Additionally, evaluating long-term performance and membrane fouling characteristics is crucial to assess the feasibility of large-scale implementation.

Based on the findings, it is recommended to optimize the pH and applied voltage to achieve maximum removal efficiency while minimizing potential drawbacks like membrane fouling and scaling. Incorporating renewable energy sources could also mitigate the high energy demands of the electrodialysis process, aligning it with more sustainable practices.

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