Multi-chamber microbial desalination cell for improved organic matter and dissolved solids removal from wastewater

Harapriya Pradhan and M. M. Ghangrekar

ABSTRACT

A five-chamber microbial desalination cell (MDC) with anode, cathode, one central desalination chamber and two concentrate chambers separated by ion exchange membranes was operated in batch mode for more than 60 days. The performance of the MDC was evaluated for chemical oxygen demand (COD) removal, total dissolved solids (TDS) removal and energy production. An average COD removal of $81 \pm 2.1\%$ was obtained using acetate-fed wastewater as substrate in the anodic chamber inoculated with mixed anaerobic sludge. TDS removals of 58, 70 and 78% were observed with salt concentration of 8, 20 and 30 g/L, respectively, in the middle desalination chamber. The MDC produced a maximum power output of 16.87 mW/m^2 during polarization. The highest Coulombic efficiency of $12 \pm 2.4\%$ was observed in this system using mixed anaerobic sludge as inoculum. The system effectively demonstrated capability for simultaneous organic matter removal and desalination along with power generation.

Key words | anion exchange membrane, cation exchange membrane, desalination, microbial desalination cell, organic matter, total dissolved solids

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INTRODUCTION

Wastewater generated from industrial, agricultural and domestic activities contain high levels of organic and inorganic matter that require treatment before discharge into water bodies. At present, organic matter is removed by conventional aerobic treatment, which consumes large amounts of electrical energy. Alternatively, anaerobic processes are more attractive than aerobic processes because of low energy consumption, low sludge production and recovery of energy in the form of methane. Wastewaters containing organic matter are currently being used as a fuel to harvest renewable electrical energy using microbial fuel cell (MFC) (Pham *et al.* 2006). The inorganic matter in the wastewater remains untouched in biological processes and needs to be removed before discharge into the environment. Various physical and chemical treatment processes such as reverse osmosis (RO), electrodialysis, distillation and ion exchange are employed for removal of inorganic matter. However, these technologies require high capital costs and energy for operation and maintenance. Therefore, an alternative renewable energy technology is required to remove inorganic matter effectively.

A new bioelectrochemical systems, the microbial desalination cell (MDC), has been developed recently that can simultaneously treat wastewater, generate electricity and desalinate saline water. The MDC consists of three chambers: anodic, middle desalination and cathodic, which are separated by an anion exchange membrane (AEM) and a cation exchange membrane (CEM). In the anodic chamber, exoelectrogenic bacteria grow on the anode, oxidize organic matter and release electrons to the anode and protons into the anolyte. At the cathode, limited protons available in catholyte are consumed, releasing hydroxyl anions. The electrons are transferred from the anode toward the cathode through an external electrical circuit due to the difference of redox potential generated between the electrodes. The ions from saline water in the middle chamber are driven to the adjacent chambers: anions through the AEM into the anodic chamber and cations through the CEM into the cathodic chamber, balancing the charge and desalinating the liquid present in this chamber. This concept of desalination was first introduced by Cao *et al.* (2009).

Artificial wastewater containing acetate has been used as anolyte for most studies testing desalination performance in the middle chamber. Since MFCs effectively removed the organic matter present in both domestic and industrial wastewaters in the anodic chamber through microbial metabolism (Pant *et al.* 2010), these wastewaters can be used in MDCs as fuel. Recently, raw wastewater (Luo *et al.* 2012) and dewatered sludge (Meng *et al.* 2014) were used as anodic substrate to reduce startup time and enhance the stability of MDCs for long-term operation over 300 days. In most of the MDCs, chemical catholytes (ferricyanide, phosphate buffer and acidified water) and catalysts (platinum) are used to decrease the reduction time (Cao *et al.* 2009; Luo *et al.* 2011; Jacobson *et al.* 2011); however, use of such chemicals is not sustainable and cannot be implemented for field-scale application. To avoid such chemicals, an air cathode can be used for practical application along with catalysts to enhance the cathodic reaction (Mehanna *et al.* 2010b).

In most MDCs, the inter-membrane distance has been relatively wide (1–2.4 cm) (Mehanna *et al.* 2010a; Chen *et al.* 2011; Luo *et al.* 2011), resulting in very high internal resistance in the system. The inter-membrane distance should be minimized to improve MDC performance by reducing internal resistance.

In a three-chamber MDC, protons released into the anolyte as a result of the oxidation of organic matter present in the wastewater are not able to migrate toward the cathode due to the AEM placed near to the anode. In addition, chloride ions accumulates in the anodic chamber from the middle desalination chamber through the AEM. Subsequently, the anolyte pH drops and affects microbial activity (He *et al.* 2008). In the cathodic chamber, hydroxyl ions are generated by cathodic reaction, increasing the catholyte pH, thus creating pH imbalances in both chambers. Problems with pH imbalance and water loss are the major limiting factor in three-chamber MDCs (Kim & Logan 2013). It was reported that one unit of pH gradient can reduce the system operating voltage (OV) by 0.06 V (Rozendal *et al.* 2007). Many approaches have been used to reduce the adverse effects of pH on electrode performance, such as increasing the anolyte volume or adding acids or bases (Cao *et al.* 2009; Chen *et al.* 2011; Jacobson *et al.* 2011). It is essential to modify the structural design of MDCs to overcome the pH imbalance.

In this study, the MDC was modified in its structural design into a five-chamber configuration with anodic, middle desalination, and cathodic chambers, as well as two concentrate chambers adjacent to the middle desalination chamber. The performance of the system was evaluated for simultaneous removal of chemical oxygen demand (COD) and total dissolved solids (TDS) from wastewater along with power generation by using saline water with different TDS concentrations in the middle desalination chamber. Hence, an attempt has been made to develop a system with the ability to remove organic matter and TDS from wastewater to produce treated water of reusable quality.

MATERIALS AND METHODS

MDC configuration

In this study, a five-chamber MDC was constructed with cubic poly-acrylic sheets with inner cylindrical chambers (cross-sectional area, 63 cm^2). The multi-chamber MDC consisted of five blocks with anodic (127 mL), cathodic (127 mL), middle desalination (32 mL) and two concentrate chambers (19 mL). All chambers were separated by two pairs of ion exchange membranes (IEMs) and a watertight seal was provided by Teflon gaskets between each chamber. The desalination chamber was separated from the two adjacent concentrate chambers by a pair of AEM (RALEX AMH) and CEM (RALEX CMH) (Figure 1). The anode and concentrate chambers were separated by placing CEM between them. Similarly, the cathodic and concentrate chambers were separated by AEM. All five chambers, along with IEMs, were clamped together. The IEMs were preconditioned by immersion in deionized water for 48 hours before being used (Pradhan & Ghangrekar 2014). The inter-membrane distance of 5 mm was provided in order to minimize the internal resistance of the MDC. Both anode and cathode (3.0 × 6.0 cm) electrodes were made from carbon cloth (Zoltek Panex 35$^\circledR$ Inc., St Louis, MO, USA) without any pre-treatment or use of catalyst. Concealed copper wires were connected to the electrodes to form a closed circuit with a fixed resistance of 100 Ω as an external load.

MDC operating condition

The five-chamber MDC was operated at an ambient temperature of 25 ± 3 °C for more than 60 days. The MDC was inoculated with mixed anaerobic sludge collected from the bottom of a septic tank. The sludge inoculum was preconditioned and added in the required volume to the anodic chamber (Ghangrekar & Shinde 2007). The MDC was
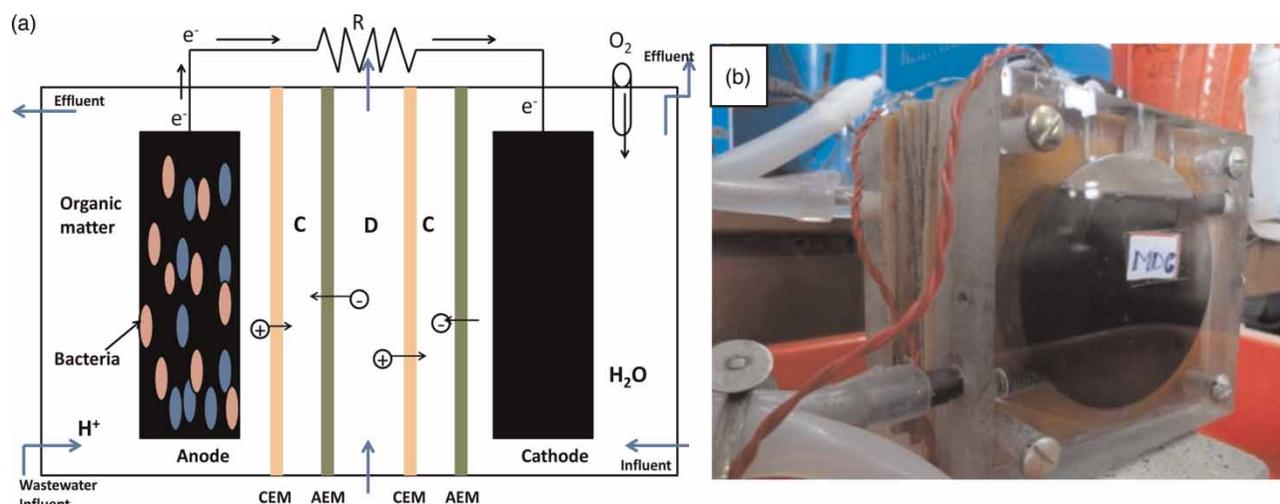
Figure 1 | (a) Schematic and (b) photograph of five-chamber MDC used for desalination (AEM: anion exchange membrane; CEM: cation exchange membrane; C: concentrated chamber; D: desalination chamber).

operated in batch mode using synthetic wastewater containing acetate as the carbon source in the anodic chamber. The anolyte was prepared using (per liter of tap water) sodium acetate, 3.8 g; NaHCO₃, 4.5 g; NH₄Cl, 0.954 g; CaCl₂·2H₂O, 0.75 g; MgSO₄·7H₂O, 0.192 g; K₂HPO₄, 0.081 g; KH₂PO₄, 0.027 g and 3 mL of trace metals solution (Ghangrekar *et al.* 2005). Aerated tap water was used as catholyte in each experimental run. Mixed ion solutions were used in the middle desalination chamber with TDS concentrations of 8, 20 and 30 g/L containing 4, 16 and 26 g/L of NaCl, respectively, along with mixed ions such as K^+, NH_4^+, Ca^{2+}, Mg^{2+}, Cl^-, NO_3^-, SO_4^{2-} and PO_4^{3-}. At a given TDS, the MDC was operated over three fed-batch cycles with a feed frequency of 4 days in the anodic and desalination chambers. The two concentrate chambers were fed with tap water initially. The concentrate was replaced completely at the end of each experimental run.

Analyses and calculations

A digital multimeter with data acquisition unit (Agilent Technologies, Penang, Malaysia) was used to measure potential and current across the external resistor of 100 Ω. The current ($I = E/R$) was determined from the measured voltage E. Power was calculated according to $P = I*E$, where P = power, I = current and E = voltage. Polarization studies were carried out by varying the external resistances from 40,000 to 1 Ω; internal resistance of the MDC was measured from the slope of the line from the plot of voltage versus current (Picioreanu *et al.* 2007). The anode and cathode potentials were measured using an Ag/AgCl reference

electrode (+197 mV vs. standard hydrogen electrode, Bioanalytical Systems Inc., West Lafayette, Indiana, USA).

The samples were collected from the anodic chamber of the MDC for initial and final COD analysis. COD was determined using the closed reflux procedure as described in *Standard Methods* (APHA 1998). TDS and the pH of the liquid present inside the anodic, desalination and cathodic chambers were measured at an interval of 24 hours in each experimental run. The pH was measured by a pH electrode (Cyber Scan, PCD 6500, Eutech Instruments, Singapore) and TDS was measured by a conductivity probe (Cyber Scan, PCD 6500, Eutech Instruments, Ayer Rajah Crescent, Singapore). The desalination efficiency was determined as the percentage of TDS decreased over the period of the 96 hours of the batch cycle.

The Coulombic efficiency (CE, %) is the fraction of electrons transferred to the anode compared to the total electron released by substrate oxidation. The CE of the MDC operated under feed batch mode was estimated as described by Logan (2008). The Faradaic efficiency or current efficiency (η_F) of the system was calculated as the ratio of the theoretical amount of coulombs (Q_t) required to remove the NaCl to the coulombs harvested through the electrical circuit ($Q = \int I dt$) assuming that removal of one mole of NaCl will require one mole of electrons (Chen *et al.* 2011; Jacobson *et al.* 2011). The Faradaic efficiency of the system was calculated as (Vaszilcsin & Nemes 2009)

$$\eta_F = \frac{Q_t}{Q}. \tag{1}$$

RESULTS AND DISCUSSION

Electricity generation and desalination performance

A maximum OV of 135 mV was produced during the MDC operation with 30 g/L of TDS concentration in the middle desalination chamber. The OV of 114 and 110 mV was produced with 20 and 8 g/L of TDS concentration, respectively (Figure 2(a)). Little change in voltage was observed during the anolyte replacement at every 96 hours due to substrate limitations for bacteria in the anodic chamber. However, with 30 g/L of TDS concentration, the change of voltage was greater when compared to operation with 20 and 8 g/L. The voltage decreased from 135 to 104 mV with 30 g/L of initial TDS concentration, while with 8 g/L the decrement was from 110 to 100 mV. This demonstrates that, apart from the substrate limitation in the anodic chamber, the voltage drop was also affected due to a change in conductivity of the electrolyte solution in the desalination chamber. It was reported earlier that the dissolved salt concentration in the desalination chamber has an impact on voltage production due to a change in internal resistance (Cao et al. 2009).

TDS removal of 58 ± 1.2, 70 ± 2.1 and $78 \pm 1.8\%$ was observed with 8, 20 and 30 g/L of initial TDS concentration in desalination chamber, respectively, (Figure 2(b)). TDS concentration of 20 and 30 g/L showed superior desalination performance than 8 g/L in all fed-batch cycles. The internal resistance of the system increased with decreasing TDS concentration. From the polarization of the system, internal resistances of 142, 127 and 110 Ω (Table 1) were observed with 8, 20 and 30 g/L of TDS concentration, respectively. High TDS concentration in the desalination chamber can

reduce the internal resistance offered by the system and generates higher OV to support higher TDS removal as compared to low TDS concentration (Cao et al. 2009; Kim & Logan 2011).

Effect of TDS concentration on system performance

It was observed that TDS removal was higher with high TDS concentration (30 g/L) in the middle chamber, as compared to low TDS concentrations (8 and 20 g/L) in the system (Figure 3). The TDS concentration in the middle chamber gradually decreased at the end of the experimental run with all salt concentrations used in the desalination chamber. In the anodic and cathodic chambers, a slight increase in TDS concentration was observed at the end of each fed-batch cycle. The potential gradient generated by electrodes transported the mixed ions present in the desalination chamber into the adjacent concentrated chambers through IEMs. The final TDS concentration in the cathode chamber was observed to be higher with 30 g/L of initial TDS concentration in the desalination chamber as compared to 20 and 8 g/L. This might be due to the non-ideal character of AEM placed near the cathode, which might have also allowed the transport of cations.

### Faradaic efficiency at different TDS concentrations

Faradaic efficiencies of 68, 201 and 294% were observed with 8, 20 and 30 g/L of TDS concentration, respectively, in the middle chamber. The theoretical coulombs required to facilitate the observed salt removal were 2.0 and 2.9 times higher than the actual coulombs observed in the system with 20 and 30 g/L of TDS concentrations, respectively. However, the Faradaic efficiency was significantly
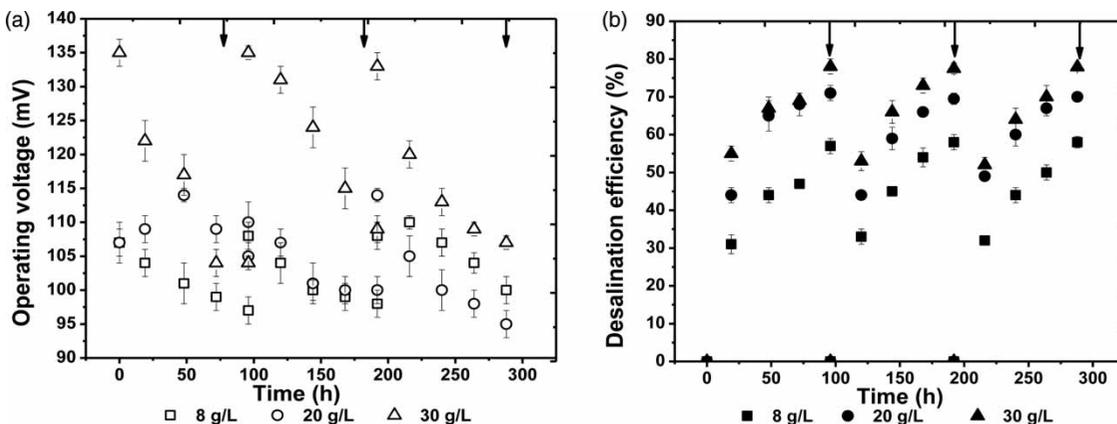
Figure 2 | (a) Operating voltage and (b) desalination efficiency over batch cycles in five-chamber MDC with initial TDS concentration of 8, 20 and 30 g/L in middle desalination chamber. Arrows indicate the electrolyte changes in MDC.

Table 1 │ Performance of five-chamber microbial desalination cell in terms of chemical oxygen demand removal, Coulombic efficiency, total dissolved solids removal, current densities and power densities in a batch cycle with 8, 20 and 30 g/L total dissolved solids concentration in the middle desalination chamber

Salt concentration (g/L)	COD removal (%)	CE (%)	TDS removal (%)	CD (mA/m²)	PD (mW/m²)	Internal resistance (Ω)
8	83 ± 2.8	10.8	58 ± 1.2	101.85	11.20	142
20	80 ± 1.7	11.7	70 ± 2.1	105.56	12.03	127
30	82 ± 1.7	14.2	78 ± 1.8	125.0	16.87	110
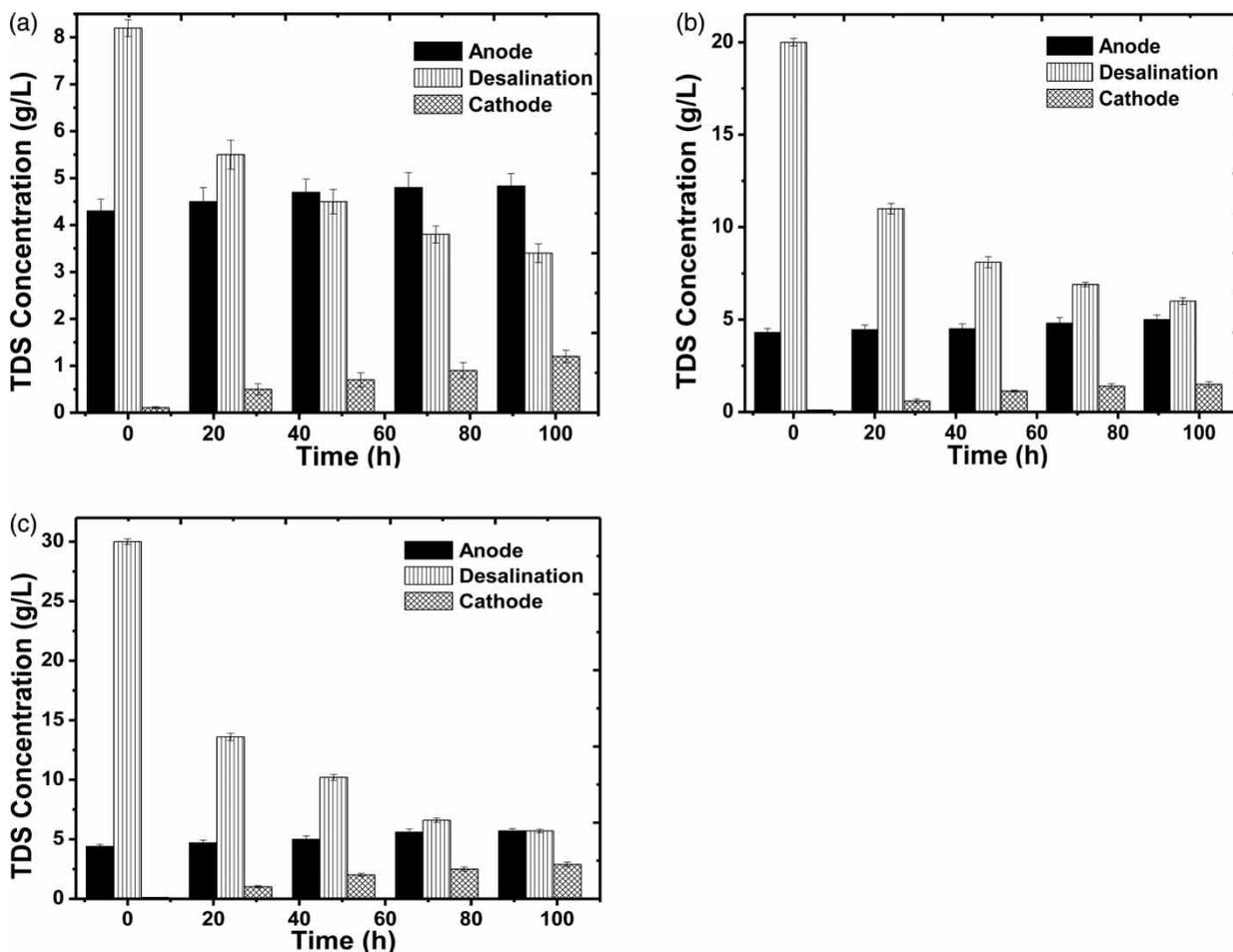
Figure 3 │ TDS concentration in anodic, desalination and cathodic chamber with (a) 8 g/L, (b) 20 g/L and (c) 30 g/L of initial TDS concentration in the middle desalination chamber.

less with low TDS concentration (8 g/L) in the middle chamber. Faradaic efficiencies of beyond 100% indicate that electric current contributed to some TDS removal while other factors such as water osmosis and dialysis also contributed to TDS removal in the MDC. The contribution of mechanisms other than electric current produced by the system itself in the desalination process has been reported previously due to a higher salinity gradient between the middle chamber and the adjacent anodic/cathodic chamber (Mehanna et al. 2010b; Jacobson et al. 2011).

COD removal and power generation

COD removal was observed in the anodic chamber for 96 hours of each batch cycle with 8, 20 and 30 g/L of TDS concentration. An average COD removal of $81 \pm 2.1\%$ was observed in the anodic chamber under all TDS concentrations tested in the desalination chamber (Table 1). No substrate loss (CH_3COO^-) occurred in the system, as the CEM was placed near to the anode. The access of proton transfer from the anode to the concentrate chamber through the CEM, helped

in maintaining the pH of the anolyte and bacterial activity (He *et al.* 2008). Hence, COD removal was unaffected by the different initial TDS concentrations in the middle chamber. The CEs were increased with higher TDS concentration in the middle chamber of the system as compared to low TDS concentration (Table 1). The highest CE of 14% was observed with 30 g/L of initial TDS concentration.

Maximum power density of 16.87 mW/m^2 was generated with 30 g/L of TDS concentration during polarization as compared to low TDS concentrations (8 and 20 g/L) in the desalination chamber. It was noticed that the performance of a five-chamber MDC improved with high TDS concentration as compared to low TDS concentration in the desalination chamber along with lower internal resistance of the system (Table 1).

pH of electrolytes

The pH inside all three chambers of the MDC (anodic, cathodic and middle desalination) was observed over each batch cycle. The initial pH of all electrolytes in the anodic, middle desalination and cathodic chambers was 8.3 ± 0.2, 8.4 ± 0.2 and 7.0 ± 0.3, respectively. The final pH values of anolyte and catholyte were slightly changed from their initial values in each experimental run. There was no drop of pH observed (pH > 7) in the anodic chamber of the MDC due to proton transport from the anodic chamber to the concentrate chamber through CEM. However, the pH of catholyte became alkaline (pH > 8.5) at the end of each experimental run. This might be due to the transport of alkali-metal cations from the concentrate chamber toward the cathodic chamber increasing the pH. Due to the concentration gradient between the cathodic and its adjacent concentrate chamber, cations might have been transported from the concentrate to cathodic chamber through non-ideal performance of the AEM. Hence, pH imbalance occurred in the cathodic chamber from the anodic and middle desalination chamber, ensuring some drop in the voltage of the system (Rozendal *et al.* 2007).

Electrode potentials

The initial anode potentials (-500 ± 15 mV vs. Ag/AgCl) were similar under all TDS concentrations in the middle chamber. However, it slightly increased at the end of the experimental run. The initial cathode potentials (76 ± 8 mV) were similar under all salt concentrations; however, it decreased (35 ± 6 mV) at the end of the cycle. Upon replacement of the catholyte in each batch, the cathode potential was restored. Oxygen was the sole electron acceptor used in the cathodic chamber. The increase of catholyte pH from the anolyte and middle saline water resulted in the voltage drop of the system and cathode potential.

CONCLUSIONS

The five-chamber MDC showed the capability of removing both organic matters from the wastewater present in the anodic chamber while removing dissolved inorganic matter from the saline water in the desalination chamber, along with electricity generation. High TDS concentration in the middle desalination chamber showed better performance in terms of TDS removal and power generation, along with lower internal resistance. The performance of COD removal was similar for all TDS concentrations in the desalination chamber. Further studies are necessary to improve the performance of the system for real wastewater application with suitable modification to the MDC configuration. Maximum TDS removal of 78% was observed, which may be acceptable under certain conditions. Nevertheless, the MDC proved to be a suitable pre-treatment method before RO.

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