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Optimizing Physical Factors for the Ammonium Removal from Wastewater Using Bio-Electrochemical Systems

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Abstract: Waste streams, leachates, and wastewater often contain high-strength ammonia, which can be challenging to manage. Microbial fuel cells (MFCs) offer a promising solution for treating such a nuisance of high-strength ammonia. However, optimizing MFC operating conditions, at lower technology readiness levels, is crucial to achieve a sustainable and economically viable application. This study investigates the factors affecting ammonia nitrogen removal in MFCs. MFCs with a cation exchange membrane (CEM) exhibit a higher diffusion rate of ammonium ions from the anode to the cathode compared to those with a proton exchange membrane (PEM). In close circuit mode (CCM), MFCs with a Pt-coated cathode electrode achieved an ammonium removal efficiency of 96% in the cathode chamber. Moreover, a plain carbon cathode electrode yielded an 87.1% removal efficiency. These results indicate that the combination of a catalyst (Pt) and oxygen in the cathode chamber can effectively remove or recover ammonia nitrogen from wastewater. Simultaneously, the removal of ammonia nitrogen in a microbial electrolysis cell (MEC) was studied. At an applied potential of 1.0 V, an ammonium removal efficiency of 87.5% was achieved. It was concluded that ammonium losses in MFCs can occur through electron migration, volatilization, and biological processes such as nitrification and denitrification.

Keywords: ammonium; diffusion; microbial fuel cells; microbial electrolysis cells; nitrogen removal; power generation; wastewater

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1. Introduction

Reactive nitrogen in the forms of ammonia, ammonium, nitrate, nitrite, and urea are widely used, ranging from industrial use to fertilizers [1]. Among them, ammonia nitrogen is a key fertilizer component for agricultural production [2]. With the degradation of nitrogenous compounds of wastewater, ammonia is ubiquitously introduced as a byproduct, entering the wastewater streams. Furthermore, about 90% of the world's ammonia is produced by using the Haber–Bosch synthesis process, which requires 37 MJ KgN^{-1} and consumes 1–2% of the world's energy use [3,4]. In addition, ammonia is the most predominant species of nutrients being released as animal or protein-rich wastes to the environment [5]. Numerous pathways result in the deliberate, as well as unintentional, release of ammonia into wastewater and, ultimately, into the environmental compartments, including into the pristine water, air, and soil [6]. Among these, the major impacts were noted in water bodies, as the presence of elevated ammonia levels in aquatic ecosystems has detrimental consequences. It is confirmed and evident that the evaluated levels of ammonia in marine water have a determinantal impact on larval development of *Paracentrotus lividus* (commonly known as sea urchins) at equivalent concentration for NH^{4+}, as low as 0.81 mg/L [7]. The acute, chronic, and sublethal effects of ammonia on fish, invertebrate, and benthic organisms are well reported [8]. Excessive levels of ammonia can cause algal blooms, depleting the dissolved oxygen and consequently creating hypoxic zones in the water bodies [9]. Moreover, higher levels of ammonia also contribute to water acidification, corrosion due to nitrification by bacteria forming nitric acid (with the potential to dissolve the chalk; metals—copper, tin, and zinc; and composites), cellulosic vessel interaction causing the wood softening, and expanding and damaging the natural rubber and plastic [10].

Ammonia can be treated or removed by physicochemical and biological methods. These methods include activated sludge application, air stripping, capacitive deionization, chlorination, electrochemical oxidation, ion exchange and adsorption, membrane transmittance, microalgae, photo-electrocatalysis, photosynthetic bacteria, struvite precipitation, and wet oxidation; further, the range of ammonia removal efficiency of these methods remains between 50 to 98% [11]. However, the biological treatment methods are the method of choice for removing ammonia from wastewater due to the possibility of operation at lower cost and co-application with other physical and chemical methods [1]. Extensive use and research have been promoted and conducted for the use of microbial fuel cells (MFCs) for the removal of ammonia nitrogen from the wastewater [1,2,5,12,13]. MFC, an example of a bio-electrochemical system (BES), is an emerging technology with which not only can the purification of pollutants be achieved but, also, it has the capacity to produce electricity while simultaneously treating wastewater [1,13]. For the removal of ammonia from wastewater, the MFC is an integrative and sustainable approach that relies on the microbial activity for ammonia removal and, simultaneously, by oxidation of the wastewater organic matter at the anode, the microbial biofilm can also release electrons that flow through an external circuit to the cathode [14]. Hence, by employing indirect oxidation via electrochemical processes, biological oxidation by nitrifying bacteria, and pH-driven ammonia stripping, ammonia removal mechanisms are activated and, simultaneously, electric current can be generated. This puts MFCs application into a superior place for ammonia removal as a promising alternative to conventional methods by combining wastewater treatment with energy recovery, potentially reducing sludge production and even enabling nutrient recovery.

Ammonium ions at the anode chamber of a two-chambered MFC can be removed by microbial growth and their transport across the CEM to the cathode compartment [15]. In MFCs, if CEM is used, cations such as protons, sodium ions, and ammonium ions will migrate from the anode to the cathode [2,16]. During electricity generation, the cathodic reaction results in the rise of catholyte pH up to 11–12, which facilitates the conversion of ammonium to free ammonia for subsequent recovery by stripping [2]. Applying these mechanisms, a series of studies were conducted in MFCs to remove ammonia nitrogen from wastewater [2,12,13,15,16]. Despite rigorous studies about the removal of ammonia nitrogen in MFCs, there still exist issues and challenges [16]. For example, the transport of ammonium ions and ammonia in two-chambered MFCs is not clear [15,17]. When a CEM is used, not only ammonium ions pass through it but, also, many different cations are transported to the cathode via CEM, presenting a possible abiotic mechanism of ammonium loss from the anode chamber in an MFC [1,16]. The use of a proton exchange membrane (PEM) was not previously examined to determine the importance of ammonia nitrogen removal or recovery in MFCs. Anaerobic oxidation of ammonium ions has not been sufficiently examined in the cathode chamber of MFCs. At present, ammonia recovery through stripping in the cathode chamber of MFCs incurs high costs. If removal or recovery of ammonia nitrogen is possible through an anoxic pathway, such a system will offer the advantage of saving costs during biological nitrification. Therefore, the main objective of this study was to investigate different factors affecting ammonia nitrogen removal in MFCs under various conditions. Ammonium removal in the MFCs was investigated under the condition of an aerobic and anaerobic cathode chamber.

2. Materials and Methods

2.1. MFC Configuration and Operation

2.1.1. Effect of Different Membrane Type in Ammonium Diffusion

An H-type two-chamber MFC was assembled by joining two Scott Duran glass bottles with a working volume of 120 mL. The MFC contained two side ports on either side of the chambers for sampling. PEM (PFSA D170-U, Fuel Cell Store, Bryan, TX, USA) and CEM (CMI 7000, Membrane International, Ringwood, NJ, USA) with 8.04 cm^2 were used in the experiments. Before use, CEM was pretreated by immersing in a 5% sodium chloride solution for 12 h while PEM was pretreated as described elsewhere [12]. Phosphate buffer saline (PBS) was used as an electrolyte in both chambers (Na_2HPO_4—4.03 g, NaH_2PO_4—3.44 g, $NaHCO_3$—0.5 g, and KCl—0.13 g, per liter), except with the addition of 85 mg/L NH_4Cl in the anode chamber to analyze the diffusion of ammonium ions from the anode to cathode chamber.

2.1.2. Effect of Circuit Connection and Different Electrode Material in Ammonium Removal

Dual-chamber H-type Scott Duran bottles were joined with a working volume of 120 mL. A carbon cloth (Fuel Cell Stores, Bryan, TX, USA) with a projected area of 2.5 cm^2 was used as the anode and cathode electrode. On the other hand, a carbon cloth (Fuel Cell Store, Bryan, TX, USA) having a projected surface area of 2.5 cm^2 that was coated with a Pt/C catalyst (0.2 mg/cm^2) was used as the cathode electrode unless otherwise stated. A copper wire (2 mm) was used as the current collector in both anode and cathode electrodes by connecting carbon cloth to it using conductive epoxy, Ecobond 56 C (Emerson and Cuming, Randolph, MA, USA), followed by waterproof nonconductive epoxy (Devcon, Solon, OH, USA). Both the chambers were inoculated with 5 mL of anaerobic sludge from the Chuncheon wastewater treatment plant (Republic of Korea) in phosphate buffer saline (PBS) solution (containing 4.33 g/L Na_2HPO_4, 3.04 g/L $NaH_2PO_4.2H_2O$, 0.31 g/L NH_4Cl, 0.13 g/L KCl, and 12.5 mL/L trace minerals solution). Open-circuit mode (OCM) was maintained by disconnecting the electrodes, whereas closed-circuit mode (CCM) was established by connecting the electrodes through a 1000 Ω resistor. These conditions were analyzed to evaluate ammonium ion removal via electron transfer.

2.1.3. Effect of Presence of Air in Ammonium Removal

In the cathode chamber after joining two Scott Duran glass bottles, the cathode chamber was analyzed for the effect of the presence of air in ammonium ion removal. To check the volatilization of ammonium ion, an MFC setup was operated in which MFC without air, meaning the cathode chamber was flushed with nitrogen gas to make anaerobic conditions, was compared with a cathode chamber provided with dissolved air. All the MFCs were operated in CCM by completing the external circuit using a 1000 Ω resistor and airflow was maintained at 20 mL/min (Dwyer adjustable flow meter). In MFCs, the external resistor serves as the electrical load, influencing current flow and electron transfer efficiency. A 1000 Ω resistor was selected to maintain a balance between stable voltage output and moderate current flow, preventing excessive voltage drops and system instability associated with lower resistances.

2.1.4. Effect of Headspace in Ammonium Removal

To analyze volatilization of ammonium ion, the headspace of a single bottle setup was analyzed. Two single bottle setups with an effective volume of 140 mL were investigated, one with and one without dissolved oxygen, to analyze the effect of air. The flow of air was maintained at 20 mL/min (Dwyer adjustable flow meter). Both the single bottles were autoclaved before experiment to avoid any type of contamination.

2.1.5. Effect of Applied Voltage in Ammonium Removal

The anode chamber was inoculated with 5 mL of anaerobic sludge taken from the Chuncheon wastewater treatment plant (South Korea) in a medium comprising 4.33 g/L Na_2HPO_4, 3.04 g/L $NaH_2PO_4.2H_2O$, 0.31 g/L NH_4Cl, 0.13 g/L KCl, 12.5 mL/L trace minerals solution, and 10 mM sodium acetate. Except acetate, the same electrolyte along with 5 mL of anaerobic sludge as inoculum was used in the cathode chamber. MFCs were operated with an aerating cathode to enrich electroactive bacteria in the anode chamber for a few weeks. An external resistance of 1000 Ω was connected between the anode and cathode electrodes to complete the electric circuit. MFCs were operated at a temperature of 30 °C in an incubator in fed-batch mode and the sodium acetate was added to the anode chamber when the voltage decreased to <20 mV. Once the MFC reached a stable phase, it was converted into a microbial electrolysis cell (MEC) by connecting a 10 Ω resistor at the anode. Two different external voltages (0.8 V and 1.0 V) were applied to evaluate their effect on ammonium removal. We selected 0.8 V and 1.0 V as they optimize electron transfer, enhance microbial ammonium removal, and minimize energy loss and undesirable side reactions. This voltage range is widely applied in MEC studies to improve nitrogen and organic pollutant degradation efficiency. Figure 1 shows the parameters investigated for ammonium removal in MFCs.

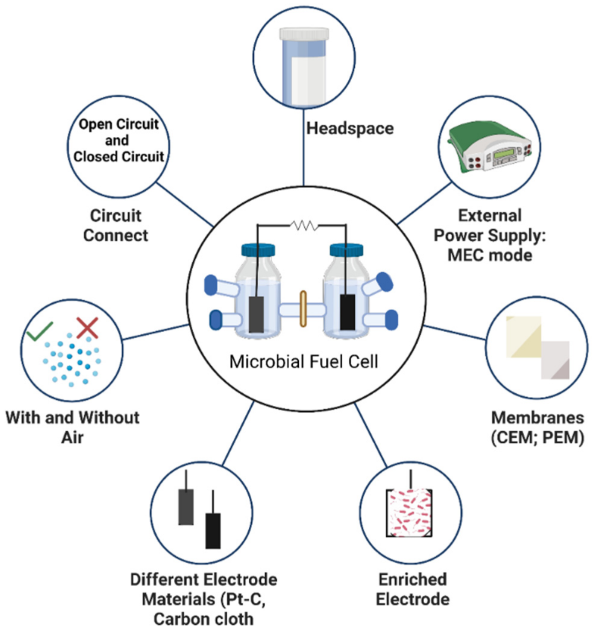

Figure 1. Impact of various parameters for ammonia removal efficiency in MFCs.

2.2. Analyses and Calculations

The potential generated was measured every 10 min using a digital precision data acquisition system (Model 2700 Keithley Instruments, Inc., Cleveland, OH, USA) integrated into a personal computer. The current generation was calculated using Ohm's law, i.e., I = V/R, where I (A) is the current, V (V) is the voltage, and R (Ω) is the external resistance.

pH was measured with an Orion Research pH meter (920A, Orion Research Inc., Boston, MA, USA). Ammonium ion was measured with an Orion Research ammonia electrode (920 A, 9512HPBNWP, Thermo Fisher Scientific Inc., Waltham, MA, USA). Nitrite and nitrate concentrations were determined using ion chromatography (IC) (Metrohm, AJ Eindhoven, The Netherlands). IC sample was filtered through a 0.45 μm filter before analysis.

2.3. Statistical Analysis

To guarantee the repeatability and dependability of the findings, every experiment was carried out in triplicate. To ascertain if the differences between the experimental groups were statistically significant, the acquired data were subjected to one-way analysis of variance (ANOVA). Statistical significance was defined as a significance level of $p < 0.05$. To find particular differences across groups, Tukey post hoc analysis was used. The SPSS program version 21.0 was used for all statistical analyses.

3. Results and Discussion

3.1. Ammonium Diffusion in Two-Chambered MFCs

Ammonium ions can be transported over the membrane to sustain a charged equilibrium across the anode, where protons are produced, and the cathode, where protons are consumed [13]. To investigate the diffusion of ammonium ions through membranes, ammonium concentration was monitored in two-chambered MFCs without electrodes and bacteria (Figure 2). Two different membranes were studied for comparison. MFC1(a) was constructed with CEM and MFC1(b) was constructed with PEM. The anode and cathode chambers were filled with MFC medium closed with a cap and then autoclaved. In the anode chamber, the initial ammonium concentration was fixed at 80 mg/L, whereas, in the cathode chamber, the initial ammonium concentration was 0 mg/L. In both MFC1(a) and MFC1(b), ammonium concentration gradually decreased in the anode chamber and increased in the cathode chamber. The diffusion process was slightly high in the MFC1 with the CEM, diffusing 84.2% of the ammonium to the cathode chamber. In the case of MFC having PEM, 72.4% of the ammonium was diffused into the cathode chamber. This finding indicated that the pore size of CEM facilitates ammonium movement through the MFC more easily when compared with PEM. Comparative study with other types of separators is needed to choose the more efficient one to remove ammonium.

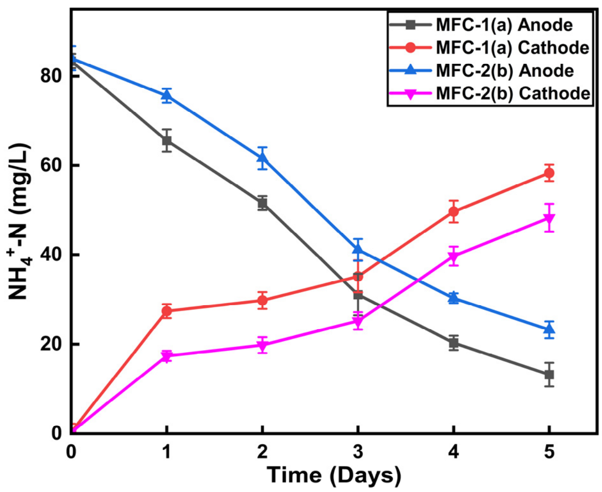

Figure 2. Ammonium diffusion in two-chambered MFC (abiotic condition) without electrodes using two different membranes: MFC-1 (a) (CEM) and MFC-1 (b) (PEM).

The characteristics of both water and ammonia molecules are fairly comparable. Both molecules are polar, with identical sizes (2.60 Å for ammonia and 2.65 Å for water), dipole moments (1.47 D for ammonia and 1.85 D for water [18]), and the ability to create hydrogen bonds. In fact, they share identical molecular orbital orientation. Because of this similarity, ammonia may pass across biological membranes that are specific for the movement of water [19]. Furthermore, research indicates that the same precise process of proton transfer that occurs in water may also occur in ammonia mediums. It was demonstrated that the Grotthus-type proton hops over a "ammonia wire" incorporating NH_3 molecules. There are not many theoretical investigations in this area, despite scientific proof of the peculiar nature of systems involving ammonia-containing fluids [20].

Liu et al. [16] investigated analytically and conceptually a comparable process of ammonium transfer over a cation-exchange membrane (CEM), accounting for protonation–deprotonation kinetics. During the investigation, it was discovered that, while the ammonium concentration in the cathode chamber stayed nearly constant and near zero, the ammonium concentration in the anode chamber dropped as a result of its movement via the CEM to the cathode chamber. The splitting of ammonium ions and subsequent conversion in the ammonia molecules in the cathode chamber, where OH^- creation on this electrode was the reason for the elevated pH value, was the proposed reason for this phenomenon [20,21]. Additionally, for future research, the Grotthus model may help to figure out how nitrogen moves through biological cell membranes [20].

3.2. Effect of Circuit Connection and Electrode Materials

Another study was set up based on the circuit connection by using two-chambered MFCs with the aerating cathode. For close-circuit mode (CCM), a 1000 Ω resistor was used to complete the external circuit of MFC, whereas, for open-circuit mode (OCM), the external circuit was kept open without any resistor or any connection between the two electrodes. Two different types of electrode materials (Pt-coated carbon cloth and plain carbon cloth) were also investigated. The experiment was conducted with bacteria using a mixed culture (enriched anode electrode). MFC 2(a) was constructed using Pt-coated carbon cloth in the cathode, whereas MFC 2(b) was constructed using carbon cloth; both were operated in CCM (Table 1). For OCM, MFC 2(c) and MFC 2(d) were constructed using Pt-coated carbon cloth and plain carbon cloth, respectively. The initial and final anode pH in CCM and OCM MFCs ranged from 6.9 to 7.1.

Table 1. Specification of the different parameters analyzed in this study.

S. No.	Anode	Cathode	Membrane	Circuit Connection	Air Sparging	MEC Mode	Inoculum (Anode Chamber)	Inoculum (Cathode Chamber)
MFC 1(a)	X	X	CEM	X	X	X	X	X
MFC 1(b)	X	X	PEM	X	X	X	X	X
MFC 2(a)	CC	Pt-C	CEM	CCM	O	X	O	New carbon cloth
MFC 2(b)	CC	CC	CEM	CCM	O	X	O	New carbon cloth
MFC 2(c)	CC	Pt-C	CEM	OCM	O	X	O	New carbon cloth
MFC 2(d)	CC	CC	CEM	OCM	O	X	O	New carbon cloth
MFC 3(a)	CC	Pt-C	CEM	CCM	O	X	O	Enriched Cathode
MFC 3(b)	CC	CC	CEM	CCM	O	X	O	Enriched Cathode
MFC 3(c)	CC	Pt-C	CEM	CCM	X	X	O	Enriched Cathode
MFC 3(d)	CC	CC	CEM	CCM	X	X	O	Enriched Cathode
MEC (0.8 V)	CC	Pt-C	CEM	MEC	O	O	O	O
MEC (1.0 V)	CC	Pt-C	CEM	MEC	O	O	O	O
MFC 4(a)	CC	Pt-C	CEM	CCM	O	X	X	X
MFC 4(b)	CC	Pt-C	CEM	CCM	O	X	X	X

The initial ammonium concentration was around 80 mg/L in both the anode and cathode chambers. When the MFC was operated in CCM, slightly higher ammonium removal was observed than in the OCM-operated MFC (Figure 3). In MFC 2(a) (CCM), ammonium ion decreased by 79% in the anode chamber and 96% in the cathode chamber over the 5 days of operation. Meanwhile, in MFC 2(c) (OCM), ammonium decreased by 60% in the anode chamber and by 76% in the cathode chamber. On the other side, MFC 2 (b) with carbon cloth cathode electrode (CCM) showed 70% ammonium reduction in the anode chamber and 87.1% in the cathode chamber, whereas, in MFC 2(d), a decrease of 45% in the anode chamber and 66% in the cathode chamber was observed. The slightly better ammonia nitrogen removal in the CCM as compared with the OCM may be either due to nitrogen loss occurring by volatilization from air sparging or the conversion of ammonium ions to free ammonia in the cathode [7,8]. This result indicates that one potential pathway for ammonia nitrogen removal could be the circuit connection, as the electron movement facilitates the ammonium ion migration from the anode to the cathode by the electric field in the two-chambered MFCs.

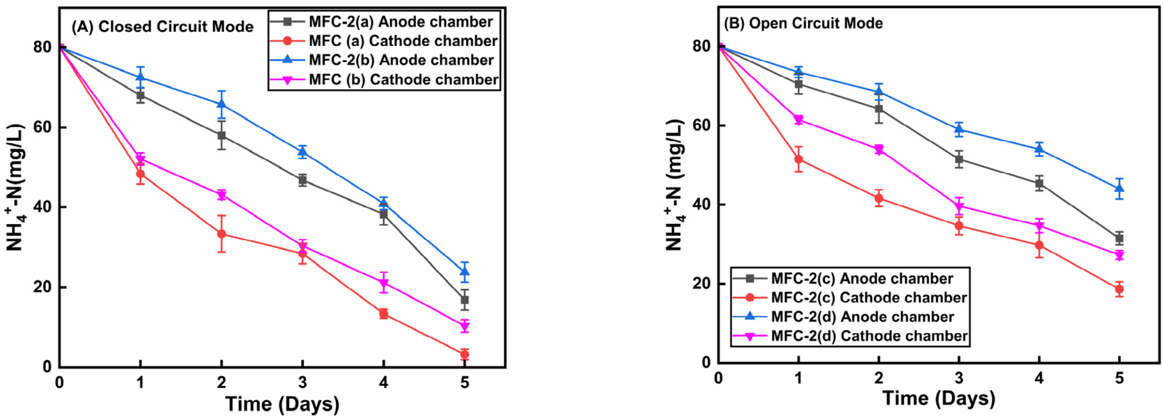

Figure 3. Analysis of ammonium concentration in the MFCs with bacteria under (**A**) closed-circuit mode and (**B**) open-circuit mode.

The most popular conductive materials for these kinds of cathodes are platinum mesh, paper, carbon cloth, and so forth. Furthermore, the binders that attach the catalysts to the electrode must meet a few requirements [22]. The high cost of employing cathodes with catalysts is one of its disadvantages [23]. Zhao et al. [24] constructed a cathode using a Pt catalyst and carbon cloth. According to the findings, the power efficiency of this catalyst was 1.2 W/m^3. According to Wang et al. [25], carbon paper with a Pt catalyst produced a power efficiency of 457.8 ± 15.2 mW/m^2. Platinum is a highly efficient catalyst that lowers the activation energy for the oxygen reduction reaction (ORR), thereby accelerating reaction rates. Pt nanoparticles offer a high density of active catalytic sites, significantly improving reaction efficiency compared to noncoated carbon cloth. Additionally, Pt exhibits a high exchange current density, facilitating rapid electron transfer between the electrode and electrolyte. Its use also minimizes overpotential, enhancing energy efficiency and reducing power losses in MECs. As a result, the anode and cathode materials can act as catalysts to reduce oxygen. Because of their lack of overpotential, platinum and gold are regarded as possible catalysts; nevertheless, their expensive cost renders them inappropriate [26,27]. Further research is needed to understand the mechanism underlying platinum's superiority in oxygen reduction and the relationship between electron transfer and ammonium migration.

During long-term MFC operation, Pt catalyst can degrade due to dissolution, sintering, or detachment from the electrode surface. Biofouling and inorganic scaling (e.g., deposition of proteins, extracellular polymeric substances, or metal ions) can reduce Pt's catalytic efficiency. Strategies like periodic electrode cleaning, alloying Pt with other metals (e.g., Pt–Ir and Pt–Ru), or using Pt-free catalysts can mitigate these effects [28]. Also, using nonprecious metal catalysts (e.g., Fe-N-C, cobalt oxides, and conductive polymers) can lower material costs while maintaining catalytic activity. Carbon-based electrodes (e.g., activated carbon, graphene, and carbon nanotubes) are promising but require optimization to match Pt performance. Since membrane fouling increases operational costs due to frequent cleaning and replacement, effective management strategies are essential. Cleaning methods such as acid washing, backflushing, and enzymatic treatments help extend membrane life but add to maintenance expenses [29]. To mitigate these challenges, alternative approaches include using low-cost separators (e.g., glass fiber and cloth-based materials) or enhancing membrane properties through hydrophilic coatings and antifouling surface modifications.

3.3. Effect of Dissolved Oxygen and Headspace

Oxygen promotes the volatilization of ammonia nitrogen; keeping this in mind, four MFCs were constructed using mixed inoculum to study the effect of oxygen under aerobic and anaerobic cathodic conditions. MFCs were operated in fed-batch mode and, for substrate, acetate was used in the anode chamber. All the MFCs were operated in CCM by completing the external circuit using a 1000 Ω resistor and airflow was maintained at 2 mL/min (Dwyer adjustable flow meter). The initial concentration of ammonium was kept at ~80 mg/L in all the MFCs (MFC3-a, b, c, and d). The ammonium concentration decreased by 73.3% in the anode chamber and by 94.5% in the cathode chamber after 5 days of operation in the MFC3 (a). In MFC3 (b), the ammonium concentration was reduced by 57.4% in the anode and 81.1% in the cathode chamber. Use of the Pt-coated cathode electrode along with aeration removed 94.5% of the ammonium ion in the cathode chamber, whereas 81.1% of the ammonium was removed in the cathode chamber of the MFC with plain carbon cloth cathode electrode (Figure 4).

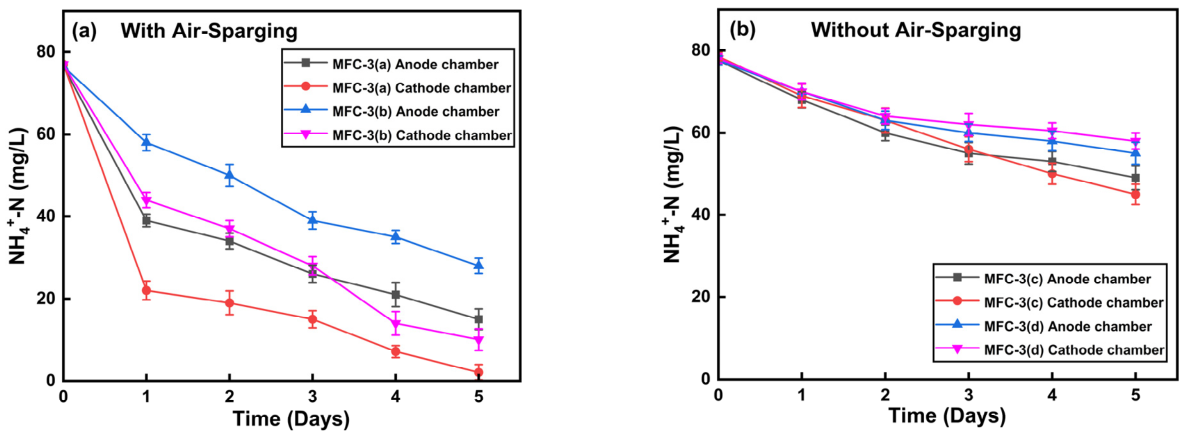

Figure 4. Concentration of ammonium in the MFCs with Pt (3(a), (c)) and carbon cloth (3(b), (d)) as electrodes: (**a**) aerobic (flowrate was maintained at 2 mL/min.) and (**b**) anaerobic conditions in the cathode.

To see the effect of oxygen on ammonia nitrogen removal, MFC 3 (c,d) was operated without aeration in the cathode chamber (no air sparging). Before sealing the cap, the cathode chambers of the MFCs were flushed with nitrogen gas (N_2) for 10 min. There was a significant change in the ammonium removal concentration in the MFCs without aeration at the same electrode condition. The ammonium concentration decreased by 35% in the Pt-coated cathode chamber (MFC 3c), while the ammonium concentration decreased by 23% in the carbon cloth cathode chamber (MFC 3d) (Figure 4). These results show that, in the absence of oxygen (aeration), ammonia nitrogen removal is not effective regardless of the electrode materials used in the MFCs.

Nitrite and nitrate concentrations were also monitored in all the MFCs. The concentrations of nitrite and nitrate were detected as less than 3.0 mg/L in all the anode chambers of the MFCs. Interestingly, the nitrification process was observed in the cathode chamber of the MFCs. The nitrate concentration increased from 0 to 105 mg/L in the cathode (Pt-coated electrode) chamber with aeration (MFC 3a). Similarly, the nitrate concentration increased from 0 to 83 mg/L in the cathode (plain carbon cloth, MFC 3b) chamber with aeration after 5 days of operation (Figure 5). However, in the absence of aeration, the nitrate concentration was less than 20 mg/L (MFC 3c, d). This result indicates that abiotic nitrification is partly responsible for ammonia nitrogen removal in the MFCs.

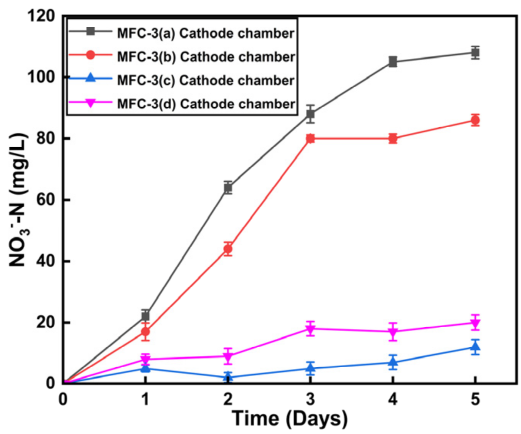

Figure 5. Analyzing bacterial activity on the formation of nitrate in the cathode chamber under aerobic and anaerobic condition.

Figure 6 presents the polarization curve comparing Pt-coated carbon and plain carbon cloth electrodes. The Pt-coated carbon electrode exhibited a higher voltage of up to 810 mV when air was sparged into the cathode chamber, with a corresponding power density of 446.5 mW/m^2. In contrast, the plain carbon cloth electrode showed significantly lower performance, with a voltage of 290 mV and a power density of 201.5 mW/m^2, highlighting the superior efficiency of the Pt-coated carbon in the MFC system. Xie et al. [30] demonstrated that the greatest ammonium–nitrogen conversion rate achieved by ammonia-oxidation microbial fuel cell (AO-MFC) throughout operation was 99.7%. In the steady phase of electricity production, the output voltage and power density were 98.5 $\pm$ 1.41 mV and 9.70 $\pm$ 0.27 mW m^2. In order to initiate ammonia oxidation, synthesize ATP, and produce electricity, the electrons from ammonia moved to ammonia monooxygenase, Cyt aa3 oxidase, and an electrode. The distribution of electrons among these three recipients was significantly influenced by molecular oxygen. It is also mentioned that, even when potassium permanganate was added to the catholyte, ammonia oxidation would not occur in the AO-MFC if the anolyte was not aerated. Hence, aeration in MFC increases overall ammonium removal efficiency. Further research needs to be conducted to analyze the saturation point at which no effective ammonium removal is observed even if the DO increases in the chambers.

Volatilization of ammonium ions might occur because of the presence of headspace in the MFC. To investigate whether headspace plays any role in ammonia nitrogen removal or not, a test was conducted in a single media bottle without electrodes (effective volume 140 mL). Two single media bottles were taken and filled with the media having an initial ammonium concentration of 83 mg/L. The experiment was conducted with aeration (air sparing) and without aeration (without air sparging). To avoid any contamination, the media bottles were autoclaved before the test. There was no significant change in the ammonium concentration in the media bottle with aeration and without aeration (Figure 7).

In the media bottle, with and without aeration, the ammonium concentration decreased by 8.4% and 4.8%, respectively, after 5 days of operation. This concludes that, in the absence of headspace, less ammonia nitrogen is removed from the MFCs due to a lack of space for volatilization. However, there is not much difference observed in case of headspace in our study; further study needs to be conducted to obtain some idea.

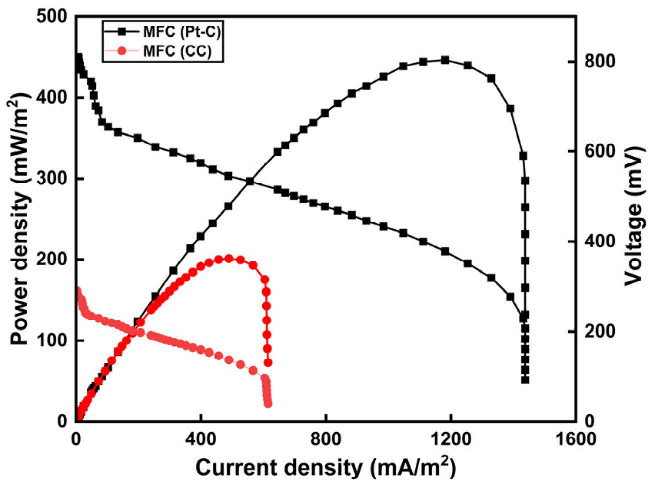

Figure 6. Polarization curve of Pt-C and carbon cloth (CC) (with air sparging).

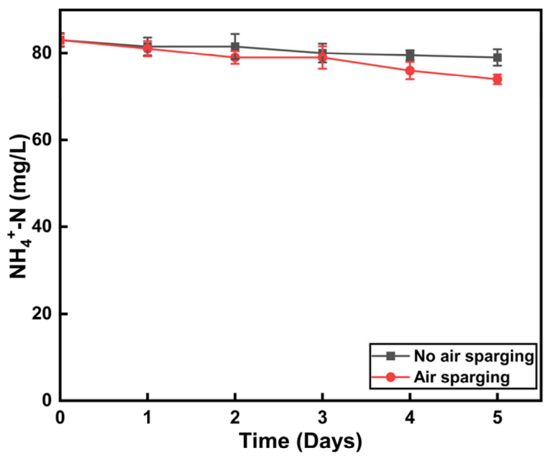

Figure 7. Effect of headspace in the single media bottle with and without air sparging.

3.4. Effect of Ammonium Removal at a Different Applied Potential

Two MECs were operated at 0.8 V and 1.0 V by applying external power. Both chambers of the MEC had enriched carbon cloth electrodes in the anode and Pt-coated electrodes in the cathode (air sparging). The ammonium concentration decreased from 80 mg/L to 10 mg/L in the cathode chamber operated at the voltage of 1.0 V (Figure 8), whereas the ammonium concentration decreased from 80 mg/L to 36 mg/L in the cathode chamber operated at the voltage of 0.8 V. A high ammonium concentration removal rate was observed in the cathode chamber of the MEC operated at the voltage of 1.0 V, achieving 87.5% of the ammonium removal efficiency. This result indicates that a high external power supply to the MEC can facilitate higher ammonia nitrogen removal in BES. The efficiency of ammonium removal in microbial electrolysis cells (MECs) is strongly influenced by the applied voltage, which drives electrochemical oxidation at the anode and hydrogen evolution at the cathode. While a higher voltage can enhance electron transfer and facilitate ammonium oxidation, it also promotes competing parasitic reactions such as nitrate and nitrite reduction, excessive hydrogen evolution, and oxygen reduction at the cathode. These side reactions can lower energy efficiency and hinder ammonium removal performance. Therefore, precise optimization of applied voltage and electrode materials is essential to maximize ammonium removal while minimizing energy losses and undesirable redox processes. In MEC mode, ammonium was mainly converted to nitrite, since nitrite was detected in the cathode chambers. The nitrite concentration increased from 0 to 105 mg/L in the cathode chamber of MEC1 (with 1.0 V) and from 0 to 66 mg/L in the cathode chamber of MEC2 (with 0.8 V) (Figure 9). In all the MEC solutions, the nitrate concentration remained lower than 3 mg/L throughout the experiment. In-detail study is needed, in case of ammonium removal by external supplied power and the process behind it. Bio-electrochemical systems (BESs) for ammonium removal are often studied using synthetic wastewater and short-term experiments, which lack the microbial diversity, competing ions, and organic contaminants present in real wastewater. These limitations prevent accurate assessment of long-term stability, electrode degradation, and energy efficiency. Future research should focus on pilot-scale trials and mixed wastewater treatment to evaluate system performance in complex environments. Additionally, optimizing electrode materials and operational parameters will enhance efficiency and scalability for practical wastewater treatment applications.

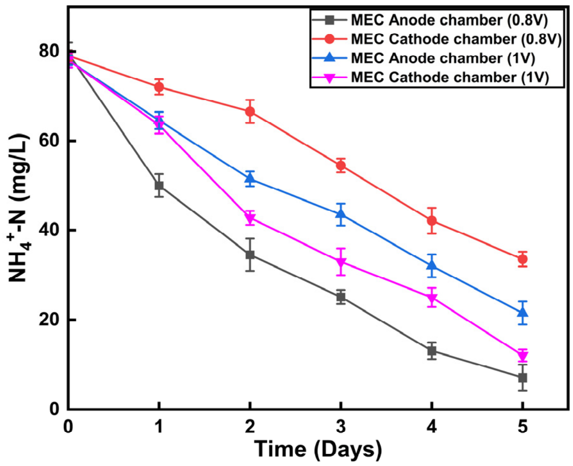

Figure 8. Effect of ammonium removal at the applied voltage of 0.8 and 1.0 V.

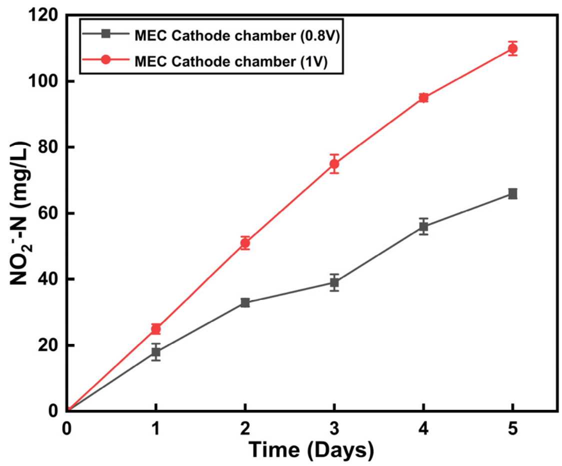

Figure 9. Analyzing bacterial activity on the formation of nitrite in the cathode chamber under MEC mode (0.8 and 1 V).

Kondaveeti et al. [31] stated that, to assess their impact on MEC performance in batch mode, MEC processes were carried out at various applied voltages (0.7 to 1.5 V) and starting ammonia concentrations (30 to 150 mg/L). The anode had the highest nitrification efficiency of 96.8% at 1.5 V, 94.11% at 1.0 V, and 87.05% at 0.7 V. Koffie and Okabe [32] stated that, at an applied voltage of 0.8 V (the anode potential Eanode = +0.633 ± 0.218 V vs. SHE), the MEC exhibited a TN reduction rate of 95 ± 42 g-TN m^3 d^1 and an NH_4^+-N oxidation rate of 151 ± 42 g NH_4^+-N m^{-3} d^{-1} without oxygen. The power supplied had a positive correlation with both the NO_3^-–N decomposition rate and the NH_4^+–N conversion rate. The findings contradicted the notion that appropriate electrical activation might increase microbial metabolism and improve biochemical efficiency [33]. The clearance rates of TN and ammonium also showed erratic patterns in comparison to nitrate. The MFC's cathode underwent electrode denitrification by anaerobic denitrification bacteria, as evidenced by the greater NO_3^--N generation and TN removal efficiency under high applied voltage circumstances [11]. A study demonstrated that carbon-nanopowder-coated electrodes without Pt showed significantly enhanced performance compared to plain electrodes for hydrogen evolution in solar-powered MECs. At applied photovoltages exceeding 0.7 V, the hydrogen conversion efficiency was almost comparable between plain carbon felt (71.3–77.0%) and Pt-loaded carbon felt (79.3–82.0%) [34]. Carbon-based anodes have been reported to achieve higher removal efficiencies for ammonia and phosphorus, reaching 98% and 99%, respectively, in bio-electrochemical systems (BESs) [35]. For instance, Fe–N–C structures, Fe phthalocyanine (FePc), and transition metal oxides (TMOs) have demonstrated high oxygen reduction reaction (ORR) activity, while AC has proven cost-effective and durable, outperforming Pt in polluted environments. PGM-free catalysts with optimized loading also enhance performance metrics like half-wave potential and current density. Additionally, carbon-based electrodes have shown high nutrient removal efficiencies (up to 99%), further supporting their viability as sustainable alternatives to Pt in MECs. These findings highlight the potential of Pt-free catalysts for cost-effective and efficient wastewater treatment applications. Future studies are required to analyze the use of different electrode material coupling with external power to achieve great results in the field of ammonium removal in MFC.

4. Conclusions

In the present study, various factors affecting ammonia nitrogen removal in MFCs were explored. Experimental results demonstrated that the use of CEM as a membrane in the MFCs is more efficient in diffusing ammonium ions from the anode to the cathode than PEM. Circuit connection also played a vital role in the removal of ammonium ions from MFCs with enriched anode electrodes. In CCM, 27.5% of ammonium ions were removed in the anode chamber, while, in OCM, only 19.8% of ammonium ions were removed in the anode chamber, which indicates that the movement of electrons enhances the removal rate of ammonium. The study results showed that there was a significant difference in the removal of ammonium ions in the MFCs with and without air sparging. An ammonium removal efficiency of 95% was achieved in the cathode chamber with aeration (Pt-coated electrode), while only 35% of ammonium removal efficiency was achieved in the cathode chamber (Pt-coated electrode) without aeration. In MEC mode, a high-power supply greatly enhances the removal rate of ammonium ions. Conclusively, Pt-coated cathode electrode along with aeration was useful for removing ammonia nitrogen from domestic wastewater using BES.

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