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Addressing Contaminants of Emerging Concern in Aquaculture: A Vacuum Membrane Distillation Approach

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ABSTRACT. The increase in contaminants of emerging concern (CECs) in agricultural and fishing waters has been causing negative impacts on aquatic and human life. Vacuum membrane distillation (VMD) has emerged as a solution for removing these components and can reject up to 99.9% of non-volatile species, such as CECs. This study evaluated VMD to treat aquaculture water, using a benchtop unit with microporous membranes (0.22 µm), operating at 75 ºC, a flow rate of 24 $L \cdot h^{-1}$ and a negative pressure of -640 mmHg. Efficiency tests showed rejection above 99% for salts and 98% for antimicrobials (sulfamethoxazole, ciprofloxacin, azithromycin and clindamycin), average flow of 7.08 $L \cdot m^{-2} \cdot h^{-1}$. The results demonstrate the potential of VMD to remove CECs and biocompounds, contributing to water safety and reducing environmental risks, with applicability on large scale.

KEYWORDS: Emerging pollutants; Wastewater treatment; Membrane distillation.

1. INTRODUCTION

Contaminants of Emerging Concern (CECs) are substances that have recently been recognized as potential environmental and health hazards, often due to advances in detection technology (Falda *et al*., Gil *et al*., 2023**)**. Some emerging contaminants are already well known, such as sulfonamides. CECs that are already well recognized include sulfonamides, which are commonly used in agriculture. In addition, other substances such as pharmaceutical and personal care products, nanomaterials, hormones, endocrine disruptors, perfluorinated chemicals, microplastics, nanoplastics, and micropollutants (which, though present in low concentrations, remain highly harmful) can contribute to the development of microbial resistomes. Furthermore, CECs typically originate from products commonly consumed by the public or mass-produced by industries.

In this context, new strategies and technologies to remove these ECs are necessary to mitigate risks and ensure the preservation and sustainability of aquatic ecosystems (Da Silva *et al*. 2025). Among these, membrane separation processes stand out, offering water decontamination through filtration with an efficiency exceeding 99.5% (Zou *et al.*, 2019). Notably, vacuum membrane distillation (VMD) uses differences in the physical properties of materials, such as liquid and vapor states of water, to achieve separation (Nariyoshi *et al.,* 2016). VMD is a technique driven by temperature gradients across the membrane and has proven highly effective in retaining ions and non-volatile organics. Compared to conventional thermal desalination technologies (e.g., multi-stage flash and multi-effect distillation), VMD operates at relatively low temperatures (30–80°C), reducing energy consumption. Compared to reverse osmosis (RO), another membrane-based process, VMD operates at low pressure, potentially resulting in lower energy consumption for this purpose (Nariyoshi *et al.*, 2016).

Beyond relatively low operational and capital costs, the highly compact and modular design of the VMD system makes it attractive for off-grid applications (Nariyoshi *et al.*, 2016). Recent research demonstrates the potential of VMD for removing ECs and decontaminating water. Zhang *et al*. (2022) assessed VMD’s efficiency in recovering wastewater from traditional Chinese medicine processing and found reductions exceeding 97% for chemical oxygen demand, total nitrogen, total phosphorus, and ammonia. Therefore, this study aims to evaluate the performance of the VMD process for the removal of CECs (specifically antimicrobial) from aquaculture water.

2. MATERIALS AND METHODS

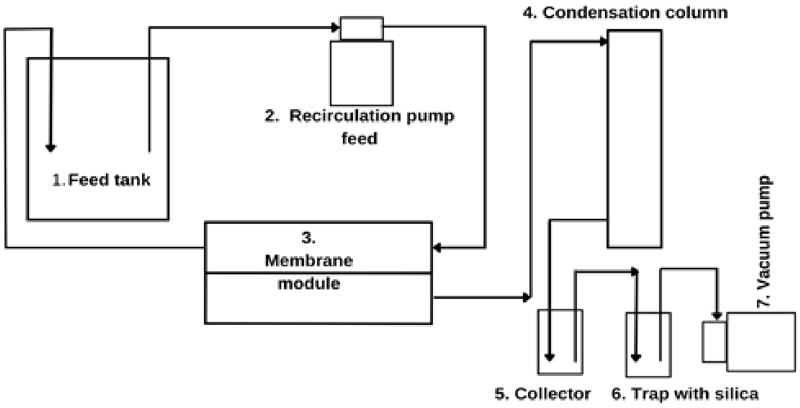
2.1 Sample Preparation

Preliminary water desalination tests were conducted to understand how the membrane unit works and the vacuum membrane distillation process. These studies were performed using a saline solution (27 $g\cdot L^{-1}$ NaCl), based on the average values found in the literature for brackish water (Kern, 2019; Lisboa *et al*., 2008). For the subsequent micropollutant removal tests, saline solutions with antimicrobials were prepared with Milli-Q ultrapure water for each of the analytes (Sulfamethoxazole, Ciprofloxacin, Azithromycin, and Clindamycin) at a concentration of 500 ppb.

2.2 Vacuum Membrane Distillation Process Performance

A bench-top flat-sheet VMD permeation system with a membrane area of 0.0086 m^2. was used for the vacuum membrane distillation tests, according to the diagram shown in Figure 1. A hydrophobic flat-sheet Fluoropore membrane (Merck Millipore) made of polytetrafluoroethylene (PTFE) and pore size of 0.22 µm was used.

Figure 1. Schematic of the vacuum membrane distillation bench system.



Permeation assays were performed for the removal of antimicrobials (Sulfamethoxazole, Ciprofloxacin, Azithromycin, and Clindamycin) at a concentration of 500 ppb. The antimicrobials were evaluated individually and concurrently in triplicate assays. The concentration of 500 ppb was overestimated to allow quantification by chromatography. The operational conditions used were the same as those in the preliminary tests, with the feed temperature set at 75 °C, vacuum pump pressure at -640 mmHg, and feed flow rate fixed at 24 $L \cdot h^{-1}$. All tests were performed by fixing the total permeation time at 2 hours, with feed recirculation. All permeation experiments were performed in triplicate. The permeate flux, J ($L \cdot h^{-1} \cdot m^{-2}$) of each experiment, was determined using the Eq. (1), where:

$$\boldsymbol{J} = \boldsymbol{V} / \boldsymbol{t}.\boldsymbol{A} \qquad \textbf{(1)}$$

Where **J** is the permeate flux ($L \cdot m^{-2} \cdot h^{-1}$); **V** is the collected permeate volume (L); **t** is the sample collection time (h); **A** is the area in m².

VMD performance was expressed by the rejection rate (%) of antimicrobials obtained by HPLC analysis. Samples were collected from the feed solution before the start of the VMD process, from the permeate at the end of the process, and from the concentrate, which consisted of the portion that did not pass through the membrane and remained on the feed side, as shown in Equation 2:

$$EF(\%) = \frac{Cinitial - Cfinal}{Cinicial} x100 \qquad \textbf{(2)}$$

Where **Cinitial** is the initial concentration of the analyte or particles in the feed solution; **Cfinal** is the final concentration of the analyte or particles in the solution (permeate).

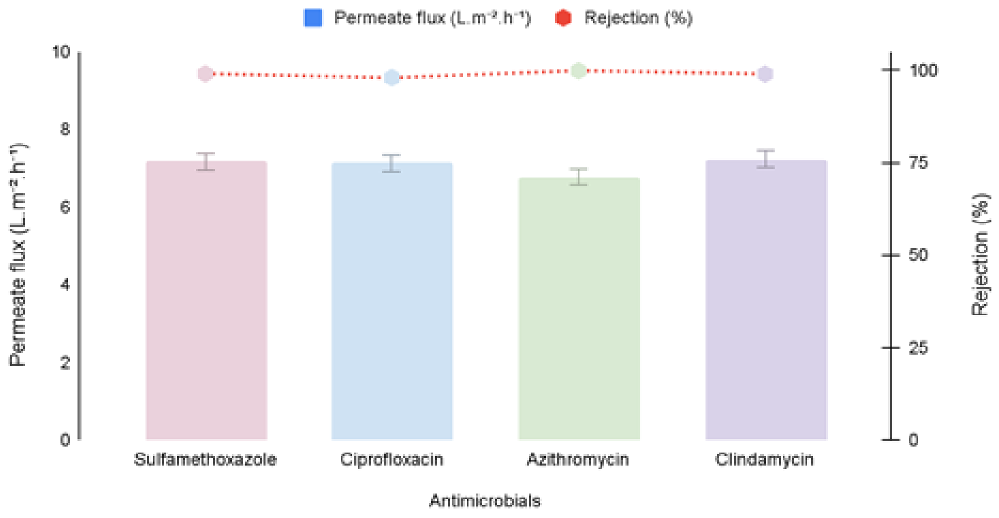
2.3 Antimicrobial Quantification by LC-MS/MS

Firstly**,** solid-phase extraction (SPE) was used to concentrate solution samples. An HPLC 290 Infinity system (Agilent Technologies, Waldbronn, Germany) coupled with a QTRAP® 5500 hybrid triple quadrupole-linear ion trap mass spectrometer (Sciex LLC, Framingham, USA) was used. Chromatographic conditions were established as described by Jank *et al*. (2014) and Hoff *et al*. (2021).

3. RESULTS AND DISCUSSION

The separation tests for the antimicrobials sulfamethoxazole, ciprofloxacin, azithromycin, and clindamycin were performed at 75 ºC, with a flow rate of 24 $L \cdot h^{-1}$ and a vacuum pressure of -640 mmHg, at a concentration of 500 ppb. Initially, the solutions containing the antimicrobials were evaluated individually, with one permeation experiment conducted for each antimicrobial in triplicate. Figure 2 presents the data on average permeate flux ($L \cdot m^{-2} \cdot h^{-1}$) and rejection (%) for each antimicrobial individually.

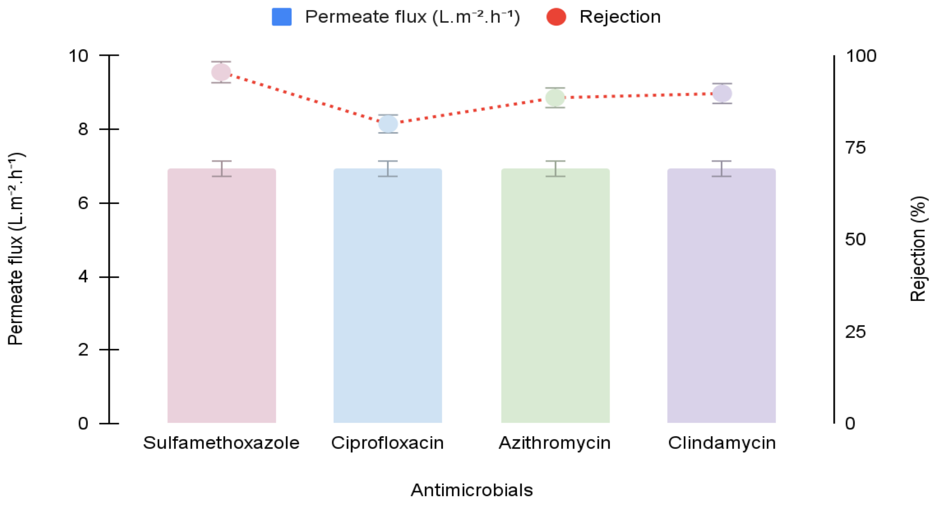
Figure 2. Permeate flux and rejection rate of each antimicrobial evaluated individually. Test conditions: antimicrobials concentration of 500 ppb, T of 75 °C, vacuum pressure of -640 mmHg, and feed flow rate of 24 $L \cdot h^{-1}$.



The average permeate flux obtained after 2 h of permeation for the antimicrobials tested sulfamethoxazole, ciprofloxacin, azithromycin, and clindamycin was 7.17 L·m^{-2}·h^{-1}, 7.13 L·m^{-2}·h^{-1}, 6.78 L·m^{-2}·h^{-1}, and 7.24 L·m^{-2}·h^{-1}, respectively. These values showed no statistical difference ($p<0.05$) among them. Regarding the rejection of antimicrobials, it was observed that the membrane presented high rejection for all analytes, with a retention rate exceeding 98% (Figure 2). The mechanisms involved in this study are size exclusion and electrostatic repulsion in separating targeted compounds from water. It was found that the difference in the compound's molecular structure played a significant role in the rejection process compared to their molecular weight.

In the test conducted with a feed solution containing all four compounds simultaneously, the permeate flux was 6.93 L·m^{-2}·h^{-1}, which showed no statistically significant difference ($p > 0.05$) compared to the fluxes obtained with the individual feed solutions. Figure 3 presents the rejection results for each component in the solution.

Figure 3: Permeate flux and rejection rate of each compound in a mixture. Test conditions: temperature of 75 °C, vacuum pressure of -640 mmHg, and feed flow rate of 24 L·h^{-1}.



The results suggest that complex interactions interfered with the rejection process, as the antimicrobials exhibited lower rejection rates when present in the mixed feed solution compared to when used in individual solutions. In the mixed solutions, containing all four antimicrobials, sulfamethoxazole showed the highest retention (95%), followed by clindamycin (88%), azithromycin (87%), and ciprofloxacin, which had the lowest rejection (80%).

4. CONCLUSIONS

The results obtained in this study indicated rejections of 99.1% for sulfamethoxazole, 98% for ciprofloxacin, 99.9% for azithromycin, and 99% for clindamycin when analyzed individually, demonstrating the effectiveness of VMD. This rejection showed a decrease when the antimicrobials were permeated simultaneously. Sulfamethoxazole showed the highest retention and ciprofloxacin, which showed the lowest rejection (80%). Based on the results of this study, new approaches for the removal of Contaminants of Emerging Concern (CECs), particularly antimicrobials, can be guided, highlighting the potential of VMD to remove organic contaminants and biocompounds from water, opening new possibilities for the treatment of contaminated water across the country.

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