



Impact of different external resistance, substrate and salt concentration on wastewater treatment and power generation in microbial desalination cell

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ABSTRACT

The increase in the population and rapid industrialization generates a significant amount of wastewater which should be treated economically. Microbial desalination cell (MDC) is a kind of technology that can treat wastewater and generate power simultaneously. It was observed that many experimental studies were lacking in findings of the variation of basic input conditions on the MDC efficiencies. The aim of the present study was to explore the impact of external resistance, electrolyte solutions and substrate concentration on power generation in an MDC system. The experimental study was conducted by using medium to high strength wastewater from distillery and brewery industry in batch-wise operation. The analysis of which resulted in medium to high-strength wastewater. The data was collected based on the experimental setup conditions. Application of different resistances on the MDC, best resulted in 82% COD removal and 57% TDS removal with 500 Ω external resistance. A COD and TDS removal efficiency of 83% and 61% was identified with an electrolyte concentration of 35,000 mg/L. The variation of substrate concentration reported a maximum COD removal of 86%, TDS removal of 62%, and current, and voltage of 1.872 mA and 628 mV with 1,500 and 8,000 mg/L, respectively.

Keywords: External resistance; Industrial wastewater; Microbial desalination cell; Salt concentration; Substrate concentration

1. Introduction

Around 97% of the water available on the planet is seawater, where the salt concentration is 35,000 ppm by weight. Less than 1% of total freshwater is accessible by humans, which is insufficient to meet the needs of the present generation. There are various methods for the removal of salt from the water such as membrane-based separation, thermal-based separation, and biological treatment. However, most of the conventional techniques for salt removal are not economically viable and/or difficult to execute on a

larger scale. When compared to the traditional methods, microbial desalination cell (MDC) offer unique advantages such as lower operation cost and effective treatment of the wastewater simultaneously. Treatments such as reverse osmosis, desalination, and electrodialysis are ineffective for industrial wastewater containing higher concentrations of organics, which can cause frequent fouling of the nanopores and choking of membrane stack [1,2]. MDC technology is the sustainable method of removing salts as this utilizes only microorganisms to degrade the organics, transfer the electrons and generate electricity from wastewater [2,3].

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Microbial desalination cell consists of an anode, a cathode chamber and a desalination chamber set at the middle of it [4,5]. The desalination chamber separates the anode and cathode chambers with anion exchange membrane (AEM) and cation exchange membrane (CEM), where the anion and cation from desalination chamber will move towards anode and cathode chambers, respectively [6]. The microbial culture contained within the anode for oxidation of the organic matter produces electrons and protons, which are then consumed in the cathode compartment to generate bioelectricity [7]. The three chambered MDC system has shown viability for actual use, but still requires additional improvements [8,9]. To improve the MDC performance, energy generation and desalination efficiency, many MDC configurations have been reported in the literature review presented in the current study [10–13].

Ragab et al. [14] conducted experiments using MDC with varying external resistance and substrate concentration, where they have reported a maximum voltage of 858 mV with substrate concentration 1,500 mg/L. They concluded that, with the increase in the external resistance for a short batch operation, maximum COD removal can be achieved. Zuo et al. [15] conducted studies using a multi-stage MDC system for the removal of organics and treatment of industrial wastewater for desalination. The result of the study reported COD removal of 97.8% with desalination efficiency of 51.7%. The reason for the higher removal efficiency was due to the alternative aerobic/anaerobic conditions provided in the experimental setup. The desalination of the wetland saline water study was reported by Salman and Ismail [16]. The maximum TDS removal of 86% with the synthetic saline water of 4,000 mg/L and power density of 527 mW/m² was reported with saline water concentration of 15,000 mg/L. The reason might be due to the presence of the extra ion which increased the ion exchange capacity in the reactor. Li et al. [17] studied the efficiency of the microbial electrolytic cell (MEC) for the desalination and nutrient removal from the municipal wastewater. They have reported a maximum COD removal of 75.5% with coulombic efficiency (CE) of 8.5% due to the stack configuration of the MEC reactor. The same technology could remove nitrate and phosphate from the wastewater sample. The unique study by Iskander et al. [18] for the improvement of forward osmosis and recovery of ammonia using MDC technology reported a maximum 24.3 mmol ammonia recovery with 64.3 recovery efficiency. The MDC system treated water improved the forward osmosis performance with the maximum water extraction. The experiment conducted by Luo et al. [19] with the comparison of microbial fuel cell (MFC) and MDC showed the MDC performance was 4 times higher than the MFC. The COD removal efficiency and CE was improved by 52% and 131%, respectively, which might be due to the presence of a diverse microbial community in the anode section. Santoro et al. [20] reported the COD removal efficiencies were ranging from 73%–83% with the presence of platinum (Pt) based metal catalyst for the anode chamber. In the same study, they have reported an increase in the pH of the desalination and cathode chamber with time. Therefore, it is especially important to investigate how substrate and salt concentration affects MDC performance in terms of removing pollutants and producing electricity.

The literature survey showed very few studies were conducted on the impact of external resistance, substrate concentration and electrolyte concentration on the desalination efficiencies. The correlation between these factors was not so well defined and how these could impact the performance was not explained with sufficient justifications. The experiments which were conducted most of them utilized synthetic wastewater and there were high variations in the reported results. To explore and stabilize these conditions, the main aim of the present study was to conduct a detailed analysis on variation of different external resistance, substrate concentration on the electricity generation from real industrial wastewaters and desalination process. However, an attempt was also made to understand the influence of different salt concentrations on the desalination efficiencies. The study provides insight on the upgradation of the present MDC techniques and to give solutions on the critical considerations for maximizing the efficiencies. The study was to explore the best-case scenario to treat the brewery and distillery industrial wastewater with maximum power output and efficient treatment which can be integrated in the existing treatment plants.

2. Materials and methodology

2.1. Sample analysis

In the present study distillery industrial wastewater, that is, spent wash was collected from Bannari Amman Sugar Industry (distillery unit), Alaganchi Village, Nanjangud, Mysuru, Karnataka, India. However, brewery industrial wastewater was collected from United Breweries Ltd, Thandya Industrial Area Chikkayana Chatra, Nanjangud, Mysuru, Karnataka, India. Initial sample characterization was conducted in the process and analysis lab, Department of Environmental Engineering, JSS Science and Technology University, Mysuru and is presented in Table 1. It was

Table 1
Initial characteristics of spent wash from Bannari Amman Sugar Industry (distillery unit) and united brewery (UB) industrial wastewater

Parameter	Distillery wastewater	Brewery wastewater
Temperature, °C	27	24
pH	2.90	3.90
Conductivity, µS/cm	17,463	687
Salinity, ppt	13	516
Turbidity, NTU	22	72
TDS, mg/L	141,160	1347
TSS, mg/L	4,987	784
Total solids, mg/L	146,147	2,131
BOD 3 d@27°C, mg/L	37,185	745
COD, mg/L	127,360	3,733
Chloride, mg/L	6,748	498
Phosphate, mg/L	2,590	1,041
Sulphate, mg/L	2,738	1,463
Nitrate, mg/L	539	672

observed from the distillery spent-wash sample that the BOD was 37,000 mg/L and COD of 125,000 mg/L, which was implying an extremely high strength wastewater. The ratio of the BOD/COD was 0.29, which showed a poor biodegradability profile of the wastewater. On the other hand, brewery wastewater sample analysis showed BOD of 745 mg/L and COD of 3,733 mg/L, respectively. The BOD and COD analysis result showed the sample was medium-strength wastewater, which can be biodegradable and incorporated in the present study.

The sea/saline water sample was collected from Kundapura, Udupi, Karnataka, India. Kundapura sea water was tested in Ganesh Consultancy & Analytical Services, Mysuru, Karnataka, India and the results are shown in Table 2. It was observed that the TDS was about 50,000 mg/L. It is inferred from a literature survey that most of the experiments were conducted with artificial saline water concentrations varying from 10,000 to 25,000 mg/L. Hence, in the present study different experiments were conducted by varying the salt concentrations to check the impact on the desalination efficiencies.

2.2. Material

In the present study, the reactor setup was made of plexi-glass with a thickness of 5 mm. The reactor setup was fabricated by RR Creation, Mysuru, Karnataka, India. Carbon rod electrodes (length 90 mm and diameter 15 mm) were procured from Vijaya Laboratory Requisites, Mysuru, India. Electrode surface was made rough and immersed into the deionized water for 24 h before its use in the experiment. In the present study, heterogeneous anion-exchange

membrane and cation-exchange membrane were used for the better ion transfer. The anion-exchange membrane (RA LEX® MEMBRANE AM(H)-PP) and cation-exchange membrane (RA LEX® MEMBRANE CM(H)-PP) were procured from Aquatreat Systems & Engineers, Delhi, India. Both the AEM and CEM were immersed into the deionized water for 12 h before using it for experimental study. Active anaerobic microbial culture was collected from the United Breweries Ltd., Mysuru, Karnataka. Microbial cultures are an important part of the MDC as this will digest the nutrients present in the wastewater and help in transferring the electron to the electrode. External resistance is one of the crucial factors that affect the performance of microbial desalination cells. External resistances were procured from Green Complex, Mysuru, Karnataka, India.

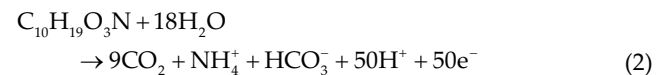
2.3. Reactor design

The designed MDC reactor had three chambers (Fig. 1) of volumetric ratios of 1:1:1, each chamber capacity with 300 mL and the total volume of the reactor was 900 mL. Anode chamber was kept anaerobic and the cathode chamber was aerobic in nature, hence it was open at top. Anode and cathode chambers were separated from the desalination chamber by AEM and CEM, respectively. Anode and desalination chambers were provided with taps for sample collection and analysis. The design was constructed using acrylic material of 5 mm thickness. The design of the reactor was made in such a way that this can be used in series connection or continuous mode of operation. The possible reactions in the MDC were considered:

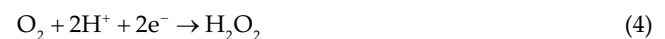
Anode



Wastewater:



Cathode



2.4. Operational condition

In the present study, ELICO LI127 pH meter was used from JSS S&TU process Lab. TDS and salinity meter of Labtronics microprocessor COND-TDS-SAL meter LT-51 was used for the TDS analysis. However, a handheld TDS meter of Remino imported TDS Meter was also used for analysis of the samples. Multimeter of DT830D LCD was used for the collection of voltage and current data. Voltage and current reading were logged in every hour with the help of a Datalogger (CEM DT-175CVS).

In the present study, three different conditions were considered. The impact of different external resistance (5, 100, 500 and 1,000 Ω), different electrolyte solution (5,000; 10,000;

Table 2

Initial characteristics of sea water used in the present experimental study

Test	Result	Test method
Sodium as Na, mg/L	6,630	IS: 3025 (P 44)
Magnesium as Mg, mg/L	1,390.08	IS: 3025 (P 46)
Potassium as K, mg/L	310	IS: 3025 (P 44)
Copper as Cu, mg/L	BDL (DL 0.01)	IS: 3025 (P 2)
Zinc as Zn, mg/L	BDL (DL 0.01)	IS: 3025 (P 2)
Iron as Fe, mg/L	0.38	IS: 3025 (P 53)
Manganese as Mn, mg/L	BDL (DL 0.01)	IS: 3025 (P 2)
Sulphur as S, mg/L	7.01	–
Chloride as Cl, mg/L	17,269	IS: 3025 (P 32)
Bicarbonate, mg/L	124	IS: 3025 (P 51)
Ammonia, mg/L	BDL (DL 0.5)	IS: 3025 (P 34)
Nitrogen as N, mg/L	0.54	IS: 3025 (P 34)
Total organic compound, mg/L	BDL (DL 10)	–
Sulphate as SO ₄ , mg/L	230	IS: 3025 (P 24)
pH value	8.14	IS: 3025 (P 11)
Nitrate as NO ₃ , mg/L	2.35	APHA (23rd ed.) P-4500NO3
Total dissolved solids, mg/L	49,260	IS: 3025 (P 16)
Total solids, mg/L	49,280	IS: 3025 (P 17)

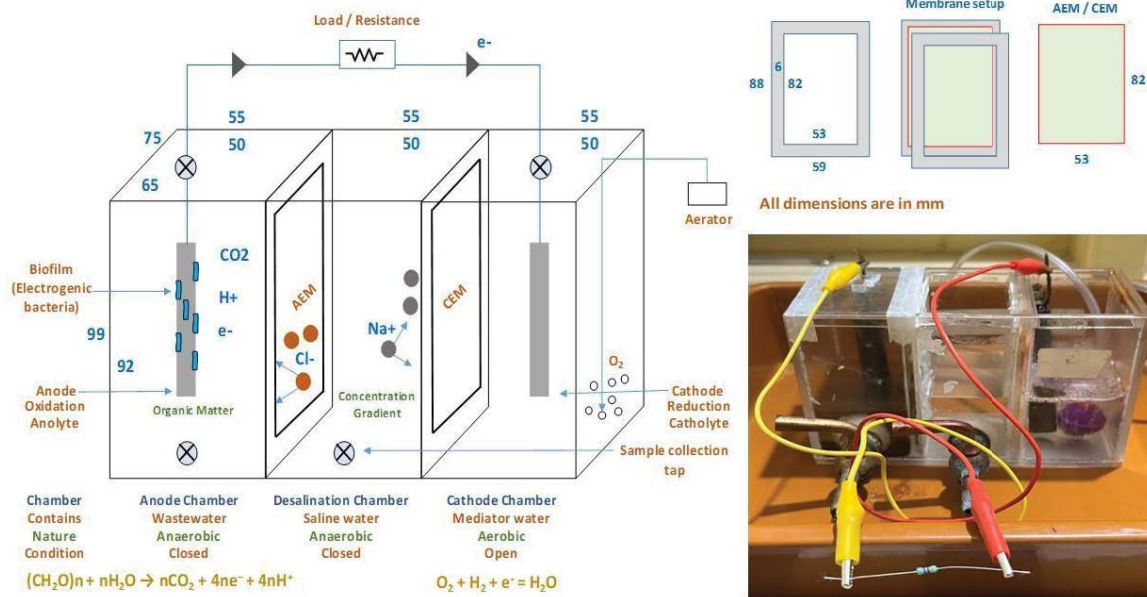


Fig. 1. Reactor design and experimental setup of the microbial desalination cell used in the present study.

20,000 and 35,000 mg/L) and different substrate conditions (1,500; 4,000; 8,000 and 12,000 mg/L) on the voltage and current generation were analyzed. An effort was also made to identify the COD and TDS removal efficiencies with the present experimental conditions. The current density, power density and coulombic efficiency were identified to analyze the best-case scenario for maximum power generation and treatment efficiencies.

The experimental setup was initiated with the placement of the reactor with the initial feeding of substrate and microbial culture in the anode chamber, electrolyte solution in the desalination chamber and tap water in the cathode chamber. Anode and cathode were connected with the external resistance. The voltage and current were measured on hourly basis with the help of datalogger. The pH and TDS of all the samples present in anode, desalination chamber and cathode were measured in every 4 h. The analysis of COD was conducted on daily basis. The collected data were recorded based on the different experimental conditions and utilized for the analysis and performance monitoring.

2.5. Performance evaluation

2.5.1. Ohm's law

The current (I) was calculated based on the Ohm's law with respect to the applied R_{ext} .

$$R_{ext} = \frac{V}{I} \quad (5)$$

$$I = \frac{V}{R_{ext}} \quad (6)$$

where R_{ext} = external resistance (Ω); V = voltage (mV); I = current (mA).

2.5.2. Nutrient removal efficiency (RE)

Percentage removal of COD in anode chamber are calculated by using Eq. (7):

$$\text{Nutrient}_{RE} (\%) = \frac{(\text{Nutrient}_{in} - \text{Nutrient}_t)}{\text{Nutrient}_{in}} \times 100 \quad (7)$$

where Nutrient_{RE} = removal efficiency of the nutrient (%); $\text{Nutrient}_{(in)}$ = concentration of the nutrient at inlet (mg/L); $\text{Nutrient}_{(t)}$ = concentration of the nutrient at outlet (mg/L).

2.5.3. Desalination efficiency (DE)

Percentage removal of salt from saline water in desalination chamber is calculated by using Eq. (8).

$$DE (\%) = \frac{C_i - C_f}{C_i} \times 100 \quad (8)$$

where C_i : initial salt concentration (mg/L); C_f : final salt concentration (mg/L).

2.5.4. Current density (CD)

The effect of current generated from the designed MDC reactor was calculated by normalizing the current values by the anode electrode surface area/volume of anode chamber using Eqs. (9) and (10).

$$CD_A \left(\frac{\text{mA}}{\text{cm}^2} \right) = \frac{I}{A_{sa}} \quad (9)$$

$$CD_v \left(\frac{\text{A}}{\text{m}^3} \right) = \frac{I \times 1000 \times 1000}{A_{vol} \times 1000} \quad (10)$$

where I = calculated current (mA or A); A_{sa} = surface area of anode electrode (cm^2); A_{vol} = volume of anode chamber (m^3).

2.5.5. Power density (PD)

The effect of power generated from the designed MDC reactor was calculated by normalizing the power values by the anode surface area/volume of anode chamber using Eqs. (11) and (12):

$$PD_A \left(\frac{\text{mW}}{\text{cm}^2} \right) = \frac{V^2}{R_{ext} \times A_{sa}} \quad (11)$$

$$PD_v \left(\frac{\text{W}}{\text{m}^3} \right) = \frac{V^2 \times 1000 \times 1000}{R_{ext} \times A_{vol} \times 1000} \quad (12)$$

where V : voltage (mV); R_{ext} : external resistance (Ω); A_{sa} = surface area of anode electrode (cm^2); A_{vol} = volume of anode chamber (m^3).

2.5.6. Coulombic efficiency (CE)

To evaluate the percentage coulombs contained in wastewater utilized to produce electricity is calculated by using Eqs. (13) and (14).

$$CE(\%) = \frac{8 \int Idt \times 1000 \times 1000}{FACOD \cdot Q \cdot T} \quad (13)$$

$$CE(\%) = \frac{C_p}{C_{th}} = \frac{M_{O_2} \int Idt \times 1000 \times 1000}{b \cdot FACOD \cdot A_{vol}} \quad (14)$$

where C_p : coulombic amount; C_{th} : total amount of electricity that can be theoretically obtained from simulated COD oxidation; M_{O_2} : molecular weight of oxygen (O_2) = 32 g; I : current (mA); b : number of electrons exchanged for oxygen used = 4; F : Faraday's constant = 96,485 C/mol; A_{vol} : volume of wastewater in anode chamber (mL); ΔCOD : change in COD concentration (mg/L).

3. Results and discussion

3.1. Effect of external resistance on MDC performance

3.1.1. Voltage and current generation

The impact of the external resistance on the voltage generation is shown in Fig. 2A. The maximum voltage of 656.25 mV was achieved for external resistance of 1,000 Ω . However, the maximum voltage of 565.5, 506.25 and 381 mV were observed for the external resistance of 500, 5 and 100 Ω , respectively. Most stable voltages were ranged from 500 to 600 mV for the external resistance 500 and 100 Ω . At the initial stage, the voltage was 312.5 mV, which increased to 656.25 mV at 73 h and then gradually decreased to 462.5 mV at 145 h.

In MDC, the voltage generation initially started low due to the build-up of microbial populations (73–273 mV) and the establishment of electrochemical gradients. As the system matured, microbial activity increased, leading to enhanced

ion transport and higher voltage generation (>500 mV). However, prolonged operation could lead to biofilm saturation, concentration polarization, and depletion of substrate, causing a decline in voltage production over time. The reason for the high voltage generation (656.25 mV) is due to substrate utilization and lower internal resistance of the system. It was observed that lower voltage was generated (506.25 mA) with the reduction in the external resistance. This could be as more electrons pass through the external circuit when the resistance is low. The generation of the voltage decreased with time (after 72 h) which might be due to the limited nutrient concentration present at the solution and microbial degradation of the wastewater.

In the research study of the Campo et al. [21] reported that with the increase in the external resistance from 120 to 560 Ω , there was a great increment in power from 3.76×10^{-4} to 1.57×10^{-3} mW. Similar observations were also made in the present study. However, Lyon et al. [22] showed that external resistance has considerable influence on the power generation. The maximum power was reported with 470 Ω external resistance followed by 100, 10,000 and 10 Ω . This study also represented the optimum external resistance which allows for the required electrons to pass and generate optimum voltage. An exceptionally low external resistance of 5 Ω allowed a higher current flow within the MDC. This high current could lead to significant internal losses, causing a voltage drop and resulting in low overall voltage and current generation. The high external resistance of 1,000 Ω limited the power transfer capability in the MDC. This high resistance value restricted the flow of electrons and decreased the overall power generation,

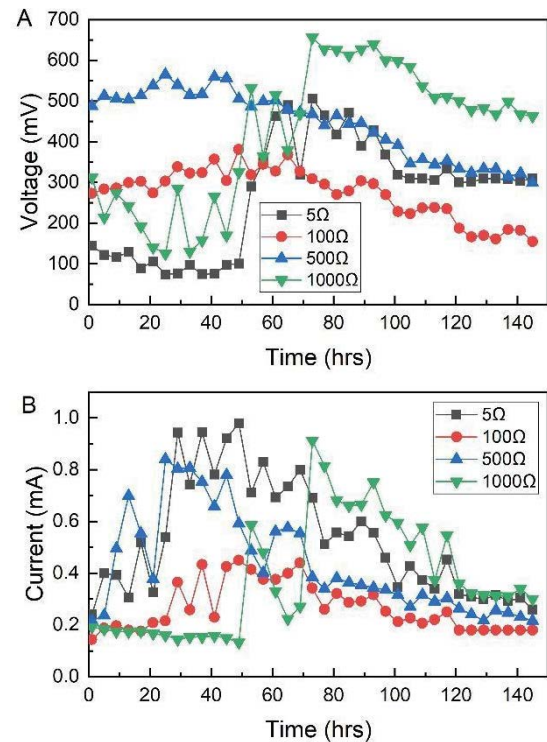


Fig. 2. Impact of 5, 100, 500 and 1,000 Ω external resistance on (A) voltage and (B) current generation.

resulting in low voltage and current generation. The 500 Ω external resistance represented a balance between low and high resistance. It allowed for optimal power transfer in the MDC, ensuring efficient conversion of microbial activity into electrical energy. In the same way, Al-Mamun [23] had conducted studies on the effect of external resistance on power generation. It was reported that, the voltage generation was maximum when the external resistance was 150 Ω and current generation was maximum when the external resistance was changed to minimum 10 Ω . The present experimental study showed a good agreement with the results found in the other scientific literatures.

The impact of current generation with the different external resistance was also checked in the present study and is shown in Fig. 2B. It was observed that, the maximum current of 0.98 mA was generated with the external resistance of 5 Ω followed by 0.912 mA, and 0.84 mA for 1,000 and 500 Ω , respectively. The initial low-to-high (0.12–0.98 mA) current generation in MDC over 50 h was observed. It has been gradually decreased (0.18–0.22 mA) which might be attributed to microbial community establishment, adaptation and death phase. During the initial phase (first 48 h), microorganisms established biofilms and optimized metabolic pathways, leading to increased ion transfer and current production. It can be deciphered that, in the presence of higher external resistances (>500 Ω), electrogenic bacteria were unable to transfer the electrons to such unfavourable electron acceptor. The situation of high external resistance (>500 Ω) hindered the electron flow from anode to cathode. In the same way, research study conducted by Chen et al. [24] demonstrated that electrogenic bacteria could behave in an unstable manner and thereby produce fewer electrons when external resistance is low (<10 Ω). It was also reported that, when the MFC was operated at low external resistance, the cell voltage decreased and the current increased [25,26]. This present study represented the similar trend for the current and voltage generation with the external resistance.

3.1.2. COD removal efficiency

The COD removal efficiency with time for different external resistance is shown in Fig. 3A. The COD removal efficiencies were identical in nature; however, the maximum removal efficiency was observed to be 82% with 500 Ω external resistance. The reason for maximum removal of COD was due to the optimum performance of the electrogenic bacteria present in the solution. The maximum COD removal efficiencies were 77%, 75% and 72% with the external resistance 1,000; 100 and 5 Ω , respectively. The gradual increase in COD reduction (3,328 to 1,656 mg/L) could be attributed to biofilm development and microbial adaptation. Initially, microorganisms established and enhanced metabolic pathways for organic matter degradation, leading to higher COD reduction rates (19%–20% reduction per day). However, with time, biofilm saturation and potential competition among microbes can moderate COD reduction efficiency (7%–8%). Fluctuations in COD reduction rates were due to varying microbial activity, influenced by factors such as substrate availability, and biofilm stability. The experimental study by Campo et al. [21] also reported that when the external resistance was increased, the COD removal efficiency

was increased. However, the quantity of the substrate consumed by the microorganisms increased accordingly.

An extremely low external resistance (e.g., 5 and 100 Ω) could lead to excessive microbial activity and substrate utilization in the anode chamber. This might also cause incomplete degradation of organic matter, resulting in lower COD removal efficiency. The 1,000 Ω external resistance could hinder efficient electrochemical reactions in the MDC. This high resistance value may disrupt the balance between substrate oxidation and reduction processes and could limit the overall COD removal efficiency. The same was also reported by Song et al. [26], where they showed that external resistance in the sediment microbial fuel cells (SMFC) was especially important to remove the readily oxidizable organic matter (ROOM). The lowest internal resistance (IR) and maximum organic removal efficiency was reported with 100 Ω external resistance.

The population and activity of exo-electrochemically active bacteria was controlled at higher applied external resistance (1,000 Ω), which resulted in a low rate of anaerobic activities. This might be the cause for higher rate of substrate removal (23%–30%/d) and a lower rate of electron transfer. Applying the larger external resistance will therefore result in high COD elimination and overall low CE. The COD removal rates were varying for different external resistance. It was observed that the maximum removal rates were varying from 20%–40% from day 1 to day 3 (Fig. 3B). This may be due to the activation of the microorganism present in the solution and their multiplication by degrading the organic matter. In the same manner Al-Mamun [23] reported that with the decrease in the external resistance from 150 to 10 Ω , the COD removal efficiency was reduced

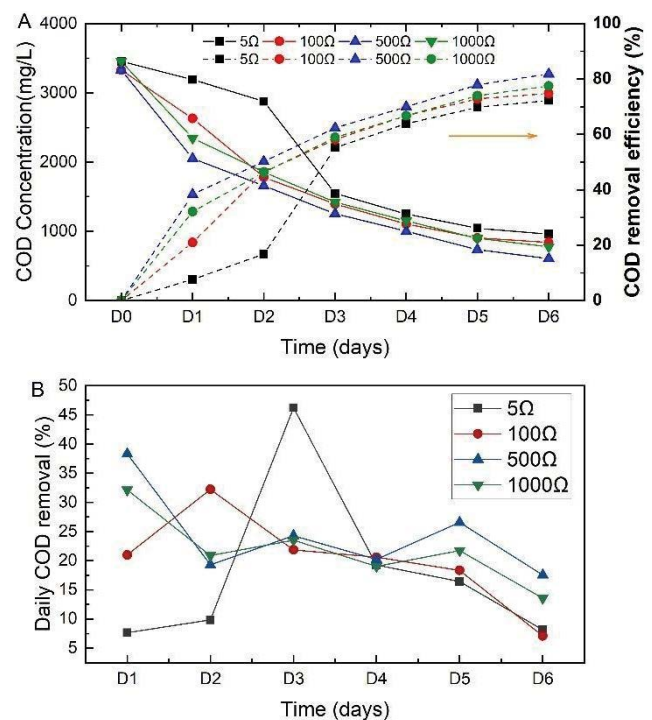


Fig. 3. Variation of (A) cumulative COD (B) daily COD removal efficiencies under 5, 100, 500 and 1,000 Ω external resistance.

from 57.14% to 16.67%, respectively. Higher external resistance resulted in lower anode potential due to lesser number of electro active bacteria (EAB) on the surface of anode and can control the electron transfer. The 500 Ω external resistance promoted efficient electrochemical reactions within the MDC. It created a favourable balance between substrate oxidation and reduction processes, which were essential for COD removal (20%–30% reduction). This optimal resistance facilitated the transfer of electrons and ions, leading to improved COD removal efficiency. Rahman et al. [27] showed that the COD removal efficiencies were 53.76%, 83.56% and CEs were 4.62%, 1.79% for the applied external resistance of 1 and 1,000 Ω , respectively, for air pumped MDC (APMDC). This result demonstrates the increase in the removal efficiency with the increase of external resistance.

3.1.3. Desalination efficiency

The TDS of the sample was checked on hourly basis with the help of a data logger. The variation of the TDS with time is shown in Fig. 4A. It was observed that the TDS concentration was reduced from 12,045 to 7,456, 12,560 to 6,435, 12,560 to 5,423 and 12,045 to 5,686 mg/L in the presence of 5, 100, 500 and 1,000 Ω , respectively. The desalination efficiencies were calculated in an interval of 4 h. The maximum desalination efficiency was observed to be 57% in the presence of 500 Ω resistance and represented in Fig. 4B.

The gradual increase in TDS reduction (from 12,560 to 7,096 mg/L) over time was due to the establishment and maturation of microbial communities. Initially, biofilm

development and ion transport mechanisms might take time to optimize, resulting in lower TDS reduction rates (10%–12%/d). As biofilms mature and microbial populations adapt, ion transfer efficiency improves, leading to higher TDS removal (16%–18%/d). Fluctuations in TDS reduction rates could stem from shifts in microbial activity influenced by substrate availability, and internal resistance. A similar study done by Chen et al. [24] reported that, specific desalination rate (SDR) increased with the reduction of the external resistance from 500 to 10 Ω and SDR was decreased when the external resistance decreased further to 5 Ω .

When the external resistance was too low (5 and 100 Ω), it could limit the migration of ions from the desalination chamber to the anode and cathode chambers. This limitation reduces the efficiency of ion removal and subsequently lowers TDS removal. On the other hand, 1,000 Ω external resistance hampered the electrode reactions in the MDC. The high resistance reduced the rate of electron transfer and limited the electrochemical processes involved in COD removal and TDS removal, leading to decreased treatment efficiency when compared with the 500 Ω . Ren et al. [28] expressed that the experimental setup can be started with higher external resistance to biofilm acclimation and power generation at the initial condition. Further the resistance can be reduced to increase current density.

3.1.4. Variation of pH and TDS

The variation of the pH of anode, desalination and cathode chamber with time presented in Fig. 5A–C. It was observed that the pH of the anode chamber decreased from 5.79 to 3.22 and 5.70 to 4.46 with time for the external resistance 100 and 500 Ω , respectively. This may be due to effective electron transfer through the AEM which produced the acidic environment in the anode chamber. On the other hand, the pH of the anode chamber increased from 6.57 to 7.62 and 6.57 to 7.95 in the case of applied external resistance 5 and 1,000 Ω . This could be the rapid take-up of the negative anion by the generated cations in the anaerobic reaction. These changes were found to be gradual with time and in similar nature. The mechanism was also explained by Mersinkova et al. [29] in their study where, in fermentation the substrate degradation at 0 and 10 k Ω of the high organic acids showed the same effect on the microbial metabolism.

The pH of the desalination chamber was observed with time and represented in Fig. 5B. pH of the desalination chamber slightly increased from 7.7 to 7.96 and 7.77 to 7.92 for external resistance 5 and 1,000 Ω , respectively. The reason for the slight changes of pH in the DC was due to reaction of the anion with cation presence in the anode chamber. On the other hand, pH of the desalination chamber decreased from 7.31 to 6.17 and 7.37 to 5.95 with an external resistance 100 and 500 Ω . Similar to the present study, Raghavulu et al. [30] conducted studies on the performance of the voltage and current generation. The result of which showed that, with the lower anodic pH, the voltage and current generation was maximum when compared with the higher pH in the anodic chamber. The oxidation reactions taking place at the anode resulted in the release of protons (H^+) and electrons (e^-). The accumulation of protons

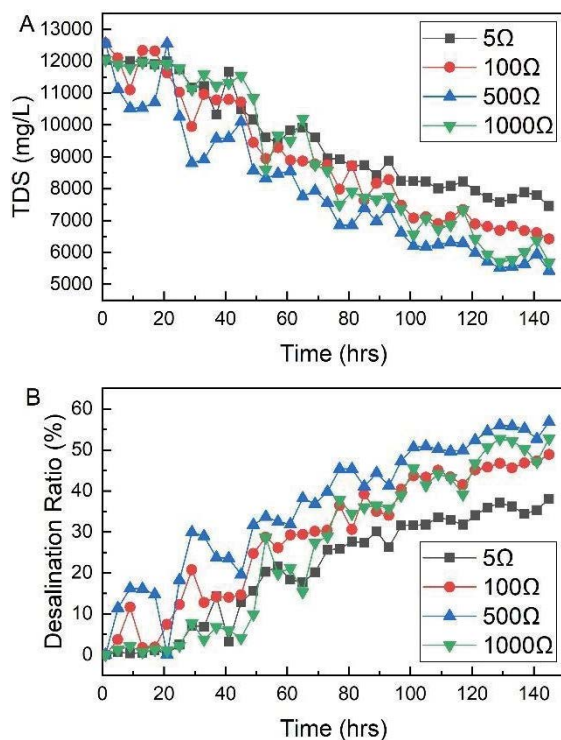


Fig. 4. Variation of (A) desalination chamber TDS and (B) cumulative TDS removal under 5, 100, 500 and 1,000 Ω external resistance.

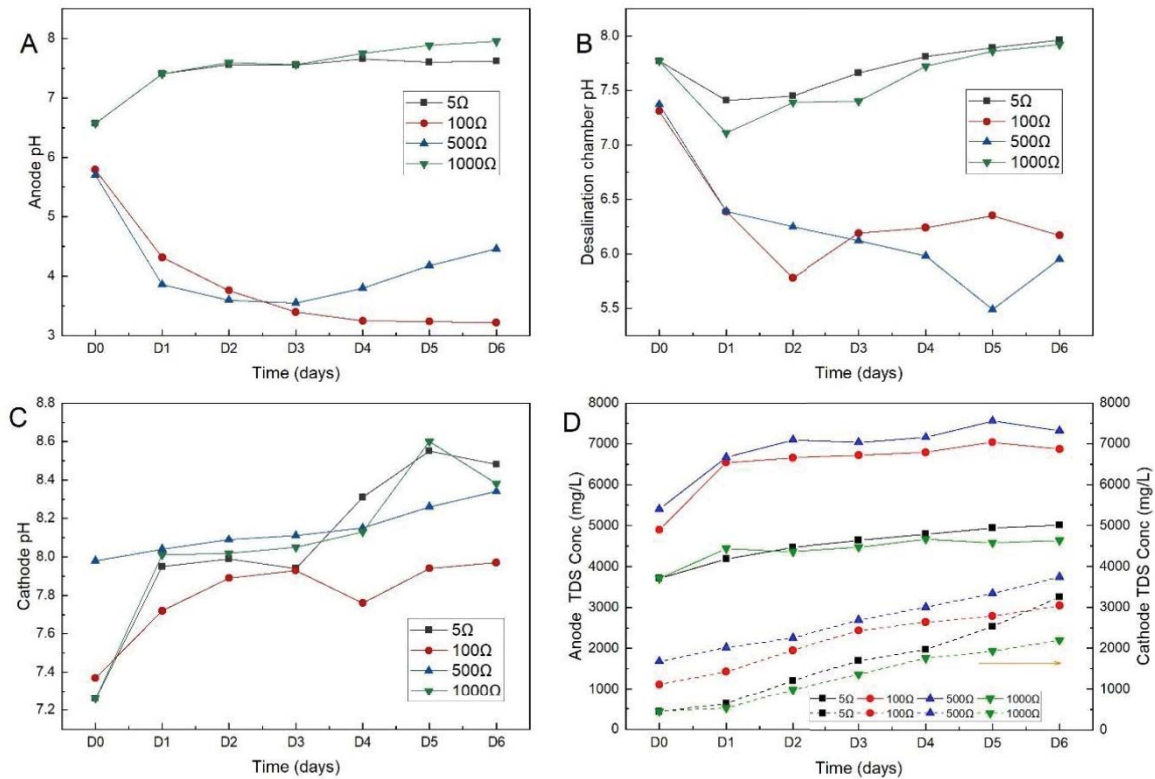


Fig. 5. Variation of (A) anode pH, (B) desalination pH, (C) cathode pH and (D) anode and cathode TDS concentration under 5, 100, 500 and 1,000 Ω external resistance.

could lead to an increase in local acidity. Further, in addition to this pH of the cathode chamber increased from 7.26 to 8.48 (Fig. 5C). However, as the protons migrated towards the cathode through the electrolyte, they could react with oxygen (O_2) and water (H_2O) to form hydroxide ions (OH^-), resulting in an increase in pH over time. Reduction reactions occur at the cathode, where electrons from the external circuit combine with protons (H^+) from the solution, forming water molecules. This reduction reaction generated hydroxide ions (OH^-) as a by-product, leading to an increase in pH over time in the cathode chamber.

It was also observed that, the anode section TDS was increased to 5,009; 6,865; 57,318 and 4,639 mg/L with the resistance 5, 100, 500 and 1,000 Ω, respectively (Fig. 5D). A similar observation was also made for the cathode section which increased from 1,675 to 3,738 mg/L for external resistance 500 Ω. The increase in cathode TDS was due to the migration of the ions from the desalination chamber to the cathode.

3.2. Effect of salt concentration on MDC performance

3.2.1. Voltage and current generation

There is an impact of salt concentration on the voltage and current generation and shown in Fig. 6A. It was observed that the maximum voltage of 723 mV generated in the case of salt concentration was 35,000 mg/L at DC. The gradual decrease in voltage over time (from 652 to 504 mV) can be attributed to ion concentration changes and electrochemical

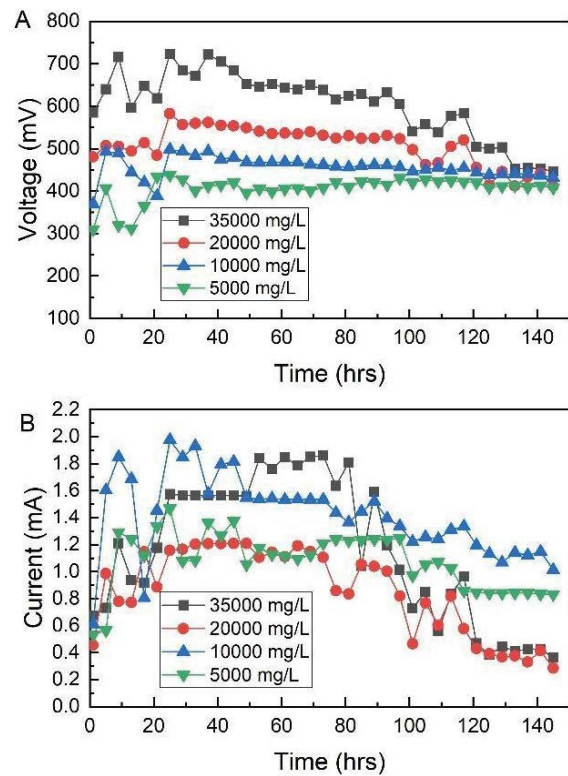


Fig. 6. Impact of 35,000; 20,000; 10,000 and 5,000 mg/L salt concentration on (A) voltage and (B) current generation.

processes. Initially, a slight voltage increase (723 mV) might occur due to higher ion mobility and conductivity of the fresh electrolyte. However, as the MDC operates, ions are transferred, leading to a gradual decrease (446 at 6th day) in their concentration in the electrolyte, resulting in reduced ion migration and drop in voltage. The maximum voltage of 582, 498, 438 mV were observed with the desalination chamber salt concentration of 20,000; 10,000 and 5,000 mg/L, respectively.

A similar study done by Yang et al. [31] showed that current generation was influenced by the NaCl concentration present in the DC. Their study reported a highest current of 3.17 mA with initial NaCl concentration of 30 g/L, followed by 3.06 and 2.82 mA with 20 and 5 g/L, respectively. The reason for higher current generation was due to the junction potential which was generated at the interface or boundary between two electrolytes. The reason for the inversely proportional relationship between current generation and applied external resistance was stated as the generated electrons can move easily when the external circuit is connected with low resistance. The reason for the maximum voltage generation (723 mV) with the maximum salt concentration (35,000 mg/L) may be due to the concentration gradient created inside the cell, which was the initial driving force for the reactions. The presence of a higher salt concentration (>20,000 mg/L) created more favourable conditions for electrochemical reactions. The increased ion concentration supported efficient electrode kinetics, resulting in enhanced electron transfer and subsequently higher voltage and current generation in the MDC.

The maximum current generation of 1.98 mA (Fig. 6B) was observed within 24 h of the reactor run and decreased with time for the DC salt concentration 10,000 mg/L. On the other hand, the maximum current of 1.57, 1.21, 1.47 mA observed within 24–48 h of the operation and decreased gradually, with the DC salt concentration 35,000; 20,000 and 5,000 mg/L, respectively. The reason may be attributed to the movement of the ions and reduction of concentration in the reactor. The graph represented that in the early phase (9–25th hour), biofilm development enhanced the microbial activity (25–40th hour) and ion exchange, resulting in higher current production. The subsequent stability phase could arise from biofilm maturation and optimal ion transfer. In this context, Lefebvre et al. [32] also reported that addition of NaCl in the system had no impact on E_{emf} . However, R_{int} was decreased and reached the minimum value of 1.2 m Ω /m³ with the NaCl concentration of 20 g/L, which was 33% reduction when compared to the initial conditions. Addition of NaCl was benefited in electricity generation and P_{max} increased by 30% as compared to the initial conditions.

Lower salt concentrations (<10,000 mg/L) resulted in reduced ion conductivity in the desalination chamber. This led to a decrease in the availability of ions for electrochemical reactions and hampered the generation of voltage and current in the MDC reactor. On the other hand, salt concentration of 35,000 mg/L enhanced the ionic conductivity of the solution in the MDC. This improved conductivity facilitated efficient electron transfer and promoted higher voltage and current generation in the cell. The same was also explained by Miyahara et al. [33], with acetate concentration containing a varying NaCl concentration of 0 to 1.8 M

and observed that the maximum current and voltage was generated with the salt concentration of 0.1 M.

3.2.2. COD removal efficiency

The COD removal with time is shown in Fig. 7A. It was observed that the maximum COD removal of 83%, 82%, 81% and 78% were noticed with 35,000; 20,000; 10,000 and 5,000 mg/L, salt concentrations, respectively. The gradual increase in COD reduction (from 2,266 to 787 and then 677 mg/L) over time can be attributed to microbial adaptation and biofilm development (24–36th h). As microorganisms colonize and biofilms are formed, metabolic pathways for organic matter degradation improve, resulting in higher COD reduction rates (27%–33%/d). The similarities in efficiencies and trends might stem from consistent microbial activity and biofilm dynamics across the range. The feed organic concentration was similar for the experimental studies and observed that the electrolyte concentration was having minimal impact on the substrate removal (78%–83%).

The COD was reduced from 3,840 to 635, 3,840 to 745, 3,950 to 852, and 3,950 to 696 mg/L for the salt concentrations 35,000; 20,000; 10,000 and 5,000 mg/L in DC, respectively. The reason for the degradation for the COD might be due to the utilization of the available substrate present in the solution by the electrogenic bacteria.

The process of microbial adaptation might be enhanced due to the higher concentration gradient in the reactor. Lower salt concentrations (<10,000 mg/L) might not provide enough ions for effective ion exchange processes in the desalination chamber. This could slow down the removal of organic compounds and result in lower COD removal efficiency. A salt concentration of 35,000 mg/L created a significant osmotic gradient between the anode and the desalination chamber. This osmotic gradient could have initiated water transport from the anode chamber to the desalination chamber and facilitated the removal of organic compounds.

The day-to-day COD removal is shown in Fig. 7B. It was observed that the COD removal efficiency was varying from 30%–40% within 24–48 h of the experimental setup. However, the COD removal efficiency was found to be reduced to 20%–30% after 72 h of the operation. This may be due to the limited substrate concentration present in the system after the operation for 72 h. Similar result obtained by Lefebvre et al. [32] reported for the removal of sodium acetate and the efficiency increased with the variation of NaCl concentration and reported 31% \pm 1%, 37% \pm 3% and 42% \pm 1% with NaCl concentration of 5, 10 and 20 g/L in DC, respectively. The improvement of performance was directly resulting from the increased power generation in the reactor which was requiring additional substrate as a source of electrons and protons. The results in literature were found to be more than that reported in the study.

3.2.3. Desalination efficiency

In the present study, the variation of the TDS concentration in the DC with time presented in Fig. 8A. It was observed that the TDS concentration was reduced from

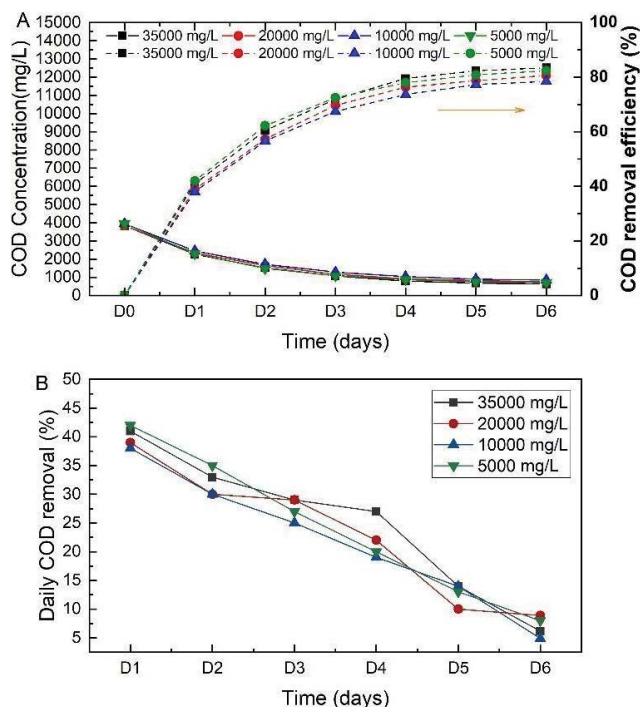


Fig. 7. Variation of (A) cumulative COD and (B) daily COD removal efficiencies with 35,000; 20,000; 10,000 and 5,000 mg/L desalination salt concentration.

38,900 to 15,100, 21,560 to 9,420, 11,460 to 5,220 and 5,445 to 2,650 mg/L for different experimental conditions. The reason for reduction in salt concentration in the desalination chamber was due to osmotic pressure and electric field action. The TDS removal was found to be gradual in nature (16%–18%/d) which can be attributed to microbial adaptation and ion transport optimization. With the maturation of the microbial culture, ion transfer mechanisms improved, leading to higher TDS removal rates. However, distinct and fluctuating trends (0–50th h) could be due to differing ion interactions, pH shifts, and biofilm responses at various electrolyte concentrations, causing variations in TDS reduction rates.

The maximum desalination efficiencies were found to be 61%, 56%, 54% and 51%, for 35,000; 20,000; 10,000 and 5,000 mg/L, respectively (Fig. 8B). The reason for maximum desalination efficiency for 35,000 mg/L was due to the concentration gradient present into the system, which was the driving force for initial movement of the ions. The daily TDS removal was found to be varying from 10%–18% within 48–72 h and then reduced to 7%–12% after 72 h (Fig. 8B). The TDS removal in the system was found to be consistent with time. The reason for the TDS removal was due to the microbial activities in the anode section which created the concentration gradient and continuously received the ions from the desalination chamber.

In the same manner, the experiment conducted by Xu et al. [34] showed that the desalination cycle and its rate happened to be shorter and slower. The salt removal efficiency increased when the salinity decreased in the desalination chamber, and highest salt removal was achieved with salinity of 5 g/L. This justified that lower salt concentrations

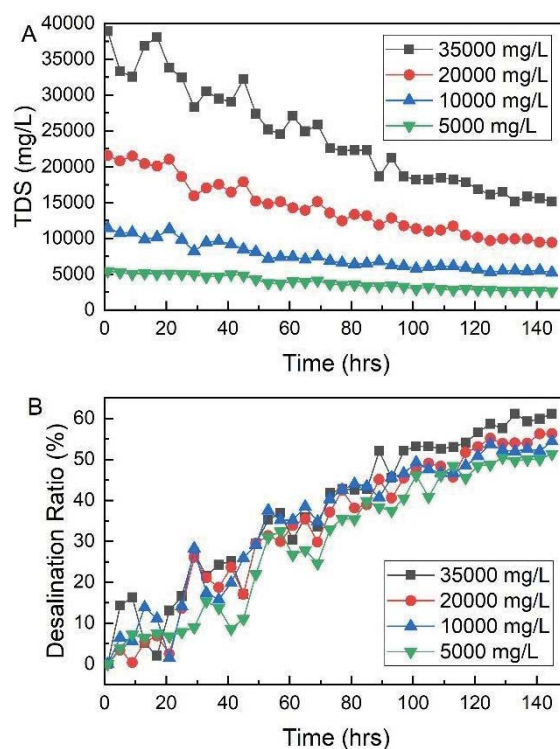


Fig. 8. Variation of (A) desalination chamber TDS and (B) cumulative TDS removal with 35,000; 20,000; 10,000 and 5,000 mg/L desalination salt concentration.

limited the availability of ions for ion exchange processes in the desalination chamber. This slowed the ion exchange capacity and reduced the effectiveness of TDS removal from the solution.

3.2.4. Variation of pH and TDS

The variation of the pH in the anode, desalination and cathode chamber are shown in Fig. 9A–C. It was observed that the pH of the anode chamber increased with time from 6.23 and 6.29 to 7.56 and 7.59 for 35,000 and 10,000 mg/L, respectively. The presence of carbon dioxide (CO_2) in the anode chamber due to anaerobic conditions, could dissolve and react with water molecules to form carbonic acid (H_2CO_3). Carbonic acid then dissociated into bicarbonate ions (HCO_3^-) and protons (H^+). The protons generated during this process could combine with electrons from the anodic reaction to produce hydroxide ions (OH^-), thereby increasing the pH in the anode chamber.

On the other hand, the pH of the desalination chamber also increased from 7.37 and 7.63 to 7.82 and 7.91 for the same experiments, respectively (Fig. 9B). The reason for the increase in the pH may be due to rapid consumption of the anions in the anode section. The pH of the cathode chamber also increased from 8.08 to 8.83 (Fig. 9C). All trends were found to be in increasing order with time. Due to the reduction process at the cathode, hydrogen gas (H_2) generated. The generated hydrogen gas could react with hydroxide ions (OH^-) present in the solution, forming water, resulting in an increase in pH.

The changes of the sample TDS with time are shown in Fig. 9D. It was observed that the anode TDS increased with time and was found to be 3,854 to 5,248 mg/L. In the cathode chamber, TDS increased from 1,788 to 5,736 mg/L and from 1,361 to 4,824 mg/L. The reason for increase in cathode TDS was due to the movement of the ions in the cathode chamber from the desalination chamber. Zhang et al. [35] have conducted studies on the impact of the anode pH on the power generation. It was observed that, with neutral anode pH, the performance of the cell was maximum and when the pH had become low, voltage generation decreased. The present study also conducted in the neutral pH for the cathode chamber, however, anode pH was found to be in increasing order along with increase in the efficiencies.

3.3. Effect of substrate concentration on cell performance

3.3.1. Voltage and current generation

The substrate concentration has a great contribution towards the voltage and current generation. The variation of the voltage and current with time is shown in Fig. 10A and B. It was observed that the maximum voltage of 628 mV was generated within 48 h of the operation for the substrate concentration 8,000 mg/L which might be due to the complete utilization of the substrate (7,790–3,056 mg/L) by the electrogenic bacteria. It may be also due to the presence of the substrate availability in the solution. The study of Ullah and Zeshan [36] reported a similar trend with the application

of glucose, acetate, and sucrose with maximum voltages of 262, 343 and 339 mV and maximum power densities of 31, 53.4 and 52.3 mW/m², respectively.

In the present study, generated voltage was stable and distinct trends could be due to variations in microbial population dynamics, competitive interactions, or substrate availability, leading to differing voltage responses. However, the maximum voltage of 560, 438, and 420 mV were observed for the substrate concentrations of 12,000; 4,000 and 1,500 mg/L, respectively. The reason for the low voltage generation was due to the inhibition concentration with 12,000 mg/L COD present in the solution and microbes were not able to digest the substrate properly. This excess substrate may exceed the capacity of the microbial community, resulting in incomplete substrate utilization and lower electron production, leading to reduced voltage and current generation.

The maximum current generation was observed to be 1.87 mA at 24 h with the substrate concentration 8,000 mg/L (Fig. 10B). In addition, maximum current of 1.21, 1.47 and 0.98 mA were observed with the substrate concentrations of 12,000; 4,000 and 1,500 mg/L, respectively. This optimal substrate availability ensured efficient substrate utilization, promoting higher rates of electron transfer, and consequently increasing voltage and current generation in the MDC.

A similar study conducted by Mokhtarian et al. [37] on various substrate utilization such as glucose, sucrose, fructose, and molasses as a carbon source for electricity production in a MFC reactor. The maximum generated bioelectricity

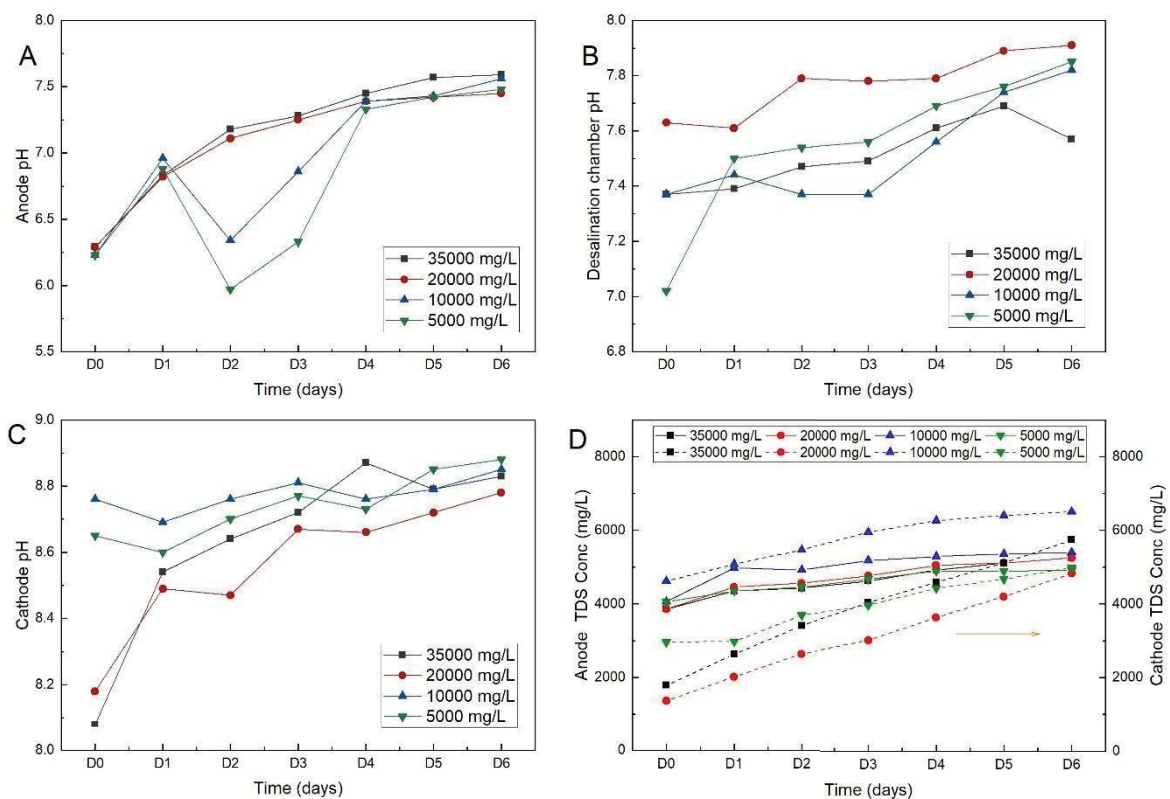


Fig. 9. Variation of (A) anode pH, (B) desalination pH, (C) cathode pH and (D) anode and cathode TDS concentration with 35,000; 20,000; 10,000 and 5,000 mg/L desalination salt concentration.

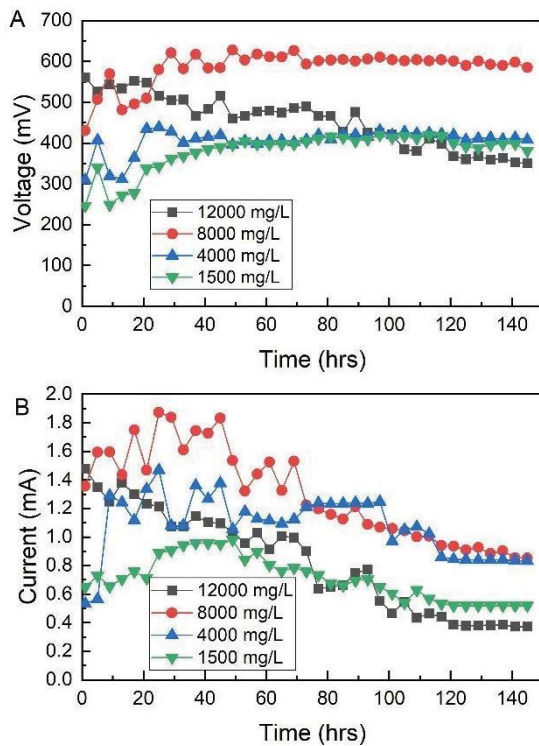


Fig. 10. Impact of 12,000; 8,000; 4,000 and 1,500 mg/L substrate concentration on (A) voltage and (B) current generation.

was reported from molasses which was in terms of an electron donor. The maximum power and current were reported as 55.25 mW/m² and 208.55 mA/m², respectively. The present study also represents similar observations in terms of the substrate concentration. On the other hand, lower substrate concentrations (4,000 and 1,500 mg/L) provide a limited supply of electron donors to the microorganisms in the anode chamber. This limited availability of electron donors hampered microbial activity and subsequent electron transfer, leading to lower voltage and current generation.

3.3.2. COD removal efficiency

The variation of COD concentration with time is shown in Fig. 11A. The maximum COD removal efficiencies were achieved 86%, 82%, 61%, 47% for the substrate concentration 1,500; 4,000; 8,000 and 12,000 mg/L, respectively. Maximum removal rates of 35%–46% were noticed with the substrate concentration 1,500–4,000 mg/L within 48 h of operation. The reason for maximum COD removal with the lower substrate concentration due to the active decomposition of the organics by the microbes present in the wastewater. The maximum removal rate (39%–46%/d) and efficiency (86%) was achieved with 1,500 mg/L substrate concentration which was in lower concentration and easily degradable. The stable COD removal (20%–27%/d) was noticed for 4,000 mg/L due to the availability of organics for the decomposition. Ullah and Zeshan [36] reported that when input wastewater with COD concentrations of 500, 2,000 and 3,000 mg/L were used in the reactor, the outlet COD of 95, 420 and 678 mg/L with the removal efficiency of 81%, 79% and 77% were achieved,

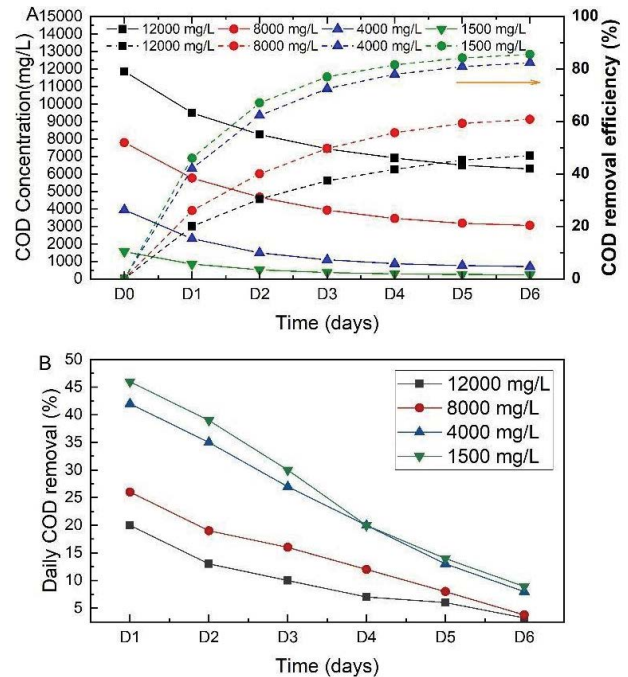


Fig. 11. Variation of (A) cumulative COD and (B) daily COD removal efficiencies with 12,000; 8,000; 4,000 and 1,500 mg/L substrate concentration.

respectively. The present experimental study was found to be in good agreement with the reported results. In the present study, insufficient substrate availability (1,500–4,000 mg/L) limited the microbial activity and metabolic processes required for COD degradation.

However, the low COD removal efficiency was noticed with maximum substrate concentration (12,000 mg/L), this may be due to the inhibition concentration of the substrate and microbes were not able to easily degrade the organic matter completely. This might result in higher food to microorganism (F/M) ratio in the reactor. Tariq et al. [38] conducted studies on the MFC system and found maximum removal efficiency when acetic acid was used and with increase in the concentration of acetate from 50 to 1,000 mg/L, the COD removal efficiency increased from 55% to 85%. Fig. 11B represents the daily reduction in COD concentration present in the anode chamber. It was observed that COD reduction was varying from 20% to 45% within 48 h and declined to 10%–20% within 96 h. The initial high COD reduction with the moderate substrate concentration was due to the organics availability in the system and later as the substrate concentration reduced, COD removal efficiency was also reduced.

The study of Khoirunnisa et al. [39] showed percentage of total COD removal varied from 48.37% \pm 6.92% at 2% (w/v) palm sugar substrate and 68.18% \pm 0.00% at 4% (w/v) molasses substrate. It was reported that molasses was proved to be a better substrate for digestion in the MFC system. In the same way, the 8,000 mg/L substrate concentration offered ample organic matter for microbial activity. This abundant supply enabled the microbial community to efficiently degrade organic compounds, resulting in higher COD removal efficiency in the MDC.

3.3.3. Desalination efficiency

The TDS reduction of the desalination chamber is presented in Fig. 12. The TDS reduction was found to be 5,220 to 1,980 mg/L and 5,100 to 2,150 mg/L with the substrate concentration 8,000 and 1,500 mg/L, respectively. The reason for the maximum TDS reduction with the substrate concentration of 8,000 mg/L was due to the maximum utilization of the substrate by the electrogenic bacteria present in the system. This drives the process fast, collecting the ions from DC and moving the reaction forward. Insufficient substrate concentrations resulted in limited electrochemical reactions involved in TDS removal, such as ion exchange. This compromised the overall effectiveness of TDS removal from the solution. The study of Santoro et al. [20] reported that the reduction in the TDS was due to electroactive bacteria on the anode surface consuming the acetate ions. This was because of the preservation of the solution's electro-neutrality, the abundance of sodium ions (Na^+) within the anode chamber may also be to blame for the delay in the transit of sodium ions from the desalination chamber to the anodic chamber.

The TDS removal rate is presented in Fig. 12B. The maximum TDS reduction was observed to be 62%, 58%, 54% and 51% for the substrate concentration 8,000; 1,500; 12,000 and 4,000, respectively. It was observed that the maximum TDS removal rate of 20%–28% was observed within 48 h of the retention time. The day wise TDS reduction was found to be declining with time (16%–20%/d). This could be due to the availability of the substrate (>4,000 mg/L) and

utilization at the initial phase (24–36th h) and lower substrate concentration present in the solution with increasing time. The reason for reduced TDS removal (54%) for higher substrate concentration (12,000 mg/L) was also due to the inhibition concentration. TDS removal was reduced with increase in the substrate concentration.

3.3.4. Variation of pH and TDS

The variation of pH for anode, desalination and cathode chamber represented that in all the chambers pH was found to be in increasing trend (Fig. 13). The pH of the anode increased from 6.23 to 7.48 in the case of substrate concentration 4,000 mg/L. Similarly, the pH of desalination chamber increased from 7.33 to 8.25 in case of substrate concentration 12,000 mg/L. A similar result was also observed for the cathode chamber and found to be 7.79 to 8.96 for the substrate concentration 12,000 mg/L and from 8.65 to 8.88 for the substrate concentration 4,000 mg/L. The reason for the increased cathode pH may be due to ion migration to the cathode chamber. Santoro et al. [20] reported the fact for pH to increase in the cathode chamber, the surplus hydroxyl ion (OH^-) flows to the desalination chamber through the anion exchange membrane for back diffusion transport phenomena after the pH rises first in the cathode chamber.

Desalination chamber pH varies from 7.33 to 8.25, 7.4 to 8.04, 7.02 to 7.85 and 7.39 to 7.82 for the substrate concentrations 12,000; 8,000; 4,000 and 1,500 mg/L, respectively. The desalination process involved the removal of salts from the solution. As the concentration of salts decreased, the relative proportion of hydroxide ions (OH^-) to protons (H^+) also changed, leading to an increased pH over time. It was observed that for both the anode and cathode chamber, the TDS was increased with time. This condition was found to be similar for the experimental conditions with applied external resistance and variation of the salt concentrations. The TDS of the anode chamber increased from 2,352 to 3,750, 2,399 to 2,860, 4,055 to 5,090 and 3,890 to 5,505 mg/L, for the substrate concentration having 12,000; 8,000; 4,000 and 1,500 mg/L, respectively. 59%, 19%, 26% and 42% increase in concentration was reported, respectively. Similarly, the cathode chamber TDS increased by 310%, 266%, 68%, 218% for the substrate concentration of 12,000; 8,000; 4,000 and 1,500 mg/L, respectively.

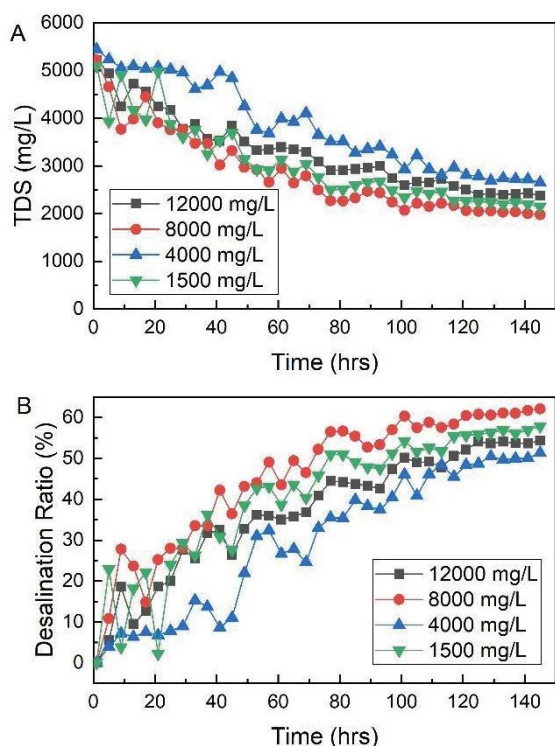


Fig. 12. Variation of (A) desalination chamber TDS and (B) cumulative TDS removal with 12,000; 8,000; 4,000 and 1,500 mg/L substrate concentration.

3.4. Current density, power density and coulombic efficiency

In the present study, based on the data collected, power and current densities were calculated and presented in Table 3. The average current density of 0.012 mA/cm² was observed with the external resistance of 5 Ω . The 5 Ω external resistance allowed a lower overall system resistance, minimizing internal losses and voltage drops within the MDC. This reduction in internal resistance enabled higher current flow and led to a higher current density. On the other hand, the impact of salt and substrate concentration showed an average current density (CD) of 0.03 mA/cm² in the presence of 10,000 and 35,000 mg/L salt concentration, 0.03 mA/cm² with the substrate concentration of 8,000 mg/L. The 35,000 mg/L electrolyte solution provided a higher concentration of ions in the desalination chamber. High ion

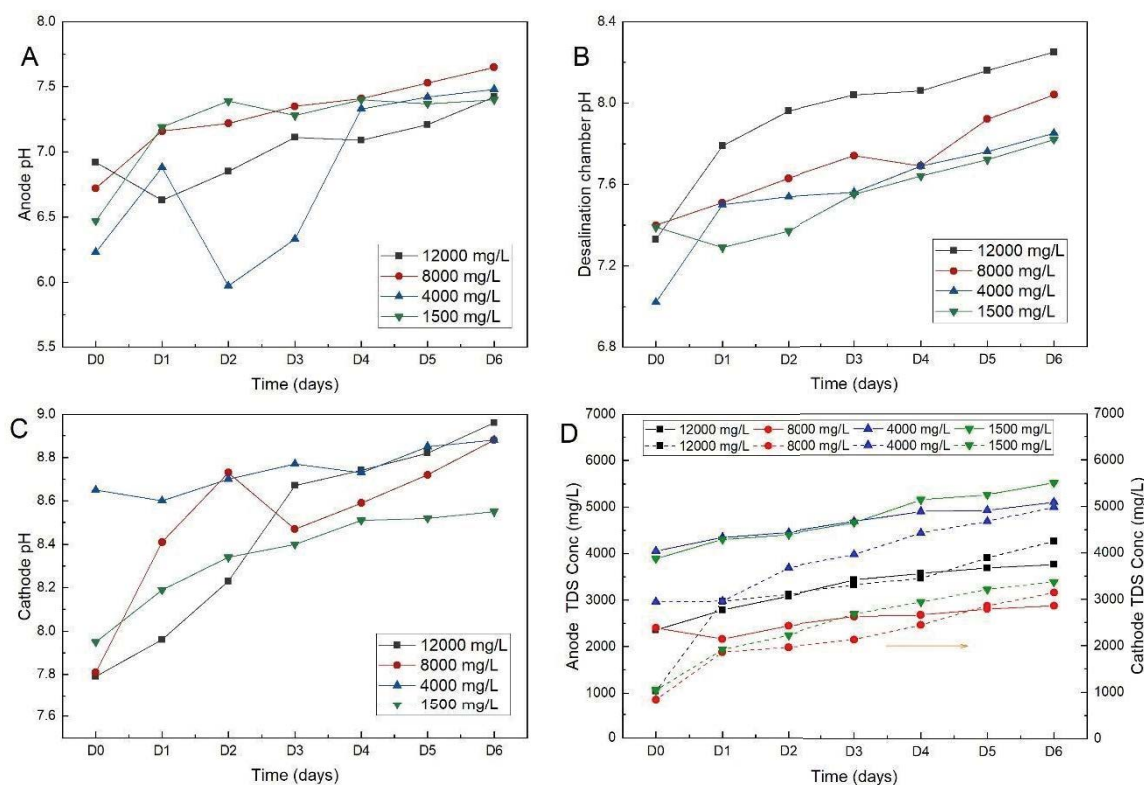


Fig. 13. Variation of (A) anode pH, (B) desalination pH, (C) cathode pH and (D) anode and cathode TDS concentration with 12,000; 8,000; 4,000 and 1,500 mg/L substrate concentration.

concentration facilitated the enhanced ion transport and promoted more efficient electrochemical reactions, resulting in higher current density. The 8,000 mg/L substrate concentration was a balance between providing an adequate amount of organic matter for microbial growth and preventing substrate left over. This balance allowed efficient substrate utilization by the microorganisms, resulting in higher current density. The 12,000 mg/L substrate concentration might lead to substrate overload, where the microorganisms were unable to efficiently utilize the excessive organic matter. On the other hand, the 4,000 and 1,500 mg/L substrate concentrations might limit the availability of organic matter, causing a decrease in microbial activity and subsequent current density.

The maximum average power density of 4.46 mW/cm² was observed in the presence of 500 Ω external resistance. The 500 Ω external resistance provided an appropriate load for the MDC system, allowing the higher voltage generation. This higher voltage, combined with the flow of current, leads to increased power density. The 500 Ω external resistance optimized the energy conversion efficiency in the MDC. It balanced the electron transfer kinetics, internal resistance, and losses, resulting in improved energy conversion and higher power density. It was observed that an average 15.87, 9.7, 14.2, and 9.54 mW/cm² power densities in the MDC were obtained with salt concentration 35,000; 20,000; 10,000; and 5,000 mg/L, respectively. The higher concentration of ions in the 35,000 mg/L electrolyte solution led to improved electrolyte conductivity. This enhanced conductivity enabled more efficient charge transfer between the electrodes, resulting in

higher power density. On the other hand, the low concentration of ions (20,000; 10,000; and 5,000 mg/L) in these electrolyte solutions led to a lower potential difference across the electrodes. This lower voltage, combined with decreased current flow, resulted in reduced power density. A maximum average power density of 16.42 mW/cm² was noticed with the substrate concentration 8,000 mg/L followed by 9.54, 8.61 and 5.85 mW/cm² with the substrate concentration 4,000; 12,000 and 1,500 mg/L, respectively. The optimal substrate concentration ensured efficient substrate oxidation by the microorganisms. The microbial community could effectively degrade the organic matter, leading to a more complete conversion of the substrate's chemical energy into electrical energy, thereby increasing the power density. Insufficient substrate availability (4,000 and 1,500 mg/L) or excessive substrate (12,000 mg/L) could hinder the microbial population's growth and activity in the anode chamber. This reduced microbial activity led to a lower electron generation and, subsequently, lower power density.

The result of the coulombic efficiency (CE) showed a maximum 17.25% with the external resistance 5 Ω followed by 5.32%, 1.57% and 0.77% with the 100, 500 and 1,000 Ω , respectively. The 5 Ω external resistance provided favourable conditions for the growth and activity of electrogenic microorganisms. The lower resistance encouraged the development of a robust biofilm on the anode electrode. It enhanced the microbial metabolism resulting in higher current density and coulombic efficiency. The impact of salt concentration on the CE showed 1.82%, 1.59%, 1.41% and 1.2% in the presence of salt concentration 35,000; 20,000; 10,000 and

Table 3
Results of desalination and power generation performance in MDC

Variables	COD (%)	TDS (%)	Current (mA)	Voltage (mV)	CD _{Avg} (mA/cm ²)	PD _{Avg} (mW/cm ²)	CE (%)
Resistance							
1,000 Ω	77	53	0.912	656	0.008	4.15	0.77
500 Ω	82	57	0.84	566	0.009	4.46	1.57
100 Ω	75	49	0.45	381	0.006	1.68	5.32
5 Ω	72	38	0.98	506	0.012	3.03	17.25
Salt concentration							
35,000 mg/L	83	61	1.859	723	0.03	15.87	1.82
20,000 mg/L	81	56	1.209	582	0.02	9.7	1.59
10,000 mg/L	78	54	1.976	498	0.03	14.2	1.41
5,000 mg/L	82	51	1.469	438	0.02	9.54	1.20
Substrate concentration							
12,000 mg/L	47	54	1.476	560	0.02	8.61	0.78
8,000 mg/L	61	62	1.872	628	0.03	16.42	1.19
4,000 mg/L	82	51	1.469	438	0.02	9.54	1.20
1,500 mg/L	86	58	0.98	420	0.02	5.85	2.73

5,000 mg/L, respectively. The higher electrolyte concentration in 35,000 mg/L solution facilitated efficient desalination and ion removal processes. It promoted effective ion migration and separation, minimizing energy losses and improving the overall coulombic efficiency. The lower electrolyte concentrations (20,000; 10,000 and 5,000 mg/L) might hinder efficient desalination and ion removal processes. Insufficient ion migration and separation could lead to energy losses and decreased coulombic efficiency. On the other hand, the impact of substrate concentration on the CE showed 0.78%, 1.19%, 1.2% and 2.73% with concentration 12,000; 8,000; 4,000 and 1,500 mg/L, respectively. The balanced substrate concentration minimized substrate losses due to incomplete utilization or excessive accumulation. This efficient substrate utilization reduced energy losses and enhanced the overall coulombic efficiency of the MDC system. The substrate concentrations of 12,000; 4,000 and 1,500 mg/L might not promote balanced microbial reactions in the anode chamber for the present scenario. Imbalances in substrate utilization, microbial community dynamics, or metabolic pathways could lead to energy losses and decreased coulombic efficiency. It was observed that a maximum CE was achieved with lower external resistance and substrate concentration and with higher salt concentration.

The comparison of the present experimental study with a few research having the same objectives are represented in Table 4. It was observed that the present experimental study was in good agreement with the result obtained in the other studies. The experiments were conducted using the real wastewater collected from the different breweries and distillery industries. There were improvements in the voltage and current generation. Further, COD and TDS removal efficiencies were also found to be satisfactory with the present experimental conditions. The desalination rate and CE were found to be lagging when compared with the results reported by the other researchers. It was reported that, CE

was inversely proportional to the COD removal and directly proportional to the current generation [23]. However, COD removal and current generation were affected by applied external resistances, and CE was also affected by the applied external resistance [21]. It was also reported that CE was negatively impacted by a relatively low salinity level 10 g/L, where the MFC's overall performance was enhanced [32]. Khoirunnisa et al. [39] showed that coulombic efficiencies range from $4.59\% \pm 0.59\%$ at 4% (w/v) sugar to maximum of $45.80\% \pm 2.17\%$ at 2% (w/v) molasses. The increased activity of methanogens, which employ electrons as an electron acceptor to consume the substrate and create methane, may be responsible for the lower CE at 45°C [8].

4. Conclusion

The present study was conducted to explore the impact of using different external resistance, substrate concentration and salt concentration on the desalination performance. The study of applying different external resistance showed a maximum voltage of 656.25 mV with 1,000 Ω and a maximum current of 0.98 mA with 5 Ω. A maximum COD and TDS removal efficiency of 82% and 57% was observed with 500 Ω, respectively. The external resistance should not be so low that the experiments would complete so fast without complete degradation of the organic matter.

On the other hand, a maximum voltage, current, COD and TDS removal of 722.88 mV, 1.895 mA, 83% and 61%, respectively was obtained in the presence of salt concentration of 35,000 mg/L. While designing the MDC for any particular system, if the salt concentration can be selected maximum, an optimum output will be generated. A maximum desalination efficiency, voltage, and current generation of 62%, 628 mV and 1.872 mA, respectively was observed with anode substrate concentration of 8,000 mg/L. Though the maximum COD removal efficiency was obtained with

Table 4
Overview of the different experimental conditions on the MDC performance

SN	External resistance (Ω)	MFC category	Substrate	Anode electrode	Cathode electrode	Catholyte	DC volume (mL)	HRT (d)	Initial substrate conc. (mg/L)	Initial salt concentration (mg/L)	Voltage (mV)	Current (mA)	Current COD removal efficiency (%)	DC efficiency (%)	Desalination rate (g/L/h)	CE (%)	References
1	1,000	3C-MDC	Synthetic wastewater	Carbon cloth	Carbon cloth coated by Pt	PBS	105	3	1,500	10,000	681	-	92.3 \pm 4.3	27.6 \pm 6.4	0.4 \pm 0.0005	5.2 \pm 1.2	[8]
2	1	3C-MDC	Synthetic wastewater	Carbon fiber brush	Carbon cloth	PBS	32	5	2,000	35,000	1001	1.5	53.76	99	2.52	4.6	[27]
3	1,000	2C-MFC	Synthetic wastewater	Toray carbon papers	Toray carbon papers	-	-	-	343	-	-	-	43.15	-	-	-	[21]
4	1,000	2C-MFC	Synthetic wastewater	Graphite rod	Graphite rod	PBS	-	4	1,000	-	781	-	50	-	-	-	[36]
5	1,000	2C-MFC	Synthetic wastewater	Carbon fiber	Carbon fiber	0.1 M KMnO ₄	-	3	-	-	789	0.48	68.18	-	-	-	[39]
6	100	3C-MDC	Synthetic wastewater	SS with silver coated	SS with pt coated	Buffer solution	108	-	-	5,000	526.9	-	-	-	-	87.2	[31]
7	2 Ω	Multi-stage MDC	Real wastewater	Conductive activated carbon granules	Conductive activated carbon granules	-	-	0.5	8,723 \pm 456	24,612 \pm 772	-	127.6	98	51.7	-	14	[15]
8	1,000	3C-MDC	Synthetic wastewater	Carbon cloth	Carbon cloth	Dipotassium hydrogen phosphate	21,000	2	600	30,000	702	-	~50	98	0.092	18.53	[34]
9	150	4C-MDC	Sewage - STP	Carbon brush	Carbon cloth	PBS	202.5	0.33	320	35,000	586.3	3.6	57.14	47	-	58.3	[23]
Resistance	1,000	3C-MDC	Actual wastewater	Carbon rod	Carbon rod	Tap water	250	6	4,000	10,000	656.3	0.91	77	53	0.065	0.77	Present study
Salt concentration	500	3C-MDC	Actual wastewater	Carbon rod	Carbon rod	Tap water	250	6	4,000	35,000	723	1.86	83	61	1.962	1.82	Present study
Substrate concentration	500	3C-MDC	Actual wastewater	Carbon rod	Carbon rod	Tap water	250	6	12,000	5,000	560	1.48	47	54	0.280	0.78	Present study

the lower substrate concentration, it is suggested to select the optimum substrate concentration as the concentration is exceptionally low, then the experiment will stop in no time and if the concentration is extremely high, this could be toxic in nature to the microbes.

The results signify that an increase in the electrolyte concentration helped in obtaining higher CD, PD and CE. Lower substrate concentration helped to increase the CE. On the other hand, lower external resistance helped to generate higher CD and CE. An optimum substrate concentration was required to maximize the CD and PD. The present experiment study provided detailed information regarding the selection of the external resistance, electrolyte concentration and substrate concentration. The findings show the requirement-based selection of the materials for the optimization of the outputs which can be implemented based on the site conditions.

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