

Available online at www.sciencedirect.com

ScienceDirect

www.elsevier.com/locate/jes

JES
 JOURNAL OF
 ENVIRONMENTAL
 SCIENCES
www.jesc.ac.cn

Application of interface material and effects of oxygen gradient on the performance of single-chamber sediment microbial fuel cells (SSMFCs)

Chin-Tsan Wang^{1,*}, Thangavel Sangeetha², Wei-Mon Yan², Wen-Tong Chong³,
 Lip-Huat Saw⁴, Feng Zhao⁵, Chung-Ta Chang⁶, Chen-Hao Wang^{6,*}

1. Department of Mechanical and Electro-Mechanical Engineering, National I-Lan University, I-Lan 26047, Chinese Taipei
2. Department of Energy and Refrigerating Air-Conditioning Engineering, National Taipei University of Technology, Taipei 10608, Chinese Taipei
3. Department of Mechanical Engineering, University of Malaya, Jalan Universiti, 50603 Wilayah Persekutuan Kuala Lumpur, Malaysia
4. Lee Kong Chian Faculty of Engineering and Science, UTAR, Kajang 4300, Malaysia
5. CAS Key Laboratory of Urban Pollutant Conversion, Institute of Urban Environment, Chinese Academy of Science, Xiamen 361021, China
6. Institute of Materials Science and Engineering, National Taiwan University of Science and Technology, No.43, Keelung Rd., Sec.4, Da'an Dist., Taipei 10607, Chinese Taipei

ARTICLE INFO

Article history:

Received 2 January 2018
 Revised 16 March 2018
 Accepted 16 March 2018
 Available online 22 March 2018

Keywords:

Single sediment microbial fuel cells
 Interface layer
 Dissolved oxygen
 Pore size
 Oxygen diffusion
 Diffusion coefficient

ABSTRACT

Single-chamber sediment microbial fuel cells (SSMFCs) have received considerable attention nowadays because of their unique dual-functionality of power generation and enhancement of wastewater treatment performance. Thus, scaling up or upgrading SSMFCs for enhanced and efficient performance is a highly crucial task. Therefore, in order to achieve this goal, an innovative physical technique of using interface layers with four different pore sizes embedded in the middle of SSMFCs was utilized in this study. Experimental results showed that the performance of SSMFCs employing an interface layer was improved regardless of the pore size of the interface material, compared to those without such layers. The use of an interface layer resulted in a positive and significant effect on the performance of SSMFCs because of the effective prevention of oxygen diffusion from the cathode to the anode. Nevertheless, when a smaller pore size interface was utilized, better power performance and COD degradation were observed. A maximum power density of 0.032 mW/m² and COD degradation of 47.3% were obtained in the case of an interface pore size of 0.28 μm. The findings in this study are of significance to promote the future practical application of SSMFCs in wastewater treatment plants.

© 2018 The Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences.

Published by Elsevier B.V.

Introduction

In recent decades, consumption of energy globally by a massive human population has followed an increasing trend, leading to an energy crisis and pollution. Fossil fuels are unreliable and

unsustainable due to their finite and diminishing supplies, and their negative impact on the environment. As a result, researchers are focusing on alternative, renewable and carbon-neutral energy sources, which are necessary for economic and environmental sustainability (Tkach et al., 2017; Wang et al.,

* Corresponding authors. E-mails: ctwang@niu.edu.tw (Chin-Tsan Wang), chwang@mail.ntust.edu.tw (Chen-Hao Wang).

2018). Microbial fuel cells (MFCs) that use certain bacteria, referred to as exoelectrogens, to produce electricity from organic matter have been widely investigated since the early 21st century as a possible method for wastewater treatment and bioenergy production. MFCs use bacteria as the catalysts to oxidize organic and inorganic matter and generate current (Mathuriya, 2016). The mechanism involves two important processes, anodic oxidation and cathodic reduction. Electrons produced by the bacteria from these substrates are transferred to the anode (negative terminal) and flow to the cathode (positive terminal) linked by a conductive material containing a resistor, or operated under a load (i.e., producing electricity that runs a device) (Huang et al., 2017). Therefore, promoting better reduction conditions (aerobic) at the cathode and oxidation conditions (anaerobic) at the anode of single-chambered MFCs is an important issue in MFC scale-up and practical application. Due to the fact that facultative anaerobic bacteria require an anaerobic environment, the presence of oxygen at the cathode may have negative effects on the anaerobic bacteria biofilm at the anode, and overall MFC performance (Logan and Regan, 2006; Dai et al., 2017; Cristiani et al., 2013). So, single-chamber MFCs should be effectively modified to enhance their power generation and organic degradation ability (Zhang et al., 2012; Rashid et al., 2013; Yang et al., in press; Tian et al., 2017).

Proton exchange membranes (PEMs) usually separate the anode and cathode chambers in an MFC, and effectively allow the selective permeability of protons (Rahimnejad et al., 2014). Research studies have reported on the utilization of various separation membranes for preventing oxygen diffusion from the cathode to the anode, including ultrafiltration membrane (Tang et al., 2010), permeable membrane (Zhang et al., 2011), anion exchange membranes (Tao et al., 2015), and J-Cloth (Qin et al., 2016). Membranes are vital for any MFC, as they transfer the produced protons from the anode to the cathode compartment. The efficiency, economic viability and feasibility of MFCs depend strongly on the performance of its PEM (Hernández-Flores et al., 2017). These features and functions of the PEM have inflated the MFC cost and made it unfeasible for practical applications. Thus, the discovery of a cheaper alternative material to PEM, with properties such as low oxygen permeability, high power generation, high chemical oxygen demand (COD) removal and coulombic efficiency (CE) has become crucial (Qin et al., 2016; Zinadini et al., 2017). Though numerous studies have been carried out using different membranes in MFCs, clear definitions regarding the quantitative indicators of the interface layer for oxygen diffusion effects are still lacking. Therefore, an attempt has been made in this study to execute and establish the effect of the oxygen gradient on the organic degradation and power performance in single-chamber sediment MFCs (SSMFCs) as a function of the pore size of the interface material. An optimized interface material can serve as an attractive alternative to the expensive PEMs being employed in MFCs.

1. Material and methods

1.1. Reactor construction and operation

Acrylic plastic sheets were used to construct five SSMFCs of size (5 mm × 55 mm × 200 mm) with a working volume of

500 mL. Each MFC had an anode chamber and cathode chamber separated by an interface membrane, except in the control reactor, which was devoid of a membrane. The MFCs had sampling ports at the anode and the cathode chambers. A schematic representation of the SSMFC is portrayed in Fig. 1. Carbon cloth and carbon felt (no wet-proofing, No. COS3001, CeTECH) were selected as anode and cathode electrodes for the MFCs respectively, and the surface area of both the electrodes was 25 cm². The carbon felt was subjected to hydrophobic treatment before the experiment. Domestic wastewater activated sludge was employed as the substrate in the SSMFCs and was collected from the Luotung Wastewater treatment plant, Yilan, Taiwan, and its characteristics are as following: Chemical Oxygen Demand (COD) 250 mg/L, Biological Oxygen Demand (BOD) 130 mg/L, Suspended Solids (SS) 100 mg/L, pH 8.08, and conductivity 0.57 mS/cm. Interface layers were inserted into the SSMFCs to determine their performance with respect to organic degradation and power generation. Cheap materials, such as scouring pads with pore sizes of 229 and 114 μm, and membrane filters with pore sizes of 0.45 and 0.28 μm, were used as the interface materials in the SSMFCs. They all possessed a uniform material thickness of 1 mm and were placed at the mid-high position of the MFCs. The immersion area of the air-cathode electrode in all the reactors was 12 cm². For dissolved oxygen (DO) analysis studies, aeration of the cathode was carried out with a fish tank aeration pump. The reactors were run for 50 days under the batch mode of operation.

1.2. Instrumental analysis

The voltage from the reactors was measured by a data recorder (data acquisition system, Jiehan 5021, Jiehan Co.). The power density of the system was analyzed by an electrochemical analyzer (electrochemical workstation, Jiehan ECW-5000, Jiehan Co.). Water testing instruments such as a pH meter (Jiehan SP-2300, Suntex), DO meter (Riki) and COD meter (V-200, Suntex) were utilized in this study. The

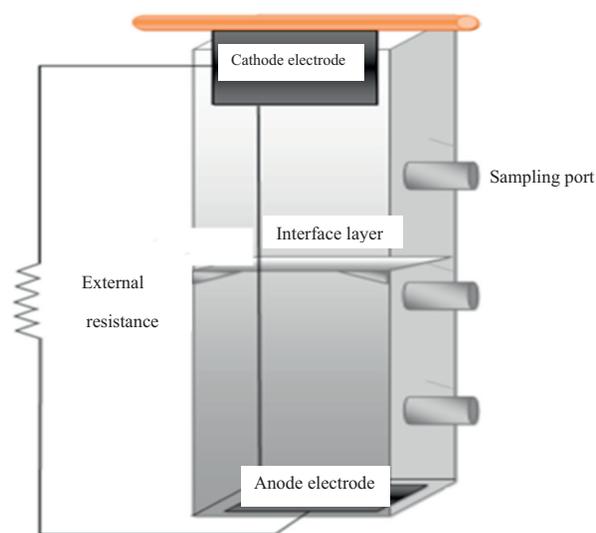


Fig. 1 – Schematic representation of the single-chamber sediment microbial fuel cells employed in the study.

DO, electrical power density (PD), and COD were measured once every two hours of operation. An external load impedance (1 kΩ) was connected to the SSMFCs to measure the output voltage of the system over a long time period. In this study the quantifiable parameter of dissolved oxygen gradient (∇_{DO}) defined in Eqs. (1) and (2) was calculated to determine the effect of employing interface layers in the SSMFCs on the diffusion of dissolved oxygen.

$$\nabla_{DO} = \Delta DO / H_{interface} \tag{1}$$

$$\Delta DO = DO_{Cathode} - DO_{Anode} \tag{2}$$

where ∇_{DO} is the dissolved oxygen gradient between the upper and lower surfaces of the interface layer. ΔDO is the deviation of dissolved oxygen value between that of the cathode ($DO_{Cathode}$) and anode (DO_{Anode}) at the lower surface of the interface layer. $H_{interface}$ is the thickness of the interface layer (1 mm).

The PD was calculated as shown in Eq. (3).

$$PD = P / A_{anode} \tag{3}$$

where the power (P) is obtained from Eq. (4) and A_{anode} is the effective working area of the anode electrode.

$$P = I \times E \tag{4}$$

where I (A) and E (V) indicated the current and voltage respectively.

2. Results and discussion

Before the study commenced, the DO at the cathode was adjusted to 3.5 mg/L. Then, interface materials with four different pore sizes and uniform thickness (1 mm) were embedded at the mid-high position of the SSMFCs. This should enhance the permeability of the interface and increase the potential difference between the anode and cathode electrodes, and possibly boost the performance of the SSMFCs. Thus, a series of studies on the effects and impacts of the interface layers on various aspects of the SSMFCs were executed and analyzed.

2.1. Impact of interface permeability on pH variations

The variations of pH in the cathode and anode chamber with respect to the four kinds of pore sizes of the interface layers between the cathode and anode are shown in Fig. 2a and b, respectively. The gradient of hydrogen ion [H^+] molarity, with a value below 10^{-6} (mol/L)/mm, indicated that the H^+ ion diffusion capacity was not affected by the interface layer regardless of its pore size. Significant studies have provided clear indications that protons [H^+] can migrate across membranes by becoming attached to water molecules and proton carriers by the Vehicle mechanism and Grotthuss mechanism (Ochi et al., 2009; Huang et al., 2017). Chen et al. (2014) have reported that temperature variations can have pronounced effects on the transport efficiency of protons across the membrane in an MFC. These valuable pieces of evidence indicated that the pore size of the embedded interface material does not affect or control the H^+ permeability and

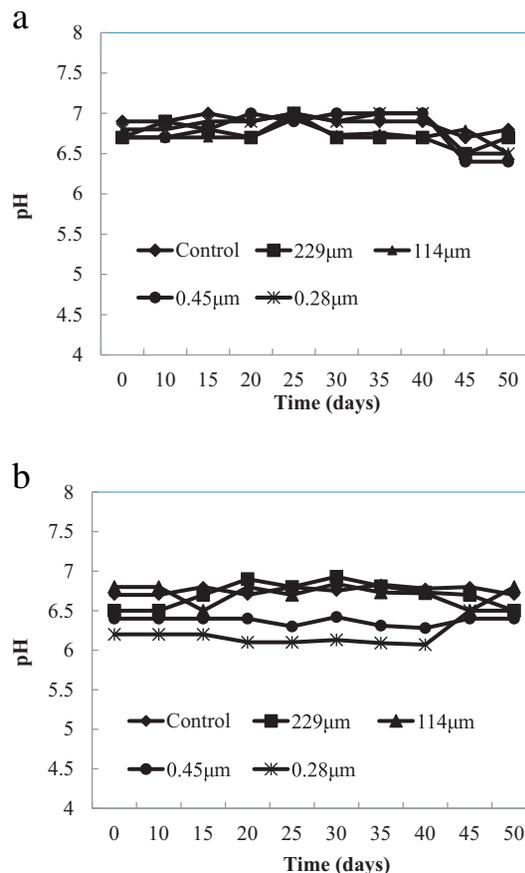


Fig. 2 – Cathodic pH variations with respect to interface layer pore sizes (a) and anodic pH variations according to the porosity of the interface layer (b).

variation of pH between the anode and cathode, possibly due to the stability of H^+ ion molarity.

2.2. Effects on oxygen diffusion efficiency

The interface layers were capable of effectively inhibiting the diffusion of oxygen from one chamber of the MFC to the other. This feature significantly affected the performance of SSMFCs in this study in a positive way. In this study, interface layers with the same thickness but different pore sizes were tested, and then the value of dissolved oxygen gradient (∇_{DO}) was obtained and listed in Table 1. Results generally showed that the SSMFCs with interface layers indeed had a lower DO gradient than the control, and this may further influence the reduction–oxidation reactions of the SSMFCs. A maximum DO gradient of 1.69 mg/L/mm was observed in the control reactor which was almost 56 times higher than the DO value of the reactor with interface layer of the least pore size (0.28 μm). Miskan et al. (2016) employed an interface layer with a pore size less than 0.45 μm, and reported that it effectively inhibited oxygen diffusion from the cathode to the anode, without affecting the mobility of the H^+ ions. This layer showed much better performance compared to larger pore size interface materials. The layers were conducive to the

Table 1 – Variations of dissolved oxygen (DO) gradient with varying interface pore sizes.

Interface layer	Porous size(μm)	$\nabla\text{DO}(\text{mg/L/mm})$
Absent	NA	1.69
Present	229	1.58
Present	114	0.18
Present	0.45	0.07
Present	0.28	0.03

growth and development of anaerobic microbes at the anode, further enhancing the redox mechanism at the anode and cathode. This feature makes the usage of interface layers very important in MFCs.

Wang et al. (2017) reported that inhibition of oxygen diffusion resulted in the formation of a biofilm at the cathode in single-chamber MFCs, thus improving the overall coulombic efficiency (CE) of the MFC. Similar results were mentioned by Rago et al. (2017), where three types of MFCs, such as air-cathode, water-submerged and photosynthetic, were employed to evaluate the influence of DO on the MFC performance. The air-cathode MFC showed the best electrical performance, due to reduced oxygen diffusion from cathode to anode and formation of an aerobic cathodic biofilm. Thus, all the above-mentioned results indicated that membranes with low oxygen diffusion capacity should be employed in MFCs. Thus in this study, decreasing the pore size of the interface layer should provide a higher DO gradient by inhibiting the oxygen diffusion from cathode to anode. It was evident that the placement of the interface layer created a clear distinction between aerobic and anaerobic environments, thereby enhancing the SSMFC performance.

2.3. Influence of interface porosity on power performance of the SSMFCs

In this study, interface materials with four different pore sizes were utilized, and their effect on the SSMFC power performance was determined. The results in Fig. 3 show that the overall performance of SSMFCs with interface layers was better compared to the control reactor. Though the voltage generation was recorded throughout the experiment (50 days), only the stable values (35–50 days) were considered for power density calculation. It was apparent from the results

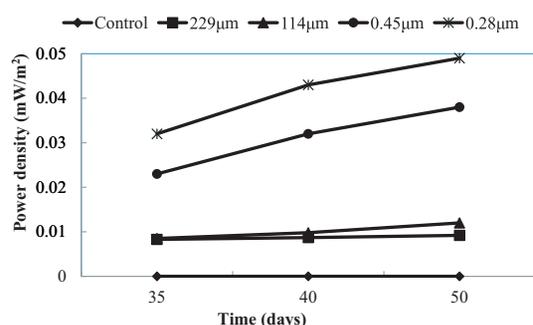


Fig. 3 – Power density productions in single-chamber sediment microbial fuel cells with different interface pore sizes.

that the smaller the pore size of the interface material, the better the electricity generation of the MFC was. No power generation was observed in the control reactor, which was devoid of an interface membrane. All the other reactors maintained an increasing and stable trend of power density generation. The pore size of 114 μm was better than 229 μm , with 0.012 mW/m^2 . A good power density production of 0.038 mW/m^2 was exhibited with the pore size of 0.45 μm , but the interface layer with a pore size of 0.28 μm was the best among all, with a maximum power density production of 0.049 mW/m^2 on day 50. Li et al. (2014) reported that membranes with large pores in MFCs can reduce the charge transfer and diffusion resistance due to increased oxygen permeability. Similar results were reported by Zinadini et al. (2017), where they employed MFCs with membranes of different porosities. They found that the membrane with lowest porosity had the highest mass transfer and diffusion coefficients compared to the other three types. This eventually led to this MFC exhibiting the maximum power output and CE. Therefore, the smaller the pore size of the interface layer, the higher the value of the DO gradient between the anode and cathode. Thus, a smaller pore size in the interface layer would effectively prevent the diffusion of oxygen from the cathode to the anode in SSMFCs and consequently result in enhanced power performance. Therefore, the choice and placement of a suitable interface layer in the MFCs was shown to be a decisive aspect in MFC construction and operation.

2.4. Impact of different pore sizes on organic degradation efficiency

This part of the study was focused on exploring the oxidation efficiency at the anode and analyzing the organic content removal from the anolyte with respect to interface layers with different pore sizes (229, 114, 0.45, 0.28 μm). The COD removal was observed in all the MFCs once a week from the start of the experiment. The values are portrayed in Fig. 4. It was observed that the MFCs with an interface layer had better organic content removal efficiency than the control MFC. COD removal also followed a similar trend as that of power generation: the smaller the pore size, the greater the enhancement of organic removal. The pore size of 0.28 μm was associated with the maximum COD removal ability (50.3%) in the last week in the experiment, compared to 0.45 μm (44.4%), 114 μm (31.8%), 229 μm (14.1%) and the

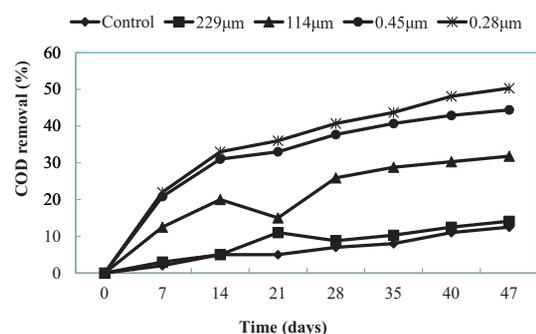


Fig. 4 – Chemical oxygen demand removal efficiencies under varying interface layer pore sizes.

control reactor (12.5%). The maximum degradation value obtained in the case of an interface pore size of 114 μm was better than interface pore size of 229 μm . But, these two cases were both inferior to the 0.45 μm pore size interface layer in COD removal efficiency, due to the fact that the oxygen diffusion might have occurred freely through the interface layer from the cathode side to the anode side. This might have hindered the growth of anaerobic microbes in the anode by creating an unsuitable and oxic environment, resulting in a weakening of the oxidation reaction in the SSMFCs and a rather poor biodegradation process (Zhang and Angelidaki, 2012). Membranes with high porosity had higher oxygen permeability and lower mass transfer and diffusion coefficients. This phenomenon has been observed to result in severely decreased COD removal efficiency by an MFC Zinadini et al. (2017). Similar results were addressed by Tang et al. (2010), and they reported that oxygen diffusion from the cathode to the anode side can be effectively prohibited when the interface layer porosity is less than 0.45 μm . Composite-based membranes with lower porosity were better than Nafion membranes in terms of COD removal efficiency (4 times higher) and CE.

The most significant phenomenon was the reduction of oxygen permeation into the anode due to small pore size (Angioni et al., 2017). The COD removal in the MFC with an interface pore size of 0.28 μm was about 48%, and it had the highest biodegradation performance compared to all other MFCs in this study. Optimization of the pore size in the interface layer of the MFCs would effectively prohibit oxygen diffusion from the cathode to the anode, while inducing a suitable condition for the growth of anaerobic microbes in the anodic biofilm of the MFCs. In addition, a distinct boundary would be created between the anode and cathode, positively affecting the redox reaction and producing better power performance in the SSMFCs.

3. Conclusions

Discovering new and inexpensive materials as alternatives to PEM can increase the practical applicability of MFCs in wastewater treatment applications. This study was an endeavour to employ alternative inexpensive materials as interface membranes in single-chamber sediment microbial fuel cells (SSMFCs). Firstly, the placement of an interface layer in SSMFCs can effectively prohibit oxygen diffusion from the cathode to the anode but can still retain the hydrogen ion permeability. The smaller the interface pore size used in the system, the better the power generation and COD removal performance obtained. A suitable pore size for the interface layer based on the experimental study was observed to be 0.28 μm . A maximum performance with a power density of 0.032 mW/m^2 and a degradation efficiency of 47.3% was achieved in the MFC with an interface layer of pore size 0.28 μm . This evidence shows that employing an interface layer with a suitable pore size in SSMFCs would have positive impacts on the performance of power generation and wastewater treatment. The SSMFC findings of this study would be helpful for improving its practical application feasibility in the future.

Acknowledgments

The authors would like to acknowledge the generous funding support from NSC Taiwan under contract number # MOST 106-2923-E-197-001-MY3, 106-2221-E-197-019, and 106-26222-E-007-CC3, and the University of Malaya for the high impact research grant HIR-D000006-16001.

REFERENCES

- Angioni, S., Millia, L., Bruni, G., Ravelli, D., Mustarelli, P., Quartarone, E., 2017. Novel composite polybenzimidazole-based proton exchange membranes as efficient and sustainable separators for microbial fuel cells. *J. Power Sources* 348, 57–65.
- Chen, L., He, Y.L., Tao, W.Q., 2014. The temperature effect on the diffusion processes of water and proton in the proton exchange membrane using molecular dynamics simulation. *Numer. Heat Transfer A Appl.* 65 (3), 216–228.
- Cristiani, P., Franzetti, A., Gandolfi, I., Guerrini, E., Bestetti, G., 2013. Bacterial DGGE fingerprints of biofilms on electrodes of membraneless microbial fuel cells. *Int. Biodeterior. Biodegradation* 84, 211–219.
- Dai, K., Wen, J.L., Zhang, F., Ma, X.W., Cui, X.Y., Zhang, Q., et al., 2017. Electricity production and microbial characterization of thermophilic microbial fuel cells. *Bioresour. Technol.* 243, 512–519.
- Hernández-Flores, G., Poggi-Varaldo, H.M., Romero-Castañón, T., Solorza-Feria, O., Rinderknecht-Seijas, N., 2017. Harvesting energy from leachates in microbial fuel cells using an anion exchange membrane. *Int. J. Hydrog. Energy* 42 (51), 30374–30382.
- Huang, D., Song, B.Y., He, Y.L., Ren, Q., Yao, S., 2017. Cations diffusion in nafion117 membrane of microbial fuel cells. *Electrochim. Acta* 245, 654–663.
- Li, X., Wang, X., Zhang, Y., Ding, N., Zhou, Q., 2014. Opening size optimization of metal matrix in rolling-pressed activated carbon air-cathode for microbial fuel cells. *Appl. Energy* 123, 13–18.
- Logan, B.E., Regan, J.M., 2006. Electricity-producing bacterial communities in microbial fuel cells. *Trends Microbiol.* 14, 512–518.
- Mathuriya, A.S., 2016. Novel microbial fuel cell design to operate with different wastewaters simultaneously. *J. Environ. Sci.* 42, 105–111.
- Miskan, M., Ismail, M., Ghasemi, M., Jahim, J.M., Nordin, D., Bakar, M.H.A., 2016. Characterization of membrane biofouling and its effect on the performance of microbial fuel cell. *Int. J. Hydrog. Energy* 2016 (41), 543–552.
- Ochi, S., Kamishima, O., Mizusaki, J., Kawamura, J., 2009. Investigation of proton diffusion in Nafion® 117 membrane by electrical conductivity and NMR. *Solid State Ionics* 180 (6), 580–584.
- Qin, M., Abu-Reesh, I.M., He, Z., 2016. Effects of current generation and electrolyte pH on reverse salt flux across thin film composite membrane in osmotic microbial fuel cells. *Water Res.* 105, 583–590.
- Rago, L., Cristiani, P., Villa, F., Zecchin, S., Colombo, A., Cavalca, L., Schievano, A., 2017. Influences of dissolved oxygen concentration on biocathodic microbial communities in microbial fuel cells. *Bioelectrochemistry* 116, 39–51.
- Rahimnejad, M., Bakeri, G., Najafpour, G., Ghasemi, M., Oh, S.E., 2014. A review on the effect of proton exchange membranes in microbial fuel cells. *Biofuel Res. J.* 1 (1), 7–15.
- Rashid, N., Cui, Y.F., Rehman, M.S.U., Han, J.I., 2013. Enhanced electricity generation by using algae biomass and activated sludge in microbial fuel cell. *Sci. Total Environ.* 456, 91–94.

- Tang, X., Guo, K., Li, H., Du, Z., Tian, J., 2010. Microfiltration membrane performance in two-chamber microbial fuel cells. *Biochem. Eng. J.* 52, 194–198.
- Tao, H.C., Sun, X.N., Xiong, Y., 2015. A novel hybrid anion exchange membrane for high performance microbial fuel cells. *RSC Adv.* 5, 4659–4663.
- Tian, C., Zhang, B., Borthwick, A.G., Li, Y., Liu, W., 2017. Electrochemical oxidation of thallium (I) in groundwater by employing single-chamber microbial fuel cells as renewable power sources. *Int. J. Hydrog. Energy* 42 (49), 29454–29462.
- Tkach, O., Sangeetha, T., Maria, S., Wang, A., 2017. Performance of low temperature microbial fuel cells (MFCs) catalyzed by mixed bacterial consortia. *J. Environ. Sci.* 52, 284–292.
- Wang, Z., Mahadevan, G.D., Wu, Y., Zhao, F., 2017. Progress of air-breathing cathode in microbial fuel cells. *J. Power Sources* 356, 245–255.
- Wang, C.T., Huang, Y.S., Sangeetha, T., Yan, W.M., 2018. Assessment of recirculation batch mode operation in bufferless biocathode microbial fuel cells (MFCs). *Appl. Energy* 209, 120–126.
- Yang, N., Zhan, G., Wu, T., Zhang, Y., Jiang, Q., Li, D., et al., 2017. Effect of air-exposed biocathode on the performance of a *Thauera*-dominated membraneless single-chamber microbial fuel cell (SCMFC). *J. Environ. Sci.* (in press).
- Zhang, Y., Angelidaki, I., 2012. Bioelectrode-based approach for enhancing nitrate and nitrite removal and electricity generation from eutrophic lakes. *Water Res.* 46, 6445–6453.
- Zhang, X., Sun, H., Liang, P., Huang, X., Chen, X., Logan, B.E., 2011. Air-cathode structure optimization in separator-coupled microbial fuel cells. *Biosens. Bioelectron.* 30, 267–271.
- Zhang, G., Zhao, Q., Jiao, Y., Wang, K., Lee, D.J., Ren, N., 2012. Efficient electricity generation from sewage sludge using biocathode microbial fuel cell. *Water Res.* 46, 43–52.
- Zinadini, S., Zinatizadeh, A.A., Rahimi, M., Vatanpour, V., Rahimi, Z., 2017. High power generation and COD removal in a microbial fuel cell operated by a novel sulfonated PES/PES blend proton exchange membrane. *Energy* 125, 427–438.