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Effect of External load and Salt Concentration on the Performance of Microbial Desalination Cell

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Abstract: Microbial desalination cell (MDC) is one of the cost and energy effective methods that can help people in countries with low income and people in rural areas without energy infrastructure, get access to desalinated water while treating their wastewater. Despite the advantages of the technology, less is known about the behavior of the internal resistance in MDCs. Therefore, this study mainly focused on the behavior of the MDC from internal and external resistance point of view. The desalination rate of saltwater at different applied external resistance (995 Ω, 464 Ω, 220 Ω, and 74 Ω) was studied. Moreover, the polarization capacity of the established MDC was investigated. The internal resistance of MDC at different salt concentrations of the desalination chamber (35-1 g/l) was also analyzed and discussed. The findings of the study showed that decreasing the external resistance could increase the current generation of the MDC as the main driving force of the desalination. Furthermore, it was found that salt concentration in the middle chamber plays a significant role on the internal resistance of MDC and hence on the desalination rate. Lower desalination rate at the lower salt concentration of the desalination chamber could be explained by the high internal resistance of the system. Therefore, integrating MDC with other suitable techniques, e.g., reverse osmosis (RO), for desalination of lower salt concentrations could overcome this challenge. MDC as a standalone desalination system at the current stage of technology might not be practical due to the low current performance of the system. However, it is worth considering it as green and low-cost technology for the pretreatment stage of the other conventional desalination systems, like RO with energy and cost savings while treating the wastewater.

Keywords: Microbial desalination cell (MDC), salt concentration, microbial desalination cell

1. Introduction

One of the biggest challenges in the world is providing affordable drinking water for human beings currently and in future. From the water resources in the planet, 97% is seawater and from the remaining share only 0.5% is freshwater which is accessible for usage [1]. Therefore, there is no choice than desalinating seawater to provide fresh water for human activities. There are several existing technologies for desalination, e.g., multi-stage flash distillation (MSF), multi-effect distillation (MED), membrane distillation (MD) and reverse osmosis (RO). At the current stage, RO is the most common desalination technology due to its lower energy consumption (4-5 kWh/m^3) compared to other stated technologies (7-18 kWh/m^3) [2]. However, there are some challenges associated with RO technology. The energy consumption of RO is still high, it needs established infrastructure due to high pressure demand and its byproduct is high salinity brine, which is usually discharged to the sea, imposing negative ecological impact [3]. On the other hand, the fast growth of industry and high rate of population growth is leading to high volume of wastewater generation. It will have positive effect on the well-being of life, yet it is toxic for both human beings and the environment. In

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addition, the existing conventional technologies are also energy consuming. Furthermore, since the supplied energy is mainly based on fossil fuels, the mentioned technologies produce huge amount of CO_2 which leads to dramatic climate change considering the fact that this is one of the considerable current century challenges [4].

Microbial desalination cell (MDC) can be considered a solution to the above-mentioned challenges. MDC is an ecofriendly method for desalination since it uses microorganisms to generate electricity from wastewater and uses it for desalination [5], [6]. The MDC is composed of three chambers of anode, desalination and cathode chamber as shown in Figure 1. The desalination chamber is positioned in the middle of the system which is separated from anode by an anion exchange membrane (AEM) and from cathode by a cation exchange membrane (CEM) [7], [8]. Oxidation of organic matters in anode results in generation of electrons, protons, and carbon dioxide. The electrons flow to the cathode through an external circuit which leads to generation of bioelectricity. Reduction of the electrons in the cathode causes a potential gradient across two electrodes. To maintain the electroneutrality, the anions in the desalination chamber move across the AEM to the anode and the cations move across the CEM to the cathode leaving the salt solution in the desalination chamber desalinated.

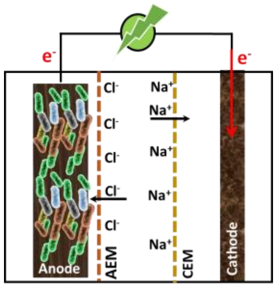

Fig. 1 - Schematic of a three-chamber microbial desalination cell

MDC is a technology that not only needs no external energy input, but also treats the wastewater simultaneously. Additionally, different value-added products can be recovered from the system, e.g. acid, and base. Despite wide range of benefits associated with MDC technology, its low performance still kept it in the lab scale. There are two main driving forces for desalination in MDCs; concentration gradient and electrical gradient [9]. Electrical gradient of MDCs is directly affected by the resistance of the system. Hence, among the factors that are affecting MDC performance, internal and external resistance are of high importance [10]. For that reason, this research is focused on studying the performance of MDC at different external resistance. Moreover, the internal resistance of the system over desalination cycle will be studied to understand the desalination behavior in MDC.

2. Methodology

2.1. Experimental MDC Setup

Two identical MDC reactors (MDC1 and MDC2) were used in this study. The MDCs were consisted of three chambers: an anode, a cathode, and a desalination chamber. The chambers were fabricated out of Plexiglas materials with internal diameter of 4 cm and thickness of 2 cm. Fiber brush electrodes were used as anode and cathode electrodes (Mill-Rose, USA). To facilitate reactors feeding and replacing the electrolyte in the cathode, anode and the desalination chambers, non-flexible rubber tubes were placed and glued in the drilled inlet and outlet ports of the chambers. The connectors were carefully fixed at two ends of each chamber using silicon sealant (Dirko, Germany).

To assemble the MDC reactor, the desalination chamber was situated in the middle while the cathode and anode chambers were located on each side of the desalination chamber. Figure 2 illustrates the components of the reactor. The silicon gaskets were used as a suitable waterproof seal to avoid leaking between the chambers. The AEM was inserted between the desalination chamber and the anode chamber, while the CEM was placed between the cathode chamber and the desalination chamber. Furthermore, the cation and anion exchange membranes were soaked in salt solution over night for possible expansion. The cathode and anode electrodes were connected at a constant external resistance by using conductive wires. To study the impact of external resistance on the desalination rate, four various resistances from high to low range (995 Ω, 464 Ω, 220 Ω, and 74 Ω) were applied in the MDC circuit for a period of 10-12 days. Each experiment was replicated two times.

2.2. MDC Operation

The anodes were inoculated with municipal wastewater collected from the secondary treatment stage of a local wastewater treatment company (Majis Industrial Services SOAC, Sohar, Oman). The biofilm for the purpose of catalyzing the anodic reaction was enriched over one month of enrichment stage in the MDC. The electrolyte used in the anode was wastewater collected from Majis. Due to low COD of the wastewater, sodium acetate trihydrate, 1 g/l, was added to the anolyte. The desalination chamber was filled with 35 g/l of NaCl as a representative of seawater. Potassium permanganate (10 mM) was added to the cathode chamber to promote the cathodic reduction half-reaction.

The reactors were operated in batch mode of operation; the anolyte and catholyte were daily refreshed over the period of the study.

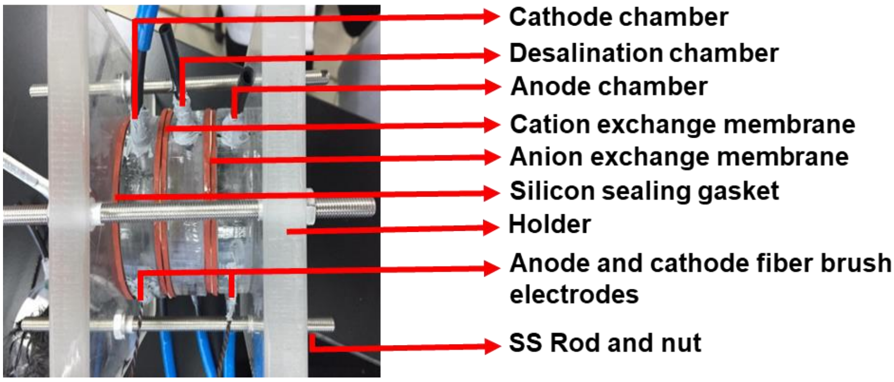

Fig. 2 - Components of the MDC setup used in this study

2.3. Analyses and Calculations

The voltage was recorded every 10 min across the applied external resistance utilizing an online data logger system (PLX-DAQ-V2, USA). The current was calculated by Ohm's law as reported in Eq 1.

$$I = \frac{V}{R_{ext}} \tag{1}$$

where V is the voltage recorded by the data logger in mV and R is the applied known R_{ext}. Electrical conductivity (EC, Max Electronics, India) was daily measured for the solution of the desalination chamber by using digital conductivity meter (Max Electronics, India). Desalination ratio was calculated based on Eq 2.

$$\eta = \frac{C_0 - C_t}{C_0} \times 100 \tag{2}$$

where C_0 indicates the initial concentration of salt solution and C_t is the concentration of salt in the desalination chamber at time t. A polarization analysis was performed to measure the electrical performance of the MDCs. Polarization curves are a powerful and known technique for analyzing and characterizing the electrical performance of the electrochemical systems. In details, a polarization curve demonstrates the voltage generated by the system versus current. Since the electrical gradient is one of the main driving forces of desalination in the MDCs, therefore studying the electrical performance of the MDC was necessary and done through the polarization curve analysis. The polarization test was completed by applying the linear sweep voltammeter at rate of 25 mV and regulated the reactor at OCV to make sure the system is at stable condition using a potentiostat (Squidstat Plus, Admiral instrument, USA). Upon deriving a polarization curve, a power curve can be plotted by drawing power as a function of current. To make the values of current and power comparable with the literature, usually the terms are normalized based on either the surface area of electrodes or the anodic volume, resulting in the current and power density terms, respectively. Both current and power densities in this study were normalized to the anode volume. Therefore, the current density (A/m^3) was calculated as shown in Eq 3, while power density (W/m^3) was calculated by using the equation that shown in Eq 4.

$$current\ density = \frac{current}{anodic\ volume} \tag{3}$$

$$Power\ density = \frac{power}{anodic\ volume} \tag{4}$$

To measure the impact of salt concentration in the middle chamber on the desalination rate, the internal resistance of the MDC at different concentrations of the salt in the middle chamber (35, 25, 15, 10, 5, 1 g/l) was measured using the polarization curve slope method. Activation overpotential and ohmic overpotential are the main losses which contributes to internal resistance of the MDC. Ohmic losses can be defined as the resistance associated with the electron transfer between the electrodes and in the electrolytes. Therefore, it will be significantly affected by the conductivity of the electrolyte and mainly with the conductivity of the middle chamber. Activation overpotential is associated with the energy required for oxidation and reduction reactions and can be overcome by efficient catalytic activity of the biocatalysts. To measure these overpotential and the sum of them as the internal resistance, the slopes of current versus voltage plot for two regions of activation loss and ohmic loss were derived from the graph [11].

3. Results and Discussion

3.1 Enrichment Stage

The identical MDC reactors were started up and went through enrichment stage at an applied resistance of 1000 Ω. High external resistance was applied to promote growth of exoelectrogenic organisms and establishment of active biofilm on the anodic electrodes. The enrichment stage is a necessary step before studying other factors since the biofilm formed on anode is the biocatalyst which catalyzes the anodic oxidation reaction. The main aim of the enrichment stage was to study the feasibility of using Majis company wastewater for electricity production in the MDCs. Figure 3 shows the trend of voltage generation in MDC reactors over the period of 26 days. The similar behavior of the two identical MDCs in terms of voltage generation proves the stability of the systems.

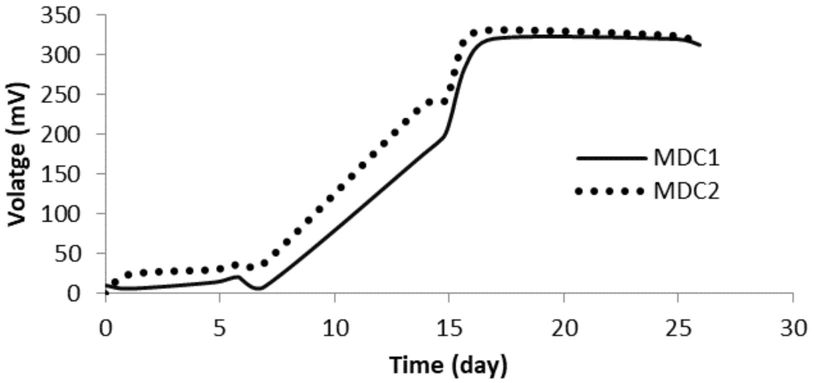

Fig. 3 - The voltage generation in MDC1 and MDC2 over the enrichment stage

In the first day of enrichment stage, the voltage of both reactors was quite low as shown in Figure 3. There was regular feeding during this week to let the exoelectrogenic organisms responsible for electricity generation grows. The main indicator of electricity generation was appeared after seven days of inoculation. The voltage generation sharply raised for both systems from day seven to the day 16th which proved that the biocatalyst was forming on the surface of the anode electrode and was catalyzing the oxidation reaction. Upon day 17, both reactors almost reached to stable voltage which was the maximum voltage generated by the MDCs. At this stage, the feasibility of using local wastewater as the source exoelectrogenic organisms was proved.

3.2. Current Generation

In the working principle of desalination in MDCs, two driving forces are involved, electrical gradient and concentration gradients [12]. While concentration gradient works due to the different concentrations of the salt in the middle chamber versus the side anodic and cathodic chambers, electrical gradient plays a crucial role for movement of the anions and cations ions of the salt towards anode and cathode chambers, respectively. One of the main factors which affects the current generation in MDCs is the external resistance applied in the system based on Ohm's law. Therefore, electrical generation out of oxidation of wastewater as a function of the applied external resistance were investigated in this stage. Upon stabilizing both reactors at the enrichment stage, different resistances were applied in the MDCs to study the current generation behavior of the systems. Figure 4 shows the trends of current generation in the MDCs over time at different applied external resistances. The enrichment of the anodic biofilm can also be approved in the current generation trend as the MDCs showed reproducible cycles of current generation upon the refreshing the systems and utilizing the feedstock available in wastewater as shown in Figure 4. Comparing the current generation trend of the systems makes it clear that the current generation of the system increased as the external resistance of the system decreased [13]. The decreasing trend of current generation in each cycle can be explained by the batch mode of operation. The source of electricity generation in an MDC is the organic carbon available in the feedstock. Since both cathode and anode were in batch mode, there was some limitation in both catholyte and anolyte reactions. Operating the systems in continuous mode could overcome such limitations and increase the performance of the system in terms of current generation [14], [15].

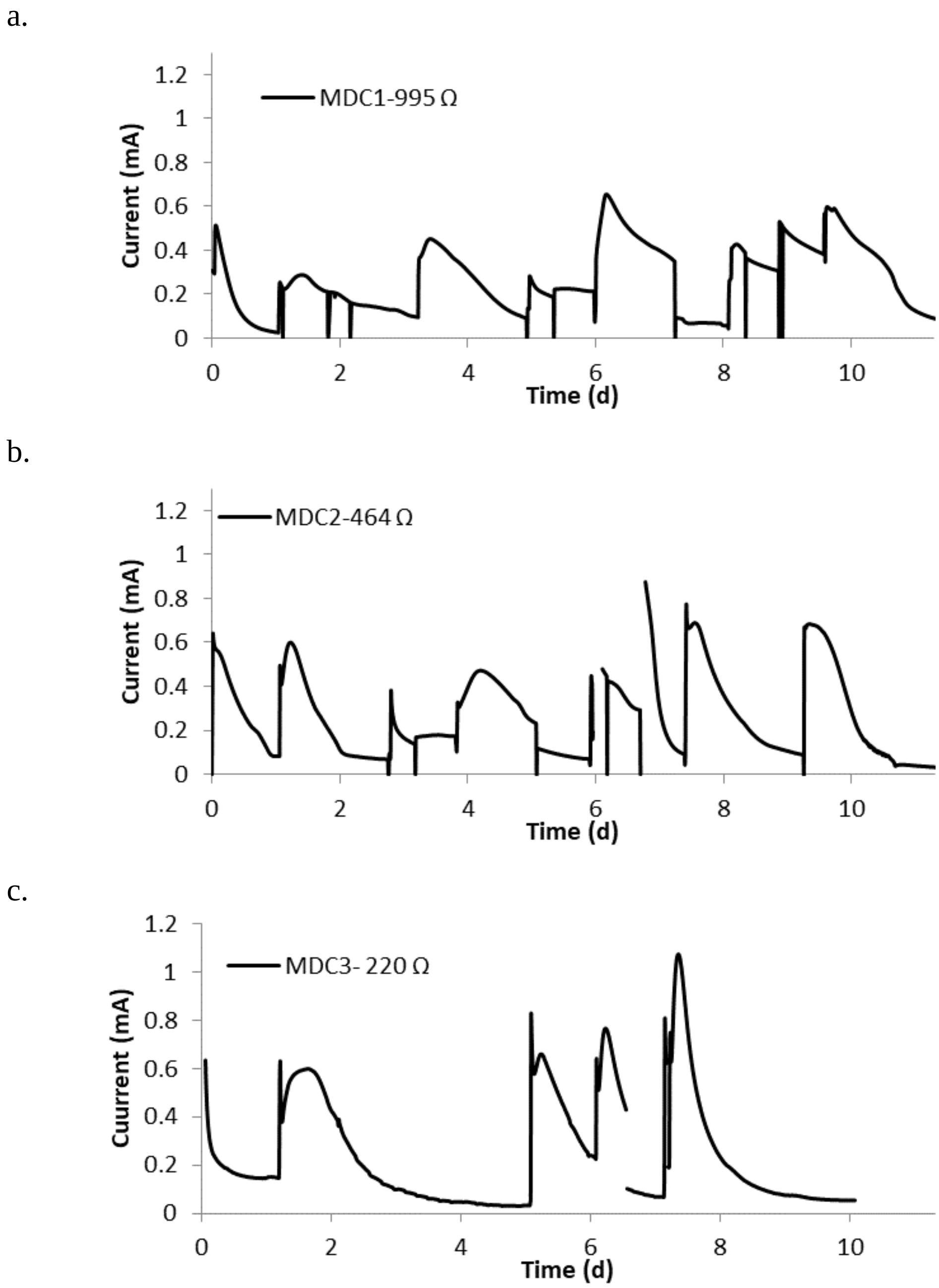

Fig. 4 - MDC current generation trends at different applied external resistances; a) 995; b) 464; c) 220 Ω

3.3. Salt Reduction

The lower external resistance applied in the MDC circuit, the lower voltage generated, and the higher current produced. To study the impact of applied external resistance on the desalination rate, the salt reduction over time at applied external resistances of 995 Ω, 464 Ω, 220 Ω and 74 Ω were monitored as shown in Figure 5. The slope of the graph shows the desalination rate in terms of g/l/d. The decreasing of applied external resistance led to increasing current generation, higher activity of exoelectrogenic microorganisms at the anode chamber, and higher rate of reduction in the cathode chamber [13]. While the resistance reduced from 995 to 464 and 220 and then 74 Ω, the desalination rate increased from 1.39, to 1.46, 1.91 and 2.04 g/l/d, respectively. The results obtained were in a good agreement with the results obtained from the current generation trends. The findings prove the effectiveness of electrical gradient in desalination rate in microbial desalination cells fed by the actual wastewater. In general, the rate of desalination in MDCs is still low and improvement in different areas of membrane, electrodes and operating conditions are required to increase the performance of MDC.

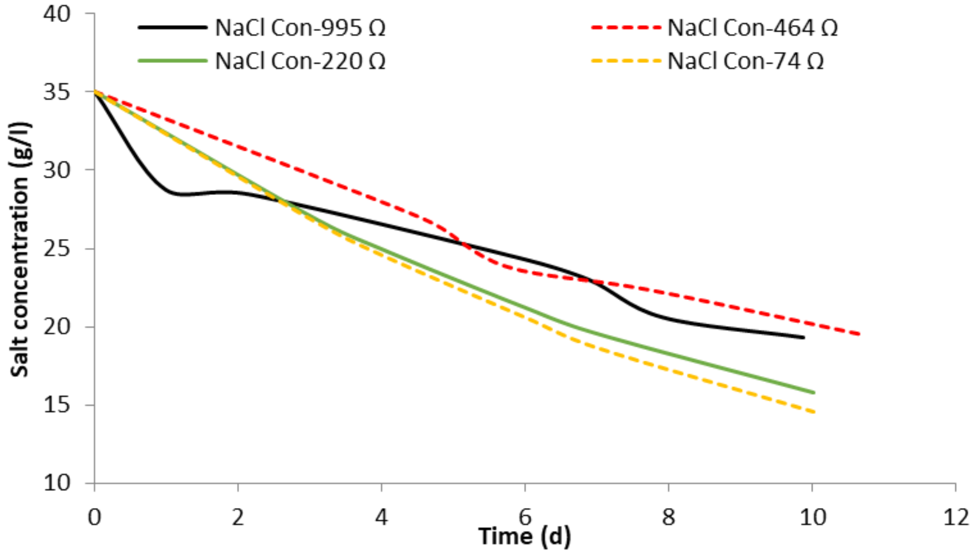

Fig. 5 - Salt removal rate in MDC with 35 g/l NaCl in different external resistance

3.4. Bioelectrochemical Analyses

A polarization review was performed to understand the electrical performance of the MDC enriched and fed with municipal wastewater. The power and polarization test were completed by applying the linear sweep voltammeter at a rate of 25 mV and regulated the reactor at an open-circuit voltage (OCV) upon completion of salt reduction study. To initially study the power generation in MDC, the polarization test was performed at the highest concentration of the salt in the middle chamber (35 g/l) to avoid any impact of low conductivity of the middle chamber on the MDC electrical performance as demonstrated in Figure 6. The maximum power density of 101 W/m^3 was produced in the MDC when the maximum concentration of the salt was available in the MDC.

Nevertheless, it is believed that as the salt concentration in the middle chamber decreases, the internal resistance of the system, gradually, increases and the current generation in the MDC reduces [16,17]. Accordingly, the polarization and power density analyses of the MDC were performed at salt concentrations of 25, 15, 10, 5, 1 g/l in the desalination chamber as shown in Figure 6.

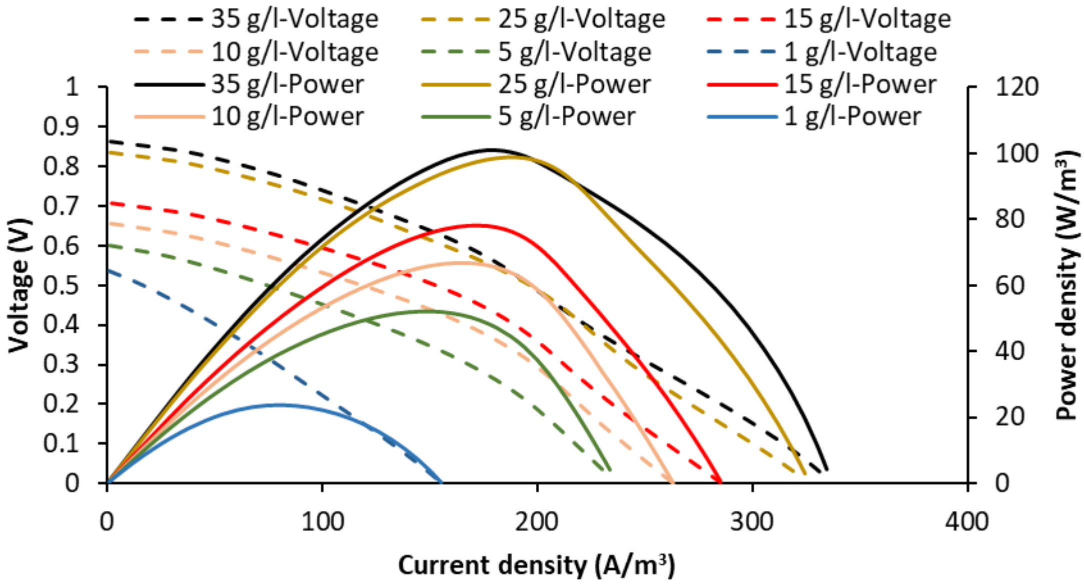

Fig. 6 - Polarization and power density analyses at different salt concentration in desalination chamber of the MDC used in this study

There was no specific change in the power and current density behavior of the MDC as the salt concentration decreased to 25 g/l, due to the high conductivity of the salt at this concentration [18]. However, the maximum power density of the MDC significantly decreased by 23%, 36%, 50% and 77% as the salt concentration reduced to 15,10, 5 and 1 g/l, respectively. In other words, the low salt concentration of the middle chamber plays as a resistance towards current generation as the main driving force of the desalination extraction. Therefore, internal resistance due to the salt concentration of the desalination is one of the major factors that influences the MDC performance [19]. The slope of polarization curve was used to measure the internal resistance of the MDC at various salt concentration. Figure 7 compares the internal resistance of the MDC at different salt concentrations (35, 25,15,10,5,1 g/l). As the salt concentration decreased from 35 g/l to 25 g/l the ohmic resistance increased slightly from 135.1 to 140 Ω. However, the increment of ohmic resistance was quite profound at lower salt concentration; 68, 182, 194 and 332 Ω at 15, 10, 5 and 1 g/l of salt concentration, respectively. Ohmic losses can be defined as the resistance associated with the electron transfer between the electrodes and in the electrolytes. As a result, it will be significantly affected by the conductivity of the electrolyte and mainly with the conductivity of the middle chamber [11]. Nonetheless, there are slight increases in activation resistance over decreases of the salt in the desalination chamber which can be explained by the efficient catalytic activity of the biocatalysts.

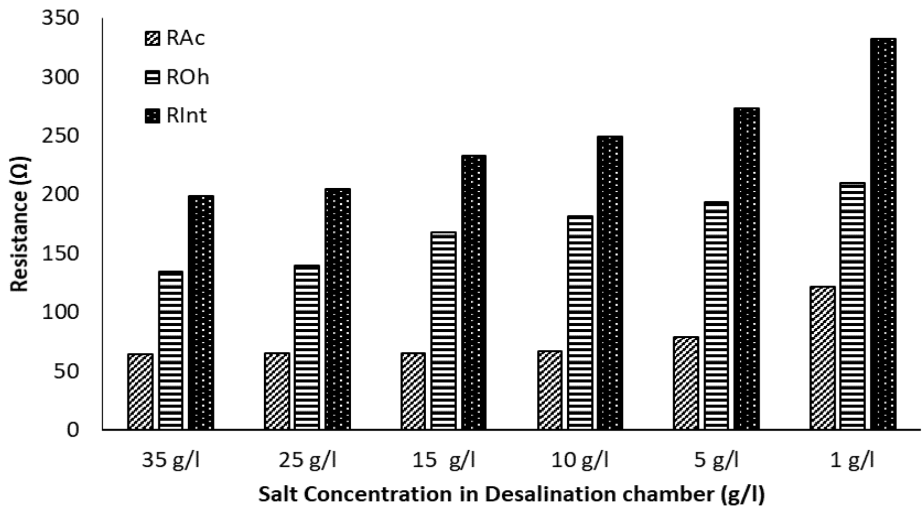

Fig. 7 - Internal resistance at different salt concentration in the desalination chamber of the MDC

The study of internal resistance at various salt concentrations in desalination chamber can demonstrate how desalination rate is affected by the operating condition of the MDC which is beyond the other constructional and material borders. Looking at the MDC as a standalone desalination system at the current stage of technology with low current performance of the system might not be practical. However, it is worth considering it as a green and low-cost technology for the pretreatment stage of the other conventional desalination systems, like RO with energy and cost savings while treating the wastewater [20]. Figure 8 shows the proposed process flow diagram of the MDC plant. The diagram demonstrates the equipment (Tanks, Pumps, MDC reactor) and instruments (flow controller, analyzers, temperature controllers, etc.) required to run an MDC based desalination system. This process can be used as a pretreatment stage of RO plant to reduce the load and the cost of this conventional desalination process.

3.5. Techno-economic Analysis of MDC

The dependency on the larger water desalination plants is increasing due to the increase in the population growth in the world. High energy consumption, which is generally generated from fossil fuel sources, in RO plants will lead to large carbon footprint. The brine that contains high concentration of organic matter and certain salts, like Ca, Cl, K, Mg, and Na is normally discharged into areas rich in marine life, and this affects the living organisms. Comparing with the conventional well developed desalination techniques, MDCs are still in pilot-scale stage. However, the economic feasibility studies indicates that MDCs have remarkable potential for the future. For instance, to compare MDC with the known RO process, RO needs 2.2 kWh of energy to be able to treat 1 m^3 of saltwater, whereas MDC produced 1.8 kWh of bioenergy. On the other hand, the capital cost of MDCs is still high [21]. The cost of electrodes and membranes are of the main cost of fabrication of the MDC systems. Redox reaction of MDC is yet slow. While the anodic reaction is catalyzed by the exoelectrogenic organisms, the cathodic reduction reaction is generally catalyzed by using a Pt coated carbon cathode. There are numerous efforts to substitute chemical cathodes with biocathodes to not only reduce the cost of MDCs, but also to increase the removal capacity of the MDCs by making the system fully biological [22]. Membrane is the other costly material used in MDCs. Decreasing the cost of membranes by increasing their lifetime and mitigating membrane fouling are looking promising to overcome on this issue. In addition, the recent advances in the field of materials and specially using natural biomasses as the economic substitutes of synthetic materials is an option to decrease the cost of materials used in MDC. It could facilitate their implementation in real scale application either as a pretreatment stage to reduce the load of conventional desalination techniques or as a standalone technology with respect to the condition [23,24].

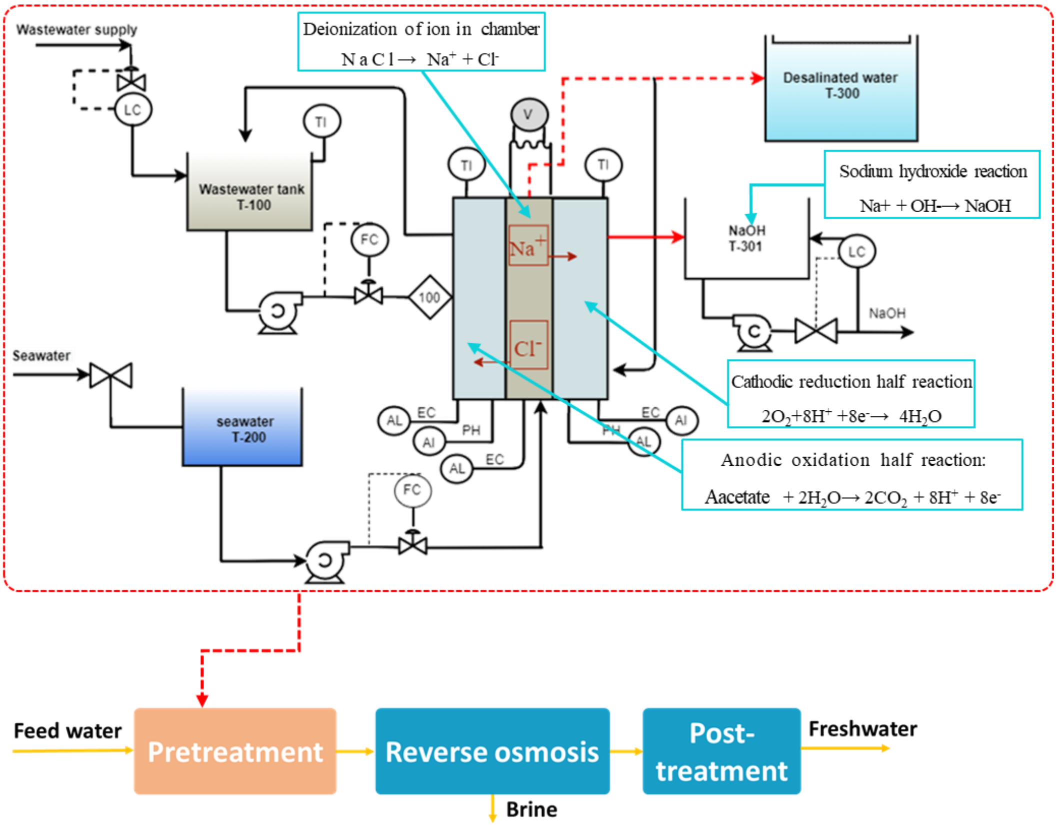

Fig. 8 - The proposed process flow diagram for MDC plant as the pretreatment stage of RO desalination process

4. Conclusion

Microbial desalination cell is an eco-friendly technology to desalinate seawater while treating wastewater and producing energy. The impact of the external resistance on the desalination rate was studied in this work. As the resistance reduced from 995 to 464, 220 and 74 Ω, the desalination rate increased from 1.39, to 1.46, 1.91 and 2.04 g/l/d, respectively. The results obtained were in a good agreement with the results obtained from the current generation trends. The results showed that decreasing external resistance could increase the current generation of the MDC as the main driving force of desalination. Additionally, the impact of the salt concentration of the middle chamber was studied. It was found that salt concentration in the middle chamber plays a significant role on the internal resistance of MDC and hence on the desalination rate. The results showed that high internal resistance (> 250 Ω) occurs when the salt concentration decreases to less than 10 g/l. Therefore, MDC is an effective technology for desalination of the saline water at higher salt concentration while an alternative technology is needed for the lower salt concentration.

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