

Enhancing the performance of microbial desalination cells using δMnO_2 /graphene nanocomposite as a cathode catalyst

Abdelsalam Elawwad , Mostafa Ragab, Ahmed Hamdy and Dalal Z. Husein

ABSTRACT

In this work, δMnO_2 was anchored into graphene nanosheets via a mediated simple and eco-friendly approach to be used as a potential low-cost cathodic catalyst in microbial desalination cells (MDC). MnO_2/G based MDC revealed a faster start-up and stable performance during the operation compared with the catalyst-free control MDC. The average chemical oxygen demand (COD) removal efficiencies were 85.11 ± 5.13 and $86.20 \pm 4.85\%$ and average coulombic efficiencies throughout the operation cycles were $1.52 \pm 0.32\%$ and $0.70 \pm 0.35\%$ for MnO_2/G based reactor and control reactor, respectively. The average desalination efficiencies were 15.67 ± 3.32 and $13.21 \pm 2.61\%$ for MnO_2/G based reactor and control reactor, respectively. The superior catalytic performance of MnO_2/G based cathode improved current generation which is the key desalination stimulus. MnO_2/G based reactor revealed a lower internal resistance of 430Ω compared with 485Ω for the catalyst-free control reactor and, similarly, the maximum power densities were found to be 12.5 and 6.5 mW/m^2 , respectively. MnO_2/G catalyst offered an improved MDC performance, however, still with uncompetitive performance in comparison with platinum group metals catalysts.

Key words | cathode catalyst, microbial desalination cells, MnO_2/G nanocomposite

HIGHLIGHTS

- Application of MnO_2/G as cathode catalyst in boosting the performance of MDCs.
- MnO_2/G nanocomposite was synthesized using simple and eco-friendly approach.
- MnO_2/G cathode improved power generation and desalination rates in MDC.
- Power densities of MnO_2/G cathode were twice those of catalyst-free cathode.

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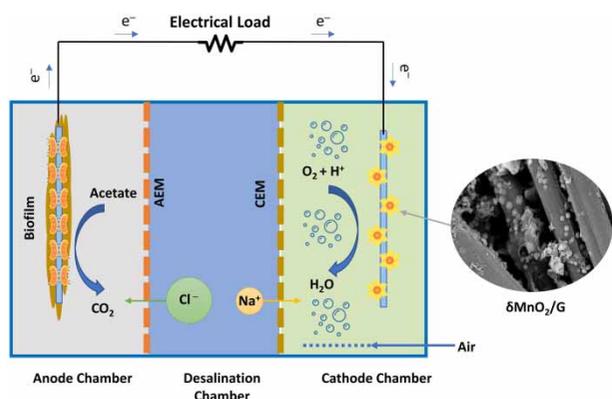
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GRAPHICAL ABSTRACT



INTRODUCTION

Freshwater demand is exaggerated due to strained population growth and rapid industrialization (Sevda *et al.* 2015; Al-Mamun *et al.* 2018). Desalination of the sea and brackish water can be a feasible solution, however, still a challenge for the developing countries (Elimelech & Phillip 2011). Desalination technologies are consuming intensive energy and accordingly contributing to climate change through greenhouse gas emissions (Cao *et al.* 2009; Subramani & Jacangelo 2015). The microbial desalination cell (MDC) is a derivative technology from the microbial fuel cell (MFC) which provides desalination with minimum external energy input. This technology was developed by Cao *et al.* (2009) to provide three main functions: wastewater treatment, energy production and desalination. The desalination process takes place through the transfer of ions from the saline water in line with the generated current by the electrogenic bacteria (Cao *et al.* 2009). Nowadays, increasing emphasis has been placed on the feasible scale-up of MDC technology for practical applications (Ragab *et al.* 2019b).

Performance and output efficiency of MDC are influenced by several factors, such as operational conditions, electrolyte conductivity, electrode materials and membrane fouling (Jingyu *et al.* 2017; Ragab *et al.* 2019b). Electrodes' materials not only affect the system performance but also the system cost efficiency. Electrodes' materials employed in MDC should have a high surface area, chemically stable

structure and with the lowest possible cost (Venkata Mohan *et al.* 2014). The reported potential achieved by MDC so far is lower than the theoretical potential which could be attributable to the system internal losses including the electrode overpotential (Scott & Yu 2015). The anodic oxidation influences the MDC performance significantly; however, the cathodic reduction is also viable for the effective and stable performance of the MDC (Pant *et al.* 2012; Scott & Yu 2015). Several studies have reported different alternatives for cathode materials; however, there are still many concerns regarding their cost, sustainability and applicability. Oxygen was used in most of the MDC studies as the terminal electron acceptor, although there are several obstacles in the application of oxygen as electron acceptor such as limitation of mass transfer in the system and high overpotential of oxygen reduction reactions (Fogel & Limson 2016). Noble metals (e.g., platinum group metals (PGM)) were applied in the cathode surfaces due to their high catalytic activity (Cetinkaya *et al.* 2015). However, these metals are impractical for wide application due to their extreme cost and poisoning sensitivity (Rismani-Yazdi *et al.* 2008; Harnisch *et al.* 2009). Significant efforts were directed to boost the oxygen reduction reaction (ORR) at the cathode surface using cheap and cost competitor catalysts. Numerous materials have been reported in the literature such as metal oxides, metals, conducting polymers, carbides and macrocycles (phthalocyanine and

porphyrines); however, they exhibited unsatisfactory performance compared with the PGM catalysts (Morris *et al.* 2007; Bashyam & Zelenay 2011; Zhang *et al.* 2011; Zhou *et al.* 2011; Khilari *et al.* 2013). The use of conductive nanomaterials and nanoparticles represents a vital solution for cathode modifications to increase their surface area and system performance (Fogel & Limson 2016). Nanotechnology approaches can play further roles in improving MDC performance and facilitate the development of large-scale MDC systems. Carbon nanomaterials have revealed possible applications as low-cost metal-free catalysts (Qu *et al.* 2010; Ben Liew *et al.* 2014).

Recent studies have shown great interest in graphene application for improving the properties of the MFCs and MDCs electrode materials. Graphene-based anodes can accelerate the anodic oxidation due to their high surface area that increases the flow of electrons from the electrogenic bacteria to the anode surface. Furthermore, the graphene can improve the cathodic reduction reactions due to its superior conductivity and surface area (Yuan & He 2015). Several studies reported the feasibility of manganese oxides (MnO_x) as cathodic catalysts in MFC due to their low cost, considerable catalytic activity and environmental friendliness (Khilari *et al.* 2013). However, due to its poor conductivity, various types of conductive supporting materials (e.g., Carbon black, Vulcan, graphite) were reported in the literature to enhance the electrochemical ORR performance (Khilari *et al.* 2013). The benefit of using MnO₂/graphene composite as a cathode in MFCs was reported in some recent studies. However, these studies used Hammer method (liquid phase exfoliation) for preparation of the graphene oxide which is reduced to graphene. This method incorporates a long pathway to prepare the graphene and usually involves highly toxic chemicals and high temperature. In this work, graphene was produced directly from graphite in one step using electrochemical exfoliation method; no toxic chemicals were used, and no high temperature was applied. In addition, the electrochemical method is time-saving. The preparation of the graphene based electrodes using direct electrochemical exfoliation is simpler and easy to implement (Zhou *et al.* 2013). Moreover, the properties of graphene produced by electrochemical exfoliation of graphite have higher quality compared to that produced by liquid-phase exfoliation

(Hammer method) (Lin *et al.* 2016). The electrochemically exfoliated graphene showed higher crystallinity and fewer defects than graphene produced by liquid-phase exfoliation (Lin *et al.* 2016). On the other hand, the electrochemical exfoliation technique is an eco-friendly approach.

In this study, graphene was prepared from graphite using electrochemical exfoliation method at room temperature, then, MnO₂ was anchored with graphene nanosheets via a mediated and simple method. The produced MnO₂/graphene (MnO₂/G) nanocomposite was characterized and then employed as a cathode catalyst in MDC. In contrast to MFCs, the performance of MnO₂/graphene nanocomposite as cathode catalyst has not been tested yet with MDC applications. This paper addresses the application of MnO₂/graphene nanocomposite as a cathode electrode catalyst and the potential improvement of system performance in terms of power generation and contaminant removals.

MATERIALS AND METHODOLOGY

System set-up and construction

Two microbial desalination (MDC#1 and MDC#2) cells were constructed using acrylic sheets, then formed and glued together in cuboid shape with the same dimension as used in our previous study (Ragab *et al.* 2019b). The three MDC chambers in both cells were separated through ion exchange membranes (AMI-7001S & CMI-7000S, Membranes International, USA) as shown in Figure 1. As per the manufacturer's recommendations, the ion exchange membranes were immersed in 5% NaCl solution before starting the experiments, to allow expansion and hydration (Ragab *et al.* 2019b). Plain carbon cloth 6 cm × 5 cm (CCP-30S, Fuel Cell Earth, USA) was employed as an anode electrode for both cells and as a cathode electrode 5 cm × 5 cm for MDC#2. MnO₂/graphene nanocomposite was prepared as a catalyst and then applied over a plain carbon cloth using Nafion[®] solution to be used as the cathode electrode 5 cm × 5 cm for MDC#1. MDC electrodes were connected externally through a titanium wire. An external resistance of 1 K kΩ was used to close the circuit, as shown in Figure 1.

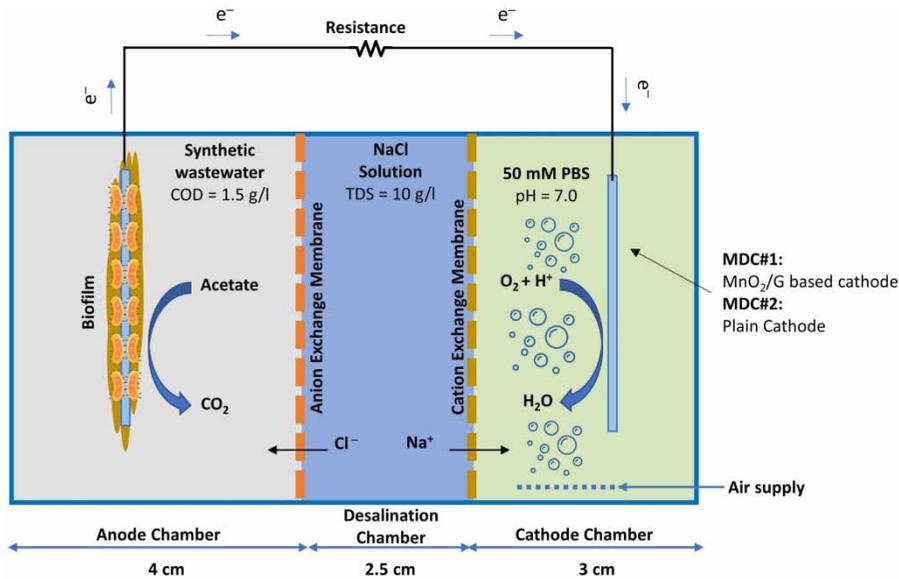


Figure 1 | Schematic of microbial desalination cell. The full colour version of this figure is available in the online version of this paper, at <http://dx.doi.org/10.2166/wrd.2020.011>.

Electrolytes and inoculum

Acetate-based synthetic wastewater (chemical oxygen demand (COD) = 1.5 gm/L) was used as the sole source of electrons in the anode chambers. The acetate had the same composition used by Ragab *et al.* (2019a). Anaerobic sludge was collected from a local wastewater treatment plant and used as inoculum to reduce the start-up period. The cathode chambers were fed with phosphate buffer solution (PBS 50 mM, pH = 7.0) and kept aerated through air blowers to ensure the availability of electrons' acceptor (i.e., oxygen). A synthetic NaCl solution with total dissolved solids = 10 g/L was used as a source of saline water in the desalination chambers.

Operation and analysis

The two cells were tested at the same operating conditions. MDC#2 (plain cathode) was used as a control reactor for comparison with MDC#1 (MnO_2/G based cathode). Both cells were operated at room temperature ($25 \pm 2^\circ\text{C}$) using the previously described electrolytes for 5 days (start-up period). Afterwards, the solutions were changed every batch cycle (3 days) throughout the experiment period (50 days including the start-up). The voltage was recorded every 1 minute through a voltage probe that was connected

to a data acquisition system (SensorDAQ, Vernier, USA) from one end and the MDCs from the other end. The current was calculated according to Ohm's law. Power and current densities (mW/m^2 and mA/m^2) were normalized to anode projected surface area. Polarization curve and internal resistance were obtained as described by Ragab *et al.* (2019a). Columbic efficiencies (CE %) were calculated by dividing the integrated measured current (C_E) over the theoretical current (C_T) based on consumed COD (Jadhav & Ghangrekar 2009) as per the following equations:

$$CE(\%) = C_E / C_T \quad (1)$$

$$C_T = (F * w * n) / M \quad (2)$$

where:

F = Faraday constant (96,485 C/mol),
 n = no. of moles of electrons produced per mole of substrate,
 $n = 4$ for wastewater,
 w = daily COD load removed in gram,
 M = molecular weight of substrate,

$$C_E = I * t$$

where:

I = current intensity,
 t = time duration (sec).

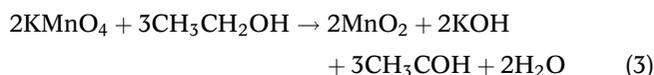
At the end of each cycle, samples were collected from the anolytes and saline water for COD measurements using a UV/VIS spectrophotometer (DR4000, Hach, Germany), and salt concentration measurements using a salinity sensor (SAL-BTA, Vernier, USA), respectively.

Preparation and characterization of the $\text{MnO}_2/\text{graphene}$ nanocomposite

The graphene powder was prepared using electrochemical exfoliation method as shown in Figure 2. Two pencil graphite rods were inserted in a parallel position in a 100 mL solution of 0.1 N Na_2SO_4 under direct-current voltage of 12 V (Figure 2(a)). With time, the anodic electrode swelled and corroded in the electrolytic cell as a black dispersion (Figure 2(b)). After 2 hours of electrolysis, the exfoliated black precipitate (graphene) was filtered and dried at 70 °C. The dried graphene (0.2 g) was dispersed in 120 mL of deionized water and stirred for 30 min. Afterwards, 2 g of KMnO_4 was added to the mixture and stirred for 10 min, then, about 30 mL of ethanol was added to the reaction mixture. After 1 hour of stirring, the reaction mixture was filtered and dried at 60 °C. The obtained dried material was labelled as MnO_2/G .

The reaction between the strong oxidizing agent KMnO_4 and ethanol is an exothermic redox reaction with

precipitation of MnO_2 and oxidized products of ethanol according to the possible reaction:



The produced MnO_2 was anchored with graphene sheets to produce MnO_2/G .

Preparation of cathode electrode

The carbon cloth surface (25 cm²) was cleaned by sequential soaking (12 h each) in 3 M HCl, acetone and ethanol, and followed by drying. About 0.08 g of dried MnO_2/G composite was dispersed in 1:1 alcohol-based Nafion[®] solution (5%) and stirred for 20 min. The cleaned and dried carbon cloth was soaked in the mixture and then dried in the air. The process of soaking/drying was repeated four times. The total loaded amount of catalyst on the carbon cloth surface was 22.6%.

Characterization of the prepared nanocomposite

The MnO_2/G composite was characterized by X-ray diffraction (XRD, Phillips; PW 1710), scanning electron

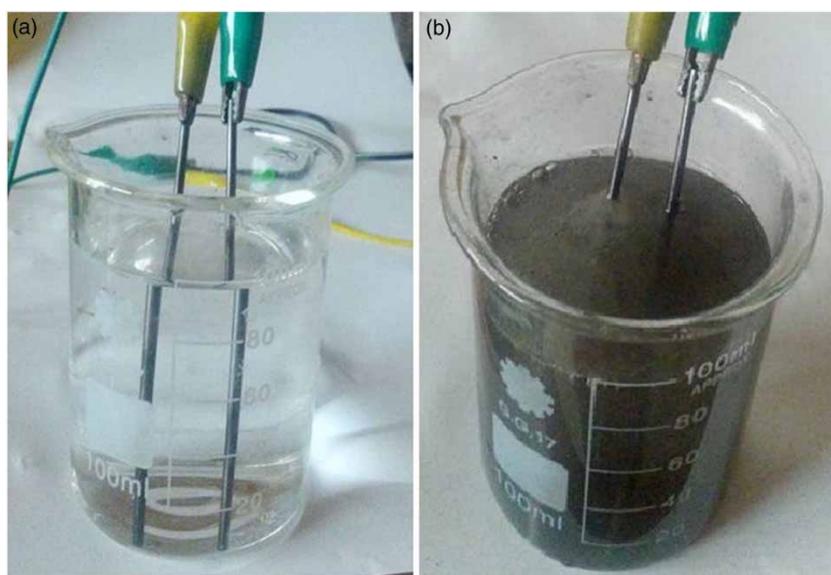


Figure 2 | Exfoliation of graphite pencils into black graphene precipitate: (a) the two parallel graphite pencils in Na_2SO_4 electrolyte and (b) black exfoliated graphene. The full colour version of this figure is available in the online version of this paper, at <http://dx.doi.org/10.2166/wrd.2020.011>.

microscope (SEM, QUANTA-FEG250) and energy dispersive X-ray analysis (EDX) techniques.

RESULTS AND DISCUSSION

MDCs voltage generation and polarization

Voltage generation during the 53 days' operation for both cells is exhibited in Figure 3. The maximum recorded voltage was 259.7 and 101.8 mV for MDC#1 (MnO₂/G based cathode) and MDC#2 (plain cathode), respectively, during the start-up. MDC#1 achieved superior voltage from the beginning of the operation while MDC#2 revealed wobbling voltage until the third cycle. The quick start-up achieved by MDC#1 could be due to the active support and electrocatalytic activity of MnO₂/G composite (Gnana Kumar et al. 2014). During the consecutive operation cycles, an average voltage of 170 and 80 mV was achieved for MDC#1 and MDC#2, respectively. MDC#1 always attained higher voltage generation during the experiment compared with MDC#2. This higher performance could be attributed to

the higher ORR of the catalyst based cathode in MDC#1 compared with the catalyst-free cathode in MDC#2. Khilari et al. (2013) and Shahbazi Farahani (2018) reported an improved ORR for cathodes using MnO₂/G composite as a catalyst. A higher voltage generation of 370 mV was reported in other studies using α -MnO₂/G catalyst in a single-chamber MFC system (Gnana Kumar et al. 2014). The increased number of chambers and ion exchange membranes in the MDC system increased the internal resistance and, consequently, decreased the voltage generation compared with the higher voltage reported by the MFC system. Moreover, the catalytic performance α -MnO₂ is higher than δ MnO₂, therefore, lowering the voltage generation (Khilari et al. 2013). As shown from Figure 3, MDC#1 demonstrated a stable voltage generation during all operation cycles which demonstrated the considerable stability achieved by MnO₂/G catalyst. Li et al. (2017) demonstrated that there was only a 5% decrease in 20 operation cycles for the MFC system using MnO₂/G as a catalyst. These results revealed that the MnO₂/G catalyst has improved the performance of the microbial desalination cell in comparison with the control reactor in terms of voltage generation.

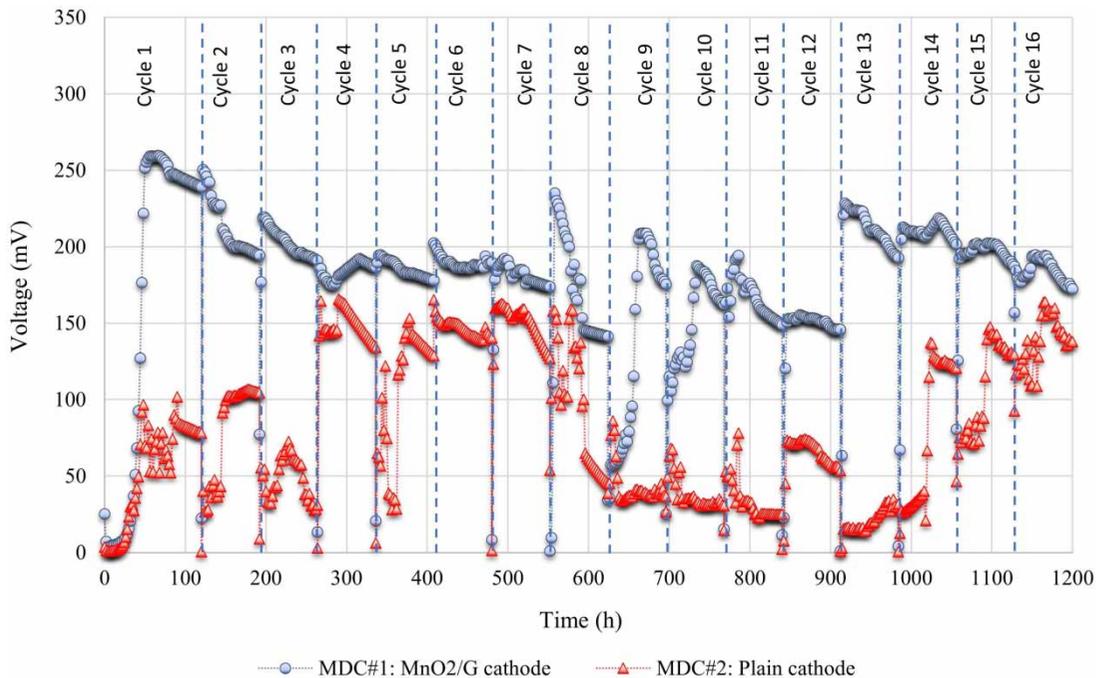


Figure 3 | Voltage generation for the cells during the operation cycles. The full colour version of this figure is available in the online version of this paper, at <http://dx.doi.org/10.2166/wrd.2020.011>.

The polarization and power curves for both MDCs are shown in Figure 4. The internal resistance was calculated by curve slope depicted in Figure 4(a). MDC#1 revealed a lower internal resistance of 430 Ω compared with 485 Ω for MDC#2. The maximum power densities were found to be 12.5 and 6.5 mW/m² for MDC#1 and MDC#2, respectively, as illustrated in Figure 4(b). It is very clear that using the MnO₂/G catalyst in MDC#1 improved the power densities significantly with a magnitude of 2:1 compared to the catalyst-free MDC#2. Hence, MnO₂/G composite can be a promising catalyst for improving MDC performance. Gnana Kumar *et al.* (2014) reported a high conductivity and large surface area for the MnO₂/G composite which enhances the contact between the electrode material and electrolyte and decreases the internal resistance. In recent studies, the maximum power density was achieved by this catalyst in the MFC system compared with other catalysts such as MnO₂ nanorods and the catalyst-free electrodes (Gnana Kumar *et al.* 2014; Rout *et al.* 2018). Kodali *et al.* (2017) reported power densities' reduction over time when the MnO₂/G composite was used as a catalyst in a single-chamber MFC system due to biofilm formation at the cathode surface. This phenomenon was not experienced in this study because the anode, desalination and cathode chambers are separated via ion exchange membranes and,

hence, the cathode is not exposed to any bacterial contamination. Khazraee Zamanpour *et al.* (2017) reported power densities of 9.5 mW/m² using catalyst-free biocathode which is considerably less than the power densities achieved in this study using the MnO₂/G catalyst. Nevertheless, in all other studies, the platinum based cathodes achieved significantly higher power densities. It is noteworthy that the power densities depend on several factors such as operation conditions, reactor size, type of electrodes and type of ion-exchange membranes.

COD removal performance and columbic efficiencies

Pollutant removal in terms of COD is one of the key MDC functions reported in the literature and has to be evaluated after using the MnO₂/G catalyst. The COD removal efficiencies were measured at the batch cycle end and the rates were calculated accordingly. The COD removal efficiencies and rates are illustrated in Figure 5. The average COD removal efficiencies were 85.1 \pm 5.1 and 86.2 \pm 4.9% while the average removal rates were 2.07 \pm 0.22 and 2.10 \pm 0.21 g/L/d for MDC#1 and MDC#2, respectively. Removal efficiencies and rates of both cells were found to be similar to each other during the different operation cycles which is congruous with the results reported in the literature. Liew *et al.* (2015)

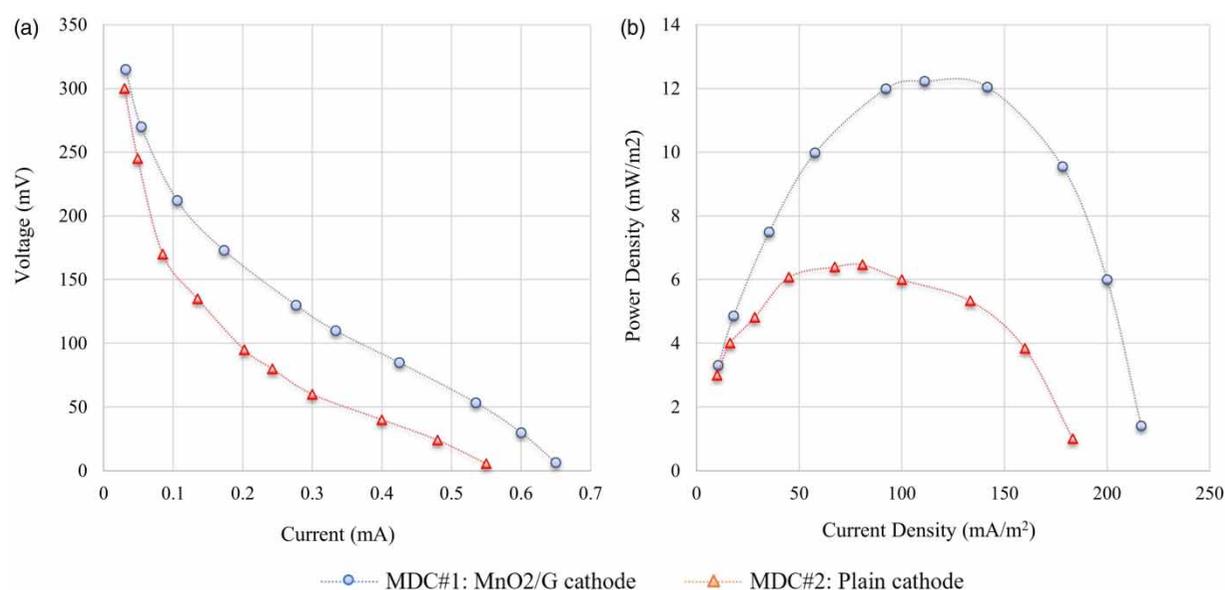


Figure 4 | (a) Polarization curve and (b) power densities curve for the two cells at various external resistances (10 Ω to 10 k Ω). The full colour version of this figure is available in the online version of this paper, at <http://dx.doi.org/10.2166/wrd.2020.011>.

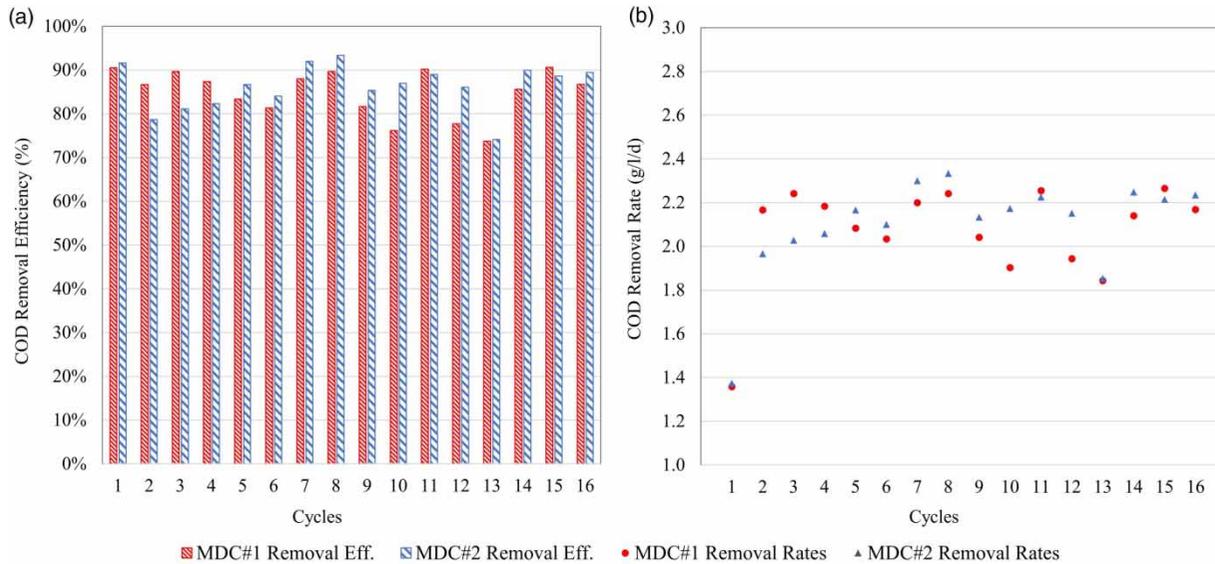


Figure 5 | (a) COD removal efficiencies and (b) COD removal rates for the two cells measured at the end of each operation cycle. The full colour version of this figure is available in the online version of this paper, at <http://dx.doi.org/10.2166/wrd.2020.011>.

reported an average COD removal efficiency of 85–86% in the MFC system despite using different cathode catalysts. Khilari *et al.* (2013) reported a COD removal efficiency of 83.7% using MnO₂/G catalyst with a very slight increase in removal efficiency of 84.4% when using the Pt/C catalyst that has superior catalytic activity. The high electrocatalytic performance would promote the electrogenic bacteria to

produce more electrons through the consumption of more anodic substrate (Li *et al.* 2017). However, this was not reflected in the COD removal rates due to the possible existence of other microorganisms (e.g., methanogens) that compete with the exoelectrogens in substrate intake. This assumption can be supported with the lower CEs reported in this study as exhibited in Figure 6.

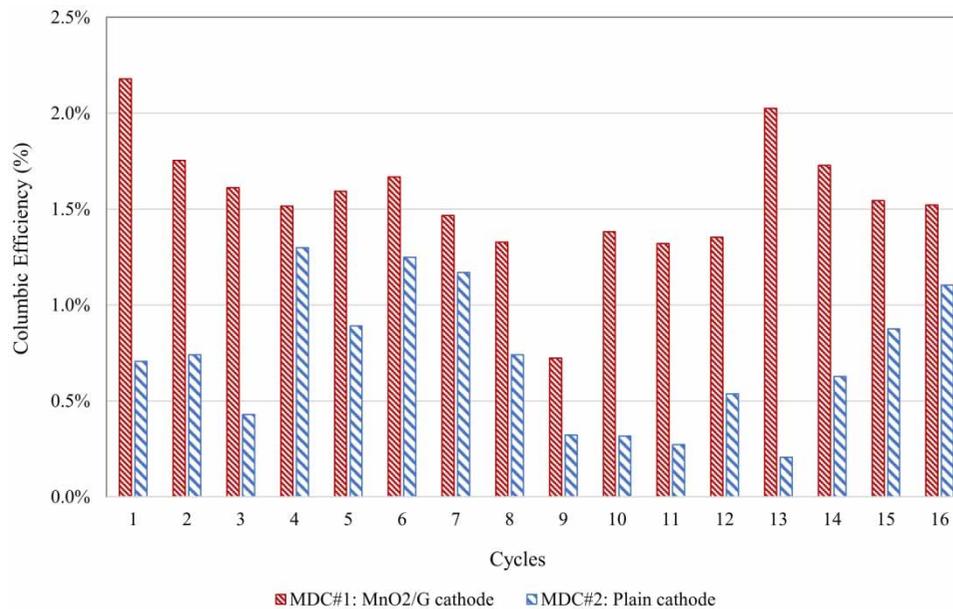


Figure 6 | Calculated columbic efficiencies for the two cells during the operation cycles. The full colour version of this figure is available in the online version of this paper, at <http://dx.doi.org/10.2166/wrd.2020.011>.

Figure 6 shows the CEs (%) of both cells per batch cycle. The CE is used to evaluate the MDC capacity in transforming the substrate into electricity (Rout *et al.* 2018). The average CEs were $1.52 \pm 0.32\%$ and $0.70 \pm 0.35\%$ for MDC#1 and MDC#2, respectively. MDC#1 always achieved higher CE than MDC#2 which indicates the superior catalytic performance of MnO_2/G based cathode compared with the free catalyst cathode. Stable CEs could be attained by MDC#1 from the first cycle. In contrast, MDC#2 started to achieve improved CE after three cycles. Higher CEs values were reported in the literature in MFC systems using MnO_2/G catalyst. The lower CEs of these MDCs could be attributed to the high internal resistance, as previously mentioned, and the electron loss due to the utilization of anodic substrate for microorganisms' growth.

Desalination efficiencies and rates

At the batch cycle end, desalination efficiencies (%) were measured and the rates (g/L/d) were determined accordingly. The results are illustrated in Figure 7. Average desalination-achieved efficiencies were 15.7 ± 3.3 and $13.2 \pm 2.6\%$ and rates were 4.05 ± 0.96 and 3.4 ± 0.76 g/L/d for MDC#1 and MDC#2, respectively. MDC#1 always achieved higher desalination efficiencies and rates than MDC#2 due to higher

current generation which is the key desalination stimulus. Higher desalination rate for the MDC#2 using MnO_2/G could be due to the higher catalytic activity which increases the difference in anode and cathode potentials and encourages the ions' migration through the ion-exchange membranes. Kokabian & Gude (2013) reported desalination rates of 0.161 and 0.076 g/L/d when using air cathode and algal-biocathode MDCs, respectively. These rates are substantially lower than the rates determined in this study. In another study, an average removal rate of 7.2 g/L/d for MDC using Pt/c as catalyst was reported which is nearly double the rates reported in this study (Ragab *et al.* 2019b).

Despite the significant difference in the current generation, the difference in desalination efficiency was not analogous. This behaviour could be attributed to the osmotic water transport across the IEMS which dilutes the middle chamber concentration and enhances the water recovery in the three MDC chambers (Kim & Logan 2013). However, it is worth mentioning that the desalination rates depend on several factors such as volume of desalination and anode chambers, salt concentration, hydraulic retention time, oxygen reduction reaction and membrane surface area (Kokabian & Gude 2013). Therefore, further investigation is still needed to investigate the technical and economic feasibility of the desalination rates achieved so far by MDCs (Ragab *et al.* 2019a).

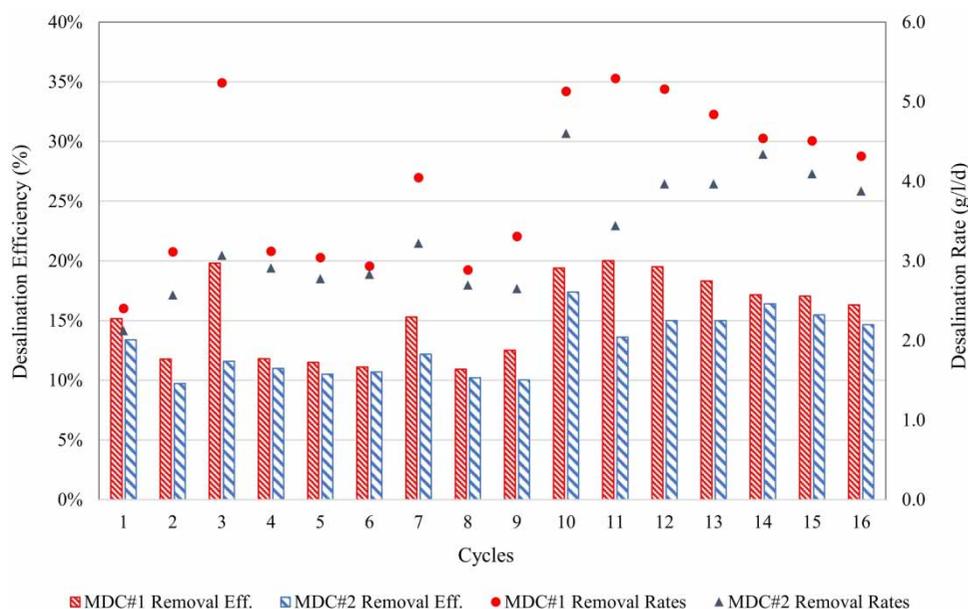


Figure 7 | Desalination efficiencies and rates for the two cells measured at the end of each operation cycle.

Characterization of MnO_2/G catalyst

X-ray diffraction analysis is illustrated in Figure 8. The XRD examination ascertained the formation of birnessite (δ -type) MnO_2 on the graphene surface, as shown in Figure 8, in which all diffraction peaks can be indexed to birnessite (δ -type) MnO_2 (JCPDS no. 42-1317). The SEM images of plain carbon cloth and MnO_2/G coated cathode at the end of the experiment are shown in Figure 9. SEM images revealed that MnO_2/G nanocomposite was successfully loaded at the carbon cloth surface (Figure 9(b)). As shown in Figure 9(c), the flower-like shape of MnO_2 was anchored onto graphene sheets and aggregations can be observed in some parts of the graphene surface. In addition, SEM

analysis showed that the MnO_2/G is tightly attached to the carbon cloth surface. The EDAX measurements (Figure 10) showed that MnO_2/G nanocomposite comprises C, O, Mn and few K and Ca, which indicates that MnO_2/G is tightly adhering to the carbon cloth. The weight percentages for C, O and Mn elements are 67.9, 24.7 and 4.0%, respectively, while their atomic percentages were 76.9, 21.0 and 1.0%, respectively.

CONCLUSION

In this paper, δMnO_2 supported on graphene sheets was synthesized and examined as a cathode electrocatalyst in MDC.

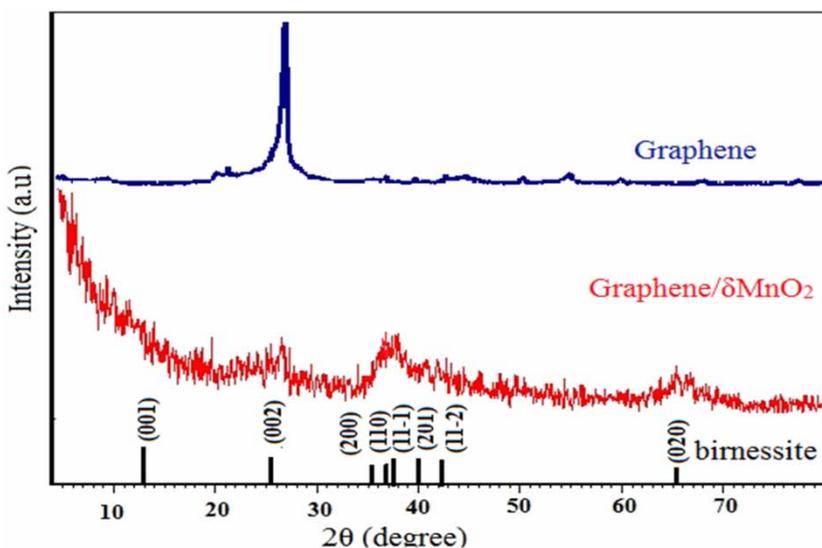


Figure 8 | XRD pattern of MnO_2/G composite and graphene. The full colour version of this figure is available in the online version of this paper, at <http://dx.doi.org/10.2166/wrd.2020.011>.

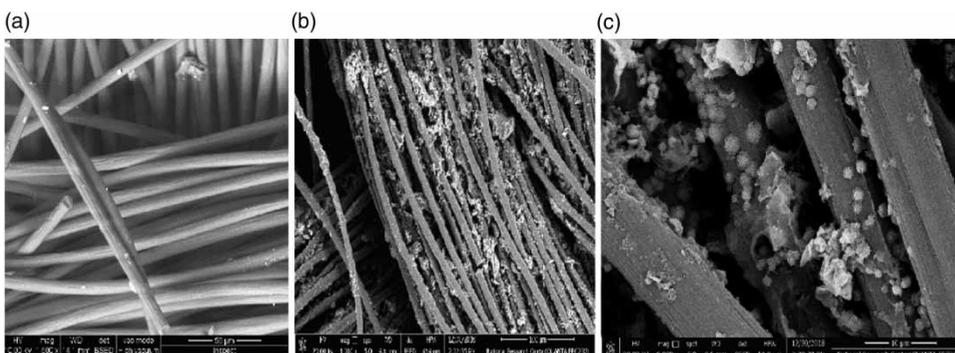


Figure 9 | SEM images of (a) plain cathode, (b) and (c) MnO_2/G coated cathode.

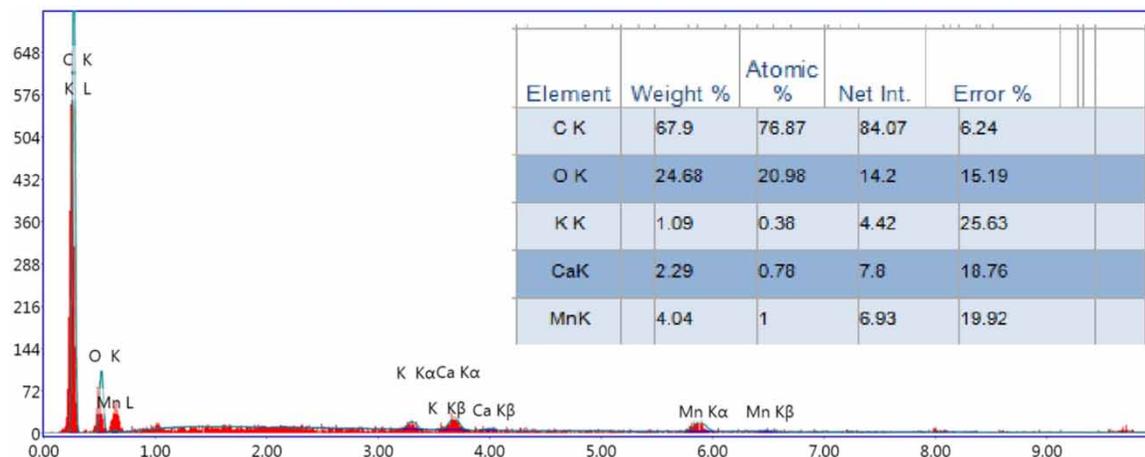


Figure 10 | EDAX analysis for the MnO₂/G coated cathode after application into the desalination cell. The full colour version of this figure is available in the online version of this paper, at <http://dx.doi.org/10.2166/wrd.2020.011>.

In contrast to the conventional chemical method (Hammer method), that produces the graphene using hazardous chemicals, this work shows the advantages of preparing graphene directly through electrochemical exfoliation method in one step. Produced graphene sheets were used as a matrix to support the growth of δ -MnO₂ onto the surface of graphene at room temperature via a mediated method which offers a simple and eco-friendly method. MnO₂/G based MDC revealed a faster start-up and stable performance during the operation compared with the catalyst-free control reactor. This stable performance could be due to the high catalytic performance demonstrated by the MnO₂/G cathode. MnO₂/G based reactor revealed a lower internal resistance and, consequently, a higher power density with a magnitude of 2:1 compared to the catalyst-free control reactor. The high catalytic performance of the MnO₂/G cathode increases the difference in anode and cathode potentials and encourages the ions' migration through the ion-exchange membranes and, thus, increased the desalination rates compared with the control reactor. Scale-up of MDCs for practical applications is still a challenge. Thus far, there are many concerns about the cost, sustainability and applicability of the MDC electrode materials. Despite the promising results reported in this study, still, the MDC-employed δ -MnO₂ cathode showed uncompetitive performance in comparison with platinum group metals in terms of CEs and desalination rates. Nevertheless, this material can be used as support for other

conductive materials to improve catalytic performance, and needs further investigation.

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DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

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