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# Desalination of actual wetland saline water associated with biotreatment of real sewage and bioenergy production in microbial desalination cell

Havan H. Salman, Zainab Z. Ismail*

*Department of Environmental Engineering, University of Baghdad, Baghdad, Iraq*

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ABSTRACT

The microbial desalination cell (MDC) can be considered as a great promising technique for the production of clean water due to the potential energy saving through the desalination process. This study assesses for the first time the desalination potential of actual wetland saline water simultaneously with biotreatment of real domestic wastewater and bioenergy generation in a continuous flow triple-compartments MDC. Two types of membranes were used in the MDC, the cation exchange membrane (CEM) and anion exchange membrane (AEM) to separate the three chambers. The results demonstrated complete removal of organic matter from real domestic wastewater. Maximum observed desalination efficiency of the actual wetland saline water achieved 93.7% with power generation and columbic efficiency of 527 mW/m$^2$ and 31.14%, compared to 373 mW/m$^2$ and 44.4%, respectively observed with synthetically prepared saline water. The observed promising results in this study highly encourages the application of the suggested approach for desalination of wetland saline waters.

## 1. Introduction

Wetlands are considered as efficacious aquatic ecosystems which could be found all over the world. A wetland is a land area that is saturated with water, either permanently or seasonally, such that it takes on the characteristics of a distinct ecosystem. Wetland habitats serve substantial functions for the ecosystem, including filtering water, help reducing flood and preventing the erosion of shoreline, as well as providing food and homes for the wildlife and fish. Wetlands can be freshwater, brackish, or saline [1].

Water and energy are the primary requirements for fulfilling modern civilization. However, due to the depletion of natural resources, increasing population, global warming, and environmental contamination, scarcities of water and energy endure an international stress. Thus, there is an urgent need to develop new techniques for simultaneous salty water desalination, wastewater treatment, and power generation [2]. Microbial desalination cell (MDC) is a new technique which integrates wastewater treatment, water desalination and production of renewable energy in a single system. Recently, MDC received considerable attention for being an environmentally friendly technology [3]. A typical principle design of MDC consists of three chambers, anode, mid (for desalination) and cathode chambers, separated by anion exchange membrane (AEM) and cation exchange membranes (CEM), respectively. In the anode chamber, bacteria degrade and oxidized the organic matter. Then after, as a result of the oxidation process the electrons release and flow towards the cathode through an external electrical circuit [4–6]. The energy stored in wastewater is directly converted to electricity by the anodic biofilm and utilizes it in situ to drive the desalination process in the MDC [7].

Cao et al. [7] achieved a salt removal efficiency of about 90% during a single batch desalination cycle, meanwhile, producing electricity. Mehanna et al. [4] studied the performance of an air-cathode MDC as a pre-treatment step preceding RO unit. Maximum power density of 480 mW/m$^2$ was produced in a single cycle of operation using acetate solution at 1000 mg/l causing conductivity reduction of the brackish water (5 g/L NaCl) by 43 ± 6%. Luo et al. [8] demonstrated that when using wastewater as the only substrate in the anodic compartment, the power output from the MDC was four times higher than its value from the microbial fuel cell (MFC) which doesn't involve the desalination process. Qu et al. [9] studied the performance of four MDCs which were connected to each other and continuously operated in order to avoid the pH fluctuation which may affect the metabolism of bacteria. An et al. [10] proposed a novel four-chamber microbial desalination cell (FMDC) for the treatment of synthetically prepared Cu (II)-loaded wastewater in the cathodic compartment and simultaneously desalinate brine or seawater in the desalination compartment. Ping et al. [11] suggested that the MDC has proved to successfully remove various inorganic ions by itself as well as remove non-dissociable

* Corresponding author.
*E-mail addresses:* zismail3@gatech.edu, dr.zainab.zead@coeng.uobaghdad.iq (Z.Z. Ismail).

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boron when coupled to other devices and the product water quality can meet irrigation guideline. Sevda et al. [12] used MDC for biotreatment of petroleum refinery wastewater (PRW), desalination of sea water, and power generation. Results revealed that complex PRW could be utilized as the substrate in the anode chamber in MDCs for producing electricity and seawater desalination. Ebrahimi et al. [13] developed a quadripartite microbial desalination cell (QMDC) for a simultaneous treatment of septic tank sludge and domestic wastewater. The results indicated that at COD concentration of 4911.6 ± 71 mg/L, the COD removal efficiency, maximum power density, and the desalination rate were 58.4%, 8.16 W/$m^3$, and 72.8%, respectively over a short-term operation. Ragab et al. [14] estimated the effect of various substrate concentrations and different external resistances on MDCs performance. The results indicated that for MDC fueled with high concentration of substrate, a lowest power generation and highest internal resistance were observed. Jafary et al. [15] demonstrated a novel design of a two-chamber tubular MDC with a new arrangement of the anion and cation exchange membranes in order to: (1) mitigate the pH imbalance through the mechanism of a self-generated pH control, (2) reduce the internal resistance, and (3) enhance the generation of bioenergy in MDC using real seawater.

To the authors knowledge none of the previously reported studies concerned of wetland saline water desalination using MDC system. This study aimed to assess and evaluate for the first time the desalination of actual wetland saline water in the desalination compartment in a three-chambers MDC simultaneously with removal of organic content from real sewage, and bioenergy production. Al-Dalmaj wetland in Iraq was considered as the study area and the near which is a very promising area for energy resources, tourism, agricultural and industrial activities.

## 2. Materials and methods

### 2.1. Substrate

Real domestic wastewater was freshly collected from the main sewage pipe in Al-Kut city, Iraq. The average quality and characteristics of the collected raw sewage are presented in Table 1. It is obvious that the most critical constituents are the chemical oxygen demand (COD) as well as the oil and grease.

### 2.2. Saline water

Two types of saline water were used subsequently in this study. The first saline water was synthetically prepared by dissolving NaCl in distilled water with an average concentration of 4000 mg/L. The second type of saline water was real samples collected from Hor Al-Dalmaj which is a vast wetland located between Tigris and Euphrates, in particular at the Middle Euphrates area, Iraq, along the drainage network in that zoon (Fig. 1). It consists of relatively deep-water lake with vast marshland habitat of dense and scattered reed beds [16,17]. Water surface area and water reservoirs volume of Al-Dalmaj estimated to be 314 $km^2$ and 429 * $10^3$ $m^3$, respectively. The maximum and average concentrations of the total dissolved solids (TDS) in the actual saline wetland water were 15,000 and 9000 mg/l, respectively at pH range of 7.4–7.5 (see Table 2).

**Table 1**
Characteristics of the real domestic wastewater.

| Constituent | Unit | Average concentration | Maximum Allowable concentration* |
|---|---|---|---|
| COD | mg/l | 420 ± 100 | < 100 |
| Oil & Grease | mg/l | 112 ± 20 | 10 |
| $PO_4^{3-}$ | mg/l | 14.5 ± 7 | 3 |
| TSS | mg/l | 780 ± 200 | 30 |
| $SO_4^{2-}$ | mg/l | 329 ± 100 | 200 |
| pH | mg/l | 7.2–7.4 | 6–9.5 |
| $NO_3^-$ | mg/l | 20 ± 5 | 50 |
| $Cl^-$ | mg/l | 195 ± 20 | 200 |

* Iraqi legislation for reservation of rivers and natural streams

### 2.3. Biocatalyst

In this study, activated sludge was exploited as the source for active microorganisms. It was collected from a local sewage treatment plant in Baghdad, Iraq. The qualitative analysis of the collected sludge demonstrated that the dominant major types of microorganisms were *Pseudomonas*, *Bacilli*, and *E-Coli*. The activated sludge samples were stored anaerobically in a tightly closed plastic container until used.

### 2.4. Catholyte solution

The catholyte solution was used as an electron acceptor in the cathodic chamber of the MDC. The catholyte was a phosphate-buffer saline (PBS) and was prepared according to Wei et al. [18] by dissolving 8.5 g NaCl, 1.91 g $Na_2HPO_4$, and 0.38 g $KH_2PO_4$, in 1 L distilled water. The final solution was autoclaved at 121°C for 15 min. The final pH of catholyte solution was in the range of 7.0–7.4.

### 2.5. MDC construction and setup

A three chambered- MDC made of transparent acrylic material was constructed and setup in this study (Fig. 2). The anode and desalination compartments had dimensions of 10 cm × 10 cm × 10 cm, whereby, the dimensions of the cathode compartment were 10 cm × 10 cm × 5 cm (see Fig. 3).

Graphite plain electrodes were used in the MDC, each electrode had a surface area of 106.4 $cm^2$. The graphite electrodes were scratched before use to enhance bacterial attachment during biofilm growth. The anode and desalination chambers were separated by a sheet of an anion exchange membrane (AEM) type AMI-7001, while cathode and desalination chambers were separated by a sheet of cation exchange membrane (CEM) type CMI-7000. Both types of membranes were provided by membrane international INC., NJ. The dimensions of sheets were 10 cm × 10 cm and each sheet was placed between two perforated Perspex sheets of size 12 cm x12 cm containing 169 pores, each pore of 5 mm diameter.

### 2.6. Operating conditions

Once the design and construction of MDC system has been completed, all the components were scoured well with favorable detergent, repeatedly washed with distilled water and tap water. The AEM and CEM membranes were immersed in 5% sodium chloride aqueous solution for 12 h before use, and then rinsed with deionized water to guarantee a good conductivity for protons and electrons. The MDC was continuously fed with actual domestic wastewater at a flowrate of 0.56 ml/min. The hydraulic retention time (HRT) was 30 h.

The desalination chamber was continuously fed with 0.05 ml/min of synthetic saline water for 60 days, and then replaced with actual saline water from Al-Dalmaj wetland for additional 125 days.

### 2.7. Analysis

The performance of MDC was evaluated by daily measurements of the chemical oxygen demand (COD) concentrations of the inlet sewage and treated effluent using COD analyzer type lovibond COD/RD/125. Continuous measurements of the total dissolved solids (TDS) concentrations was carried out on a daily basis for the inlet and outlet of the desalination chamber. The voltage was continuously measured using voltage data logger (EL-USB-3) as well as by a multimeter, and then the voltage values were converted to power according to the

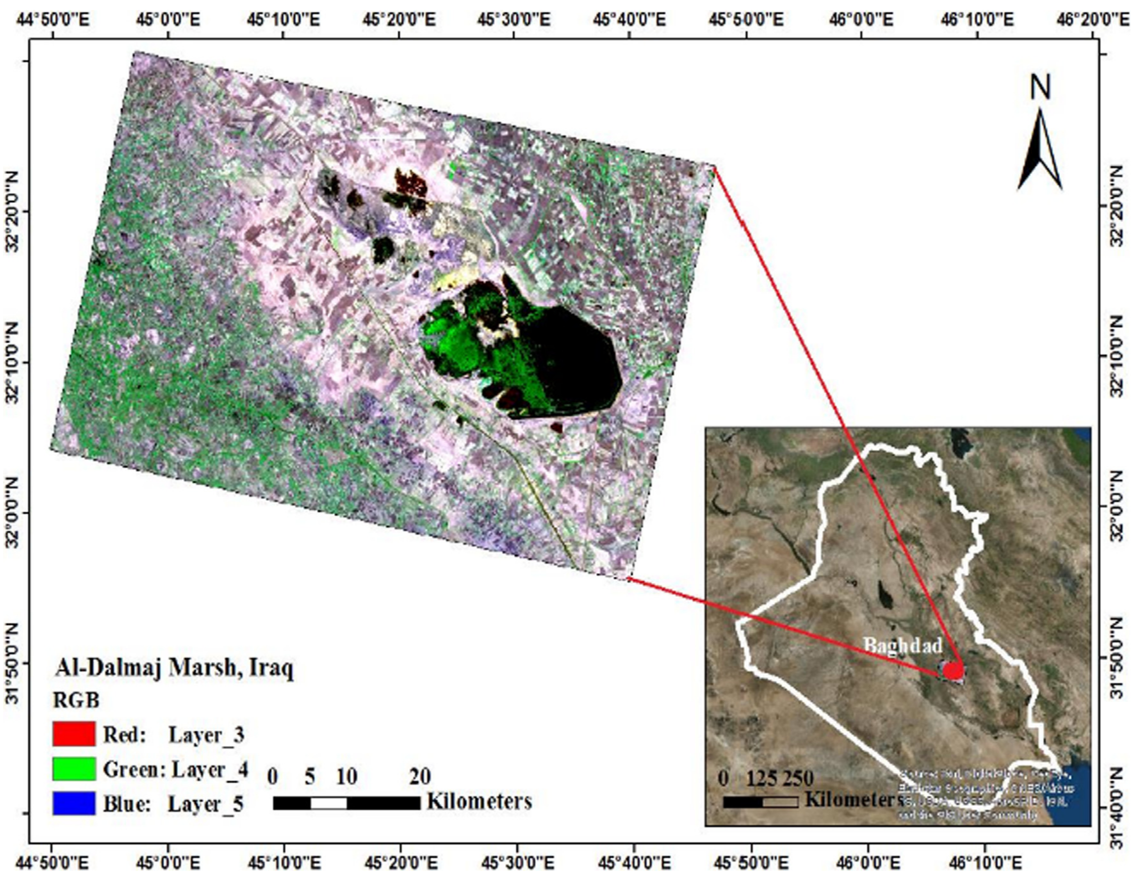


**Fig. 1.** Al-Dalmaj wetland location.

**Table 2**
Characteristics of Al-Dalmaj wetland saline water.

| Constituent | Unit | Concentration range |
|---|---|---|
| COD | mg/l | < 50 |
| $SO_4^{2-}$ | mg/l | 1700–5472 |
| $NO_2^-$ | mg/l | 1.3–2.4 |
| $NO_3^-$ | mg/l | 20–42 |
| $Cl^-$ | mg/l | 2170–9500 |
| TDS | mg/l | 4000–15000 |
| pH | mg/l | 7.4–7.5 |

following equation:

$$P = V_{cell} * I \tag{1}$$

where; P is the power, I is the electrical current, and $V_{cell}$ is the cell voltage.

The power density was calculated by normalizing the power values by the anode surface area.

The coulombic efficiency (CE) of a cell represents the amounts of electron which can be recovered from the cell. It is also, substantive as the percentage of total charge which transferred to the anode surface over the maximum charge extractable upon complete oxidation of the substrate to electricity as reported by Kassongo et al. [19]. For the continuous flow, CE can be calculated as given by Eq. (2) [20]:

$$CE = \frac{M * I}{Fbq\Delta COD} * 100\% \tag{2}$$

where; M = 32 the molecular weight of oxygen, I is the generated current in the MFC system (mA), F is Faraday's constant (96,485 C/mol electron), b = 4 is the number of electrons exchanged per mole of oxygen, q is the volumetric influent flow rate, and ΔCOD is the difference in the influent and effluent COD.

## 3. Results and discussion

### 3.1. Removal of COD

MDC was continuously operated with real domestic wastewater for 180 days. Fig. 2 presents the profile of COD removal from the real wastewater in the anodic chamber. The results revealed that the removal of COD was clearly observed after the first day of MDC operation. This could be related to the fact the components of the real domestic wastewater might be favorable to the active microorganisms of the anodic biofilm in MDC. Maximum and average COD removal achieved 100% and the 84%, respectively. The efficiencies of COD removal in this study were comparable and even higher than the values ranged between 62% and 92% reported in previous studies [21–26]. Also, samples of the treated effluent indicated a complete absence of oil and grease with a removal efficiency up to 100%. These results demonstrated the validity of the suggested approach for the treatment of the domestic wastewater.

### 3.2. Desalination performance

The desalination performance of MDC was evaluated and presented as TDS removal efficiency. As given in Fig. 4, in spite of feeding the desalination chamber with a synthetic saline solution of constant TDS concentration, a relatively high fluctuation in the TDS removal was clearly observed during the first 20 days of MDC operation. This observation could be attributed to the fact there is a lag time until the general performance of MDC system stabilized and settled down. On the other hand, a comparatively low overbalance in the TDS removal efficiency was noticed during the remaining 160 days of operation except a clearly observable sharp drop was recorded at the day 60. This steep drop in the TDC removal efficiency may related to the sudden

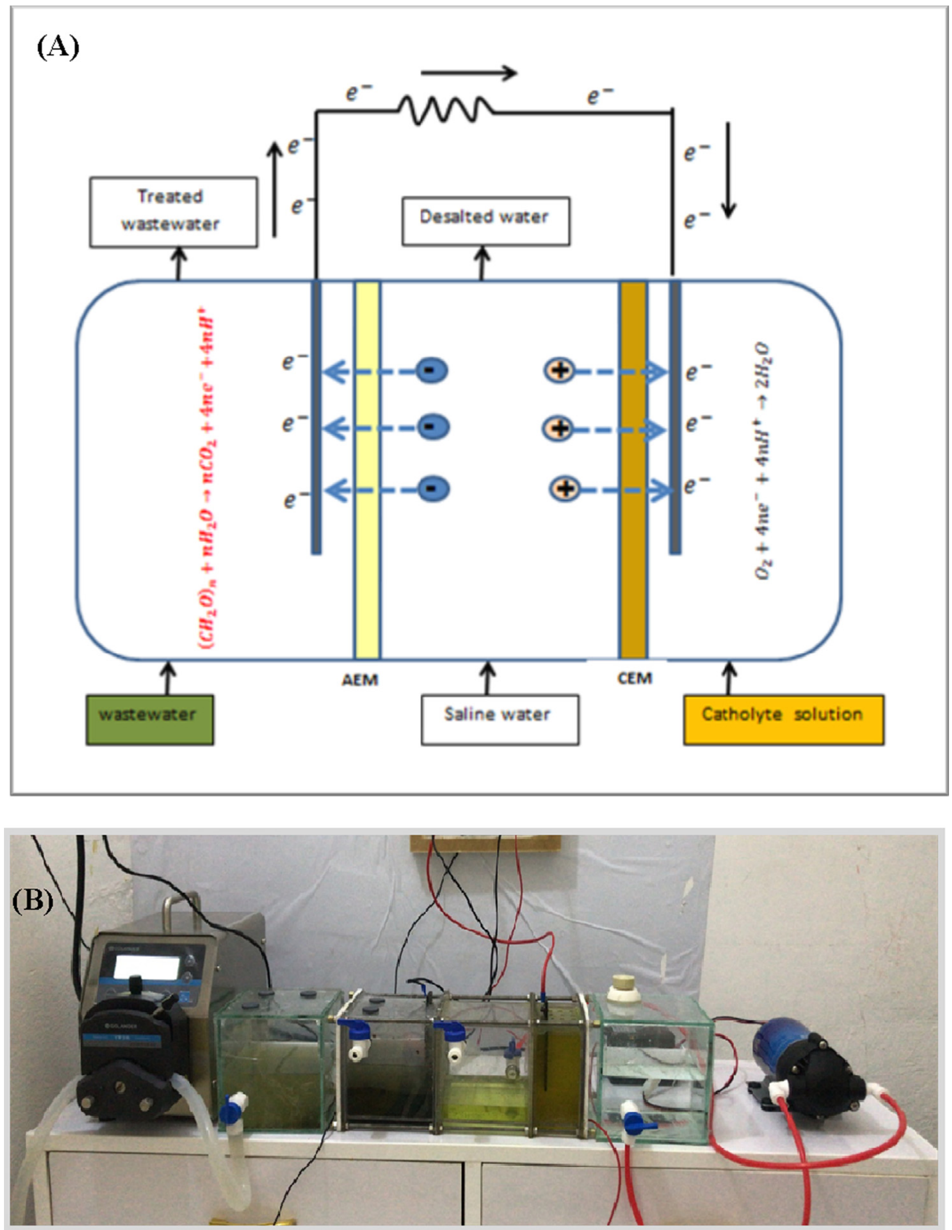


**Fig. 2.** (A) Scheme of the MDC; (B) Photo of the MDC.

replacement of the synthetic saline water by actual saline wetland water having all unexpected species within its composition. However, almost a relatively stabilized performance of MDC was obtained until the end of operation period in spite although there was a high fluctuation in TDS concentration in the actual saline wetland water. The results indicated that for the actual saline wetland water, maximum removal efficiency of TDS achieved 93.7%. This observation could be attributed to the fact that the extra number of ions resulted from the multiplication of the actual saline water species may cause an increase in the ion exchange, which in turn lead to higher TDS removal.

The results of TDS removal efficiency obtained in this study were higher than those reported in previous studies. Pradhan et al. [27] demonstrated that with salt concentration of 8, 20 and 30 g/L, the TDS removal efficiencies were 58, 70 and 78%, respectively in MDC cell fueled with acetate-loaded wastewater as the sole substrate in the anodic compartment bio-catalyzed with mixed anaerobic sludge. Meng et al. [28] found that during the steady state operation period of a two-phase microbial desalination cell (TPMDC), the desalination efficiencies in 3 days operation for various concentrations of saline solutions were 6.00 ± 0.05% for 35 g/L, 10.75 ± 0.76% for10 g/L, and 19.80 ± 0.64% for 2 g/L, respectively. Brasted and He [29] reported 90% removal efficiency of hardness from water at different concentrations ranged from 220 to 2080 mg/L as $CaCO_3$ using a bench-scale laboratory MDC.

### 3.3. Power generation and polarization curves

Electricity generation in the MDC during the entire 180 days- operation were shown in Fig. 5. A rapid increase was observed in the first 3 days and continue until almost the power generation achieved steady state after 12 days of operation. Maximum power generation was 373 mW/m$^2$ observed during the operation of MDC with synthetic saline water. Then a notable drop was observed after replacement of the synthetic saline water with actual wetland saline water. This could be due to the change of the saline water quality, in particular the TDS concentration and the existence of other species in the actual wetland saline water. However, some slight voltage drops were observed during the steady state and stabilization of power until the end of the operation

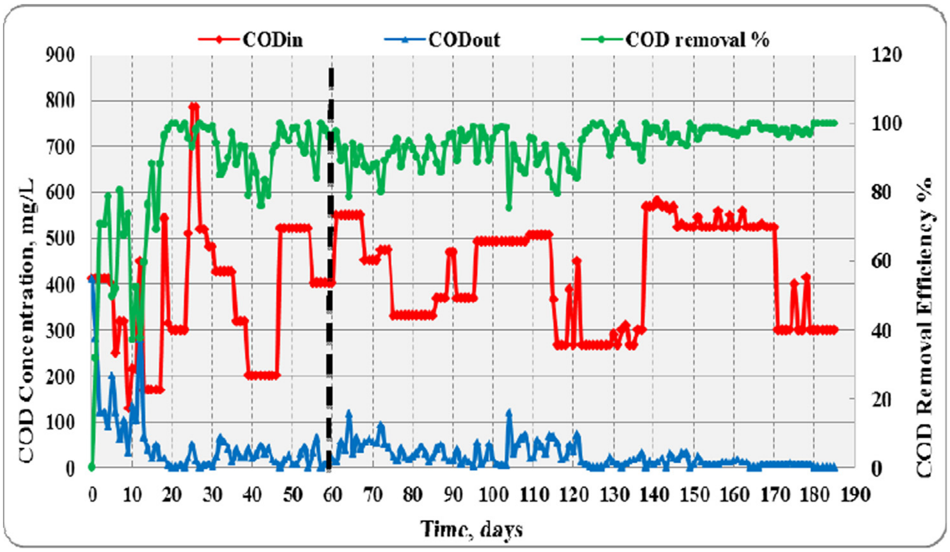


**Fig. 3.** Profile of COD removal from real domestic wastewater in the anodic chamber.

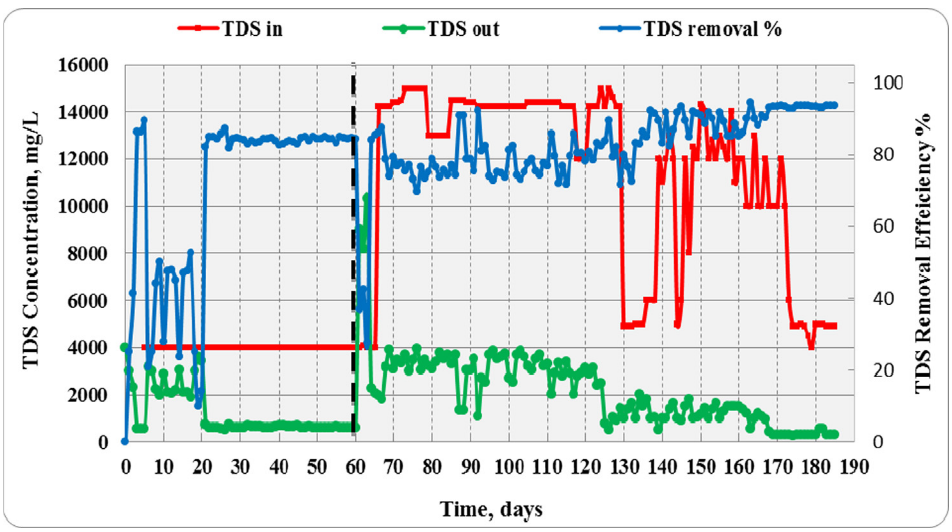


**Fig. 4.** Profile of TDS removal in the desalination compartment.

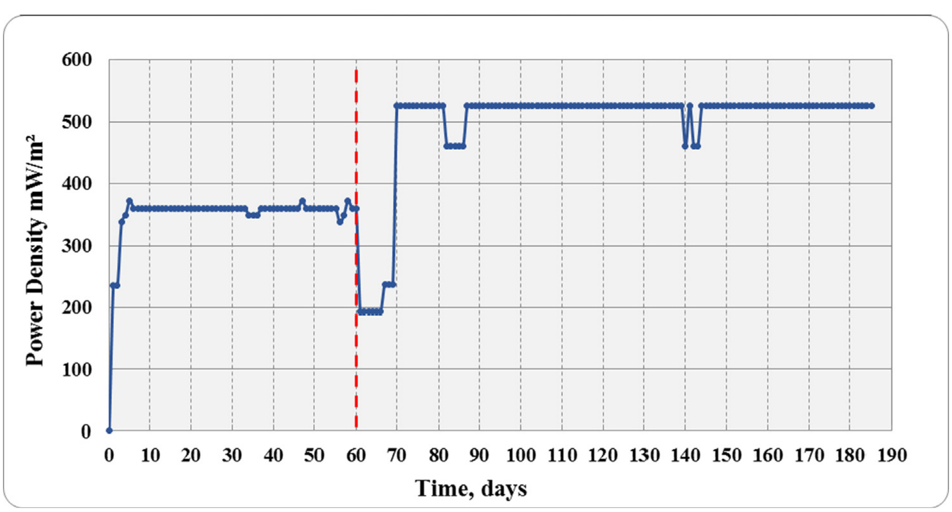


**Fig. 5.** Profile of power generation in MDC.

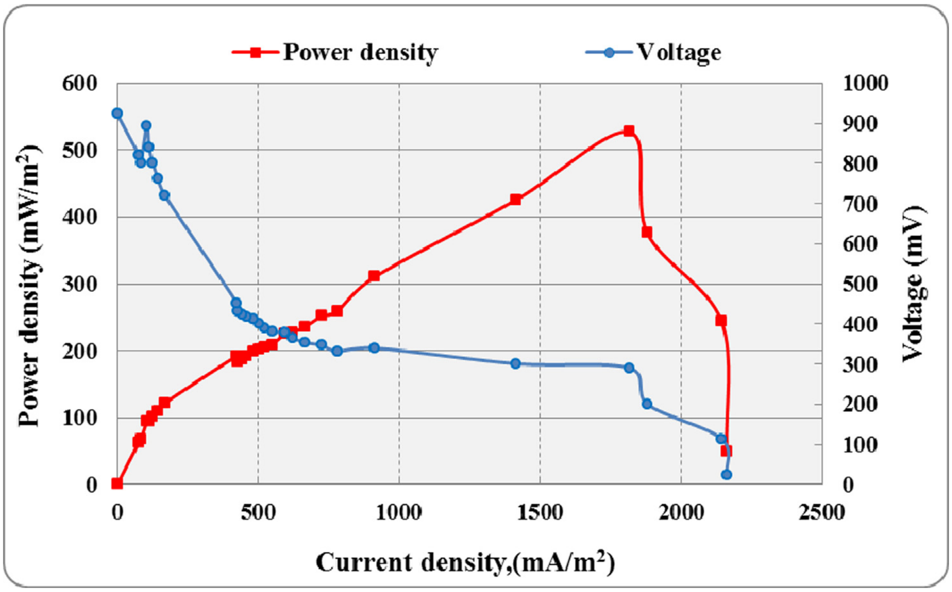


**Fig. 6.** polarization curve in the MDC.

period with maximum obtained power density of 527 mW/m$^2$ which is comparable, almost higher than 424 mW/m$^2$ reported by Mehanna et al. [4] using 5000 mg/l NaCl solution in the desalination chamber of MDC. However, it higher than a power density of 48.52 mW/m$^2$ suggested by Ismail and Ibrahim [30] in MDC coupled with FO membrane used for treatment of domestic wastewater in the anodic chamber simultaneously with the desalination of produced water in the desalination chamber. Sevda et al. [12] reported a 9.5 W h/m$^3$ with respect to the total volume of the desalinated water in MDC fueled with petroleum refinery wastewater.

Polarization curve and power density can reflect the performance of the MDC. The polarization curve presents the voltage output of the fuel cell for a certain current density loading. The relationship between the cell voltage and the power density versus the cell current density is given in Fig. 6. Variable external resistances ranged from 1 to 1000 Ω was applied to demonstrate the data required for the polarization curve of the MDC.

A maximum power and current density achieved were 172.08 mW/m$^2$, 1099.43 mA/m$^2$ for synthetic saline water and 526.94 mW/m$^2$, 2161.65 mA/m$^2$ for actual saline wetland water, respectively.

### *3.4. Coulombic efficiency*

The maximum coulombic efficiency of MDC obtained in this study under steady conditions for synthetic saline water and actual saline wetland water were 44%, 31.14%, respectively.

The overall CE was a function of substrate concentration and circuit resistance. CE is inversely proportional with COD removal and substrate flow rate. Previous studies [31–34] demonstrated that the consumption of organic substrates by non-electrogenic bacteria which may divert the electron flow toward other metabolic process could be a potential reason for observing low CE values with higher COD removal efficiencies.

## 4. Conclusion

This study was developed to assess the performance of a triple-chambers MDC for simultaneous desalination of wetland saline water, domestic wastewater treatment and power generation. The results revealed that a complete COD removal up to 100% from the real domestic wastewater was obtained in the anodic chamber. Also, the results demonstrated that the maximum removal efficiency of the TDS achieved 86% for synthetic saline water at TDS initial concentration of 4000 mg/l. However, in case of the actual saline wetland water, the TDS removal efficiency increased to 93.7% for initial concentration of TDS ranged from 3000 to 15,000 mg/l. The maximum recorded power outputs were 373 mW/m$^2$ and 527 mW/m$^2$ in MDC operated with synthetic saline water and factual saline wetland water, respectively.

## Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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