BioOne COMPLETE

Performance of Microbial Reverse-Electrodialysis Cells for Power Generation at Different External Resistance

Authors: Effendi, Agus Jatnika, Hidayat, Syarif, Syafrudin, ., Ramadan, Bimastyaji Surya, Purnawan, Candra, et al.

Performance of Microbial Reverse-Electrodialysis Cells for Power Generation at Different External Resistance

Agus Jatnika Effendi[1], Syarif Hidayat[1] (ID), Syafrudin[2], Bimastyaji Surya Ramadan[2], Candra Purnawan[3] and Joo-Yang Park[4]

[1]Faculty of Civil and Environmental Engineering, Institut Teknologi Bandung, Bandung, Indonesia. [2]Department of Environmental Engineering, Faculty of Engineering, Universitas Diponegoro, Semarang, Indonesia. [3]Department of Chemical Sciences, Faculty of Mathematics and Natural Sciences, Universitas Sebelas Maret, Surakarta, Indonesia. [4]Department of Civil and Environmental Engineering, Hanyang University, Seoul, Republic of Korea.

ABSTRACT: In this study, the effect of external resistance on the microbial reverse-electrodialysis cell (MRC) performance using organic-rich wastewater as an electron donor was examined. The optimum of external resistance was determined to be $300\,\Omega$. In such condition, the power density of $1.53 \pm 0.198\,W/m^2$, substrate removal of $52 \pm 2.3\%$, Coulombic efficiency of $70 \pm 2.6\%$, energy recovery of $3.0 \pm 0.4\%$, and energy efficiency of $53 \pm 7.1\%$ were obtained in the MRC. The differences in power density at different external resistances were mainly due to the changes in internal resistance and ion flux efficiency in the MRC. The external resistance affected substrate removal and Coulombic efficiency through the length of batch cycle time, and current density exchanged as well as the Tafel slope. Furthermore, the proper external resistance applied to the reactor created high power production; thus, high energy efficiency and energy recovery were achieved. These results demonstrated that selecting proper external resistance was an essential key for a successful MRC operational.

KEYWORDS: Renewable energy, bioelectrochemical systems, salinity gradient energy, energy efficiency, energy recovery

Introduction

Bioelectrochemical systems (BESs) is considered as one of the most promising technologies that can be used to extract the energy in organic/inorganic wastes as electrical power or chemicals.[1] Over the last decade, microbial fuel cells (MFCs) have gained extensive attention from researchers, representing over 75% publication of the BESs research area in 2016.[2] Microbial fuel cells are unique devices of BESs that can convert the chemical energy stored in biodegradable materials into direct electrical power while simultaneously treating wastewater.[3] In this system, the direct electrical power is generated as a result of simultaneous processes oxidation of biodegradable materials by exoelectrogens and oxygen reduction in the anode and cathode electrodes, respectively. However, in the MFC pilot scale using organic materials of wastewater as an electron donor, to date, the highest power densities reached approximately 7 to $60\,W/m^3$ as normalized by volume of the reactor.[4-6] The operational strategy with series mode has been done to improve the performance of the reactor in terms of voltages and power densities.[7] In such a condition, the reactors have a significant performance in treating wastewater; however, this is not the case for power production.

Salinity gradient power (SGP) is a method to convert the Gibb free energy from the mixing of water with different salinity concentrations into electrical power.[8] Reverse-electrodialysis cell (RED), as a representation of SGP is the most recommended technology to harness the energy from salinity gradients.[9] In such a system, the cell comprises several pairs of anion- and cation-exchange membrane, which stacked alternately each other and situated in between an anode and a cathode chamber. When the solutions with different salinity concentrations were introduced to the flow channel between these membranes, electrochemical potential energy was generated across the membranes as a result of selective ion transport from the solutions.[10] The corresponding potential energy is theoretically around 0.1 to $0.2\,V$ for each pair of membranes for 15 to 150 salinity ratios of seawater and river water.[11] This potential can rise by increasing the number of cell pairs; however, efficiency and operational power production become lower than expected due to the hydrodynamic and ohmic losses as well as overpotential.[12] For instance, in the pilot applications (125-500 cell pairs), the power output of the RED stack reached $700\,W$ and decreased to $330\,W$. It occurred when the system operational shifted from the artificial brine and brackish water to real solutions with the expected energy output of $1\,kW$.[13] Hence, a different approach is needed to optimize the RED's potential as a power source.

Recently, several studies have been demonstrated to prove that the combination of a small number of RED stacks with an MFC could synergistically enhance the potential electrical power generation compared with the individual systems.[14,15] In such a system, when 5 membrane pairs of RED stacks were
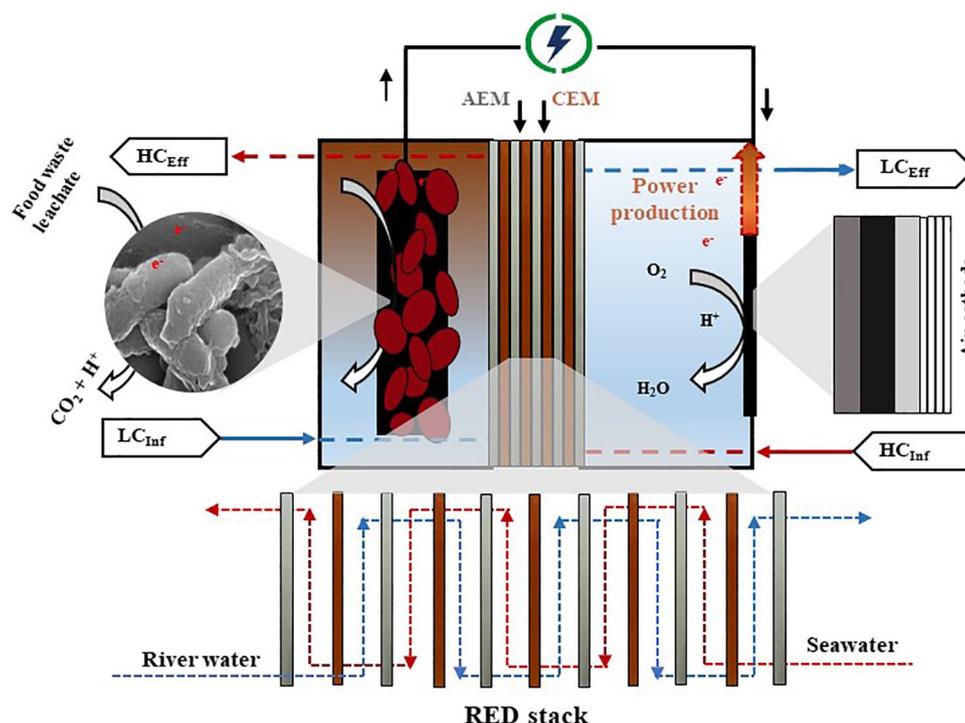
Figure 1. Schematic diagram of microbial reverse-electrodialysis cell (MRC). HC indicates high concentration; LC, low concentration; MRC, microbial reverse-electrodialysis cell; RED, reverse-electrodialysis cell, AEM, anion exchange membrane; CEM, cation exchange membrane.

used for the electrical power production, the maximum voltage and power density reached 1.3 V and 4.3 W/m², respectively. The values were higher than those obtained from MFC alone (0.5 V, 0.7 W/m²).[14] Confirmed by further research, when a microbial reverse-electrodialysis cell (MRC) used ammonium bicarbonate in the RED stack and domestic wastewater as an electron donor, the result showed that even with a single pair of RED stacks, the performance of reactor significantly improved.[16] In addition, the energy efficiencies (35%-42%) and energy recoveries (10%-21%) of the corresponding system were relatively comparable with the RED systems (14%-35% and 9%) than MFCs, as those 2 figures for MFCs were generally low (<7.2% and <6.5%).[14,17-19]

In this study, the effect of external resistance on the MRC reactor performance using organic-rich wastewater as an electron donor was examined. Because it has high organic content, food waste leachate as a representation of organic-rich wastewater is highly potential to be used as a substrate for the microorganism in the MRC reactor. Preliminary studies were conducted in the fed-batch mode using a different number of membrane pairs to determine the optimum cell pairs. In further experiments, the reactor was operated under various external resistance. The reactor performance was evaluated by measuring power density, substrate removal, Coulombic efficiency (CE), energy recovery, and energy efficiency.

Materials and Methods

Reactor setup

The MRC reactor was constructed as previously described with minor modifications.[20] The reactor consisted of an anode chamber, a cathode chamber, and a small number of the RED stack (Figure 1). The anode and cathode chambers were constructed using poly(methyl methacrylate) with a working volume of 30 mL. A heat-treated graphite fiber brush, 3 cm in diameter and 2.5 cm long, was used as the anode electrode following the method from a previous study and placed vertically in the middle of anode chamber.[21] The wet-proofed (30%) carbon cloth (1071 HCB; AvCarb, United States) was used as a cathode electrode with a modification of 4 polytetrafluoroethylene diffusion layers on air-side and a Nafion binder mixed with platinum catalyst on solution-side. The Ag/AgCl reference electrodes were assembled on each of the chambers to measure the electrode potentials. The RED stack consisted of 3 cell pairs (except as noted) made of alternation anion and cation exchange membrane (Selemion AMV and CMV, Asahi Glass, Japan). Each membrane had an essential area of 12.25 cm² (3.5 cm × 3.5 cm). These membranes were separated by silicone gaskets and a nylon mesh spacer with a thickness of 0.18 mm, forming flow channels for alternating high-concentration (HC) and low-concentration (LC) solutions.

Solutions

The anode was enriched with exoelectrogens in a single chamber of an MFC at fix external resistance 1000 Ω and fed with 1 g/L of sodium acetate (CH_3COONa). The MFC reactor was fed with gradual increased concentrations of NaCl (0.10-0.35 M) to acclimate the exoelectrogens to chloride ions. The adapted anode was transferred to the MRC after reproducible maximum voltages on the MFC were stable at least for 3 consecutive batch cycle.

The anolyte solution was prepared by dissolving the following chemicals in 1 L of deionized water: 1.90 g CH_3COONa except as noted, 0.31 g NH_4Cl, 0.13 g KCl, 6.60 g $NaH_2PO_4.2H_2O$, 8.19 g Na_2HPO_4, as well as 12.5 g minerals and vitamins. A 1.0 M $NaHCO_3$ solution was used as catholyte (conductivity ~50.6 mS/cm; pH ~8.03). The HC solution was 35.0 g/L NaCl (~53.6 mS/cm), whereas the LC solution was 0.70 g/L NaCl (~1.39 mS/cm), creating a salinity ratio of 50. Leachate, as a representation of organic-rich wastewater, was used as an electron donor (substrate). The characteristic of leachate is as follows: soluble biochemical oxygen demand (COD) = 2100-2300 mg/L; nitrogen (NH_3) = 130 mg/L, nitrogen (NO_3^-) = 6.5 mg/L, phosphate (orthophosphate) = 86.4 mg/L, conductivity = 13.91 mS/cm, and pH = 7.15.

Reactor operation

Preliminary experiments were conducted to determine the optimum membrane pairs in the RED stack. The MRC reactor was operated using different numbers of the RED stack (1, 3, and 5 cell pairs). The reactor was fed with 1.9 g/L of CH_3COONa and connected to 1000 Ω external resistor. In further experiments, the MRC reactor was operated with different external resistances (150 Ω, 300 Ω, 650 Ω, and 1000 Ω). Food waste leachate was used as a substrate in the anode chamber and was replaced when the generated current decreased to less than 0.5 mA. In the RED stack, HC and LC were used as a feed solution and continuously supplied at a fixed rate of 1.2 mL/min during reactor operation. All of the MRC experiments were done in a constant room temperature (26 ± 1°C).

Experimental analysis and calculations

The potential difference (U) between anode and cathode was monitored and recorded every 5 minutes using a voltage recorder (VR-71; T&D Corporation, Japan) connected to a personal computer. The current was determined as $i = U/R$, and the current density was normalized by the cathode projected surface area (7 cm²). The maximum power density was obtained from the polarization curve, which was determined using variable external resistance (5-40.000 Ω) at 20-minute intervals. The effluent anolyte, catholyte, HC, and LC solutions were measured for pH and conductivity using a pH meter (Orion 720A+; Thermo Scientific Co.) and a conductivity meter (Orion Three-star, Thermo Scientific Co., United States). The COD of influent and effluent anolyte was measured according to the standard method (DR-2800; Hach Company, Indonesia). Ion flux efficiency (η_{flux}), CE, energy recovery (r_E), and energy efficiency (η_E) were described as follows.[14]

The chemical activity of ion (α_i) was determined by multiplying the chemical concentration in molarity by the activity coefficient (γ_i). The extended Debye-Huckel equation was used to determine the activity coefficient[22]:

$$\log \gamma_i = -\frac{A|z_i|^2 \sqrt{I_s}}{1 + B\alpha^0 \sqrt{I_s}} - \log(1 + 0.018 m_i) + K_i I_s \qquad (1)$$

The Debye-Huckel constants are $A = 0.5085$ kg$^{1/2}$/mol$^{1/2}$ and $B = 0.3282$ kg$^{1/2}$/A.mol$^{1/2}$. The ion size parameter (α^0) was 0.78 Å for both sodium (Na^+) and chloride (Cl^-), whereas K_{Na} and K_{Cl} are 0.105 and –0.009 kg²/mol², respectively. I_s is the ionic strength in molality, and m is the molal concentration. This equation is valid for a NaCl solution up to 1 molality.[23]

The ion flux efficiency (η_{flux}) is a ratio of the current generation in the MRC to the ion flux through the ion-exchange membrane and determined as

$$\eta_{flux} = \frac{N_{MP} i}{FQz\left(c_{in}^{river} - c_{eff}^{river}\right)} \qquad (2)$$

where N_{MP} is the number of cell pairs, i is the current generation in MRC (A), Q is the flow rate of feed stack (L/s), and c is the molar concentration of NaCl (mol/L).

The CE was calculated based on the COD removal and the number of coulombs produced during the reactor operation as previously described[23]:

$$CE = \frac{8\int i dt}{FV_{An}\Delta COD} \qquad (3)$$

where 8 is the number of electrons for substrate oxidation, i is current produced during the operational time (A), V_{An} is the volume of the anolyte (L), and ΔCOD is the change of substrate during operational time (g-COD).

The energy recovery (r_E) is the ratio of power production to the total energy provided in the MRC, and it was defined as

$$r_E = \frac{P}{\Delta H_c n_s^{in} / t_B + X^{in}} \qquad (4)$$

where P is the power produced from the MRC (W), ΔH_C is the heat of combustion of the substrate (kJ/mol), n_s^{in} is the mol concentration of substrate at the initial of operational time (mol), and t_B is the operational time of reactor (day). X^{in} is the theoretical energy (W) provided by the differences in salinity concentration of seawater and river water, and it was determined as[24]

$$X^{in} = 2RTQ\left(c_{in}^{river} \ln \frac{\alpha_{in}^{river}}{\alpha^{mixed}} + c_{in}^{sea} \ln \frac{\alpha_{in}^{sea}}{\alpha^{mixed}}\right) \qquad (5)$$

Energy efficiency (η_E) is the ratio of the power production to theoretically extractable energy provided by MRC, and it was determined as[12]

$$\eta_E = \frac{P}{\Delta H_c \left(n_s^{in} - n_s^{out} \right) / t_B + X^{in} - X^{out}} Seq \qquad (6)$$

where n_s^{out} is the mol concentration of substrate at the end of operational time, X^{out} is the theoretical energy (W) of the salinity gradient energy remaining in seawater and river water effluents.

A Tafel plot test was conducted to investigate bioelectrochemical kinetics of anode biofilm electrode using a potentiostat (DY2300; Digi-Ivy, Inc., Austin, TX, USA) in 3-electrode conventional cells. The anode, saturated calomel electrode, and the cathode served as the working electrode, reference electrode, and counter electrode, respectively.

Results and Discussion

Performance of MRC using different numbers of membrane cell pairs

The reactor was operated under fed-batch mode with different membrane cell pairs (1 MP, 3 MP, and 5 MP) and fixed external resistance (1000 Ω). As shown in Figure 2, the cell current tended to increase as the number of membrane cell pairs increased. The MRC with 5 MP produced a maximum cell
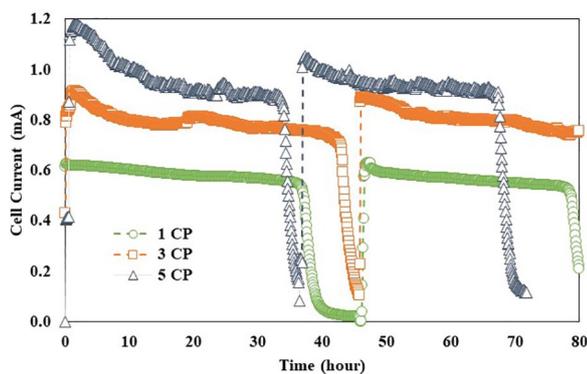
Figure 2. Current generation in MRC reactor at the indicated number of membrane cell pairs (external resistance of 1000 Ω). MRC indicates microbial reverse-electrodialysis cell.

current of 1.12 ± 0.09 mA, which was 1.2- and 1.9-fold higher than that of obtained using 3 MP (0.9 ± 0.02 mA) and 1 MP (0.60 ± 0.03 mA), respectively.

The polarization curve was measured by varying an external resistance in the MRC reactor to determine the maximum power density. It was observed that the maximum cell potentials produced during the polarization test increased as the number of membrane pairs increased (Figure 3A). Furthermore, adding more membrane pairs increased the maximum current density from 0.51 mA/cm² (1 MP) to 0.85 mA/cm² (5 MP). Meanwhile, consistent with previous research,[25] the cell potential decreased with increasing current density due to the activation losses, ohmic losses, and concentration losses during MRC operation. The power density of the MRC reactor was inclined to follow the previous results of maximum cell potentials (Figure 3B). The MRC with 1 MP produced the maximum power density of 1.19 W/m² as normalized by 7 cm² of cathode area or 30 W/m³ as normalized by anolyte volume. Meanwhile, the MRC with 3 MP produced the maximum power density of 2.31 W/m² (58.3 W/m³). Furthermore, the MRC with 5 MP achieved higher power densities, with a maximum power density of 2.75 W/m² (69.4 W/m³). However, the increase in power density as a result of an increase in the number of membrane pairs from 3 to 5 (0.44 W/m²) was smaller than that obtained when increasing membrane pairs from 1 to 3 (1.12 W/m²), suggesting that further increase in membrane pairs did not significantly increase power density.

These values of power density were relatively higher compared with power density produced by the MFC with the same operational conditions (reactor working volume and electron donor). Based on the previous study,[26] 2 chambers of MFC produced 0.45 W/m² of power density. Subsequently, Choi and Ahn[27] also reported that the MFC reactor produced 0.77 W/m² of power density with food waste leachate as substrate and 24 mL of working volume reactor. The research from Moharir and Tembhurkar[28] also showed relatively the same result, claiming that the MFC reactor produced 0.29 W/m² of power density. These results confirmed that the high power density produced in the MRC reactor is
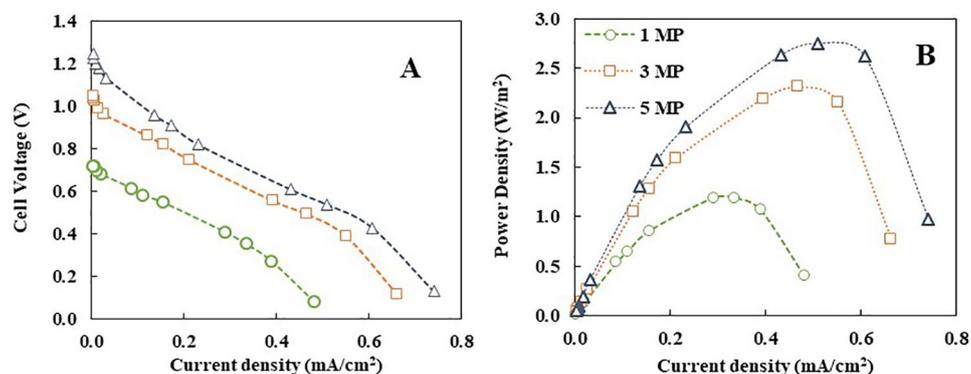
Figure 3. (A) Polarization and (B) power densities of MRC at different number of membrane cell pairs. MRC indicates microbial reverse-electrodialysis cell.
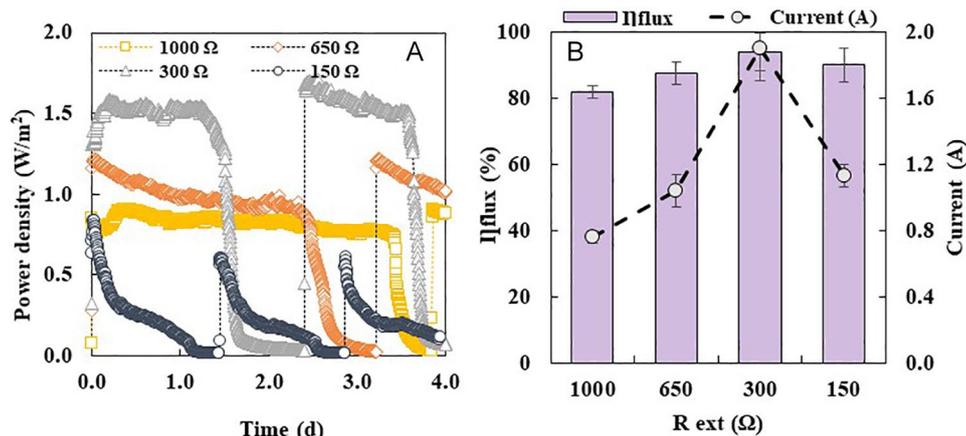
Figure 4. (A) Power density and (B) ion flux efficiency of MRC reactor at the indicated external resistance. MRC indicates microbial reverse-electrodialysis cell.

due to the salinity energy created from the small number of membrane pairs (RED stack).

According to the above results, 3 MP was selected as the optimum operational condition as the increase in the number of membrane pairs to 5 MP did not substantially increase the reactor performance. Therefore, in further experiments, the reactor was operated using 3 MP with different external resistors ($150\,\Omega$, $300\,\Omega$, $600\,\Omega$, and $1000\,\Omega$).

Effect of external resistance on power generation

In this section, the MRC reactors were operated for several cycles with food waste leachate as a donor electron and were connected to different external resistors ($150\,\Omega$, $300\,\Omega$, $600\,\Omega$, and $1000\,\Omega$). Figure 4A shows that the power density increased from $0.82 \pm 0.038\,W/m^2$ to $1.53 \pm 0.198\,W/m^2$ as the external resistance decreased from $1000\,\Omega$ to $300\,\Omega$. Furthermore, the power density significantly decreased to $0.34 \pm 0.067\,W/m^2$ as the external resistance decreased to $150\,\Omega$. These results indicated that when external resistance dropped, power density would increase as a result. However, a fall in power density occurred when the external resistance exceeded its optimum point. The differences in power density produced were likely due to the changes in the internal resistance of the MRC reactor. Based on the slope of the polarization curve, the total internal resistance of the reactor was $544.9\,\Omega$, $507.7\,\Omega$, $372.0\,\Omega$, and $401.1\,\Omega$ for the MRC with the external resistance of $1000\,\Omega$, $600\,\Omega$, $300\,\Omega$, and $150\,\Omega$, respectively. The MRC reactor with the external resistance of $300\,\Omega$ achieved higher power production, compared with the other reactors, as the total internal resistance in this reactor was close to the value of its external resistance. This result was consistent with the previous study[29]; it is stated that the reactor's power density was maximized when the external resistance connected to it was equal or close to the total internal resistance.

To determine the influence of external resistance to the salinity energy created by the RED stack, the ion flux efficiency

was measured. Ion flux efficiency is a ratio of the current generation in the MRC reactor to the ion flux through the ion-exchange membrane. Based on the concentration change in the LC effluent, the ion flux efficiency was $82 \pm 2\%$, $88 \pm 3\%$, $94 \pm 6\%$, and $90 \pm 5\%$ with the average currents produced were $0.74 \pm 0.038\,mA$, $1.04 \pm 0.098\,mA$, $1.90 \pm 0.198\,mA$, and $1.13 \pm 0.067\,mA$ for the MRC reactor with the external resistance of $1000\,\Omega$, $600\,\Omega$, $300\,\Omega$, and $150\,\Omega$, respectively (Figure 4B). These results showed that the ion flux efficiency increased (from $82 \pm 2\%$ to $94 \pm 6\%$) with a decrease in the external resistance (from $1000\,\Omega$ to $300\,\Omega$). This increase led to a rise in the cell current produced in the MRC reactor ($0.74 \pm 0.038\,mA$ to $1.90 \pm 0.198\,mA$). The ion flux efficiency dropped to $90 \pm 5\%$ as the external resistance fell to $150\,\Omega$; thus, the cell current produced decreased to $1.13 \pm 0.067\,mA$. When the reactor was operated with low external resistance, the reactor generated a higher current due to the more frequent electron transfer from anode to an electrode, which then would support faster cathode reaction and high electrogenic activity.[29] According to the above results, it can be concluded that the external resistance affected the ion flux efficiency through the magnitude of current produced in the reactor.

Effect of external resistance on CE and COD removal

Coulombic efficiency is the ratio of the total recovered coulombs to the theoretical amount of coulombs provided by the substrate. Generally, the CE value is influenced by substrate removal (as the soluble COD removal) in the reactor. Based on the calculation of initial and effluent of soluble COD in the MRC reactor, the substrate removal reached up to $73 \pm 2.8\%$, $62 \pm 2.1\%$, $52 \pm 2.3\%$, and $41 \pm 2.6\%$ for the reactor with external resistance of $1000\,\Omega$, $650\,\Omega$, $300\,\Omega$, and $150\,\Omega$, respectively (Figure 5A). It was observed that the COD removal increased as the external resistance increased. The higher COD removal was likely a result of the longer batch cycle time of the
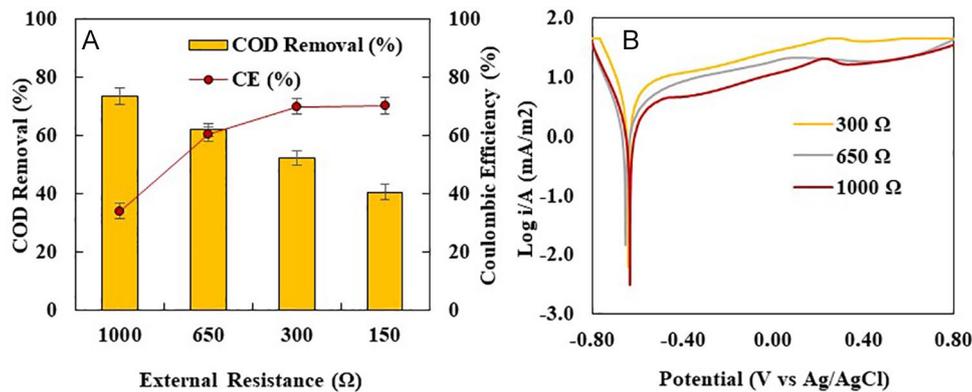
Figure 5. (A) COD removal and CE and (B) Tafel plots of MRC reactor at the indicated external resistance. CE indicates Coulombic efficiency; MRC, microbial reverse-electrodialysis cell.

MRC reactor with $1000\,\Omega$ than those of other reactors. The longer the cycle time of the reactor, the more substrate was consumed by the bacteria; thus, high-soluble COD removal in the reactor was achieved.

The CE value of the MRC reactor at different external resistance can be seen in Figure 5A. The CE obtained from the MRC reactor with $300\,\Omega$ ($70 \pm 2.6\%$) and $150\,\Omega$ ($70 \pm 2.9\%$) was higher than that of the reactor with $1000\,\Omega$ ($34 \pm 2.7\%$) and $650\,\Omega$ ($60 \pm 2.3\%$). The higher CE value on the MRC reactor with $300\,\Omega$ and $150\,\Omega$ was considered to be a result of the shorter batch cycle time. Low external resistance would bring a high electron transfer rate in the reactor; thus, it probably resulted in a shorter batch cycle time. The batch cycle time would affect the CE value as the reactors were started with a mixed culture inoculum. The substrate removal by the non-exoelectrogen caused substrate loss to non-current-generating processes, which resulted in high COD removal and low CE.

To determine the electron transfer rate in the MRC reactor, the bioelectrokinetic of the anode was then analyzed using Tafel plots in terms of exchange current density (i_o) and anodic Tafel slope (b_a) as shown in Figure 5B. Exchange current density is a parameter related to the bioelectrochemical activity of the anode at the equilibrium condition. Based on the Tafel plots shown in Figure 5B, the exchange current density of biofilm at $300\,\Omega$ MRC reached $23.2\,\text{mA/m}^2$, which was higher than those of other reactors ($18.6\,\text{mA/m}^2$ and $12.0\,\text{mA/m}^2$ for the MRC reactors with $650\,\Omega$ and $1000\,\Omega$, respectively). In terms of anodic Tafel slope (b_a), the biofilm at the MRC reactor with $300\,\Omega$ revealed a lower value of $0.73\,\text{V/decade}$ than the reactors with $1000\,\Omega$ and $650\,\Omega$ ($0.93\,\text{V/decade}$ and $0.84\,\text{V/decade}$, respectively). These results indicated that the reactor with lower external resistance could easily detach the electron from the biofilm into the anode electrode compared with the reactor with higher external resistance.

According to the results above, it can be concluded that external resistance affected the CE value of the MRC reactor through the length of batch cycle time and bioelectrokinetic anode value (exchange current density and Tafel slope). When
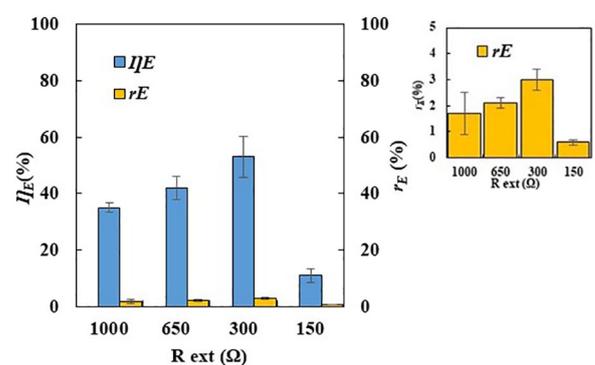

Figure 6. Energy efficiency and energy recovery (inserted picture) of MRC reactor at the indicated external resistance. MRC indicates microbial reverse-electrodialysis cell.

the MRC reactor was connected to a high external resistance, the reactor would have a longer batch cycle as the exchange current density was low; thus, large COD removal and low CE value were achieved (and vice versa).

Effect of external resistance on energy recovery and energy efficiency

The energy recovery (r_E) is the ratio of power production to the total energy provided in the MRC. Meanwhile, energy efficiency (η_E) is the ratio of the power production to theoretically extractable energy provided by MRC. The energy efficiency and energy recovery of the MRC reactor at different external resistance are shown in Figure 6. It was observed that the energy recovery increased from $1.7 \pm 0.1\%$ to $3.0 \pm 0.4\%$ as the external resistance decreased from $1000\,\Omega$ to $300\,\Omega$. The energy recovery then significantly decreased to $0.6 \pm 0.1\%$ when the external resistance decreased to $150\,\Omega$. Compared with another study with 3-membrane pairs of MRC conducted by Liu et al,[17] energy recovery results from this study were significantly lower. This low energy recovery was likely due to the relatively high feed stack flow rate used here ($1.2\,\text{mL/min}$ compared with $0.80\,\text{mL/min}$) compared with the lower power produced in the reactor ($1.03\,\text{mW}$

compared with 2.4 mW). The high feed stack flow rate resulted in higher energy input creating from the RED stack (34 mW compared with 24 mW). Moreover, Kang et al[30] reported that the MRC reactor with 5 mL/min of feed stack flow rate and 2.4 mW of power produced achieved 2.0% energy recovery, which was lower than the result of the recent study. In this case, this result proves that the feed stack flow rate significantly affected the energy recovery of the MRC reactor compared with the energy produced in the reactor. In this study, the value of energy efficiency mainly depended on the power production in the MRC reactor (P varied from 0.22 to 1.03 mW) as the summation of energy created from salinity gradient (X^{in}) and substrate loading ($\Delta H_c \, x \, n_s^{in}/t_b$) was relatively constant (0.034 W). These calculations suggested that the MRC reactor with high power production would achieve high energy recovery.

Based on the calculation of energy recovered in the system compared with the energy available on the substrate, the energy efficiency of the MRC reactor tended to follow the trend of the energy recovery result. The energy efficiency increased from $35 \pm 1.6\%$ to $53 \pm 7.1\%$ as the external resistance decreased from 1000 Ω to 300 Ω. The energy efficiency then significantly decreased to $11 \pm 2.4\%$ when the external resistance decreased to 150 Ω. The higher energy efficiency was observed in the MRC reactor with the external resistance of 300 Ω, which was 1.5, 1.3, and 4.8 times larger than the MRC reactors with the external resistance of 1000 Ω, 650 Ω, and 300 Ω, respectively. Similar to energy recovery, the value of energy efficiency in the reactor mainly depended on the power production compared with the energy input (based on the entering minus leaving) to the reactor. The power production in the reactor varied from 0.22 mW to 1.03 mW, while the energy input was relatively constant (1.30 W). Thus, the relatively higher power production of the reactor with external resistance of 300 Ω resulted in larger energy efficiency compared with other reactors.

According to the above results, it can be concluded that the external resistance affected the value of energy efficiency and energy recovery through the magnitude of power production in the reactor. When the reactor was connected to the proper external resistance, the reactor created high power production; thus, the high energy efficiency and energy recovery were achieved.

Conclusions

The applied external resistance was optimized to determine its effect on the MRC reactor performances. Based on the evaluation of the reactor performance, the optimum condition was achieved when 300 Ω of external resistance was applied. In such conditions, the power density of 1.53 ± 0.198 W/m², substrate removal of $52 \pm 2.3\%$, CE of $70 \pm 2.6\%$, energy recovery of $3.0 \pm 0.4\%$, and energy efficiency of $53 \pm 7.1\%$ were obtained in the MRC reactor. The external resistance affected the power density as it changes the internal resistance and ion flux

efficiency of the MRC reactor. Improper selection of external resistance would lead to high losses in power output. When the MRC reactor was connected to a high external resistance, the reactor would have a longer batch cycle as the exchange current density was low; thus, large COD removal and low CE value were achieved (and vice versa). Moreover, the proper external resistance applied to the reactor created high power production, which resulted in high energy efficiency and energy recovery. Therefore, this study shows that selecting proper external resistance was an essential key for a successful MRC reactor operational.

Author Contributions

AJE and SH conceived and designed the research and analysed the data and wrote the first draft of the manuscript. SS, BSR, CP, and JYP made critical revisions and approved the final version. All the authors contributed to the writing of the manuscript, revisions, and agree with manuscript results and conclusions. All authors reviewed and approved the final manuscript.

ORCID iD

Syarif Hidayat (iD) https://orcid.org/0000-0003-1611-6887

REFERENCES

1. Logan BE, Rabaey K. Conversion of wastes into bioelectricity and chemicals by using microbial electrochemical technologies. *Science*. 2012;337:686-690.
2. Santoro C, Arbizzani C, Erable B, Ieropoulos I. Microbial fuel cells: from fundamentals to applications. A review. *J Power Sources*. 2017;356:225-244.
3. Lu M, Chen S, Babanova S, et al. Long-term performance of a 20-L continuous flow microbial fuel cell for treatment of brewery wastewater. *J Power Sources*. 2017;356:274-287.
4. He W, Zhang X, Liu J, Zhu X, Feng Y, Logan BE. Microbial fuel cells with an integrated spacer and separate anode and cathode modules. *Environ Sci Water Res Technol*. 2016;2:186-195.
5. Estrada-Arriaga EB, Guillen-Alonso Y, Morales-Morales C, et al. Performance of air-cathode stacked microbial fuel cells systems for wastewater treatment and electricity production. *Water Sci Technol*. 2017;76:683-693.
6. Liang P, Duan R, Jiang Y, Zhang X, Qiu Y, Huang X. One-year operation of 1000-L modularized microbial fuel cell for municipal wastewater treatment. *Water Res*. 2018;41:1-8.
7. An BM, Heo Y, Maitlo HA, Park JY. Scaled-up dual anode/cathode microbial fuel cell stack for actual ethanolamine wastewater treatment. *Bioresour Technol*. 2016;210:68-73.
8. Pattle RE. Production of electric power by mixing fresh and saltwater in the hydroelectric pile. *Nature*. 1954;174:660.
9. Post JW, Vermaan J, Hamelers HVM, et al. Salinity-gradient power: evaluation of pressure-retarded osmosis and reverse electrodialysis. *J Membr Sci*. 2007;288:218-230.
10. Veerman J, Vermaas DA. Chapter: 4. Reverse electrodialysis: fundamentals. In: Cipollina A, Micale G, eds. *Sustainable Energy From Salinity Gradients*. Cambridge, UK: Woodhead Publishing; 2016:77-133.
11. Veerman J, Saakes M, Metz SJ, Harmsen GJ. Electrical power from sea and river water by reverse electrodialysis: a first step from the laboratory to a real power plant. *Environ Sci Technol*. 2010;44:9207-9912.
12. Veerman J, de Jong RM, Saakes M, Metz SJ, Harmsen GJ. Reverse electrodialysis: comparison of six commercial membrane pairs on the thermodynamic efficiency and power density. *J Membr Sci*. 2009;343:7-15.
13. Tedesco M, Cipollina A, Tamburini A, Micale G. Towards 1 kW power production in a reverse electrodialysis pilot plant with saline waters and concentrated brines. *J Membr Sci*. 2017;522:226-236.
14. Kim Y, Logan BE. Microbial reverse electrodialysis cells for synergistically enhanced power production. *Environ Sci Technol*. 2011;45:5834-5839.

15. Cusick RD, Kim Y, Logan BE. Energy capture from thermolytic solutions in microbial reverse-electrodialysis cells. *Science*. 2012;335:1474-1477.

16. Cusick RD, Hatzell M, Zhang F, Logan BE. Minimal RED cell pairs markedly improve electrode kinetics and power production in microbial reverse electrodialysis cells. *Environ Sci Technol*. 2013;47:14518-14524.

17. Liu J, Geise GM, Luo X, et al. Patterned ion exchange membranes for improved power production in microbial reverse-electrodialysis cells. *J Power Sources*. 2014;271:437-443.

18. Liu H, Cheng S, Logan BE. Production of electricity from acetate or butyrate in a single-chamber microbial fuel cell. *Environ Sci Technol*. 2005;39:658-662.

19. Kim JR, Premier GG, Hawkes FR, Rodríguez J, Dinsdale RM, Guwy AJ. Modular tubular microbial fuel cells for energy recovery during sucrose wastewater treatment at low organic loading rate. *Bioresour Technol*. 2010; 101:1190-1198.

20. Hidayat S, Song YH, Park JY. Performance of a continuous flow microbial reverse-electrodialysis electrolysis cell using a non-buffered substrate and catholyte effluent addition. *Bioresour Technol*. 2017;240:77-83.

21. Feng Y, Yang Q, Wang X, Logan BE. Treatment of graphite fiber brush anodes for improving power generation in air-cathode microbial fuel cells. *J Power Sources*. 2010;195:1841-1844.

22. Zhuo K, Dong W, Wang W, Wang J. Activity coefficients of individual ions in aqueous solutions of sodium halides at 298.15 K. *Fluid Phase Equilib*. 2008;274:80-84.

23. Logan BE. *Microbial Fuel Cell*. Hoboken, NJ: John Willey & Sons; 2008.

24. Escobar I, Schafer A. *Sustainable Water for the Future: Water Recycling Versus Desalination*. Amsterdam, The Netherlands: Elsevier; 2010.

25. Kim KY, Yang W, Logan BE. Impact of electrode configurations on retention time and domestic wastewater treatment efficiency using microbial fuel cells. *Water Res*. 2015;80:41-46.

26. Li XM, Cheng KY, Selvam A, Wong JWC. Bioelectricity production from acidic food waste leachate using microbial fuel cells: effect of microbial inocula. *Process Biochem*. 2013;48:283-288.

27. Choi J, Ahn Y. Enhanced bioelectricity harvesting in microbial fuel cells treating food waste leachate produced from biohydrogen fermentation. *Bioresour Technol*. 2015;183:53-60.

28. Moharir PV, Tembhurkar AR. Effect of recirculation on bioelectricity generation using microbial fuel cell with food waste leachate as substrate. *Int J Hydrog Energy*. 2018;43:10061-10069.

29. Gonzalez del Campo A, Canizares P, Lobato L, Rodrigo M, Fernandez FJ, eds. *Effect of External Resistance on Microbial Fuel Cell. Environment, Energy and Climate Change II: Energies from New Resources and the Climate Change*. Berlin, Germany: Springer International Publishing; 2016.

30. Kang H, Kim E, Jung SP. Influence of flow rates to a reverse electro-dialysis (RED) stack on performance and electrochemistry of a microbial reverse electrodialysis cell (MRC). *Int J Hydrog Energy*. 2017;42:27685-27692.