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Analysis of Membranes of a Microbial Desalination Cell for Fouling

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Abstract
Membrane fouling studies are needed to bring microbial desalination cell technology (MDC) to commercialisation. Thus, this study investigated membrane fouling in a five-chamber MDC. Scanning electron microscope and energy dispersive spectroscopy were used for the membrane analysis of the MDC. It was found that the anion exchange membrane facing the anode chamber was biofouled by bacteria, and the side facing the desalination chamber was scaled with O, Na, Cl, K, and Mg. The cation exchange membranes predominantly had C, F, and O on their surfaces. It was concluded that irrespective of MDC design and type of catholyte used, membrane fouling is bound to occur in the technology. The development of self-healing membranes can, however, help overcome this problem.
Keywords: Membranes, biofouling, scaling

Introduction

In the last few decades, evolving technologies like microbial fuel and microbial desalination cells have increased the relevance of membranes in water and wastewater treatment (Cao et al., 2009). According to Imoro et al. (2021a), the most popularly used membranes in microbial cell technologies are cation exchange membranes (Membrane International Inc, USA), anion exchange membranes (Tienwei membrane, China) and proton exchange membranes (Sigma-Aldrich, India).

Despite the usefulness of membranes in microbial cell technologies, a critical problem facing these technologies, especially microbial desalination cells (MDC), is membrane biofouling (Ping et al., 2013) and scaling (Luo et al., 2012). Scaling is caused mainly by the precipitation of ions, especially cations (Zuo et al., 2013), whiles biofouling is caused by bacteria in wastewater contained in the anode chamber (Ping et al. (2013). Scaling and biofouling reduce microbial desalination cells' electricity generation and desalination efficiencies (Kokabien and Gude, 2015).

A survey of the available literature showed that studies addressing the fouling problems of MDCs had been skewed towards MDCs working with chemical (potassium ferricyanide-based) catholyte and MDCs with the classical three-chamber configurations. Thus, this work was carried out to investigate membrane fouling in a five-chamber MDC with water as its catholyte.

Methods

Sample Preparation for SEM Analysis

A five-chambered MDC (Fig. 1) operated for three batch cycles (150 days) was dismembered, and its membranes (AMI 70001 and CMI 7000, Membrane International, USA) were analysed for fouling. This MDC worked under an average anolyte pH of 5.72 ± 0.91 and average catholyte pH of 8.36 ± 0.83. Its reproducible peak voltage was 343.57 ± 0.25 V, and its desalination efficiency was 50.01%. Its anolyte was wastewater and catholyte tap water (Imoro et al., 2021b). A Scanning Electron Microscope (SEM) with Energy Dispersive Spectroscopy (EDS) (Phenom ProX Generation 5, mag. 80 – 150,000x) was used to examine it for scaling and biofouling. A sterilised scissor was used to carefully cut the middle portions of the membranes (AEM and CEM) for air drying overnight (Luo et al., 2012). The cut membranes were mounted on aluminium stubs with adhesive carbon paper for SEM analysis. Optical and electron images of samples were obtained with the SEM and elemental compositions with EDS. With information from SEM and EDS, the nature and compositions of used and unused membranes were compared to detect fouled layers.

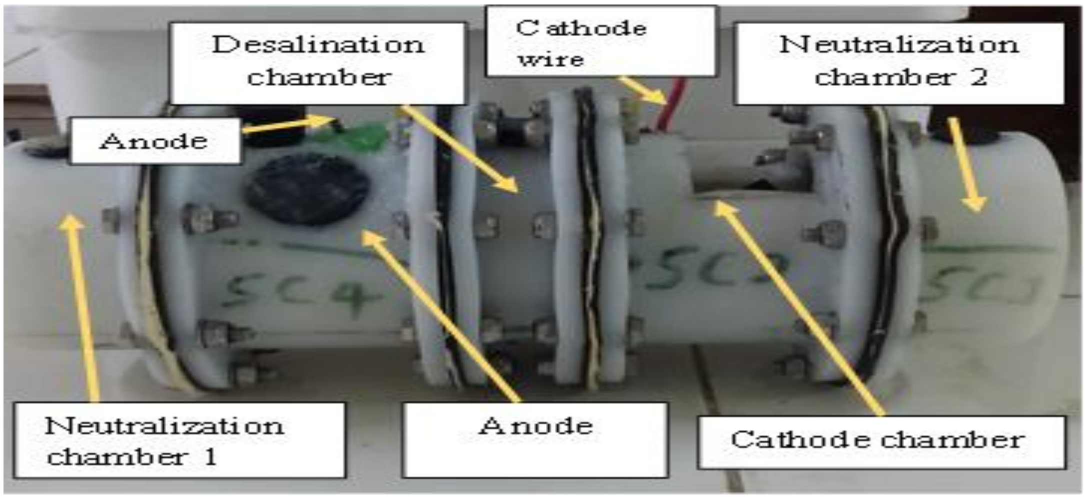

Plate 1. Five-Chamber water catholyte MDC (MDC)

Biochemical Identification of Bacteria on Fouled Membranes

Used anion exchange membranes (AEM) were aseptically rinsed thoroughly in sterilised distilled water to transfer the attached bacteria in water. This preparation's serial dilutions (10^{-5}) were plated on Plate Count Agar (PCA) for bacteria growth and identification. According to Smith and Hussey (2005) protocols, Gram staining was carried out for bacteria identification. The bacteria isolates were subjected to citrate, catalase, and indole tests as described in MacWilliams (2009a-c) and the triple sugar iron test described in Lehman (2005).

Results

Comparison between used and unused Anion Exchange Membranes (AEMs)

Used AEM of the anode chamber was fouled on both sides (Plate 3 and 4). The side of the AEM facing the anolyte was fouled predominantly by rod, spherical and short rod-shaped bacteria (Table 1). This observation was attributed to bacteria in the anolyte. A thin layer of debris (from wastewater) formed on the AEM with cracks on it. The cracks (Plate 3) resulted from the subjection of the membranes to dryness. Inorganic scales were observed on the side of the AEM facing the desalination chamber, primarily due to the presence of salt (NaCl) in the desalination chamber (Plate 4).

Energy dispersive spectroscopy (EDS) revealed that the side of the used AEM facing the anolyte contained C, O, Ca, P, F, Na, Cl, whiles the side facing the desalination chamber contained O, Na, Cl, K, Mg. The detection of C, O, and F was expected because these elements are part of the composition of ion exchange membranes (Zuo et al., 2013). The detection of especially Ca, C and O was possible because of their increased concentration due to bacteria growth (Luo et al., 2012).

The presence of Na and Cl on membranes was due to the use of NaCl solution in the desalination chamber, while the precipitation of Mg on the membrane side facing the desalination chamber was probably due to high pH (9.60 ± 0.7) in the desalination chamber. According to Ping et al. (2013), a high pH of approximately 10.2 can facilitate the precipitation of Mg on cation exchange membranes.

The AEM of the neutralisation chamber facing the catholyte had numerous patches of inorganic scales (Plate 5) with C, F, O, S, K, and Na detected on it. The detection of S and K was not expected because the catholyte did not contain these elements. Thus, their presence on the AEM could be due to cross-contamination from the anolyte. The unused AEM (Plate 1) analysis showed no apparent fouling layers; thus, it provided the required contrast for assessing used membranes.

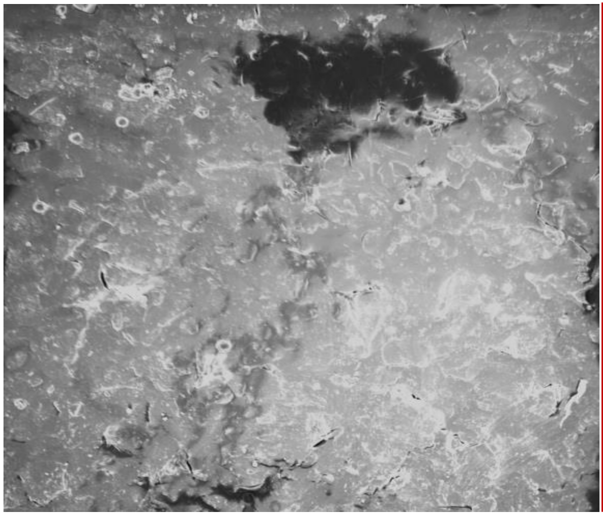

Plate 2. Unused AEM

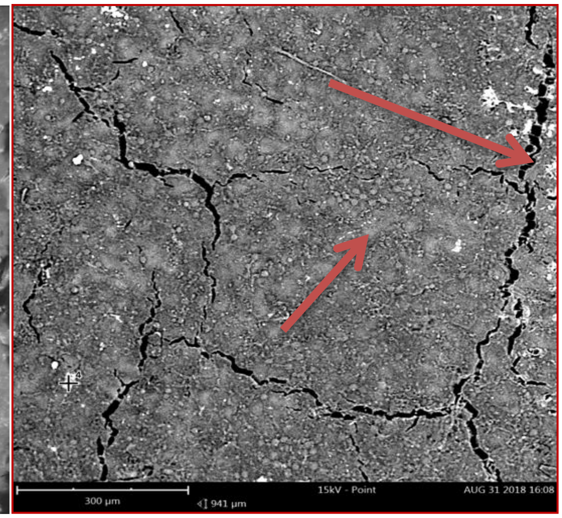

Plate 3. Used AEM (Side facing anolyte)

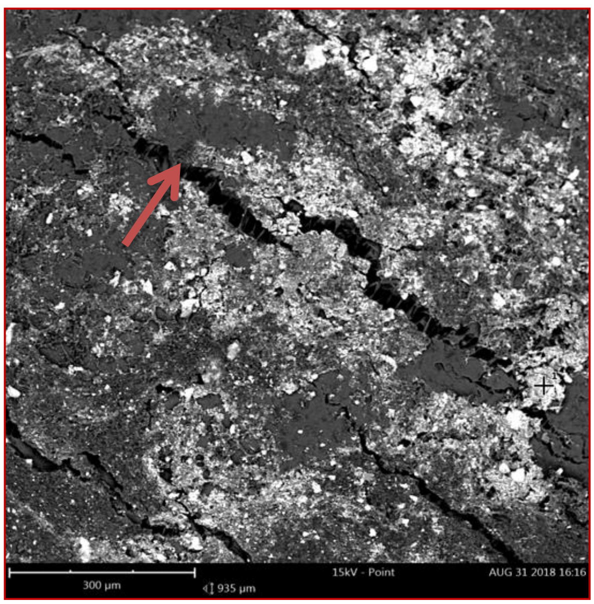

Plate 4. Used AEM (Side facing desalination chamber)

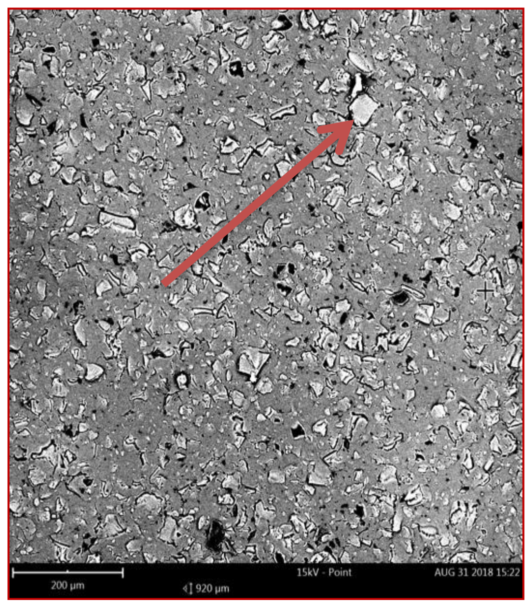

Plate 5. Used AEM of neutralization chamber (side facing catholyte)

Comparisons between unused and used Cation Exchange Membranes (CEMs)

The side of the CEM facing the catholyte had dark patches all over its surface (Plate 6) because of the use of Vulcan carbon in the cathode compartment. It contained N, S, F, O and C (Table 2). As indicated earlier, C, F, N and O form a part of the composition of ion exchange membranes, so their detection was expected. S was from Vulcan carbon because it has traces of S in it. On the other hand, the side of the CEM facing the desalination chamber had patches of inorganic scales (Plate 7) with C, F, O, Fe, Na, S, Ca and Cl on it (Table 2).

The detection of Fe on the CEM was not expected and could represent a case of cross-contamination from the catholyte. The neutralisation chamber's CEM (Plate 8) (side facing anolyte) had a thin layer of debris with cracks. These cracks were a result of dryness. On the other hand, the unused CEM did not have apparent layers of fouling (Plate 9).

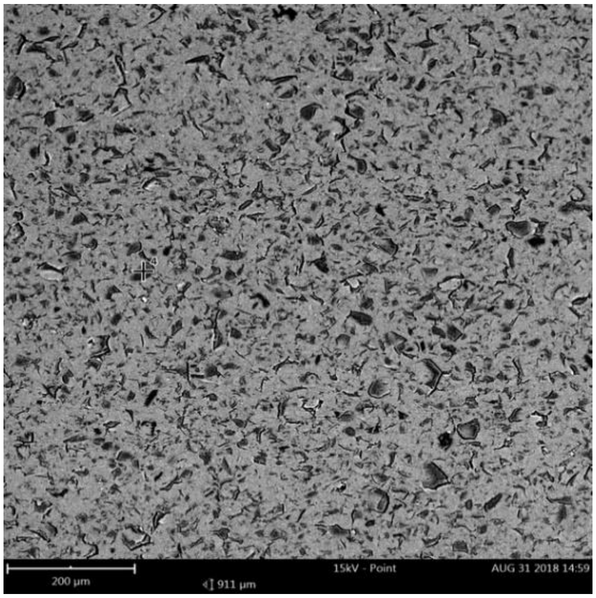

Plate 6. Used CEM (Side facing catholyte)

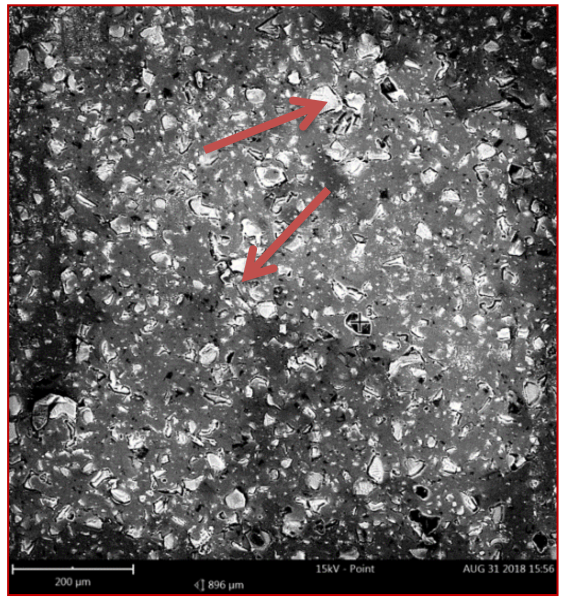

Plate 7. Used CEM (Side facing desalination chamber)

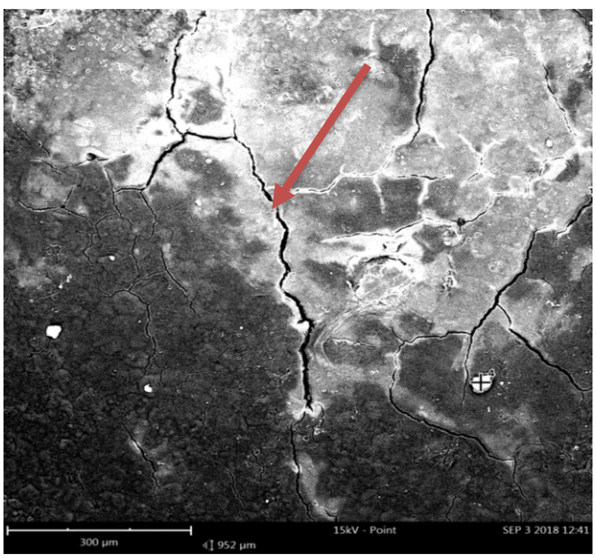

Plate 8. CEM of neutralization chamber (side facing anolyte)

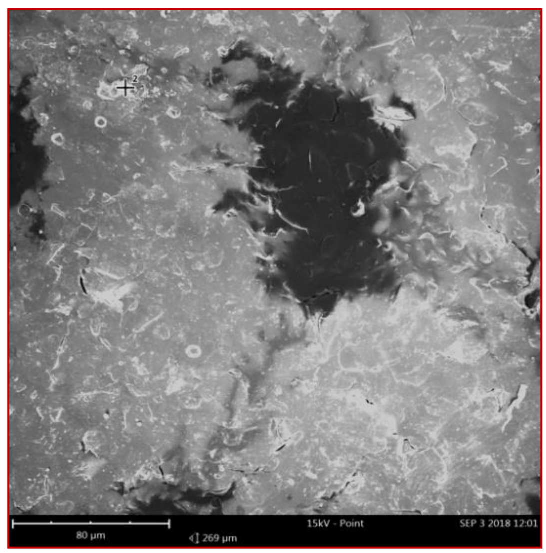

Plate 9. Unused CEM

Table 1 Predominant Bacteria on Fouled Membranes

Morphology	Citrate	Catalase	Gram reaction	Shape	Spore	Indole	TSI fermentation	Suspected Bacteria
White dense	+	+	+	Rod	X	-	No	*Pseudomonas aeruginosa*
Swammy (slightly peach)	+	+	+	Cocci	X	-	Slant and butt	*S. aureus*
Yellow dense colonies	+	+	+	Short Rod	X	+	Slant	*E. coli*
White with translucent outline	+	+	+	Rod	X	-	No	Bascillus/ Clostridum

Table 2: Atomic concentrations of elements on ion exchange membranes

Elements	Atomic concentration (%) of CEM (Side facing desalination chamber)	Atomic concentration (%) of AEM (Side facing anolyte)
C	40.53	77.37
F	17.03	15.63
O	33.24	4.23
S	0.12	0.23
K	-	0.04
Na	8.06	0.34
Fe	0.08	-
Cl	0.06	5.80
Ca	0.04	0.11
P	-	0.04

General Discussion

The discovery of fouled layers on used membranes of the five-chambered MDC demonstrated some setbacks with this technology. However, this is not the first study to observe fouled layers on used membranes. Luo et al. (2012), working on the long-term performance of MDC, reported both biofouling and inorganic scaling. Further, Ping et al. (2013) also reported that when anion and cation exchange membranes were used for a long time, they got fouled by bacteria and ion precipitates.

This study showed that AEMs were predominantly biofouled, while CEMs were more affected by inorganic scaling. These observations are generally associated with the constituents of the anolyte and catholyte of the MDC technology (Ping et al., 2013). Both bio and inorganic fouling can reduce the permeability of membranes to the migration of ions through them (Choi et al., 2011). These problems are part of why the technology has not yet reached commercialisation. The development of membraneless MDC or self-healing membranes will significantly advance the MDC technology towards large-scale use.

Conclusion

Membrane fouling studies are necessary to guide the development of MDC technology towards commercialisation. This study proved that scaling can occur on CEMs even when water is the catholyte. Moreover, it was shown that irrespective of MDC design; biofouling can occur on AEMs of MDCs after prolonged use. Self-healing membranes or membrane-less MDCs are needed to overcome the fouling problems of the technology.

References

Cao, X., Huang, X., Liang, P., Xiao K., Zhuo, Y., Zhang, X., Logan, B. E., 2009. A New Method for Water Desalination using Microbial Desalination Cells, *Environmental Science Technology*, 43, 7148 – 7152. doi: 10.102/es901950j.

Choi, M. J., Chae, K. J., Ajayi, F. F., Kim, K. Y., Yu, H. W., Kim, C. W., Kim, I. S., 2011. Effects of Biofouling on Ion Transport through Cation Exchange Membranes and Microbial Fuel Cell Performance, *Bioresource Technology*, 102 (1), 298–303.

Imoro, A. B., Mensah, M., Buamah, R., 2021a. Developments in the Microbial Desalination Cell Technology: A Review, *Water-Energy Nexus*, 4, 76 -87.

Imoro, A. B., Mensah, M., Buamah, R., 2021b. Assessment of the Electricity Generation, Desalination, and Wastewater Treatment Efficiencies of a Microbial Desalination Cell Operating with Electrolyte Dilution as pH Control Measure, *Journal of Fundamental and Applied Sciences,* 13(1), 185-198.

Kokabian, B., Gude, V. G., 2015. Sustainable Photosynthetic Biocathode in Microbial Desalination Cells, *Chemical Engineering Journal*, *262*, 958–965.

Lehman, D., 2005. Triple Sugar Iron Agar Protocols, *American Society of Microbiology,* 1-7.

Luo, H., Xu, P., Ren, Z., 2012. Long-Term Performance and Characterization of Microbial Desalination Cells in Treating Domestic Wastewater, *Bioresource Technology*, *120*, 187–193.

MacWilliams, M. P., 2009. Catalase Test Protocol, *American Society of Microbiology*, 1-9.

MacWilliams, M. P., 2009. Citrase Test Protocol, *American Society of Microbiology,* 1-7.

MacWilliams, M. P., 2009. Indole Test Protocol, *American Society of Microbiology,* 1-9.

Ping, Q., Cohen, B., Dosoretz, C., He, Z., 2013. Long-Term Investigation of Fouling of Cation and Anion Exchange Membranes in Microbial Desalination Cells, *Desalination*, 325, 48–55.

Smith, A. C., Hussey, M., A., 2005. Gram Stain Protocols, *American Society of Microbiology,* 1-9.

Zuo, K., Yuan, L., Wei, J., Liang, P., Huang, X., 2013. Competitive Migration Behaviors of Multiple Ions and their Impacts on Ion-Exchange Resin Packed Microbial Desalination Cell, *Bioresource Technology*, *146*, 637–642. https://doi.org/10.1016/j.biortech.2013.07.139.