Study of Microbial Desalination Cell Performance; Power Generation and Desalination Efficiency using Pure Oxygen in a Cathode Chamber

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Abstract

Microbial Desalination Cell (MDC) is capable of desalinating seawater, producing electrical power and treating wastewater. Previously, chemical cathodes were used, which were application restrictions due to operational expenses are quite high, low levels of long-term viability and high toxicity. A pure oxygen cathode was using, external resistance 50 and 150 kΩ were studied with two concentrations of NaCl in the desalination chamber 15-25 g/L which represents the concentration of brackish water and sea water. The highest energy productivity was obtained, which amounted to 44 and 46 mW/m³, and the maximum limit for desalination of saline water was (31% and 26%) for each of 25 g / L and 15 g / L, respectively, when using an external resistance of 150 KΩ. At 50 KΩ, 13 and 12 mW/m³ were obtained, and the maximum desalination limit were 20% and 2% when using 25 g / L and 15 g / L, respectively. The concept of the mixing process was introduced in the desalination chamber to improve the performance of the system, where the highest energy productivity was obtained, which amounted 45 and 47 mW/m³, and the percentage of salt removal in the desalination chamber were 40% and 55% when using 15 g/L and 25 g/L and 150 KΩ, respectively. This study demonstrated a promising approach to using the mixing process in the desalination room in order to increase the desalination and electrical productivity.

Keywords: Microbial desalination cell (MDC), Biocathode, oxygen cathode, Voltage, external resistance.

1. Introduction

Energy has become an essential and integral part of society's life to maintain economic growth and a good quality of life. The International Energy Agency (IEA) has published that the global need for energy in 2030 will be 50% higher than it is at now [1], [2]. In addition, there has always been an urgent need to discover meaningful and creative solutions to get fresh water in the previous years, until its true implications emerged in the last few years, since fresh water accounted for just around 2% of total surface water in the world, it has resulted in a genuine focus for researchers on developing innovative and effective methods for water purification and treatment with low waste [3]. Aside from the energy component and acquiring clean energy from sustainable sources, which the modern world deems a necessary for reducing pollutants and avoiding the use of oil sources. For example, the desalination process using conventional technology (e.g.: reverse osmosis process) requires about 3.7 watt per hours of electrical energy to treat 1 cubic meter of salt water [3]. This led to the development of a
number of technologies, including the microbial desalination cell (MDC) system [8, 9], a modified version of the microbial fuel system (MFC) and the bio-electrochemical system (BES) system [2], [4], [5]. Even with water that has less than 2000 mg/L of COD, MDC has shown excellent effectiveness in decreasing pollutants in wastewater by transforming it into electrical energy. This system will aid in the processing and generation of electrical energy and wastewater, respectively. Over time, it has demonstrated encouraging outcomes in the generation of energy and wastewater treatment [6]. The anode chemical equation is expressed as:

Active microorganisms + biodegradables organics + anaerobic condition $\rightarrow n\text{CO}_2 + 4n\text{e}^- + 4n\text{H}^+ \quad(1)$ [2], [7].

The cathode chemical equation is expressed as:

$\text{O}_2 + 4n\text{e}^- + 4n\text{H}^+ \rightarrow 2\text{H}_2\text{O} \quad(2)$ [8], [9].

Alternative methods for desalination processes were found from the introduction of the concept of the microbial desalination cell in 2009 for water desalination and wastewater treatment, as well as the production of electrical energy [3]. Cao et al. (2009) were successful in removing more than 90% of (total dissolved solids) TDS using a ferricyanide catholyte with initial TDS concentration 35 g/L [10]. Mehanna et al. (2010) used platinum (Pt) catalysts to replace the ferricyanide cathode with an air cathode. Using same amounts of anode solution and saline solution, the air cathode microbial desalination cell eliminated 43–67% of the TDS from saline solution [11]. Jacobson et al. (2011) built a L$^{-1}$ Upflow Microbial Desalination Cell (UMDC) for continuous mode (with 2.75 L) and catalyzed the air cathode using a Platinum/carbon (Pt/C) solution combination. Found that the (TDS) removal rate was 11.61 ± 1.69 NaCl L/day when the salt solution’s initial conductivity was 56.7 ± 1.4 mS$	ext{cm}^{-1}$ [12]. Chen et al. (2011) developed a stacked MDC (SMDC), By inserting pairs of cells between the anode and cathode of the air. It was concluded that the introduction of additional pairs of cells led to an increase in the internal resistance, so the best number of pairs was 1.5 per cell for SMDC. Microbial desalination cell is considered as one of the promising technologies because it is versatile and produces electrical energy and can be applied on a large scale [13].

However, there is a negative aspect of the system when using chemical cathodes such as ferricyanide cathodes as they are toxic and harmful to the environment [14]. For this reason, alternatives have been found, such as using aerobic cathodes, pure oxygen, algae, bacteria, and others. The most often used reaction acceptor is oxygen because of its high reduction potential as well as low saving cost and air being a free and permanent resource [14]. In this study, a pure oxygen cathode was introduced as an electron acceptor to work as a catalyst to improve the desalination process and remove organic matter from the anode chamber.

2. Method

2.1 MDC structure

Three cubic chambers MDC with (10×7×10) cm were made using plexiglass. (6×6) cm (AMI-7000, Membranes international) and (CMI-7001, Membranes international) as anion exchange membrane and cation exchange membrane respectively used to separate between the chambers. Before usage, the membrane was soaked in a 5% NaCl solution for 24 hours and washed with distilled water, which aids in hydration and expansion. Graphite plate cut as (8×0.5×5) cm shape as anode and cathode electrodes, the working volume of anode chamber is 350mL, desalination chamber is 250 mL and cathode chamber are 350 mL.

2.2 Microorganisms and electrolyte

All microbial desalination studies used 45 mL of acclimatized anaerobic sludge taken from the first gas power plant in southern Baghdad, Iraq. A synthetic wastewater solution containing (2.778g/L) of sodium acetate was used in the anode chamber. In the cathode chamber, pure oxygen was supplied at a rate of 1 L/min; both electrodes utilized in the anode and cathode chambers were pure graphite plates with dimensions of (8*0.5*5) cm.

2.3 MDC start-up and operation

In earlier investigations, the microbial desalination cell was operated in a biofuel cell mode compared with the MDC cell. All experiments were performed in batch process. The start-up phase consisted of introducing all essential solutions just once during the whole experiment, with no addition or replacement of solutions during the experiment. Two concentrations of salts were studied in the desalination chamber at (15 g/L), which
represents turbid water, and at (25 g/L), which represents sea salt. The external resistance was changed with two values of 150 KΩ and 50 KΩ, and the influence of the mixing process was introduced into the desalination chamber to evaluate the efficiency of the desalination process and to increase electrical energy productivity. The system was set to run at a temperature of 25 ± 3 degrees Celsius.

2.4 SEM analysis

X-ray spectroscopy in conjunction with scanning electron microscopy (SEM) (EDX) A scanning electron microscope was used to examine the surface shape and topographical details (SEM). The generated images are three-dimensional and accurately depict the surface contour. The Energy Dispersive X-ray Spectrophotometer is used to examine the precursor elements (EDS). SEM-EDS analysis was performed using TESCAN, Vega III, Czech Republic.

3. Result

3.1 Electricity Performance for MDC

The system was operated in the first experiment when a concentration of NaCl 25 g/L was used in the middle chamber and 50 KΩ as an external resistance for 12 hours continuously. In the second experiment, the system was operated for 24 hours when using 15 g/L of desalination in the desalination chamber and 50 KΩ as an external resistance. The rest of the experiments lasted about 48 hours of operation. In the first hours of operation, a rise in the peak level of the microbial desalination cell was observed, and then gradually decreased throughout the rest of the operating period, as shown in Figure 1 and 2. The maximum power generated in the first experiment with 150 KΩ at a salt concentration of 15 g/L reached 44 mW/m³ and at 25 g/L of salt concentration it reached 46 mW/m³, while in the second experiment the maximum power generated reached 13 and 14 mW/m³ for each of 15 and 25 g/L of salts, respectively. The pH values of the system showed a decrease in its value as a result of the transfer of chlorine ions derived from middle chambers to an anode chamber which caused a decrease the pH value from 8.31 to 7.01. The lower power was caused primarily by the lower potential of the cathode with ventilation. As shown in the Figure 3, introducing the mixing process in the desalination chamber to positively influence the production of electrical power. An experiment was studied using two concentrations of salts in the desalination chamber (15-25 g/L) with a fixed external resistance of 150 KΩ. This change led to an increase in electrical power production by about 45 and 47 mW/m³ for each of 15 and 25 g/L, respectively.

Fig. 1 show the performance of the MDC with 150 KΩ of the external resistance and with 25-15 g/L of NaCl in desalination chamber with continuous pure O2.
Fig. 2 show the performance of the MDC with 50 KΩ of the external resistance and with 25-15 g/L of NaCl in desalination chamber with continuous pure O2.

![Power density vs. time](image)

Fig. 3. show the performance of the power generation in MDC with 150 KΩ of the external resistance and with 25-15 g/L of NaCl in desalination chamber with mixing.

3.2 TDS concentration removal

The conductivity of saline for concentrations of NaCl 15 g/L and 25 g/L when using the mixing process and without using the mixing process is shown in Figure 4 and 5. The percentage of desalination depends on a change in the conductivity of the solution, as the decrease in the conductivity in the desalination chamber leads to a decrease in the desalination rate. Because a small part of the water may move from the middle chamber to the cathode chamber. In the current study, the minimum conductivity reached was 24.5 mS and 16.8 mS when use 150 k Ω as external resistance and 25 g/L and 15 g/L of NaCl concentration in the middle chamber, respectively, and the desalination was 31% and 26% at 25 g/L and 15 g/L of TDS concentration in the middle chamber after 48 h operation, respectively; the minimum conductivity achieved was 29.9 mS and 22.09 mS when using 50 k Ω as external resistance and 25 g/L and 15 g/L of NaCl concentration in the middle chamber, respectively, the maximum desalination obtained was 20% when 25 g/L of TDS concentration in the middle chamber with 24 h of operation time and 2% when 15 g/L TDS concentration in the middle chamber with 12 h of operation time. The effect of mixing improves decreasing in the conductivity in the desalination chamber, 16 mS and 24 mS when using 150 K Ω and with 25 g/L and 15 g/L of TDS concentration in the desalination chamber, respectively, the mixing improves the desalination efficiency and reached 55 % and 40 % when 25 g/L and 15 g/L of TDS concentration used in the
middle chamber, respectively. As shown in the Table 1 the comparison of the desalination rate and efficiency that obtained from this study and previses studies. The presence of Na$^+$ and Cl$^-$ ions in its composition are just a small part of the sea water content. It is nevertheless possible to present ions such HPO$_4^{2-}$, PO$_4^{3-}$, Cl$^-$, K$^+$, and NH$_4^+$. When using real wastewater, it may contain a number of complex elements, such as CaSO$_4$, CaCO$_3$, MgCO$_3$, Ca(NO$_3$)$_2$, and MgSO$_4$, among others. During the desalination process, some of these ions may be transported from saltwater to freshwater, increasing the possibility of water contamination and IEM pollution.

Fig. 4. Shown the conductivity of the MDC without using mixing in the desalination chamber.

Fig. 5. Shown the conductivity of the MDC using mixing in the desalination chamber.
3.3 Percentage of COD removal in MDC

The maximum COD removal value reached in the anode chamber was 35.5% when use 50 KΩ as external resistance with 25 g/L of TDS concentration for 24 h operation time, and 8% when 50 KΩ as external resistance with 15 g/L of TDS concentration for 12 h operation time. 40% and 25% maximum COD removal were achieved when use 150 KΩ as external resistance with TDS concentration (25 g/L and 15 g/L), respectively, for 48 h operation time. The air cathode has become the focus of attention for researchers because of its high potential in oxidation and reduction processes. However, the crossing of oxygen from the cathode chamber to the anode chamber in the MFC system may be the only major drawback of oxygen cathodes [14], [20]. The structure of the microbial desalination cell provides an additional intermediate chamber between the anode chamber and the cathode chamber, which is a buffer zone for the diffusion of oxygen from the cathode chamber to the anode chamber, so it is possible that the anaerobic cathode is promising in the microbial desalination cell. Zhang et al. 2014 studied the efficiency COD removal in the anode chamber with air cathode microbial fuel cell (MFC) the maximum COD removal achieved was 78 % with 100 Ω as external resistance and 91% with 1000 Ω as external resistance this different in the rustles may due to the different in the construction of the cells in the MDC have an addition chamber case increasing in the internal resistance and the time of operation [21].

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Table 1, Comparing the performance of microbial desalination cell (MDC).

| Desalination rate (%) | TDS concentration (mg/L) | TDR (mg/h) * | cathode | Ref. |
|-----------------------|--------------------------|--------------|--------|-----|
| 77                    | 35                       | 2.3          | Air cathode | [15] |
| 100                   | 30                       | 109.4*       | Air cathode with pt | [16] |
| 99b                   | 10                       | 1.8*         | Air cathode with pt | [17] |
| 80                    | 20                       | 25.2         | Air cathode with pt | [13] |
| 98                    | 35                       | -            | Air cathode with pt | [18] |
| 63                    | 20                       | -            | Air cathode with pt | [19] |
| 37                    | 20                       | 1.7*         | Air cathode with pt | [11] |
| 44                    | 35                       | -            | Air cathode with pt | [18] |
| 31                    | 25                       | 0.112c       | Pure O₂ cathode | This study |
| 26                    | 15                       | 0.02c        | Pure O₂ cathode | This study |
| 55                    | 25                       | 0.21c        | Pure O₂ cathode with mixing in the desalination chamber | This study |
| 40                    | 15                       | 0.045c       | Pure O₂ cathode with mixing in the desalination chamber | This study |

* Data calculated according to figures and profiles presented in corresponding articles.

b with 0.8 V as additional voltage.

c with 150 KΩ as external resistance.

* TDR (Total Desalination Rate).
3.4 Biofouling analyses

Figure 7 (A&B) shows the SEM image for the fresh membrane (AEM) that used in the MDC and used (AEM). Figure (7 A) shows the SEM image examination of a fresh anion exchange membrane and an unused AEM revealed evident differences between the membrane surface and a cracked detected for the new anion exchange membrane. Figure (7 B) Clearly indicate the fouling layer for the anion exchange membrane employed. The surface of the anion exchange membrane exhibited both biofouling, which are often generated by bacteria aggregating in the shape of rodes, and inorganic crystalline crusts, which are formed by the deposit of inorganic compounds in synthetic wastewater. Figure (7 C) revealed clearly the variation in pore size in the anion exchange membrane (AEM) before and after usage. Figure (7D) after applying the pore size range of (28.56 µm – 12.17 µm), the pore size range is (26.61 µm – 54.19 µm). This difference is the fundamental reason for lowering the rate of desalination during working hours, since the highest rate is achieved in the early hours.
Fig. 7. The SEM & the pore size for the Anion Exchange Membrane before and after used.
4. Conclusion

The air cathode of MDC can be an effective method for sewage treatment, electric power production and water desalination, as oxygen has a great ability to reduce electrons. The external resistance and mixing processes in the desalination chamber can also have the ability to directly affect the efficiency of the MDC system: the maximum power generation obtained 47 mW/m$^3$, the maximum COD removal was and the maximum desalination 40% water obtained 55% with 150 KΩ as external resistance after 48 h operation time. The results obtained in this study will enable the system to be developed to make it more efficient and sustainable for both sewage treatment processes, electric power production and desalination of salt water.

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دراسة أداء خلية تحلية المياه الميكروبية ؛ كفاءة توليد الطاقة وتحليل المياه باستخدام الأكسجين

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الخلاصة

خلية التحلية الميكروبية (MDC) قادرة على تحلية مياه البحر وإنتاج الطاقة الكهربائية ومعالجة مياه الصرف الصحي. في السابق ، تم استخدام الأكسجينات الكيميائية ، والتي كانت في الغالب على التدفقات السطحية مربعة جدة ، ومستويات منخفضة من الصالحة بحرية أطول وعملية عالية. تم إدخال كتلة أكسجين نقي ودروس المقاومة الخارجية (KΩ) 0.05 و 0.15 (متر) و 0.25 (متر) مع تركيز من كودر الصوديوم في غرفة التحلية 20.15 جم/لمتر والتي يمثل تركيز الماء كمليواد و مياه البحر. تم الحصول على أعلى إنتاجات الطاقة والتي بلغت 44 و 46 ميغاواط / متر. وكان الحد الأقصى للنسبة المائية للماء المحلة (KΩ = 0.5 و 0.6) لكل من 55 و 56 جم/لمتر و 15 جم/لمتر على التوالي. عندما امتداداً مقداراً خارجية قدرها 500 كم/المتر ، تم الحصول على 13 و 14 و 15 جم/لمتر و 16 جم/لمتر على التوالي. تم إدخال مفهوم عملية التحليل في غرفة التحلية لمعدات الأكسجين أداء الماء. أظهرت هذه النشاطة نهجاً واعياً لاستخدام عملية التحليل في غرفة التحلية من أجل زيادة واعدة لاستخدام هيئة التحليل والكهرباء.