The operation characteristics of air cathode Microbial Desalination Cell to treat oil refinery wastewater

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Abstract. This system [microbial desalination cell (MDC)] is considered an excellent sustainable process to treat wastewater by biological anaerobic oxidation of the organic material by electroactive bacteria, desalinate saltwater, and electrical power generation. In the present work, MDC was used for treating oil refinery wastewater in the anode chamber by anaerobic bacteria. Simultaneously, an air pump was used to provide the oxygen to the cathode chamber as an electron acceptor to generate bioelectricity power. The power density generated by this air cathode MDC with 1KΩ external resistance at the 1st experiment was 71.11 μW/m². It increased to a peak value of 570.86 μW/m² at the last experiment. The maximum chemical oxygen demand (COD) removal percent of oily wastewater was 96%. The higher salinity removal rate 150.39 ppm/h with a first salt concentration in a desalinating chamber of 35000 ppm.

1. Introduction
Oil refineries usually generate a significant quantity of wastewater from different refining processes, for example, percolation, desalting, distillation, thermal cracking, and other treatment processes used in oil refining to produce beneficial products [1,2]. The quantity of the generated wastewater is estimated to be as high as 1.6 times the crude oil volume remedied [3]. Discharging this type of wastewater into surface water bodies without treatment causes significant damages to environmental and human health due to the poisonous contaminants such as (hydrocarbons, phenol, and dissolved minerals) [4,5]. Therefore, this wastewater most has sufficiently remedied to satisfy the environmental regulations standards [6]. Different physical and chemical oily wastewater treatment processes are implemented utilizing different electrocoagulation methods, electrochemical oxidation, and dissolved air flotation [7]. However, these processes are costly due to the enormous quantities of chemicals are used and expensive pieces of equipment, and extravagant sludge production amounts. So, biological methods are an excellent alternative to the chemicals and physical processes due to modest and uncostly with friend-environment operating conditions [2-8]. Biological processes use aerobic, anaerobic, or semi aerobic microorganisms to transform complex organic material into simple materials (CO₂, H₂O, and CH₄) [9]; a bioelectrochemical system one of the current biological treatment methods to treat many types of industrial wastewater.

Bioelectrochemical systems can produce the excellent value of chemical energy products or clean electricity from different wastewater sources. Organic or inorganic wastes can avail to use by electroactive bacteria as fuel [10,11]. The microbial desalination cell (MDC) combines wastewater and saltwater treatment to benefit from electrical power recapture without any exterior electrical power chip or mechanistic activity or pressure implementation [12]. MDC is progressed from the microbial fuel cell
(MFC) by adding the desalination compartment in the middle of the anode and cathode compartments [13,14]. The anode chamber used many types of wastewater as a substrate, synthetic wastewater, or real wastewater. The anode chamber is considered a powerhouse for the MDC; microbes donate their electrons to the chamber's electrode. The electrons later pass to the electrode of the cathode chamber through an outer circuit. In the cathode chamber, the definitive response happens at the cathode compartment's electrode in the oxygen existence. Air cathode is utilized in MDC; this supplies a more suitable and efficient system to reduce the synoptic cost [15,16].

Moreover, many MDC designs are suggested by many researchers to promote the process’s execution, and one of these designs air cathode MDC. This design has two ways to supply the oxygen in the cathode chamber: exposing the cathode's electrode to the air directly. The second way was used in this research; an air pump provides the oxygen to the cathode chamber. While widely utilizing synthetic wastewater as a substrate in MDCs [17,18], little works focus on treating actual wastewater. For example, Surajbhan et al., [15] studied seawater desalination with simultaneous bioelectricity generation from MDC treatment. In this work, MDC was used to treat petroleum refinery wastewater and study the saltwater desalination and catholyte solution's effect on the treating process. Ateh et al., [19] compared the execution of an MDC under batch and continuous municipal wastewater feeding conditions. The results of this study presented relatively improve MDC performance by anolyte enrichment under controlled continuous feeding conditions. Long-term execution and description of this system in domestic wastewater remediation studied by Haiping et al., [20]. This work described MDC’s long-term execution pending wastewater treatment and determined the critical factors of execution decrease. The 8-month was the operation period for this work, and during this period, the MDC execution declined by time. The dropping in current density was 47%, the decline in Columbic efficiency was 46%, and the decline in desalination rate was 27%. Haiping et al., [17] studied MDCs for improving the execution in municipal wastewater treating, desalination, and electric power generation.

This work investigates air cathode MDC's performance to treat oil refinery wastewater, desalination of salty water, and electric power production by recording COD removal percentage, desalination rate, and amount of electrical power produced.

2. Materials and method
2.1. MDC consistency
In this study, the air cathode MDC was constructed of plexiglass chambers (anode, desalination, and cathode chamber). The anode and the cathode chambers each have dimensions of 10x10x7 cm, while the desalination chamber has a size of 10x10x3 cm, as described in figure 1-a [21]. Two types of ion-exchange membranes supplied from Membrane International Ltd., were used, anion exchange membrane (AEM, AMI 7001) and cation exchange membrane (CEM, CMI 7000). The AEM disconnected the anode and desalination chambers; the CEM disconnected the cathode and desalination chambers. Before use, the membranes were preconditioned for 24h by flooding in a 5% salt (NaCl) solution and swilled with deionized water as recommended by the supplier to allow membrane hydration and expansion. The anode and cathode were made of graphite sheets; each has a 9x9 cm (length x width) dimension and 2 mm (thickness). The distance between each electrode and the adjacent membrane was 1 cm. Copper filaments with sealed contact were utilized to connect the external resistance to the electrodes.

All chambers were provided with inlet and outlet ports of 1 cm in diameter, except the cathode chamber has a 3 cm diameter inlet port suitable for dissolved oxygen (DO) meter. The anode chamber was sealed from ambient air to attain the required anaerobic conditions. The anolyte and catholyte volume was 650 mL, while the desalination chamber solution volume was 300 mL. The air cathode MDC is shown in figure 1-b.
2.2. The materials
In this study, the experimental work consists of three experiments in the same conditions to treat the same wastewater. The three chambers of air cathode MDC have the following:

1. Microbial consortium and anolyte solution:
   A mixed culture microbial consortium was used; it was obtained from the conventional activated sludge of the Al-Doura refinery wastewater treatment plant in Baghdad city. Acclimation of the sludge was done in anaerobic conditions for one week. For the biofilm development on the anode, the acclimation process is done inside the MDC's anode chamber. After that, the oily wastewater treatment was started by feeding the anode chamber with oily wastewater of COD 75 mg/L (oil refinery wastewater after pretreated with dissolved air flotation). The characteristics of oily wastewater are illustrated in Table 1.

Table 1. The characteristics of oily wastewater.

|       | COD (mg/L) | Oil (mg/L) | Ph (mg/L) | S.S (mg/L) | S² (mg/L) |
|-------|------------|------------|-----------|------------|-----------|
|       | 75         | 6          | 1.02      | 124        | 0.09      |

2. Catholyte solution:
The buffer solution was used as a catholyte solution composed of 2.25 g/L KH₂PO₄, 2 g/L K₂HPO₄·3H₂O dissolved in 1L of DI water [22].

3. Desalination chamber solution:
The NaCl solution with 35000 ppm was used in the desalination chamber to simulate seawater.

2.3. Analyses and calculations
A digital multimeter (Aswar, DT860D) was used to record the voltage with a 1KΩ external resistance was used in closed circuit tests to connect the anode and the cathode. Ohm's law determined the electric stream, I = E/R, where E is the voltage and R is the external resistance. The power density was studied as per the electrode surface area. The coulombic efficiency (CE), a portion of the electrons recovered as an electric stream from the substrate, was estimated using eq. (1) [23]:

$$\text{CE} = \frac{\text{I}_{\text{elec}}}{\text{I}_{\text{theoret}}}$$
\[ CE = \frac{M \int_{t_0}^{t} I \, dt}{nFV_a(COD_0 - COD_t)} \times 100\% \]  

(1)

Where (M) is the oxygen molecular weight, (I) is the electric stream, (F) is Faraday’s constant, \( n = 4 \) is the electrons numbering mutual per mole of oxygen, and \( V_a \) is the anolyte volume. COD\(_0\) appears to influence anolyte chemical oxygen demand, and COD\(_t\) is the COD value after the time (t). The MDC was operated on for several days to reach a steady state. The polarization curves were determined with the aid of variable external resistance ranged from 10 kΩ to 100 Ω in steps (leaving about 20 min between successive steps to attain a steady-state). The COD was measured by utilizing a standard method. The multimeter (Lovi Bond Senso Direct 150) was used to measure TDS, Electrical conductivity, DO in the cathode chamber, and pH of the samples. The TDS removal was calculated as follows:

\[ \text{TDS removal rate (ppm/h)} = \frac{C_0 - C_t}{t} \]  

(2)

Where \( C_0 \) is the initial TDS, and \( C_t \) is the final TDS of NaCl solution in the desalination chamber over a batch cycle of time t.

3. Outcomes and discussion

3.1. Power generation of the MDC

Figure 2-a shows the voltage generated across the MDC, while figure 2-b shows the power density during three successive experiments. At the beginning of each experiment, the three chambers fed with the solutions were illustrated in section 2.2. These two figures show that the maximum voltage difference between the electrodes in the anode and cathode chamber for a fixed value of the external electrical resistance at 1 KΩ was 24 mV, 56 mV, and 68 mV for experiments 1, 2, and 3, respectively; for three days of each experiment. Similarly, the maximum power density was 71.11, 387.2, and 570.86 μW/m² for experiments 1, 2, and 3, respectively. The voltage and power density values increased at the beginning over time until they reach the maximum value. After that, the values dropped over time due to the substrate’s depletion in the anode chamber.

It was clear that the electricity production effectiveness has developed between the 1\(^{st}\) and the 2\(^{nd}\) to the 3\(^{rd}\) experiment, which may be the reason is due to the biofilm layer thickness increasing on the anode with time, so the number of ions migrating between chambers increased, and electrical power production efficiency improved.

![Figure 2](image_url)

**Figure 2.** a- The voltage generation, and b- The power density for all experiments vs. time.
The previous study by Surajbhan et al., [15] treated the petroleum refinery wastewater in the MDC with the maximal value of power density was 243.4 mW/m² more than the power density in this study might be attributed to the difference of the initial value of substrate COD of the anolyte (the COD was 806 mg/L of the prior study and 75 mg/L of the present study).

After the reach of each experiment's steady-state operation, the polarization curve was drawn using the way presented in section (2.3), and it was illustrated in figure 4. While the voltage values vs. multi-resistance for all experiments as shown in figure 3. The maximal values of power density were 100, 707, and 436 μW/m² for the experiment 1, 2, and 3, respectively.

**Figure 3.** The voltage values of the three experiments vs. multi-resistance values.

**Figure 4.** The polarization curves of all experiments, a- experiment 1, b- experiment 2, and c- experiment 3.
3.2. Salinity removal rate of the MDC

The salinity removal rate accomplished was different for each experiment. The salt removal values were 150.39, 149.25, and 147.92 ppm/h for the 1st, 2nd, and 3rd experiment, respectively, with a first salt concentration, which was 35000 ppm for all experiments as illustrated in figure 5-a. The results appear little difference in the salinity removal rate between the three experiments due to the fouling and scaling on the AEM and CEM, respectively. The desalination process affected the cathode and anode chamber's pH values, and the pH changed in all experiments.

During the 3rd experiment, the anolyte solution's pH value decreased from the first value of approximately 7 to 6.13 and increased the catholyte solution from 7 to 8.2 figure 5-b. A accumulation of $H^+$ ions in the anode chamber was produced from biodegradation of the substrate by bacteria caused the pH to decline. The AEM prevents $H^+$ ions from migrating to the desalination chamber; conserve charge neutrality allows chloride ions to transfer from saltwater in the desalination compartment to the anolyte. On the other hand, the depletion of $H^+$ ions in the cathode chamber due to stimulating them with oxygen caused the pH to increase. The CEM prevents $OH^-$ ion from migrating to the desalination chamber; conserve charge neutrality allows sodium ions to transfer from the saltwater in the desalination compartment to the catholyte.

![Salinity removal rate](image_url)

**Figure 5.** a- Salinity removal rate from the desalination chamber for the three experiments, and b- The pH changes of anolyte and catholyte for the 3rd experiment.

3.3. COD removal efficiency of the MDC

The air cathode MDC performance to treat oil refinery was monitored by recording the COD removal percentage of anolyte. The COD removal was 53.33%, 74%, and 96% for the 1st, 2nd, and 3rd experiments, respectively, each with three days cycle as illustrated in figure 6-a. The COD removal activity in this study developed by the time, the COD removal percentage of the 2nd experiment better than the 1st experiment, and the 3rd experiment were the best. The increasing of the biofilm thickness and biofouling on the walls and membrane of the anode chamber and the improving bacteria's ability to consume this kind of wastewater over time are the reasons for this development in the COD removal efficiency. Surajbhan et al., [15] used MDC to treat petroleum refinery wastewater, and the maximal COD removal percentage was 64%. Haiping et al., [20] investigated the MDC performance to treat domestic wastewater in long-term operation, and the percentage of COD removal was 55%. On the other hand, Haiping et al., [17] investigated the MDC performance to remedy municipal wastewater, and the COD removal activity was 53%. So, the COD removal efficiency in this work better than other works due to the difference in the initial COD; in this work, the initial concentration of COD lower than in other works.

The values of COD reduction in the anode chamber and the achieved cumblic efficiency (CE) values versus time for the 3rd experiment are illustrated in figure 6-b. The highest value of CE was 13.6%. This value was less than the value achieved by Haiping et al., [17] (25.4%). That may be due to the significant
variation between COD's first value in both works (for the sitting work was 75 mg/L while for the prior work was more than 2700 mg/L).

Figure 6. a- The three experiments' COD removal efficiency and b- COD with columbic efficiency values of the 3rd experiment.

4. Conclusions
This work investigated the air cathode MDC's performance in oil refinery wastewater treatment, simulated seawater desalination, and electrical power generation. The peak of power density generated by this MDC with 1KΩ resistance was 570.86 μW/m². The COD percentage removal of the oily wastewater was 96%. The MDC achieved a maximum TDS removal rate of 150.39 ppm/h for the first TDS was 35000 ppm of saltwater in the desalination chamber. This work proved air cathode MDC's conceptual capability to remedy actual oil refinery wastewater by the anode chamber's microbial community. MDC is an environmental-friendly method to treat actual wastewater, desalination sea, or brackish water and power generation.

Acknowledgment
The University of Technology, Iraq, supported this work.

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