

EXPLORING FACTORS AFFECTING NITROGEN ISOLATION BY CATION EXCHANGE MEMBRANE AND THEIR IMPLICATIONS FOR MICROBIAL FUEL CELL PERFORMANCE IN WASTEWATER TREATMENT

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Abstract

This study explores the utilization of a cation exchange membrane (CEM) in a microbial fuel cell (MFC) system to isolate nitrogen from wastewater influents. While employing a CEM in an MFC system has drawbacks, such as increased internal resistance and reduced power output, it also provides a means for optimal energy recovery from organics while allowing isolated nitrogen to be treated in subsequent steps. This study evaluated the diffusion of ammonium through CEM in a dual-chamber MFC under different operating conditions. Results indicated that the MFC reactor with CEM as a separator isolated 88-93% of the nitrogen input, demonstrating the feasibility of this approach for nitrogen separation in wastewater treatment applications. Factors affecting nitrogen isolation, including COD input at the anode, dissolved oxygen (DO) at the cathode, and external resistance (ER), are identified. Higher COD input at the anode and the DO at the cathode were found to enhance nitrogen separation, while increased ER had an adverse effect on nitrogen isolation capacity. Additionally, changes in the surface characteristics of the CEM during operation could impact nitrogen isolation, emphasizing the need for careful monitoring and maintenance of the CEM to ensure consistent performance over time. In conclusion, this study highlighted the potential of using a CEM in MFC systems for nitrogen isolation, provided insights into the factors affecting the efficacy of nitrogen separation, and underscored the need for monitoring and maintenance of the CEM. These results could significantly impact the development of more efficient and sustainable wastewater treatment using the MFC system.

Keywords: Cation exchange membrane; microbial fuel cell; nitrogen isolation; wastewater treatment

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Introduction

Microbial fuel cell (MFC) reactors use separation between chambers to prevent crossover activities that might affect MFC performance (Santoro *et al.*, 2017). To maintain electrical neutrality in MFC, the separator must allow for the free flow of ions. Therefore, ion exchange membranes like cation exchange membranes (CEMs) are effective barriers. Although crucial to the operation of MFC systems, their high price is a significant downside. In addition, the high concentrations of common cations in the wastewater and the poor selectivity of CEMs may contribute to a low proton transfer efficiency (Rozendal *et al.*, 2006). In an MFC reactor, the oxidation process at the anode produces protons, and the reduction process at the cathode consumes protons. Therefore, the low protons transfer efficiency of CEM results in a disparity in pH between the two regions, affecting MFC performance (Nguyen and Babel, 2022). However, nitrogen isolation from wastewater influents utilizing CEMs can potentially convert this vulnerability into an asset. The oxidation of isolated ammonium at the cathode can aid in pH balance. This allows an MFC reactor to be set up for maximum energy recovery from organics while nitrogen oxide compounds such as nitrate and nitrite can be treated downstream. Recent research has also looked at the possibility of removing nitrogen in a dual-chamber MFC by using ion exchange membrane penetration of nitrogen (Jin *et al.*, 2022). Our study investigated the diffusion of ammonium through CEM in an MFC under the influence of different COD inputs at the anode, dissolved oxygen (DO) concentrations at the cathode, and values of external resistance (ER).

Materials and Methods

MFC reactor configuration

A dual-chamber MFC was constructed using 10 mm thick acrylic plates. Each chamber had a working capacity of 1 L. A 185 cm² area sheet of CEM (CMI-7000S, Membrane International, USA) was used as a separator between two chambers. CEM was turned to boil for 30 min in 10% H₂O₂ solution, distilled water, 1 M H₂SO₄ solution, and finally distilled water again before being installed (Yoshitake *et al.*, 1996). The anode and cathode were made from 162 cm² carbon cloth with a thickness of 1.5 mm. Two electrodes were connected via an external copper circuit and a resistor. Using a fine bubble air stone and an air valve, the DO level in the cathode chamber was stabilized via aeration. All of the vents on the MFC reactor was plugged up with rubber buttons to prevent the ingress of outside air.

Inoculation and Medium

The anode chamber and cathode chamber were respectively inoculated with 100 ml anaerobic sludge (MLSS = 14.31 g L⁻¹) and 100 ml anoxic sludge (MLSS = 29.98 g L⁻¹). The carbon cloths were immersed in the sludge overnight to facilitate microbial attachment. The stock medium contains (per L tap water) 6 g Na₂HPO₄, 3 g KH₂PO₄, 0.5 g NaCl, 0.1 g MgSO₄·7H₂O, 0.015 g CaCl₂·7H₂O, and 1 mL trace nutrients solution (Virdis *et al.*, 2011). The trace metals solution consisted of (per L tap water): 1.5 g FeCl₃·6H₂O, 0.15 g H₃BO₃, 0.03 g CuSO₄·5H₂O, 0.18 g KI, 0.12 g MnCl₂·4H₂O, 0.06 g Na₂MoO₄·2H₂O, 0.12 g ZnSO₄·7H₂O, 0.15 g CoCl₂·6H₂O, and 10 g Ethylenediamine tetra-acetic acid (EDTA) (Lu *et al.*, 2006).

Table 1. Four different operating conditions

	COD inputs at the anode (mg L ⁻¹)	DO at the cathode (mg L ⁻¹)	ER (Ω)
First condition	2,000	4	50
Second condition	2,000	4	100
Third condition	2,000	0.6	100
Fourth condition	1,500	0.6	100

Operation Method

The input of the anode chamber was medium with supplementing 1.92 or 2.56 g L⁻¹ sodium acetate (COD of 1,500 or 2,000 mg L⁻¹, respectively) and 0.4 g L⁻¹ ammonium chloride to obtain NH₄⁺-N concentrations of 100 mg L⁻¹. The input of the cathode chamber was medium without addition. Four different operating conditions with different COD inputs at the anode DO concentrations at the cathode, and values of ER were applied in Table 1.

Every two days, wastewater in each chamber was withdrawn and replaced by new wastewater. Wastewater samples were collected from each chamber at the start and end of each batch for analysis. The operation process above is summarized in Figure 1. This process was performed thrice for each operational condition.

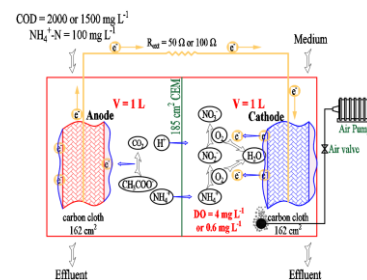


Figure 1. Functional diagram of the MFC reactor

Analysis and Calculations

Before analyzing chemical parameters such as COD, $\text{NH}_4^+\text{-N}$, $\text{NO}_2^-\text{-N}$, and $\text{NO}_3^-\text{-N}$ following the APHA method (Baird *et al.*, 2017), the sample from each chamber was filtered using a 2.5 μm paper filter (Whatman Grade 42, Cytiva, UK) for particle elimination. A distillation machine (Vapodest 10s, Gerhardt, Germany) was used for ammonium analysis. UV-visible spectrophotometer (Genesys 10s, Thermo Fisher Scientific, USA) was used for nitrite and nitrate analysis. DO was determined by a DO meter (550A, YSI, USA). pH was determined by a pH meter (Mettler Toledo, Switzerland). The cell voltage (E_{cell} or U) was monitored by a data recorder (Grant Instruments, Cambridge Ltd., Co, UK). The current (I) and the power density (P) are calculated by Ohm's law.

$$I = U/R_{\text{ext}}$$

$$P = UI/V_A$$

Where I (A) is the current, U (V) is the voltage, R_{ext} (Ω) is ER, P (W m^{-3}) is the power density, and V_A (m^3) is the liquid volume of the anode chamber.

After an operation, the CEM in the reactor was uninstalled to observe the surface under a scanning electron microscope (SEM) (JEOL JSM-7800F, Japan). It was washed and then dehydrated, and finally, gold coated before the SEM observation, following the procedure of Jin *et al.* (2019).

Results and Discussion

Table 2 shows the output of the chemical analysis of the anode chamber and cathode chamber. With ammonium influent of 100 mg L^{-1} , it can be observed that only a small amount of ammonium remained in the effluent of the anode chamber (ranged from 7.0-11.2 mg L^{-1} in different conditions tested). It is important to note that no nitrite or nitrate was detected in the output of the anode chamber, indicating that nitrification did not occur here. Meanwhile, at the output of the cathode

Table 2. Chemical analysis of anode chamber and cathode chamber effluent (n.d.: not detectable)

		Anode chamber (mg L^{-1})	Cathode chamber (mg L^{-1})
First condition	COD	447 $\pm$ 12	43 $\pm$ 5
	$\text{NH}_4^+\text{-N}$	7.0 $\pm$ 1.4	n.d.
	$\text{NO}_2^-\text{-N}$	n.d.	0.1 $\pm$ 0.1
	$\text{NO}_3^-\text{-N}$	n.d.	80.6 $\pm$ 1.1
Second condition	COD	444 $\pm$ 14	40 $\pm$ 0.0
	$\text{NH}_4^+\text{-N}$	7.9 $\pm$ 0.8	n.d.
	$\text{NO}_2^-\text{-N}$	n.d.	0.8 $\pm$ 0.6
	$\text{NO}_3^-\text{-N}$	n.d.	79.6 $\pm$ 1.5
Third condition	COD	453 $\pm$ 12	43 $\pm$ 9
	$\text{NH}_4^+\text{-N}$	8.9 $\pm$ 0.8	4.7 $\pm$ 0.8
	$\text{NO}_2^-\text{-N}$	n.d.	51.5 $\pm$ 1.4
	$\text{NO}_3^-\text{-N}$	n.d.	24.9 $\pm$ 1.4
Fourth condition	COD	264 $\pm$ 0.0	40 $\pm$ 8
	$\text{NH}_4^+\text{-N}$	11.2 $\pm$ 0.0	5.1 $\pm$ 0.8
	$\text{NO}_2^-\text{-N}$	n.d.	49.6 $\pm$ 0.3
	$\text{NO}_3^-\text{-N}$	n.d.	24.8 $\pm$ 0.7

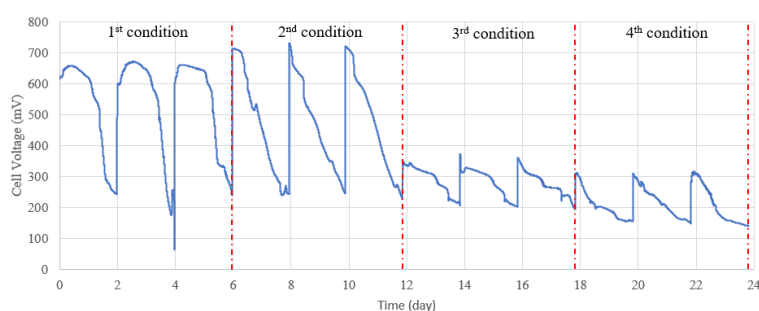


Figure 2. Cell voltage generated during the operational process

chamber, the amount of nitrogen increases sharply from the initial medium without nitrogen. This suggested that there was a diffusion of ammonium from the anode chamber to the cathode chamber through the CEM. It is clear that MFC with CEM as a separator effectively isolated nitrogen (88-93%) from wastewater, simultaneously generating cell voltage from organic removal, as shown in Figure 2.

Electricity Generation and COD Removal

The cell voltage generated in the first and second conditions (DO at the cathode of 4 mg L⁻¹) was significantly greater than in the third and fourth conditions (DO at the cathode of 0.6 mg L⁻¹). It has been reported that DO at the cathode has a significant effect on the power generation of the MFC reactor (Nguyen and Babel, 2022). The higher DO encouraged cathodic reaction to reduce oxygen to water, thereby minimizing internal resistance and enhancing electricity production. The ER interfered with the flow of current through the outer circuit (Virdis *et al.*, 2008). As a result, the first condition with a lower ER of 50 Ω produced a larger current compared to the second condition with a higher ER of 100 Ω . The average current generated was 10.7, 4.7, 2.8, and 2.1 mA, respectively, for the first to fourth operating conditions. COD removal efficiency in the anode chamber was 77.3-82.3% within two days of treatment. From this organic matter removal, the MFC reactor recovered an average power density of 6.2, 2.4, 0.8, and 0.5 W m⁻³ corresponding to the first to fourth operating conditions. At the same time, utilizing the excess oxygen in the cathode chamber, more than 95% ammonium diffused via CEM from the anode chamber was oxidized to nitrite and nitrate.

Factors Affecting Nitrogen Isolation

With the same COD at the anode and DO at the cathode in the first and second conditions, the ammonium concentration in the output of the anode chamber slightly increased from 7 $\pm$ 1.4 mg L⁻¹ to 7.9 $\pm$ 0.8 mg L⁻¹ when ER increased from 50 Ω to 100 Ω . Virdis *et al.* (2011) reported that a lower value of ER reduces the overall system impedance, with more electron flow through the external circuit. This promoted more ammonium diffusion via CEM to achieve charge equilibrium. Compare the second and third conditions with the same COD input at the anode and the same value of ER, the ammonium at the anode chamber rose from 7.9 $\pm$ 0.8 mg L⁻¹ to 8.9 $\pm$ 0.8 mg L⁻¹ when DO at the cathode chamber declined from 4 mg L⁻¹ to 0.6 mg L⁻¹. One possible explanation is that less oxygen was present in the cathode chamber, decreasing the reduction rate of protons to water ($O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$) (Nguyen and Babel, 2022). It decreased electricity generation

by the MFC reactor and diminished ammonium transport driving force across the CEM. In addition, a small amount of unoxidized ammonium at the cathode chamber output in the third condition (Table 2) indicated that low DO slowed the ammonium oxidation rate. This also impeded the diffusion of ammonium from the anode chamber to the cathode chamber. Compared to the third condition, the fourth condition had a lower COD influent of 1,500 mg L⁻¹, while DO at the cathode and ER were unchanged. As a consequence, the ammonium concentration in the anode chamber jumped from 8.9 $\pm$ 0.8 mg L⁻¹ to 11.2 $\pm$ 0.0 mg L⁻¹. Exoelectrogenic bacteria that oxidized organic materials and produced electrons for the fuel cell may be less active due to a decrease in organic matter in the anode chamber (Nguyen and Babel, 2023a; 2023b; 2024). Therefore, less electrons were sent via an external circuit to the cathode chamber, where they reacted with oxygen to form water, leading to a decrease in the cation gradient across the cation exchange membrane. As a result, ammonium ions had a lower driving force to move to the cathode chamber through CEM, increasing the effluent concentration of ammonium in the anode chamber. In summary, COD input at the anode, DO at the cathode, and ER had an impact on the nitrogen isolation by CEM because they directly affected the MFC's ability to generate electricity. In general, nitrogen isolation efficiency increased as COD at the anode and DO at the cathode increased. In contrast, nitrogen isolation capacity decreased as the value of ER increased.

Characterization of Membrane Surface

It is essential to recognize that the COD input at the anode, DO at the cathode chamber, and value of ER in the relationship with nitrogen isolation is qualitatively complex due to the influence of many other variables. These variables include but are not limited to, the properties of the CEM, the variation in pH at the anode chamber, and the concentration of competing ions. By adjusting the pore size, thickness, and charge of a CEM, ammonium ions may be selectively transported while other ions are blocked. When organic materials are oxidized, the pH in the anode chamber may drop (Ren *et al.*, 2020). Because of this, the CEM's characteristics alter, decreasing its efficiency for ammonium diffusion. The SEM images of the CEM before and after the operation in this study (Figure 3) showed a marked change in the membrane surface. After the operation, large cracks were detected, causing damage to the membrane surface. In addition, deposits adhered to the membrane surface, compared to the clean surface before operation. High concentrations of competing ions, such as

potassium and sodium, may reduce the cation exchange membrane's selectivity and hence its ability to isolate ammonium ions (Rozendal *et al.*, 2006). Besides, the ammonium diffusion rate is also affected by the hydraulic retention time of the treatment procedure and the substrate type utilized in MFC. Additional research is required to comprehend the effect of other factors on nitrogen sequestering and optimize the operational parameters for improving performance. Additionally, the potential effects of this ammonium diffusion on subsequent processes should be investigated.

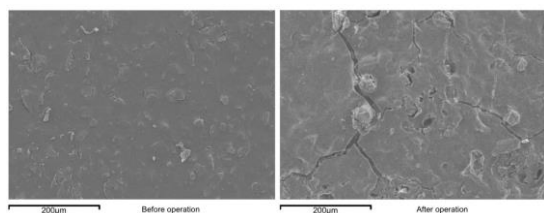


Figure 3. SEM images of CEM before and after the operation

Challenges and Future Perspectives

The successful integration of CEM in MFC systems for nitrogen isolation from wastewater presents a promising avenue for sustainable wastewater treatment. However, as with any innovative technology, several challenges and opportunities for improvement emerge. One notable challenge lies in ensuring the long-term durability and effective maintenance of CEMs within MFC reactors. The observed changes in surface characteristics, including cracks and deposits, highlight potential issues that may impact membrane integrity over time. The high cost associated with CEMs remains a significant impediment to their widespread implementation. As a crucial component in MFC systems, the economic viability of CEMs needs improvement. The low proton transfer efficiency of CEMs poses challenges to maintaining electrical neutrality within MFC reactors. This inefficiency can result in pH imbalances between chambers, affecting overall MFC performance. The selectivity of CEMs, particularly in the presence of common cations and competing ions in wastewater, requires careful consideration. High concentrations of ions like potassium and sodium may reduce the membrane's selectivity, affecting its ability to isolate ammonium ions effectively.

Advancements in membrane materials hold immense potential for addressing durability concerns and reducing costs. Research should focus

on the development of novel materials with improved resilience to operational stresses, ensuring prolonged membrane life. Additionally, exploring cost-effective alternatives or manufacturing processes can contribute to making CEMs more economically viable. Efforts to enhance the proton transfer efficiency of CEMs should be a key research priority. Modifying membrane properties or exploring innovative proton-conductive materials can contribute to achieving better electrical neutrality in MFC systems. Improved proton transfer efficiency would positively impact electricity generation and nitrogen isolation capabilities. Research initiatives should aim to optimize the selectivity of CEMs for effective ammonium ion isolation. This involves fine-tuning membrane properties to selectively transport ammonium ions while blocking competing ions. Understanding the intricate interplay of membrane characteristics and ion interactions will guide the development of membranes with superior selectivity.

Conclusions

The MFC reactor with CEM as a separator has successfully produced power and simultaneously isolated nitrogen from wastewater. About 90% of the input nitrogen was sequestered by CEM membrane diffusion under various operating conditions. Based on the study findings, important parameters, including COD input at the anode, DO at the cathode, and ER were identified as having an impact on ammonium isolation in the N-MFC. Nitrogen isolation efficiency increased with COD input at the anode and DO at the cathode. However, the higher value of ER decreased nitrogen isolation capacity. In addition, nitrogen isolation could be affected by changes in the surface characteristics of the CEM that occurred during operation.

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