

Combination of a novel electrode material and artificial mediators to enhance power generation in an MFC

Ergin Taskan, Bestamin Ozkaya and Halil Hasar

ABSTRACT

This study focuses on two main aspects: developing a novel cost-effective electrode material and power production from domestic wastewater using three different mediators. Methylene blue (MB), neutral red (NR) and 2-hydroxy-1,4-naphthoquinone (HNQ) were selected as electrode mediators with different concentrations. A tin-coated copper mesh electrode was tested as anode electrode. Maximum power density of the microbial fuel cell (MFC) with 300 μM MB was 636 mW/m^2 . Optimal mediator concentrations with respect to the achieved maximum power output for MB, NR and HNQ were 300 μM , 200 μM and 50 μM , respectively. The results demonstrate that tin-coated copper mesh showed a higher biocompatibility and electrical conductivity.

Key words | microbial fuel cell, mediator, power output, internal resistance

Ergin Taskan (corresponding author)

Halil Hasar

Department of Environmental Engineering,
Firat University, Faculty of Engineering,
Elazig 23119,
Turkey
E-mail: etaskan@firat.edu.tr

Bestamin Ozkaya

Department of Environmental Engineering,
Yildiz Technical University,
Istanbul,
Turkey
and
Department of Chemistry and Bioengineering,
Tampere University of Technology, Faculty of
Science and Environmental Engineering,
Tampere,
Finland

INTRODUCTION

The microbial fuel cell (MFC) is a promising technology for alternative energy options due to its electricity generation from organic matter by bacterial metabolism. In this technology, inadequate power densities have constituted the greatest challenge for constructing a pilot- or real-scale reactor. In an MFC, it has been thought that the electron transfer and electrode material are two important factors that influence the power generation. To date, two mechanisms for electron transfer from bacteria to electrodes have been found to be important: direct electron transfer (DET) and mediated electron transfer (MET) (Schröder 2007). Since DET (upon which means the active membrane enzyme is directly connected to the electrode and/or the fibrous protein structure of nanowires) facilitates the transfer of electrons to the electrode that naturally forms in an MFC, MET entails the external addition of an artificial mediator to an electrode to reach the electrons released in the anode because MET is involved in the redox mediator, which can be used as an electron shuttle between bacteria and the electron acceptor (Rabaey *et al.* 2005; Burns *et al.* 2009; Babanova *et al.* 2011). Studies so far have been widely carried out on the mediators with synthetic wastewater at stable concentration; methylene blue (MB) at 80 μmol by Sund *et al.* (2007), neutral red (NR) at

250 μmol by Wang *et al.* (2011) and 2-hydroxy-1,4-naphthoquinone (HNQ) at 500 μmol by Lee *et al.* (2002).

On the other hand, the anode electrode should have some properties for transporting electrons from the anode electrode to the cathode electrode, such as: (i) good electrical conductivity and low resistance, (ii) strong biocompatibility, (iii) chemical stability and anti-corrosive, (iv) a large-surface area, and (v) appropriate mechanical strength and toughness (Zhou *et al.* 2011). Copper could be used as an effective electrode material because of its high-electrical conductivity in MFC studies, but it was stated that copper is not suitable electrode material for MFC application because of its corrosive effect (Zhu & Logan 2014). Therefore, coating the copper electrode would be a good alternative approach to prevent corrosion. In recent studies, different anode electrode materials have coated different materials by using different techniques. For example, Guo *et al.* (2014) tested a new carbon paper electrode modified with graphene using a layer-by-layer assembly technique, which achieved a maximum power density of 368 mW/m^2 . In another study, Hidalgo *et al.* (2014) used ceramic berl saddles covered by a thin and conductive carbon layer and achieved a maximum power density of 130 mW/m^2 .

The present study used novel cost-effective electrodes; a tin-plated copper electrode for anode and titanium electroplating with platinum for the cathode because they have high conductivity and biocompatible capacities. In addition, three artificial mediators with the properties of biocompatibility and electrochemically active (Schröder 2007; Schaezle *et al.* 2008; Tang *et al.* 2010; Babanova *et al.* 2011; Rahimnejad *et al.* 2011) such as MB, NR, and HNQ were tried to define the effect of MET on power generation in a dual chamber MFC by considering total internal resistance, current densities, and mediator concentrations. Therefore, this study presents an instructive contribution to power generation using different mediator types and new electrode materials.

MATERIAL AND METHODS

Dual chamber MFC

For the dual chamber MFC used in this study, each effective volume of 300 mL is shown in Figure 1. Electrodes were tin-coated copper mesh in the anode chamber and platinum-coated titanium in the cathode chamber. Two compartments were separated by a proton exchange membrane (Ultrex CMI7000, Membranes International, Inc., Ringwood, NJ, USA). Ultrex membrane has a functional group of sulphonic acid, total exchange capacity (meq/g) of 1.6 ± 0.1 , standard thickness (μm) of 0.45 ± 0.025 , water permeability (ml/h/ft² at 5 psi) of <3 and a chemical stability range (pH) of 1–10. The membrane was preconditioned by immersion in 5% NaCl solution at 40 °C for 24 hours. The anode compartment of the MFC

was seeded with anaerobic sludge. The MFC reactor was covered by aluminum foil during operation.

Artificial mediators and electrodes

MB, NR, and HNQ used as artificial mediators were supplied by Sigma-Aldrich, Steinheim, Germany. In order to reduce changes in pH and keep a pH value of nearly 7, 50 mM phosphate buffer was added to the anode and cathode solutions. Tin-coated copper mesh was used as an anode electrode. The copper mesh has 16 wires per inch and a wire diameter of 0.27 and 1.32 mm openings. The physical characteristics data were obtained from the manufacturer's datasheet. The tin-coated copper mesh was obtained from LessEMF Inc. (Albany, NY, USA). In this study, the MFC reactor was operated for 90 days. The scanning electron microscopy (SEM) images were obtained before and after the operation. The SEM image of the copper mesh electrode is shown in Figure 2.

A platinum-coated titanium plate electrode was used as a cathode electrode to catalyze the reduction of molecular oxygen to water in the cathode chamber. The platinum concentration on the titanium plate electrode was 0.30 mg of Pt/cm². The anode and cathode electrodes were fixed with an external resistance of 10 Ω . The feed was delivered into the MFC from a 0.5 L tank by using a peristaltic pump (Watson Marlow, Wilmington, MA, USA). The pH was measured by a pH meter (Thermo Scientific, Waltham, MA, USA). Voltage (V) and current (A) across an external resistor were measured at 1 minute intervals using a data acquisition system (FLUKE 8846A, Everett, WA, USA) connected to a computer. The power generation of the MFC was calculated according to $P = IE$, where I (A) is the current and E (V) is voltage. The

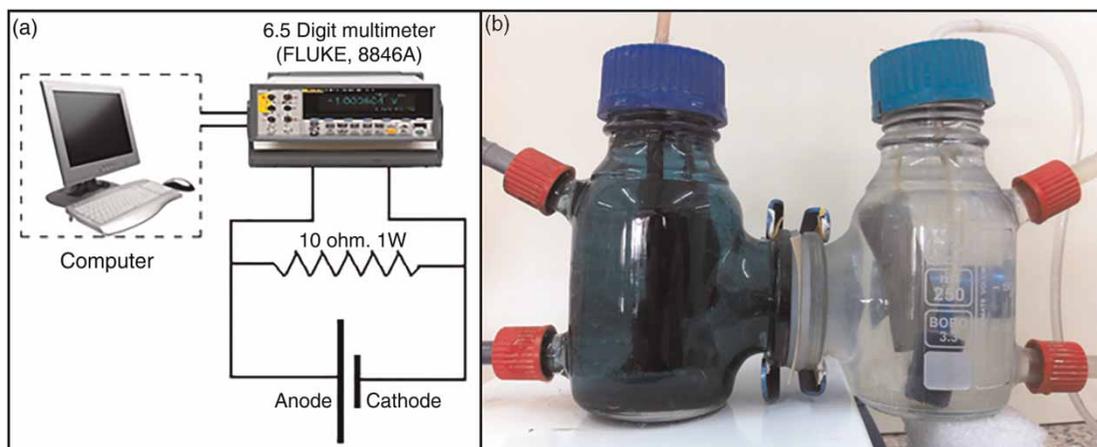


Figure 1 | (a) Voltage monitoring system and (b) a photograph of a laboratory-scale two-chamber microbial fuel cell.

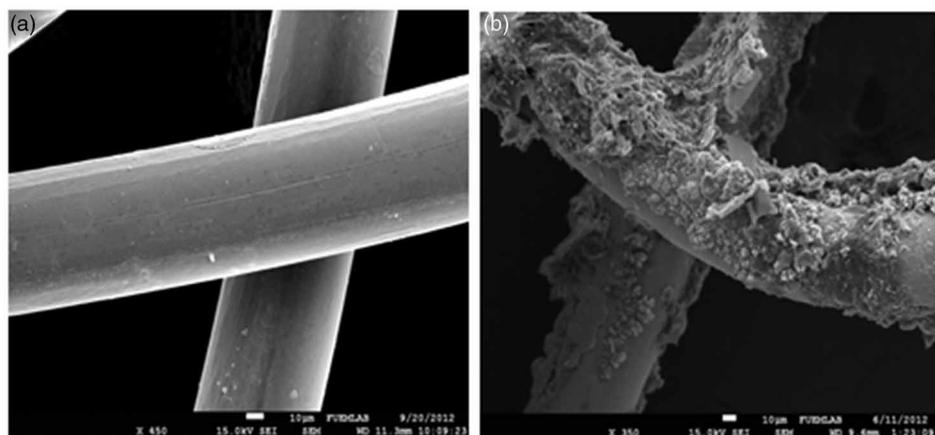


Figure 2 | SEM images of copper mesh electrode surface before (a) and after (b) operation.

power density was normalized to the cathode surface area as mW/m^2 (Rismani-Yazdi *et al.* 2008). Polarization data can be used to examine the internal resistance of the reactor using polarization curves. Polarization measurements at variable resistances from 1 to 50,000 Ω were carried out using a potentiometer. The coulombic efficiency (CE) was calculated on the basis of the measured chemical oxygen demand (COD) removal as described by Logan *et al.* (2006) and the COD was determined in accordance with *Standard Methods for the Examination of Water and Wastewater* (American Public Health Association Water Environment Federation 1995). The mediator cost was calculated for a power density increase of $1 \text{ mW}/\text{m}^2$ for each mediator type. Chemical costs were calculated in EU (Euro), using Sigma-Aldrich (2014).

Operation of dual chamber MFC

The MFC reactors were fed with domestic wastewater supplied from Elazig Wastewater Treatment Plant (Turkey) and the wastewater was kept in a deep refrigerator at $+4^\circ\text{C}$ in order to avoid any decomposition. The anode chamber was seeded with anaerobic sludge from Diyarbakir Wastewater Treatment Plant (Turkey), and sparged with nitrogen gas for 10 min to remove dissolved oxygen. The buffered MQ water was used in the cathode section and aerated by air pump during the operation. The MFC was operated at room temperature and a hydraulic retention time (HRT) of 2 days. After the end of each period, the anode medium was replaced to carry out further experiments to take measures against residuals from previous conditions. The MFC reactor was operated for about 90 days to define the long-term stability of the tin-coated copper mesh electrode.

RESULTS AND DISCUSSION

Electrode performance

The electrode used in the anode was copper mesh and provides a high porosity (see Figure 2). The tin-coated copper mesh has a high-specific surface area of $0.65 \text{ kg}/\text{m}^2$. This increases the electrode surface to improve the performance of MFCs because it enhances microbe attachment and the bio-electron transfer area and decreases internal resistance of the MFC. In addition, tin plate has another advantage for the copper mesh electrode. Tin plate protects the copper electrode from corrosion and helps chemical stability. SEM results (Figure 2(b)) showed no corrosive impact on the tin-coated copper mesh electrode. In addition to this, biofilm formation on the electrode surface demonstrated no toxic effect on the tin-coated copper mesh electrode because microorganism injuries from corrosion formation on the copper electrode, which is known to be toxic to microorganisms, and decreases performance of the MFC. Zhu & Logan (2014) indicated that corrosion of the copper anode adversely affected the current generation of the MFC and reported that the copper anode showed initial high-current generation, but subsequently they produced little power ($2 \text{ mW}/\text{m}^2$). In another study, Kargi & Eker (2007) achieved tiny power density ($2.9 \text{ mW}/\text{m}^2$) by using a copper anode. In the current study, we achieved a maximum power density of $110 \text{ mW}/\text{m}^2$ during the mediator-less operation. Figure 2 shows that a good biofilm accumulation was established on the electrode surface. This shows that electrode configuration and coating with tin are very effective for the performance of the copper electrode by preventing its

corrosion. The electrodes used have a large-specific surface area, chemical stability, excellent conductivity and they are anti-corrosive. In our study, power density and SEM results demonstrated that a tin-coated copper mesh electrode has good stability, and it is suitable electrode material for MFC application.

Electron transfer mechanisms in power generation

For the DET mechanism, the MFC reactors were operated without the addition of an artificial mediator. The results showed that the maximum power density in the case of DET varied in the range of 110 and 135 mW/m^2 after MFC seeded with anaerobic sludge received a steady-state current generation. Conversely, it has been observed that all three mediators contributed to the power generation. While the maximum power generation was about

110 mW/m^2 without an external mediator, it increased to 125 mW/m^2 at 50 μM of MB. In order to determine the effect of mediator concentration on the power generation, MB concentration was increased progressively from 50 to 400 μM . The maximum power increased sharply to 460 mW/m^2 at 100 μM MB. At concentrations of MB of 200 and 400 μM , it varied in the range of 506–519 mW/m^2 . Alternatively, the maximum power generation and current density generation achieved about 636 mW/m^2 and 1.26 A/m^2 at 300 μM MB, respectively (Figure 3). The results showed that the MET effect at 300 μM MB was almost six-fold better than the DET mechanism.

Before the NR was added to the MFC, the maximum power density was 135 mW/m^2 and current density was 0.62 A/m^2 . By adding the NR, it increased to 400 mW/m^2 and 1 A/m^2 at 200 μM NR (Figure 4), which means an approximate three-fold power increase.

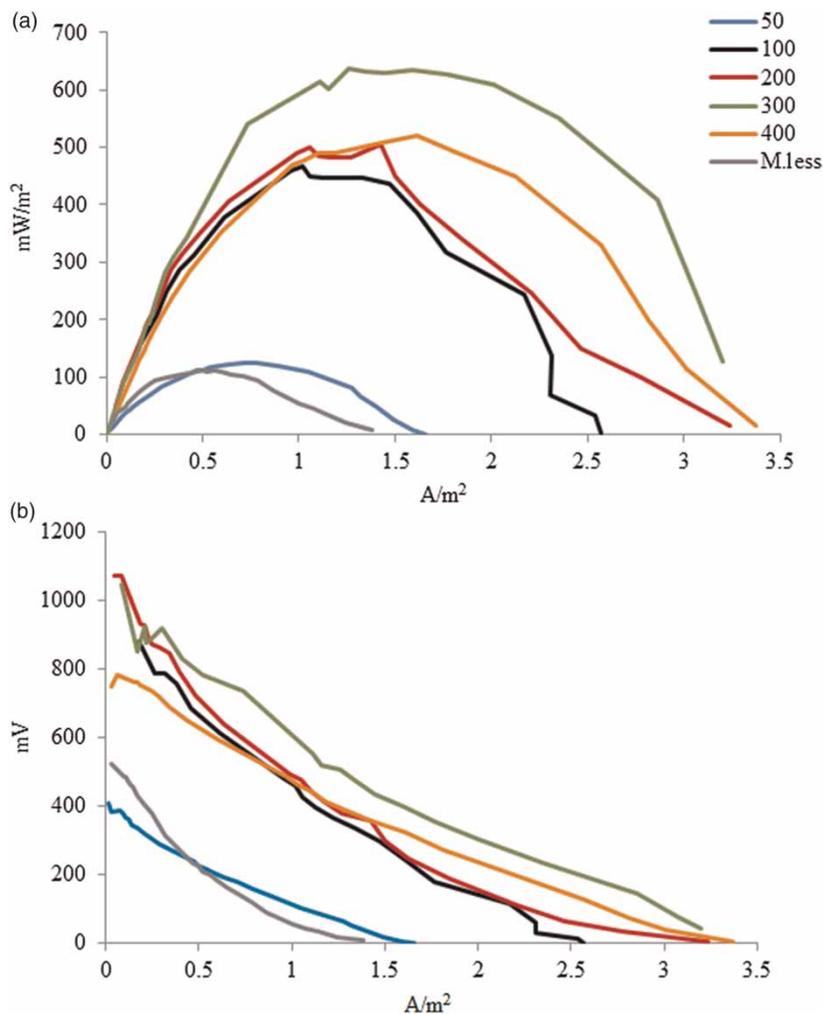


Figure 3 | Polarization curves of MFC depending on MB concentrations. Power curves (a) and potential curves (b) of MFC fed with mediatorless and different mediator concentrations.

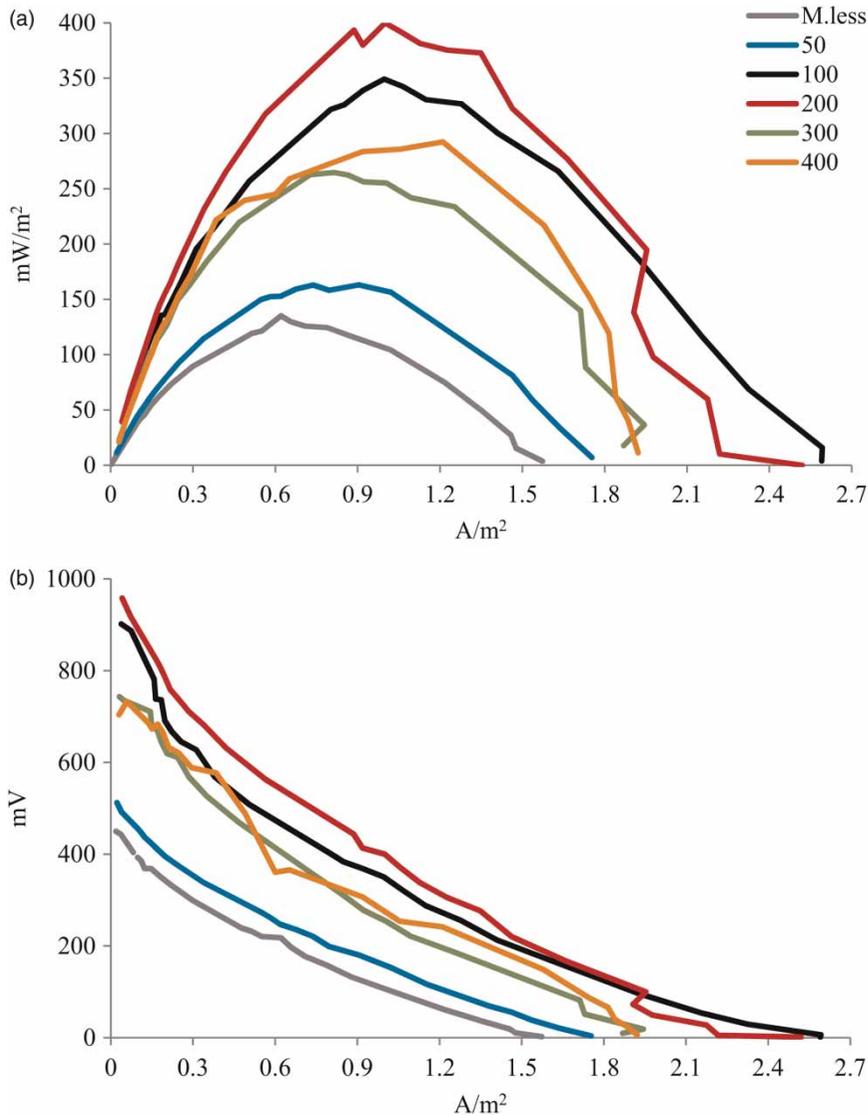


Figure 4 | Polarization curves of MFC depending on NR concentrations. Power curves (a) and potential curves (b) of MFC fed with mediatorless and different mediator concentrations.

The lowest power output increment was observed with the HNQ mediator. The power generation of MFC with 50 μM HNQ was one-half-fold of the increase of a mediator-less operation (Figure 5).

It was indicated that the best generation of power and voltage was obtained by the MB mediator. Conversely, the lowest enhancement of the power density in comparison with the mediator-less MFC was achieved with the supplement of HNQ. Daniel *et al.* (2009) reported that the open circuit potential in a single MFC with MB was almost the double that generated with NR as mediator. Wilkinson *et al.* (2006) proposed that, in the presence of NR, respiration would shut down because the potential of NR was too low to enable it to oxidize any electron transport molecules.

Our results showed that the direct electron transfer rate was very low. This could be due to two reasons: first is that it resulted from the over-potential effect and second is that it resulted from insulation of the active-side enzyme in the anode environment. Since either oxidation or reduction of organic matter at the anode surface and the bacterial surface require a certain amount of energy to activate oxidation reactions, a transfer resistance forms and this situation also causes potential losses between the bacteria and electron surface, which are called over-potentials. The second reason results from the active side of the enzyme being significantly insulated in the protein medium. This also causes isolation of the enzyme from the electrode surface by its relative burial in the bacterial membrane. When

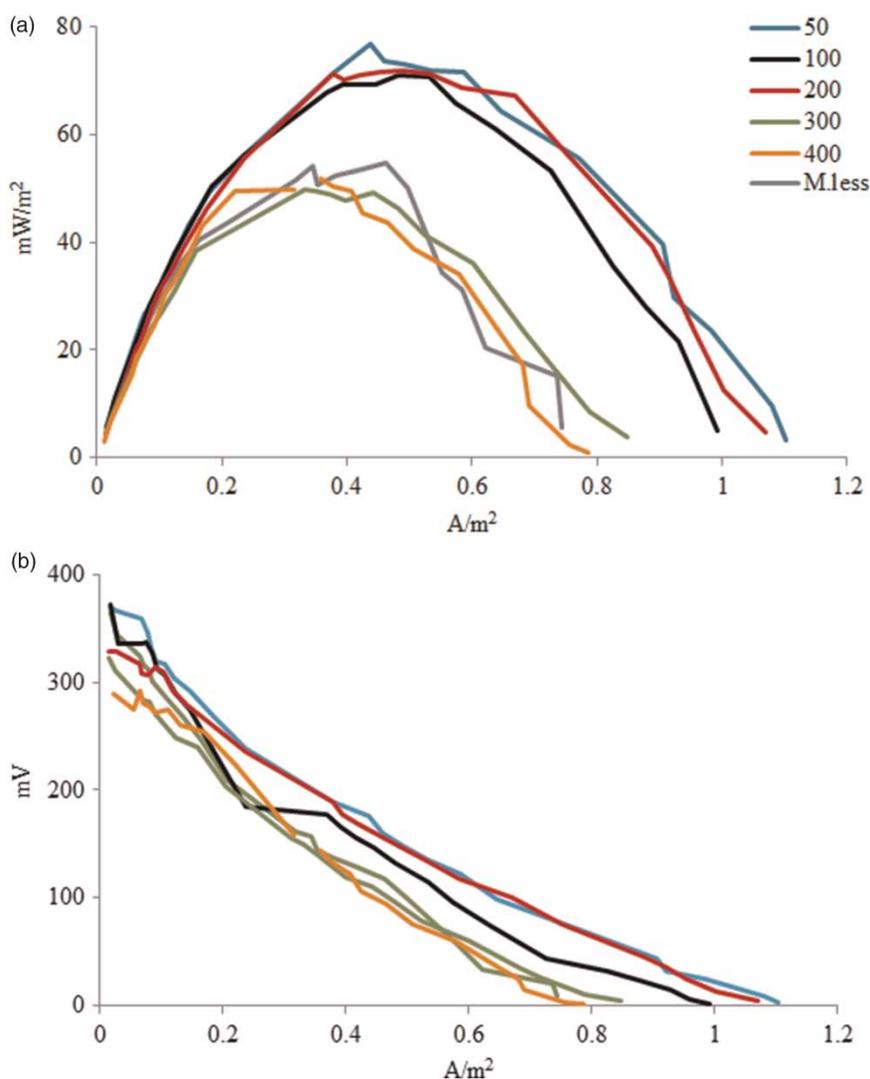


Figure 5 | Polarization curves of MFC depending on NR concentrations. Power curves (a) and potential curves (b) of MFC fed with mediatorless and different mediator concentrations.

we added the external mediators into the medium, the results demonstrated that MET proceeds much faster than DET because the addition of the mediator: (i) accelerates the oxidation reactions at the electrode surface, which causes a decrease in over-potentials, (ii) realizes rapidly the electron transfer between enzymes of an electrode using a small redox molecule, and (iii) encounters and overcomes transfer resistance by diffusing quickly in and out of the enzymatic channels (Schaetzle *et al.* 2008). Therefore, the voltage generation of MFC increased rapidly and stabilized after adding the mediators. In particular, a stable voltage output for the NR mediator was obtained within 2 hours of the MFC being operated while it took more than 10 hours for the MB mediator. Voltage generation in the MFC remained stable with 300 μM NR and HNQ at

approximately 17 hours and 18 hours, respectively (Figure 6).

Effect of different mediators on internal resistance

Internal resistance is an important parameter to determine the performance of MFCs because an MFC produces maximum power output when external resistance is equal to internal resistance (Resnick *et al.* 1988). Internal resistance includes four resistances: anode resistance, cathode resistance, electrolyte resistance, and membrane resistance. Logan *et al.* (2006) demonstrated that it clearly limited the power output of an MFC. However, Logan *et al.* (2007) and Oh & Logan (2006) also suggested an alternative solution whereby internal resistance can be reduced by

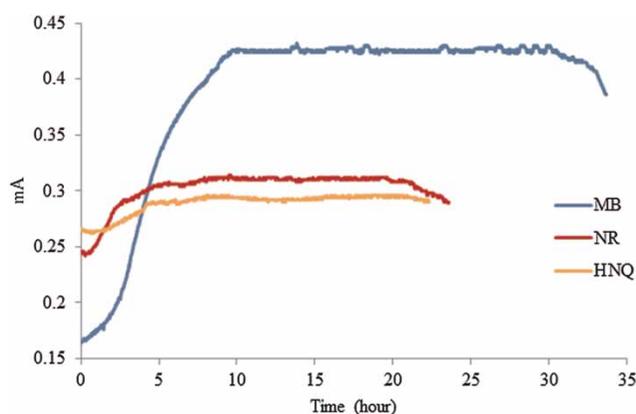


Figure 6 | Voltage generation of MFC with 400 μM MB, 300 μM NR, and 300 μM (HNQ).

increasing the anode surface area, which is a limiting factor. Instead of this solution, polarization data can be used to examine internal resistance because our results showed that internal resistance changed with mediator concentration. Polarization curves were obtained at all stages to investigate the effect of different mediators and their concentrations on internal resistance. With the addition of 50 μM mediator, internal resistance decreased rapidly (Figure 7).

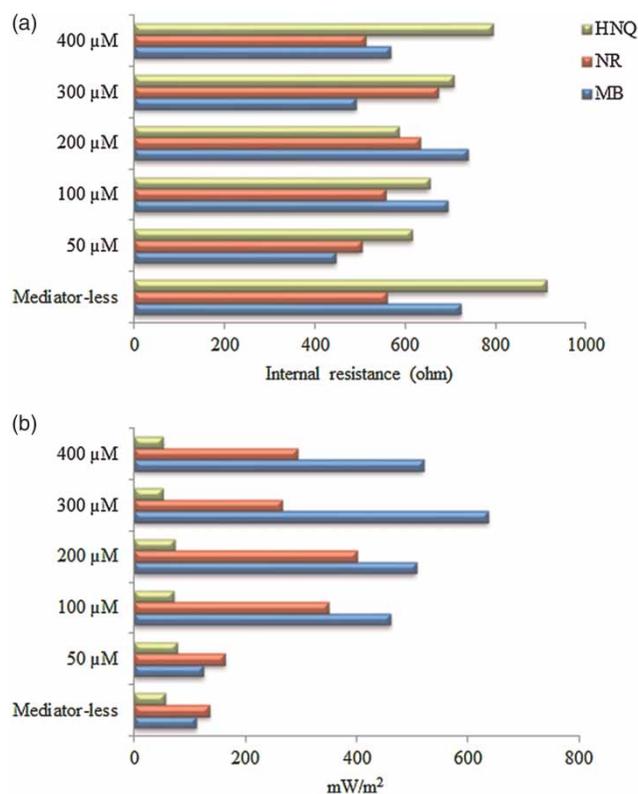


Figure 7 | Power density (a) and internal resistance (b) depending on mediator concentrations.

Conversely, if an excessive amount of mediator is used, it covers the electrode surface and decreases the active surface. This situation reduces the fuel cell performance. Observed results supported the hypothesis that adsorption of the mediator to the electrode surface affected internal resistance of the MFC. Ho *et al.* (2011) reported that HNQ has minimal adsorption to the electrodes and is less prone to adsorption over the surface of the electrode than thionin. In another study, Popov *et al.* (2012) reported that MB can be adsorbed onto the carbon anode surface more efficiently than NR. The results showed that internal resistance decreased with the addition of 50 μM HNQ. With the addition of 100 and 200 μM HNQ, internal resistance stayed almost stable. After the addition of 300 and 400 μM HNQ, internal resistance increased to 707 and 792 Ω because the mediator might have adhered to the electrode surface. With addition of 50 μM MB, internal resistance decreased rapidly and then stayed almost stable for 100 and 200 μM concentrations. With the addition of 300 and 400 μM MB, internal resistance decreased to 490 and 567 Ω while it increased when applying HNQ at the same concentrations. While internal resistance decreased rapidly with the addition of 50 and 100 μM NR, it increased to 632 and 672 Ω with the addition of 200 and 300 μM NR, respectively.

In order to achieve better performance of MFCs, the internal resistance should have a lower value. Figure 6 shows that decreasing internal resistance is associated with increasing power output due to an increase of electron transfer from the microorganisms to the electrode. Power output and internal resistance varied with different mediators and their concentrations. Figure 7 shows that the power output and vice versa increased in the case of decreasing internal resistance. The lowest internal resistance values of all mediators were obtained with the addition of 50 μM MB, 200 μM NR, and 200 μM HNQ.

The CE of the MFC increased with the increase of mediator concentration. CE increased accordingly and reached the maximum of about 21.06% at 300 μM MB concentration (Table 1).

Cost analysis of the mediator-MFC

The cost of mediators used in the MFC represents an important factor for the successful large-scale application of this technology. Thus, there is a continued need for inexpensive mediators for efficient cost-effective operations of the MFC. The cost analysis of mediators was calculated based on the power output and dosage. Our findings indicate that MB is

Table 1 | COD and CE variations in MFC under different mediator concentrations

Mediators → Concentration (μM) ↓	MB			NR			HNQ		
	COD _{in}	COD _{out}	CE	COD _{in}	COD _{out}	CE	COD _{in}	COD _{out}	CE
0	300 ± 10	170 ± 10	3.69	300 ± 10	160 ± 10	4.47	300 ± 10	160 ± 10	1.81
50	300 ± 10	160 ± 10	4.14	300 ± 10	160 ± 10	5.40	300 ± 10	160 ± 10	2.54
100	300 ± 10	160 ± 10	15.47	300 ± 10	160 ± 10	11.56	300 ± 10	160 ± 10	2.35
200	300 ± 10	160 ± 10	16.76	300 ± 10	160 ± 10	13.24	300 ± 10	160 ± 10	2.38
300	300 ± 10	160 ± 10	21.06	300 ± 10	160 ± 10	8.76	300 ± 10	160 ± 10	1.65
400	300 ± 10	160 ± 10	17.19	300 ± 10	190 ± 10	9.68	300 ± 10	150 ± 10	1.56

COD_{in}: influent COD.COD_{out}: effluent COD.

CE: coulombic efficiency.

Table 2 | Power increase and cost comparison of mediators

Mediator type	Price (EU/g)	Optimum dosage (μmol)	Power increase	Cost for (EU/m ²)
Methylene blue	2.47	300	Six-fold (524 mW/m ²)	0.00015
Neutral red	54.30	200	Three-fold (265 mW/m ²)	0.00355
HNQ	3.21	50	One-half-fold (24 mW/m ²)	0.00036

2.4 and 24 times cheaper than HNQ and NR, respectively, in terms of power increase. The cost analysis showed that the optimal mediator according to cost, power output, and dosage is MB (Table 2).

CONCLUSIONS

This study is a comprehensive demonstration power production in an MFC using a tin-coated copper mesh anode under artificial mediators, i.e. MB, NR and HNQ. The results showed that MB significantly increases the power output in comparison with other mediators; maximum power output with the addition of 300 μM is about six-fold higher than a mediator-less MFC. The power output order in an MFC using different mediators is MB > NR > HNQ. The high power density was achieved with tin-coated copper mesh. This result demonstrated that tin-coated copper mesh is an effective electrode material for MFC

applications in terms of high-power density, biocompatibility, and electrical conductivity.

ACKNOWLEDGEMENTS

This paper includes some data from Ergin Taskan's PhD thesis. The authors gratefully acknowledge the financial support from FUBAP, Project Number MF. 12.10.

REFERENCES

- American Public Health Association Water Environment Federation 1995 *Standard Methods for the Examination of Water and Wastewater*. Washington, DC, USA.
- Babanova, S., Hubenova, Y. & Mitov, M. 2011 Influence of artificial mediators on yeast-based fuel cell performance. *Journal of Bioscience and Bioengineering* **112** (4), 379–387.
- Burns, J. L., Ginn, B. R., Bates, D. J., Dublin, S. N., Taylor, J. V., Apkarian, R. P., Amaro-Garcia, S., Neal, A. L. & DiChristina, T. J. 2009 Outer membrane-associated serine protease involved in adhesion of *Shewanella oneidensis* to Fe (III) oxides. *Environmental Science & Technology* **44** (1), 68–73.
- Daniel, D. K., Das Mankidy, B., Ambarish, K. & Manogari, R. 2009 Construction and operation of a microbial fuel cell for electricity generation from wastewater. *International Journal of Hydrogen Energy* **34** (17), 7555–7560.
- Guo, W., Cui, Y., Song, H. & Sun, J. 2014 Layer-by-layer construction of graphene-based microbial fuel cell for improved power generation and methyl orange removal. *Bioprocess and Biosystems Engineering* **37** (9), 1749–1758.
- Hidalgo, D., Tommasi, T., Cauda, V., Porro, S., Chiodoni, A., Bejtka, K. & Ruggeri, B. 2014 Streamlining of commercial Berl saddles: a new material to improve the performance of microbial fuel cells. *Energy* **71** (15 July 2014), 615–623.
- Ho, P. I., Gnana Kumar, G., Kim, A., Kim, P. & Suk Nahm, K. 2011 Microbial electricity generation of diversified carbonaceous

- electrodes under variable mediators. *Bioelectrochemistry* **80** (2), 99–104.
- Kargi, F. & Eker, S. 2007 Electricity generation with simultaneous wastewater treatment by a microbial fuel cell (MFC) with Cu and Cu–Au electrodes. *Journal of Chemical Technology and Biotechnology* **82** (7), 658–662.
- Lee, S., Choi, Y., Jung, S. & Kim, S. 2002 Effect of initial carbon sources on the electrochemical detection of glucose by *Gluconobacter oxydans*. *Bioelectrochemistry* **57** (2), 173–178.
- Logan, B. E., Hamelers, B., Rozendal, R., Schröder, U., Keller, J., Freguia, S., Aelterman, P., Verstraete, W. & Rabaey, K. 2006 Microbial fuel cells: methodology and technology. *Environmental Science & Technology* **40** (17), 5181–5192.
- Logan, B., Cheng, S., Watson, V. & Estadt, G. 2007 Graphite fiber brush anodes for increased power production in air-cathode microbial fuel cells. *Environmental Science & Technology* **41** (9), 3341–3346.
- Oh, S.-E. & Logan, B. E. 2006 Proton exchange membrane and electrode surface areas as factors that affect power generation in microbial fuel cells. *Applied Microbiology and Biotechnology* **70** (2), 162–169.
- Popov, A. L., Kim, J. R., Dinsdale, R. M., Esteves, S. R., Guwy, A. J. & Premier, G. C. 2012 The effect of physico-chemically immobilized methylene blue and neutral red on the anode of microbial fuel cell. *Biotechnology and Bioprocess Engineering* **17** (2), 361–370.
- Rabaey, K., Clauwaert, P., Aelterman, P. & Verstraete, W. 2005 Tubular microbial fuel cells for efficient electricity generation. *Environmental Science & Technology* **39** (20), 8077–8082.
- Rahimnejad, M., Najafpour, G., Ghoreyshi, A., Shakeri, M. & Zare, H. 2011 Methylene blue as electron promoters in microbial fuel cell. *International Journal of Hydrogen Energy* **36** (20), 13335–13341.
- Resnick, R., Halliday, D. & Walker, J. 1988 *Fundamentals of Physics*. John Wiley, New York, NY, USA.
- Rismani-Yazdi, H., Carver, S. M., Christy, A. D. & Tuovinen, O. H. 2008 Cathodic limitations in microbial fuel cells: an overview. *Journal of Power Sources* **180** (2), 683–694.
- Schaetzle, O., Barrière, F. & Baronian, K. 2008 Bacteria and yeasts as catalysts in microbial fuel cells: electron transfer from micro-organisms to electrodes for green electricity. *Energy & Environmental Science* **1** (6), 607–620.
- Schröder, U. 2007 Anodic electron transfer mechanisms in microbial fuel cells and their energy efficiency. *Physical Chemistry Chemical Physics* **9** (21), 2619–2629.
- Sigma-Aldrich 2014 Analytical, Biology, Chemistry & Materials. <http://www.sigmaaldrich.com/european-export.html> (accessed 20 October 2014).
- Sund, C. J., McMasters, S., Crittenden, S. R., Harrell, L. E. & Sumner, J. J. 2007 Effect of electron mediators on current generation and fermentation in a microbial fuel cell. *Applied Microbiology and Biotechnology* **76** (3), 561–568.
- Tang, X., Du, Z. & Li, H. 2010 Anodic electron shuttle mechanism based on 1-hydroxy-4-aminoanthraquinone in microbial fuel cells. *Electrochemistry Communications* **12** (8), 1140–1143.
- Wang, K., Liu, Y. & Chen, S. 2011 Improved microbial electrocatalysis with neutral red immobilized electrode. *Journal of Power Sources* **196** (1), 164–168.
- Wilkinson, S., Klar, J. & Applegarth, S. 2006 Optimizing biofuel cell performance using a targeted mixed mediator combination. *Electroanalysis* **18** (19–20), 2001–2007.
- Zhou, M., Chi, M., Luo, J., He, H. & Jin, T. 2011 An overview of electrode materials in microbial fuel cells. *Journal of Power Sources* **196** (10), 4427–4435.
- Zhu, X. & Logan, B. E. 2014 Copper anode corrosion affects power generation in microbial fuel cells. *Journal of Chemical Technology and Biotechnology* **89** (3), 471–474.

First received 26 June 2014; accepted in revised form 18 November 2014. Available online 2 December 2014