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EFFECT OF METHYLENE BLUE ADDITION AS A REDOX MEDIATOR ON PERFORMANCE OF MICROBIAL DESALINATION CELL BY UTILIZING *TEMPE* WASTEWATER

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ABSTRACT

The microbial desalination cell (MDC) is a modification of the microbial fuel cell (MFC) system. The microbial desalination cell is a sustainable technology to desalinate saltwater by directly utilizing the electrical power generated by bacteria during the oxidation process of organic matter. In this study, *tempe* wastewater will be used as a substrate. Methylene blue (MB) at concentrations of 100 μM, 200 μM, and 400 μM in the anolyte is added as a redox mediator, and the effect on electricity production and desalination performance are evaluated. The average power density increases by 27.30% and 54.54% at MB concentrations of 100 μM and 200 μM, respectively. On the other hand, the increase of the MB concentration in the anolyte results in a decrease in the salt removal percentage. The observation made using a scanning electron microscope showed the presence of MB adsorption on the surface of the anion exchange membrane (AEM) and is suspected to be the cause of the disruption of anion transfer between MDC chambers causing a decrease in the salt removal percentage.

Keywords: AEM; Desalination; Methylene blue; Microbial desalination cell; *Tempe* wastewater

1. INTRODUCTION

The microbial desalination cell (MDC) is a modification of the microbial fuel cell (MFC) system (Cao et al., 2009). MDC is a sustainable technology to desalinate saltwater by directly utilizing the electrical power generated by bacteria during the oxidation process of organic matter. This enables the MDC system to carry out the desalination process without external electrical energy (Luo et al., 2012). The simple MDC reactor was first introduced by Cao et al. (2009). It consists of three chambers separated by an anion exchange membrane (AEM) next to the anode chamber, a cation exchange membrane (CEM) next to the cathode chamber, and the center chamber containing saline solution between the two membranes.

The potential of using waste as a substrate in the MDC has begun to attract a great deal of attention. Luo et al. (2011) have successfully tested the MDC by utilizing domestic wastewater as a substrate to carry out the desalination process. Other waste that can be used is *tempe* wastewater. In Indonesia, there are a great number of *tempe* industries; however, the wastewater produced by these industries is unutilized and directly dumped into the environment. Yet, it contains nutrients, such as nitrogen, phosphor, and other organic materials as carbohydrates, vitamins, and proteins that act as nutrients for the growth of microorganisms. Moreover,

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previous studies proved that *tempe* wastewater as a substrate can produce electricity that can be tested on the microbial fuel cell system (Utami, 2013). This electricity production will be further used for the desalination process in the MDC system.

Researchers have developed various ways to improve the desalination performance of the MDC. Jacobson et al. (2011) made a tubular reactor design in continuous flow, which is known as the upflow microbial desalination cell (UMDC). Moreover, Ge et al. (2014) changed the membrane structure to a stacked membrane arrangement in the MDC reactor. Both of these methods utilize the same mechanism to improve desalination performance, with the intention of gaining ion migration efficiency by changing the membrane and reactor construction. Actually, the basic driving force of ion transfer in a bio-electrochemical system is electricity generation within that system. Therefore, this study will focus on the effect of desalination performance on electricity generation.

The ease of the electron transfer process in a bio-electrochemical system is an important stage in electricity production (Liu, 2008). However, most microorganism species are inactive in transferring electrons towards the anode (Patol et al., 2012). Various redox mediators such as methylene blue (MB), neutral red, thionin, and humic acid are proven able to improve the productivity of the electricity generated (Park & Zeikus, 2000; Taskan et al., 2014). The addition of redox mediators has been widely tested on the MFC system, but their use in the MDC has not been well explored. MB was chosen because of its biocompatibility, relatively cheap price, easy obtainability, and wide usage in MFC research with positive results (Permana et al., 2013; Rahimnejad et al., 2011; Taskan et al., 2014). Moreover, MB has an oxidized and reduced form which easily passes both in and out through a bacterial cell membrane, and another important factor is that MB is not absorbed by the cell wall or the electrode surface. These criteria are necessary for an efficient redox mediator. Thus, an increase in electricity production caused by MB is expected to improve the performance of desalination for the MDC systems.

Therefore, this study aims to evaluate the effect of MB addition at concentrations of 100 μM, 200 μM, and 400 μM as a redox mediator for electricity production and desalination performance in the MDC which utilizes *tempe* wastewater as a substrate. The main goal of this study is to find an alternative way to perform a desalination process without high energy use, while at the same time solving an environmental problem through effective wastewater utilization. Therefore, the most significant impact of this study will be to explore the feasibility of the potential use of *tempe* wastewater as an organic source or fuel for the MDC system as a means of waste utilization. The second will be exploring the status of MB usage as a means to improve desalination performance, which has not been done to any degree in connection to the MDC.

2. EXPERIMENTAL METHODS

2.1. MDC Construction

A three-chamber MDC reactor is used in this study, consisting of an anode chamber, a middle chamber (desalination chamber), and a cathode chamber with the respective volume ratio of 9:1:9, which was first introduced by Cao et al. (2009). The effective solution volumes used are 1,800 mL of anolyte, 200 mL of saline solution, and 1,800 mL of catholyte, separated by an AEM membrane (AMI-7001S) and a CEM membrane (CMI-7000S) received from Membranes International, Inc.

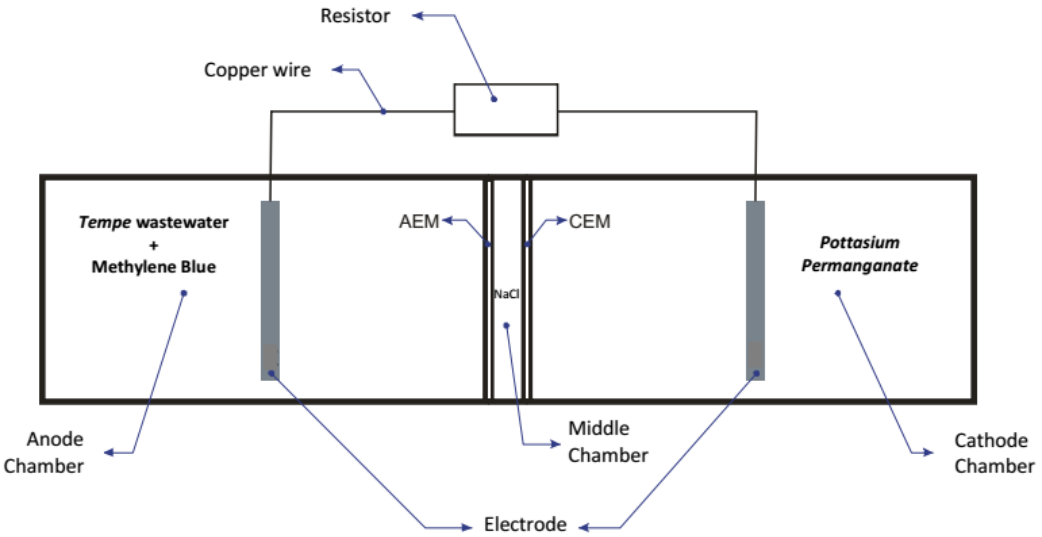


Figure 1 MDC reactor construction

The cross-sectional area of AEM and CEM are equal, which is 38.47 cm^2 at a distance of 3.1 cm between the membranes. A graphite rod is used as the anode-cathode pair with an effective surface area for each electrode of 145.6 cm^2. The distance between the electrodes is approximately 26.5 cm with each electrode placed at the midpoint of the anode chamber and a cathode chamber, respectively. The anode and cathode are interconnected by a copper wire, and a 10 Ω resistor is fitted as an external resistance (Figure 1).

2.2. MDC Operation

Batch operation is applied in the MDC reactor at room temperature (~27^{o}C) for 65 h. The salt solution (as NaCl) will be desalinated with an initial concentration of 30 g/L by 200 mL in the middle chamber. Membranes are prepared prior to usage by soaking them in a 5% NaCl solution at 40°C for 24 h. Graphite electrodes are also prepared by soaking them in a solution of 0.1 M HCl for 1 d, and after that soaking them again in 0.1 M NaOH for 1 d.

Tempe wastewater that is used in this study is synthetic wastewater, made by boiling soybeans (*Glycine max*) with a ratio of the mass of soybeans to the volume of water of 3:5 for 15 min. The stew water is then incubated for 3 d in anaerobic conditions. Therefore, some characterization of the wastewater model is done due to ensure its quality by maintaining optical density (OD) and pH after incubation at constant variables with OD at 6.5 and pH at 4.8.

The incubated wastewater is then fed into the anode chamber along with a phosphate buffer solution ($NaH_2PO_4.H_2O$ and $Na_2HPO_4.2H_2O$) of a 0.1 M concentration, a pH of 7, and a volume ratio of 1:1. MB is added to the anolyte until its concentration reaches 100 μM, 200 μM and 400 μM. The control that used in this study is MDC without MB addition (0 μM in anolyte as a control). In the cathode chamber, potassium permanganate ($KMnO_4$) is used as an electrolyte along with a 0.1 M phosphate buffer solution with a volume ratio of 1:1.

2.3. Measurements and Data Calculations

The conductivity of the saline solution is measured using a conductivity meter (ORION 150 Plus, Thermo Fisher Scientific, USA) while the voltage is measured using a wireless multimeter (Model EX540, EXTECH Instruments, USA).

$$I = \frac{V}{R_{ex}} \quad (1)$$

where I is the current (mA), R_{ex} is the external resistance (**Ω**), and V is the voltage (mV). After obtaining the value of I, the power density can be calculated using the following equation (Wei et al., 2012):

$$P_d = \frac{IV}{v} \tag{2}$$

where P_d is the power density (mW/m^3), V is the voltage (mV), I is the current (mA), and v is the volume of anolyte (m^3).

From the obtained value of conductivity, the concentration of NaCl as the salt solution can be calculated through the equation of the standard curve (data not shown), and then the data can be processed to obtain the % of salt removal value by the following equation (Jacobson et al., 2011):

$$SR = \frac{c_o - c_i}{c_o} x\ 100\% \tag{3}$$

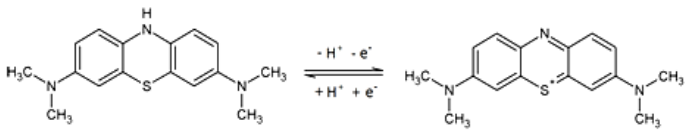
where SR is the removal percentage of the initial salt concentration to the final salt concentration (% of salt removal), and C_o (g/L) and C_i (g/L) are the initial and end concentrations, respectively, during one batch operation.

Scanning electron microscope (SEM) imaging from the surface of the AEM is also captured to investigate the MB interaction with the membrane surface. The AEM sample that is used has been cleaned and dried before observation using the SEM.

3. RESULTS AND DISCUSSION

3.1. Effect of MB Addition on Electricity Production

Figure 2 shows the profile of voltage generated during the batch operation for 65 h at various MB concentrations. MDC with MB addition shows higher voltages at concentrations of 100 μM and 200 μM, with maximum voltages of 77.90 mV and 63.15 mV, respectively, compared to the voltage of control 49.43 mV. This happens because there is MB presence in the anolyte, and this increases electron transfer from bacteria cells onto the anode surface as a mediator substance. Glucose, as a substrate which is oxidized by microorganism metabolism, produces electrons.



(4)

According to Equation 4, the reaction of MB as a redox mediator is a reversible reaction. Electrons from the electron chain transport of a microorganism will be captured by MB in oxidized form (MB_{ox}), so that the mediator substance changes to a reduced form (MB_{red}). Then, the reduced form of the mediator re-oxidizes in the anode to become an oxidized form. Electrons which are released from this process will pass an electrical circuit through the anode and generate more electricity as current. This can be used as a driving force in salt ion migration between MDC chambers because of the difference in ionic concentration.

Maximum voltage often occurs early in the operation. Mehanna et al. (2010) reported in a previous research, which operated in a feed-batch mode that maximum electricity is always obtained at the beginning of the cycle, which is during the first period of substrate addition.

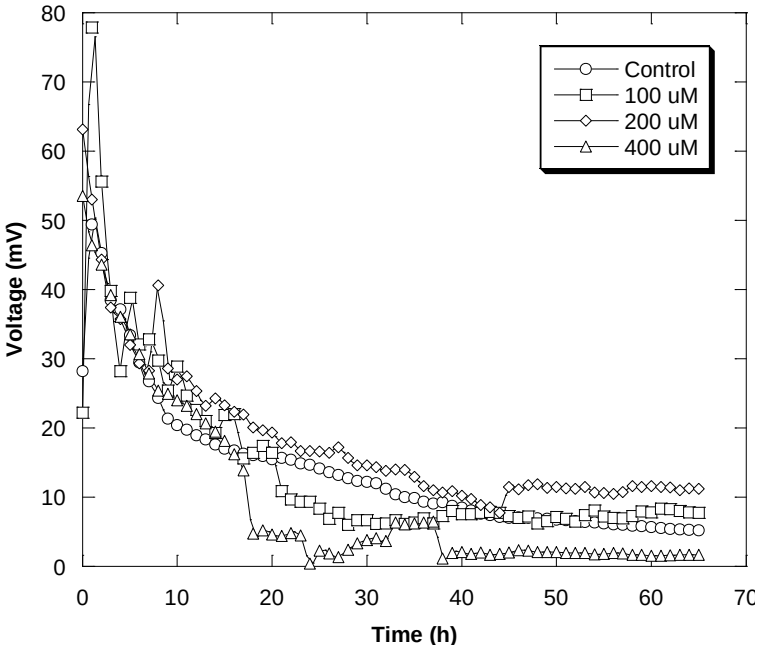


Figure 2 Profile of voltage generated at various MB concentrations

Figure 3 shows that the value of maximum power density increases at all MB concentrations. The comparison value between maximum and average power density indicates the first shoot in the initial period compared to its stability in average value. During the first period, it is important to observe electron transfer efficiency when the number of microorganisms is at its maximum and there is a high substrate presence in the anolyte. The highest maximum power density is obtained at 100 μM, which is 337.13 mW/m^3. Then the maximum power density at 200 μM, 400 μM, and control, respectively, are 221.53 mW/m^3, 159.19 mW/m^3, and 135.74 mW/m^3. However, with an increasing amount of MB concentration, the increment of maximum power density becomes smaller. This is suspected to happen due to an increased amount of MB adsorbed by the surface of the anode because of the increasing concentration of MB. Moreover, this increases the amount of resistance at the anode. An increase of resistance at the anode will have an impact on the maximum voltage by decreasing it.

The highest average power density is obtained at a concentration of 200 μM, shown by the 54.54 % increment from the average power density of 16.22 mW/m^3 (control) to 25.06 mW/m^3, whereas the average power density at a concentration of 100 μM is 20.65 mW/m^3 with a 27.30% increment from the control (Figure 3). Although the highest maximum power density is obtained when the MB concentration is 100 μM, the highest average power density is obtained when the MB concentration is 200 μM. This is because the average voltage generated until the end of the operation at an MB concentration of 200 μM is at a higher value compared to the one at an MB concentration of 100 μM (Figure 2).

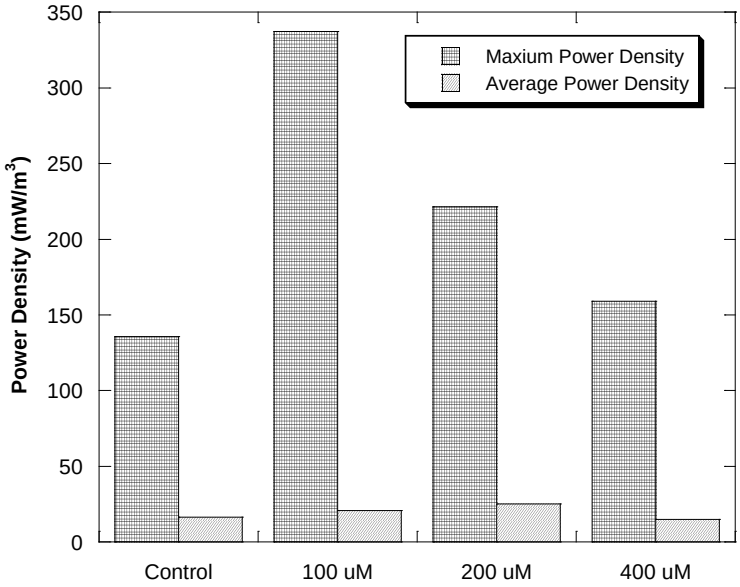


Figure 3 Comparison between average and maximum power density generated at various MB concentrations

Different results are obtained when MB with a concentration of 400 μM is added. The average power density is lower than the control, which is a decrease by 8.84% from 16.22 mW/m^3 to 14.79 mW/m^3, despite the fact that the maximum power density generated in the early period of the operation is higher than the control. If we look at the voltage profile at an MB concentration of 400 μM (Figure 2), there is a significant voltage drop at the 16th hour in a short period, and this causes the value of the voltage to become very small. This phenomenon of voltage drop is suspected to be caused by a decrease in bacterial activity due to toxicity from the addition of MB at higher concentrations (Li, 2013). In the same study, Li (2013) also reported that the addition of an MB concentration at more than 300 μM did not have any significant impact on the increase of the electricity generated.

3.2. Effect of MB Addition on Desalination Performance

The addition of MB at various concentrations is also evaluated for its effect on desalination performance. An increase in the average power density at MB concentrations of 100 and 200 μM does not cause an increase in the % of salt removal; it actually shows the opposite result. Figure 4 shows that there is less of a decrease in salinity when MB is added to all concentrations used in the MDC.

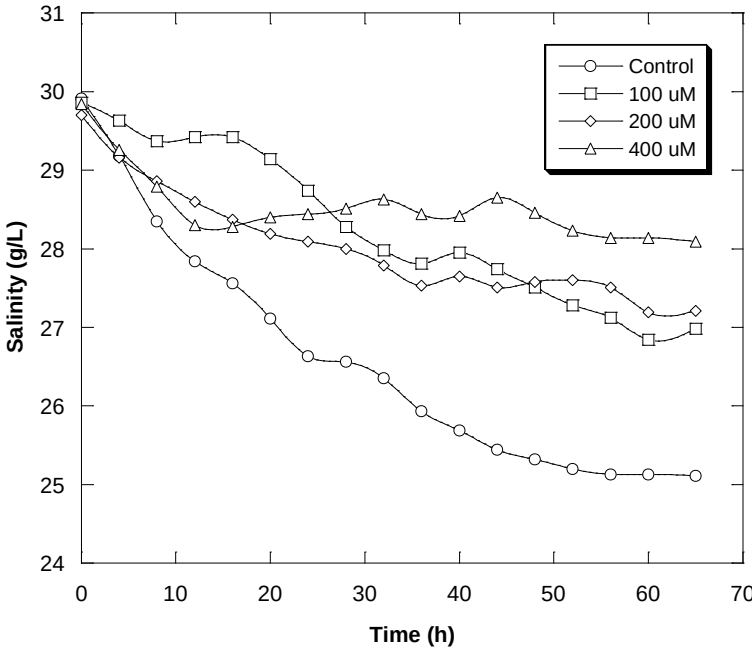


Figure 4 Profile of salinity at various MB concentrations

The results show that the % values of salt removal during 65 h of operation for the control, 100 μM, 200 μM, and 400 μM MB concentrations, respectively, are 16.10%, 9.66%, 8.38%, and 5.86%. The highest % of salt removal is obtained when the MDC operates without any MB addition. The results show that, with an increasing concentration of MB addition, the % of salt removal value obtained decreases (Figure 5).

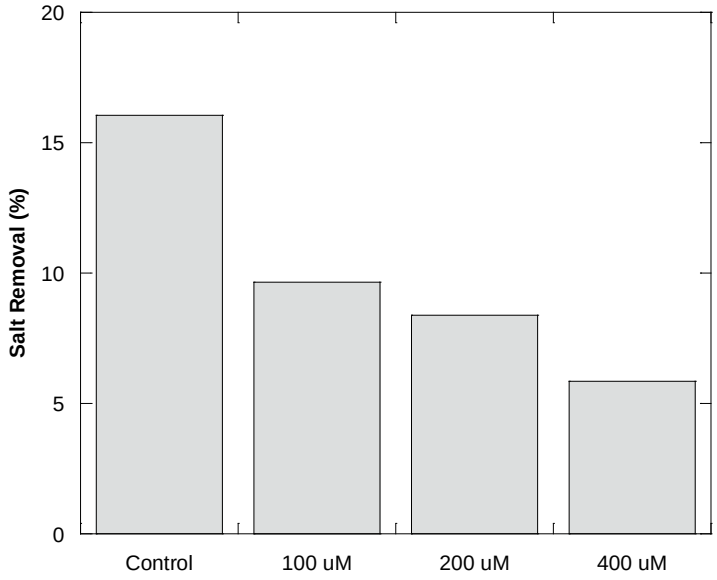


Figure 5 Comparison of the % of salt removal at various MB concentrations

The existence of MB adsorbed by the membrane surface is suspected to cause disruption of the interaction of the anion with a quaternary ammonium group in AEM. An image of the AEM unexposed and exposed to MB after use is also observed (Figures 6a and 6b). The dark blue color shows the MB adsorption by the membrane surface during operation. The phenomenon of fouling by MB was also observed by Rahimnejad et al. (2011) in the MFC research using a Nafion 117 membrane.

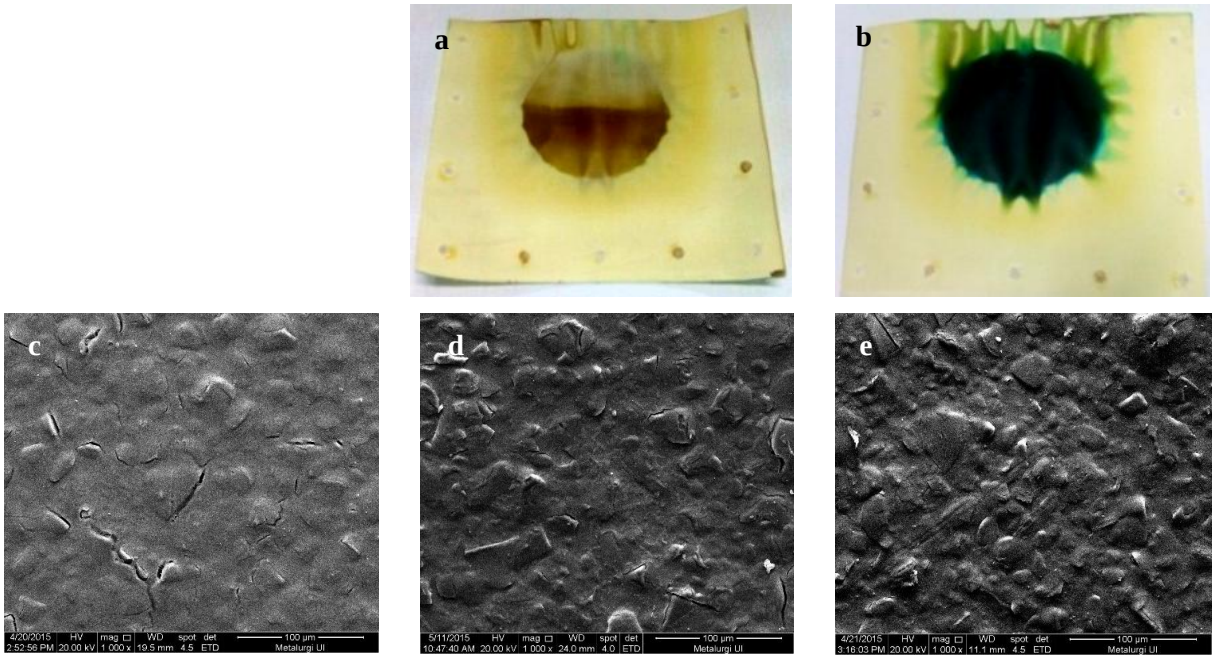


Figure 6 Photographic image of the AEM: (a) after being used in the anode chamber without methylene blue; and (b) with MB. SEM images of the AEM surface: (c) before being used; (d) after being used; and (e) after being used with MB in the anolyte

SEM imaging is also done to observe changes in the morphology of the membrane surface after being exposed to MB. Figure 6c shows the AEM surface before use (raw membrane). The AEM has a surface that is slightly cracked. These results are consistent with what has been previously investigated by Wang et al. (2011) and Ping et al. (2013). Figure 6d shows the AEM after use with the anolyte containing *tempe* wastewater without MB. The membrane surface looks rougher and has more cracks in comparison to Figure 6c. Figure 6e shows the membrane surface after use with the anolyte containing *tempe* wastewater and MB. The characteristic cracks on the surface of the membrane exposed to MB are no longer visible. This may occur because MB adsorption by the membrane surface covers the existing gaps and cracks, and then it coats the surface of the membrane, which causes disruption of ionic interactions on the AEM so that the movement of ions between chambers becomes inhibited.

4. CONCLUSION

The effect of MB addition with various concentrations in the anolyte of MDC has been investigated. MB at concentrations of 100 μM and 200 μM is able to increase the power density generation to 27.30% and 54.54%, respectively. However, the salt removal percentage value decreases along with the increasing concentration of MB in the anolyte. Adsorption of MB found on the surface of AEM is suspected to be the cause of the disruption of anion transfer between MDC chambers. The optimum electricity production is obtained at an MB concentration of 200 μM with an average power density of 25.06 mW/m^3. However, the optimum condition for desalination performance is obtained without the addition of MB with salt removal reaching 16.10%.

5. ACKNOWLEDGEMENT

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