Available online at www.sciencedirect.com

ScienceDirect

Procedia Chemistry 16 (2015) 640 – 647

Procedia Chemistry

International Symposium on Applied Chemistry 2015 (ISAC 2015)

MnO_2/CNT as ORR Electrocatalyst in Air-Cathode Microbial Fuel Cells

Chee Wai Woon[a], Huei Ruey Ong[a], Kwok Feng Chong[b], Kar Min Chan[a], Md. Maksudur Rahman Khan[a,*]

[a]*Faculty of Chemical and Natural Resources Engineering, Universiti Malaysia Pahang, Lebuhraya Tun Razak, 26300 Kuantan, Pahang, Malaysia*

[b]*Faculty of Industrial Science and Technology, Universiti Malaysia Pahang, Lebuhraya Tun Razak, 26300 Kuantan, Pahang, Malaysia.*

Abstract

Air-cathode microbial fuel cell (MFC) is a potential electrochemical device for green power generation simultaneously conducting wastewater treatment. In the present work, the MnO_2 catalyst has been prepared and modified by inducing carbon nanotube (CNT) via sonochemical-coprecipitation method. The as-prepared catalyst (MnO_2/CNT) was characterized by x-ray powder diffraction patterns (XRD), field emission scanning electron microscope (FESEM), energy-dispersive x-ray spectroscopy (EDS), transmission electron microscopy (TEM) and cyclic voltammetry (CV) to examine its morphological surface, crystal structure, elemental analysis and oxygen reduction reaction (ORR) activity of the catalyst, respectively. The CV results revealed that MnO_2/CNT catalyzed ORR at potential of -0.45 V. The effect of catalyst loading on the chemical oxygen demand (COD) removal efficiency of palm oil mill effluent (POME) and MFC performance were studied. The maximum power density and open circuit voltage (OCV) generated from with the as-prepared MnO_2/CNT were measured to be 215.57 mW/m^3 and 582 mV, respectively.

Peer-review under responsibility of Research Center for Chemistry, Indonesian Institute of Sciences

Keywords: MFC; MnO_2/CNT; Oxygen reduction reaction; Polarization curves; POME

* Corresponding author. Tel.: +60-16-9596643; fax: +609 549 2889.
E-mail address: mrkhancep@yahoo.com

Peer-review under responsibility of Research Center for Chemistry, Indonesian Institute of Sciences
doi:10.1016/j.proche.2015.12.003

Nomenclature

MFC	Microbial fuel cell	CV	Cyclic voltammetry
CNT	Carbon nanotube	COD	Chemical oxygen demand
MnO_2	Manganese dioxide	POME	Palm oil mill effluent
XRD	X-ray powder diffraction patterns	OCV	Open circuit voltage
FESEM	Field emission scanning electron microscope	ORR	Oxygen reduction reaction
EDS	Energy-dispersive X-ray spectroscopy	PACF	Polyacrylonitrile carbon felt
TEM	Transmission electron microscopy	MEA	Membrane-electrode-assembly

1. Introduction

The diversion of non-renewable energy to green energy has become one of the alternatives to solve the world's energy crisis. Solar, wind, biomass and hydroelectric power were the targeted green energy sources which could be used to replace the dependency of fossil fuels. On the other hand, the aggressive industrialization generated large amount of biomass wastewater which created a severe environmental problem. Therefore, microbial fuel cell (MFC) has gained a great advertency attributable to its ability in generating bioelectricity directly from and potentially enhancing the biomass wastewater treatments. It is a bio-electrochemical cell which utilize microorganism in the anolyte to generate electricity from the degradation of organic substances[1]. Artificial anolytes such as glucose solution, acetate solution and artificial sucrose wastewater were used in previous studies[2, 3, 4] and limited studies were conducted on real industrial wastewater as anolyte in MFCs[5, 6, 7, 8]. High strength in chemical oxygen demand (COD) such as palm oil mill effluent (POME) served a good source of organic matter for electricity generation[9]. The POME abundance in Malaysia, Indonesia and Philippine provide availability of biomass wastewater resources which could be used for power generation.

Besides, ameliorations were done on MFC such as MFC designs[10, 11], type of inoculums[5, 12], and electrons acceptors[3, 7, 13] to the air-cathode MFC in order to optimize the performance of cells. Single chambered MFC especially air-cathode MFC has drawn increasing attention due to the simple construction, sustainable sources, better performance and lower cost [4, 14, 15, 16]. Oxygen has been used as electron acceptors in air-cathode which enables the air-cathode MFC to have a sustainable source because of its availability in the environment[4]. However, slow oxygen reduction reaction (ORR) on the surface of air-cathode is one of the drawbacks in the air-cathode MFCs[17, 18]. Therefore, electrocatalyst which acts as the heart of the fuel cell is needed in order to catalyse the ORR activity in the air-cathode MFC. Platinum (Pt) is the best ORR electrocatalyst and conventionally used in fuel cells because it exhibits good activity and stability under operating conditions[19]. However, the applications of Pt catalyst as the catalyst in industrial scale are not promising as Pt catalysts can even account for half of the MFCs cost and it has low catalytic stability which due to catalyst poisoning [16, 20, 21].

Hence, the development of lower cost electrocatalyst with high ORR activity is one of the main objectives of most of the electrocatalysts studies. Electrocatalyst materials such as metal oxides[8, 22, 23], metal complexes[24, 25] and carbon based catalyst[26, 27, 28] were developed and studied throughout the decades. In our previous studies, manganese dioxide (MnO_2) and Pt doped MnO_2 (Pt/MnO_2) were reported to be promising electrocatalysts which are active in ORR activities and have the ability of generating high power output in air-cathode MFC[7, 10]. In recent, carbon based catalyst are widely used as ORR catalysts as it has good conductivity, high stability with lower cost which is potentially to be substituting the Pt catalyst[27]. The development of carbon based catalyst has drawn the attention of scientist. In this context, carbon nanotube supported manganese dioxide (MnO_2/CNT) was developed and used as electrocatalyst in the air-cathode MFC for power generation and simultaneously for palm oil mill effluent (POME) treatment. The as-prepared catalyst was characterized by field emission scanning electron microscope (FESEM), x-ray powder diffraction patterns (XRD), energy-dispersive x-ray spectroscopy (EDS) and transmission electron microscopy (TEM). The performance of MnO_2/CNT in air-cathode MFC and ORR activity were determined by polarization measurement and cyclic voltammetry (CV), respectively. The COD removal efficiency of the air-cathode MFC was investigated.

2. Materials and methods

2.1. Chemicals and raw materials

Carbon nanotube (CNT), potassium permanganate ($KMnO_4$, 99%), sulphuric acid (H_2SO_4, 98%), Manganese (II) sulfate ($MnSO_4$), isopropanol (C_3H_8O, 96%), Nafion solution (5 wt%) and digestion solution were purchased from Sigma Aldrich and used without further purification. Polyacrylonitrile carbon felt (PACF) and Nafion 117 membrane were procured from Du Pont (USA). Palm oil mill effluent (POME) and anaerobic sludge were collected from FELDA palm oil plant located at Panching, Pahang.

2.2. MnO_2/CNT preparation and characterization

MnO_2/CNT was synthesized with the method as described by Lv et al. (2013)[29] via sonochemical-coprecipitation. In brief, 15.64 mg of CNT was mixed in $KMnO_4$ aqueous solution (0.36 mM, 50 mL) and sonicated for 30 min. The mixture was then added to $MnSO_4$ aqueous solution (0.84 mM, 50 mL). Then, 50 mL of 0.01 M H_2SO_4 aqueous solution was added in under stirring at room temperature for 1 h. The black precipitates were filtered and washed thoroughly with deionized water. The obtained precipitates were dried overnight in an oven at 65 °C and denoted as MnO_2/CNT.

The as-prepared MnO_2/CNT was then characterized by field emission scanning electron microscopy (FESEM), X-ray powder diffraction patterns (XRD), energy-dispersive x-ray spectroscopy (EDX) and transmission electron microscopy (TEM) to examine its morphological surface, crystal structure and elemental analysis, respectively.

2.3. Electrode preparation

The electrode was prepared with the method as described by Woon et al. (2015)[7, 8] and Khan et al. (2015)[10]. In brief, the catalyst ink was prepared by mixing as-prepared MnO_2/CNT with 0.15 mL of 5 wt% Nafion solution and 0.15 mL of isopropanol. The catalyst ink was ultrasonicated for 20 min. The prepared MnO_2/CNT ink was evenly dispersed evenly onto a 2 mm thick PACF surface with the area dispersion of 7 cm^2.

2.4. Air-cathode MFC set-up and operation

Nafion 117 membrane was pre-treated with the method as described by Woon et al., (2015)[7, 8]. In brief, the Nafion 117 membrane with a dimension of 5 cm x 5 cm was boiled in 0.1 M of H_2SO_4 solution for 30 min, followed by boiling in deionized water for 1 h. Pre-treated membranes were soaked in deionized water overnight at room temperature before use. The as-prepared electrode was hot pressed with the pre-treated membrane for 2 min as the catalyst-coated side facing the pre-treated membrane. The press temperature and pressure were set to 100 °C and 1 bar respectively to develop a membrane-electrode-assembly (MEA).

The air-cathode MFC was built with a cubic plexi glass into a dimension of 5 cm x 5 cm (Shanghai, Sunny Scientific, China) and a total working volume of 20 mL. Carbon brush was inserted into the anode chamber and used as the anode electrode. MEA was placed at the opening of cubic air-cathode MFC with the membrane facing the anode chamber. Titanium wire of 5 cm was then inserted into the MEA as the current collector, connected to the external wire. Electric circuit with a resistor was connected from the carbon brush to the titanium wire. Raw POME was diluted with deionized water in the ratio of 1:49 and anaerobic sludge was mixed with the diluted POME solution in the ratio of 1:25. The substrate was fed into the anode chamber and flushed with N_2 gas to remove the oxygen content and tightly closed. Air-cathode MFC was operated at room temperature.

2.5. Electrochemical characterization and analysis

The ORR activity of the catalyst was examined by using cyclic voltammetry (CV) by using a three-electrode configuration (Ag/AgCl as reference electrode, catalyst coated on carbon paper as working electrode and platinum mesh as counter electrode) in an oxygenated 0.1 M of Na_2SO_4 solution.

Polarization measurement was conducted to determine the power generation of MFC at different external resistance using an external resistor. The polarization curves were obtained from the corresponding voltage data. The open circuit voltages (OCVs) of MFCs were measured using a potentiostat.

2.6. COD removal efficiency

MnO_2/CNT with different loading of 0.10 g, 0.15 g and 0.20 g were prepared as the air cathode to determine the effect of catalyst loading towards the COD removal efficiency. Catalyst loading of 0.10 g, 0.15 g and 0.20 g were labelled as 14.28 mg/cm^2, 21.43 mg/cm^2 and 28.57 mg/cm^2, respectively. The COD was determined using digestive solution (0 – 1500 mg/L range; Hach, USA) and measured using a COD reactor (HACH DRB 200, USA) and calculated with the following equation: , USA) and calculated with the following equation:

$$COD\ removal\ efficiency = \frac{COD_i - COD_f}{COD_i} \times 100\% \qquad (1)$$

where COD_i = initial COD (mg/L) of the effluent in anode chamber and COD_f = COD of the effluent (mg/L) in the anode chamber at any time.

3. Results and discussion

3.1. X-ray powder diffraction pattern (XRD) of MnO_2/CNT

The XRD patterns of MnO_2/CNT are presented at 2θ = 15°-65° in Fig. 1. In general view over the XRD patterns reveals that the synthesized samples show MnO_2 and CNT peaks. The XRD patterns of the as-prepared MnO_2/CNT sample showing five main MnO_2 peaks of (2 0 0), (3 0 1), (3 1 0), (4 0 0) and (5 2 1), confirming the present of MnO_2 phases which was similar to that reported by[9, 30, 31, 32]. The diffraction peaks at 2θ of 26° and 43° are ascribed to the (0 0 2) and (1 0 0) plane of carbon, respectively which is in agreement with[33, 34, 35]. The result from XRD analysis also indicates that high purity of MnO_2/CNT was successfully synthesized.

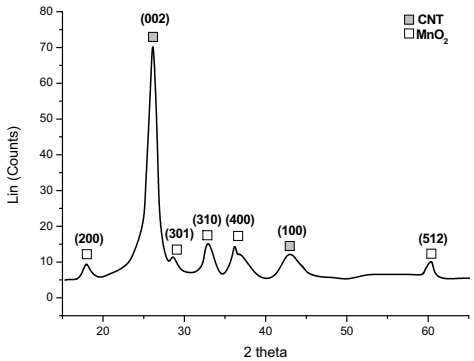

Fig. 1: The XRD pattern of MnO_2/CNT

3.2. Morphology and elemental analysis of MnO_2/CNT

Field emission scanning microscopy (FESEM) was used to examine the morphologies of as-prepared MnO_2/CNT catalyst. From Fig. 2a, it can be seen that CNT was roughened by the formation crystal structures of MnO_2[16]. The actual size of the MnO_2 crystals on the CNT surface cannot be observed by FESEM due to its nano-sized structure.

Therefore, the particle size of MnO_2 was further visualized by TEM. In a glance in Fig. 2b, the particle size of MnO_2 is about 10-20 nm. This observation implies the as-prepared catalysts are in nanoscale. As seen, MnO_2 was dispersed on the surface of CNT. Besides, elemental analysis of the MnO_2/CNT by EDS confirmed the present of C, O_2, and Mn which is shown in Fig. 2c. From the EDS pattern, it can be concluded that high purity of MnO_2/CNT was synthesized. The result obtained is in consistence with XRD result (Fig. 1).

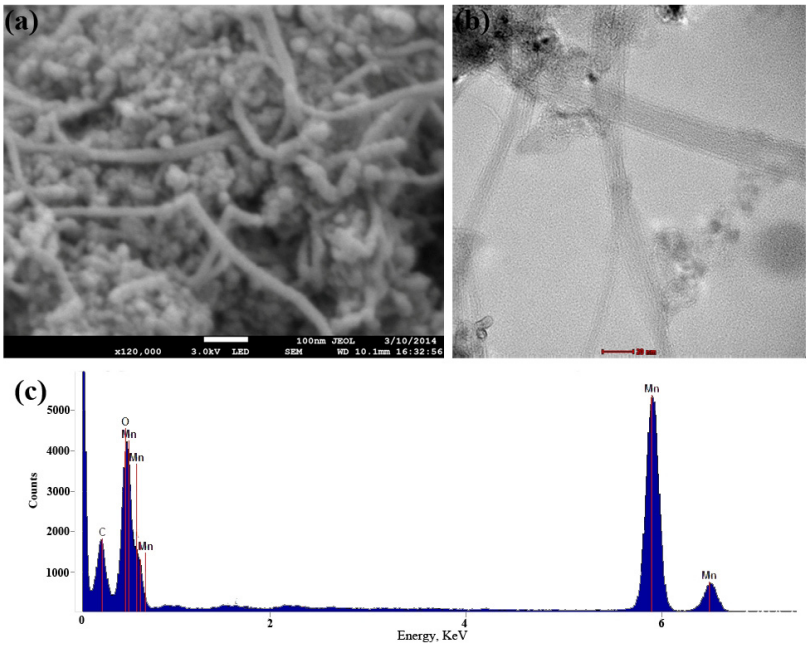

Fig. 2: Morphology and elemental analysis of MnO_2/CNT by (a) FESEM, (b) TEM and (c) EDS

3.3. *Cyclic voltammetry*

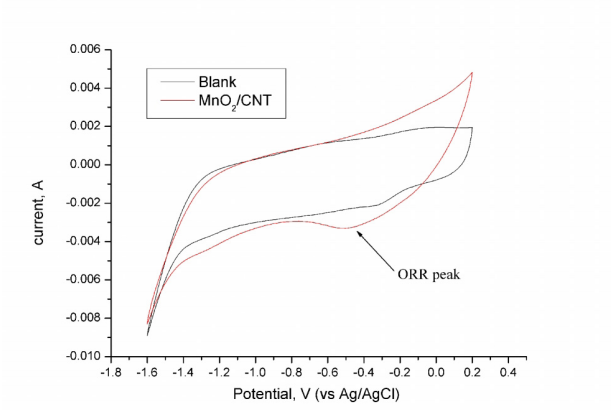

Fig. 3: Cyclic voltammogram for ORR in 0.1 M Na_2SO4 saturated by O_2 with scan rate of 30 mV/s

The ORR activity was then evaluated by cyclic voltammetry (CV) technique on a three-electrode system in O_2 saturated 0.1 M Na_2SO_4 solution with the scan rate of 30 mV/s. At the potential of -0.45 V, the current of the ORR at the electrode with catalyst MnO_2/CNT is -0.0032 A, which is 0.52 times higher than that of the electrode with CNT catalyst (-0.0021 A). The ORR peak current of MnO_2/CNT catalyst is bigger than that of CNT catalyst. The increase of the current indicates the increase of ORR rate as reported by Khilari et al. (2014)[36]. It can be concluded that MnO_2/CNT is an active ORR catalyst.

3.4 COD removal efficiency

The COD removal efficiency and MFC performance on different catalyst loadings were illustrated in Fig. 4. From Fig. 4, the highest catalyst loading of 28.57 mg/cm^2 provides the highest COD removal efficiency (22%) with the highest power generation. This indicates that higher catalyst loading could enhance the performance of air-cathode MFC by increasing the ORR activities in the air-cathode[7]. The results suggest that the air-cathode was the limiting element of the cell. While higher catalyst loading was used in the cathode, the electrons produced from anode could be utilized through ORR which caused enhanced microbial activity in the anode chamber and as a result the COD removal efficiency was increased.

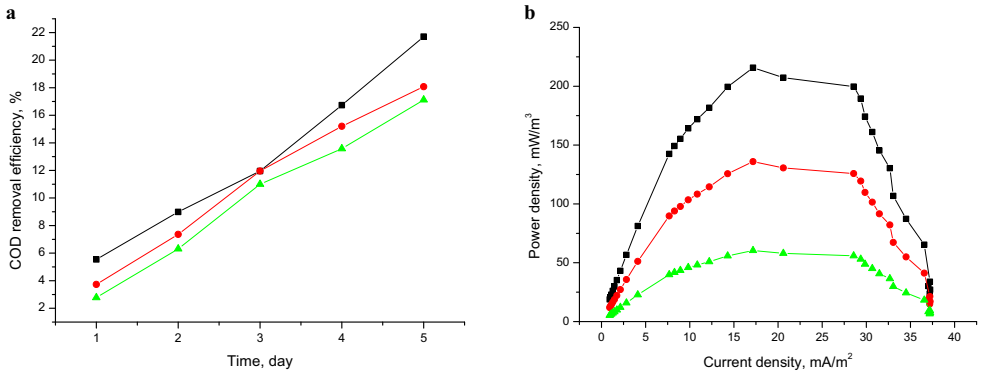

Fig. 4: COD removal efficiency on different catalyst loadings [■ - 28.57 mg/cm^2, ● - 21.43 mg/cm^2, ▲- 14.28 mg/cm^2 (MnO_2/CNT)]

3.5. Air-cathode MFC performance

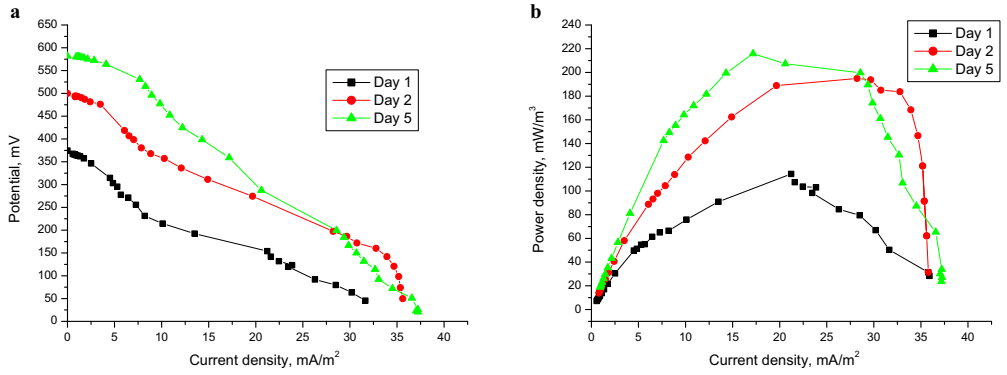

Fig. 5: a) Polarization curve b) power output profile for the closed circuit MnO^2/CNT catalysed air-cathode MFC for 5 consecutive days

The polarization curve and power output profile for the closed circuit air-cathode MFC is shown in Fig. 5. The highest open circuit voltage recorded in the MnO_2/CNT catalysed air-cathode MFC was 582 mV which obtained on the 5th day. As seen in Fg. 5 (a), the drop of the voltage as the increasing current density is due to the ohmic resistance by the wire connections and materials. The maximum power output was determined by the polarization curves as presented in Fig. 5 (b). The maximum power output on the first, second and fifth day recorded were 114.48 mW/m^3, 196.01 mW/m^3 and 215.57 mW/m^3, respectively.

When comparing the power generation from the current study with the literature (Table I), it can be seen that the MnO_2/CNT has a great potential to be used as the electrocatalyst in air-cathode MFC as it could produce higher energy output compared to other catalysts. The maximum output for MnO_2 and 0.4 wt% Pt/MnO_2 reported by Khan et al. (2015)[10] were 95 mW/m^3 and 165 mW/m^3, respectively.

Table 1. Performance comparison of MFC to literature

Type of electrocatalyst	Type of substrate	Max. power density (mW/m^3)	Reference
MnO_2/CNT	POME	215.57	Current study
MnO_2	POME	95	Khan et al., (2015)[10]
0.4 wt% Pt/MnO_2	POME	165	Khan et al., (2015)[10]

4. Conclusion

In this study, MnO_2/CNT was successfully developed and characterized. XRD and EDS confirmed that the as-prepared MnO_2/CNT was high in purity. The morphology of MnO_2/CNT was visualized by FESEM and TEM. The CNT was roughened by the formation of nanoscale structure of MnO_2. The CV results presented that MnO_2/CNT shows ORR activity with the ORR peak at potential of -0.45 V. The COD removal efficiency and MFC performance were studied. Approximately 22 % of COD removal efficiency and 215.57 mW/m^3 were achieved with the catalyst loading of 28.57 mg/cm^2. The maximum power density and maximum open circuit voltage OCV generated from the as-prepared MnO_2/CNT catalyzed air-cathode MFC were 215.57 mW/m^3 and 582 mV, respectively. It can be seen that MnO_2/CNT catalyst has a great potential air-cathode MFCs.

Acknowledgements

This work was supported in part by Department of Higher Education, Ministry of Education (Grant NO: RDU 120611) and Universiti Malaysia Pahang (Grant No: RDU 140322 and GRS 150321).

References

[1] Li X, Hu B, Suib S, Lei Y, Li B. Manganese dioxide as a new cathode catalyst in microbial fuel cells. *J. Power Sources* 2010; **195(9)**: 2586–2591.

[2] Kim S-I, Roh S-H. Multiwalled carbon nanotube/polyarcylonitrile composite as anode material for microbial fuel cells application. *J. Nanosci. Nanotechnol.* 2010; **10(5)**: 3271–3274.

[3] Wei L, Han H, Shen J. Effects of cathodic electron acceptors and potassium ferricyanide concentrations on the performance of microbial fuel cell. *Int. J. Hydrogen Energy* 2012; **37**: 12980–12986.

[4] Su Y, Zhu Y, Yang X, Shen J. A highly efficient catalyst toward oxygen reduction reaction in neutral media for microbial fuel cells. *Ind. Eng. Chem. Res.* 2013; **52**: 6076–6082.

[5] Baranitharan E, Khan MR, Yousuf A, Teo WFA, Tan GYA, Cheng CK. Enhanced power generation using controlled inoculum from palm oil mill effluent fed microbial fuel cell. *Fuel* 2015; **143**: 72–79.

[6] Sciarria TP, Tenca A, D'Epifanio A, Mecheri B, Merlino G, Barbato M, Borin S, Licoccia S, Garavaglia V, Adani F. Using olive mill wastewater to improve performance in producing electricity from domestic wastewater by using single-chamber microbial fuel cell. Bioresour. Technol. 2013; **147**: 246–253.

[7] Woon CW, Lim JH, Ong HR, Khan MR. Simultaneous power generation and wastewater treatment by using air-cathode single chamber microbial fuel cell. *Int. J. Mat. Sci. Inn.* 2015; **03(01)**: 33–41.

[8] Woon CW, Lim JH, Ong HR, Khan MR, Rahman W. Manganese dioxide as a cathodic catalyst in microbial fuel cell: Characterization and effect of catalyst loading. Sci. Technol. Prog. 2015; **1**: 18-23.

[9] Baranitharan E, Khan MR, Prasad DMR, Teo WFA, Tan GYA, Jose R. Effect of biofilm formation on the performance of microbial fuel cell for the treatment of palm oil mill effluent. *Bioprocess Biosyst. Eng.* 2014; **38**: 15–24.

[10] Khan MR, Chan KM, Ong HR, Cheng CK, Rahman W. Nanostructured Pt/MnO_2 Catalysts and Their Performance for Oxygen Reduction Reaction in Air Cathode Microbial Fuel Cell. *Int. J. Electr., Comput., Electron. Commun. Eng.* 2015; **9(3)**: 247–253.
[11] Rabaey K, Clauwaert P, Aelterman P, Verstraete W. Tubular microbial fuel cells for efficient electricity generation. *Environ. Sci. & Technol.* 2005; **39(20)**: 8077–8082.
[12] Cercado-quezada B, Delia ML, & Bergel A. Testing various food-industry wastes for electricity production in microbial fuel cell. *Bioresour. Technol.*2010; ***101(8)***: 2748–2754.
[13] Li J, Fu Q, Liao Q, Zhu X, Ye DD, Tian X. Persulfate: A self-activated cathodic electron acceptor for microbial fuel cells. *J. Power Sources* 2009; **194(1)**: 269–274.
[14] Du Z, Li H, Gu T. A state of the art review on microbial fuel cells: A promising technology for wastewater treatment and bioenergy. *Biotechnol. Adv.* 2007; **25(5)**: 464–482.
[15] Hampannavar US, Anupama, Pradeep N. Treatment of distillery wastewater using single chamber and double chambered MFC. *Int. J. Environ. Sci.* 2011; **2(1)**: 114–123.
[16] Zhang P, Li K, Liu X. Carnation-like MnO_2 modified activated carbon air cathode improve power generation in microbial fuel cells. *J. Power Sources* 2014; **264**: 248–253.
[17] Lee K, Zhang L, Lui H, Hui R, Shi Z, Zhang J. Oxygen reduction reaction (ORR) catalyzed by carbon-supported cobalt polypyrrole (Co-PPy/C) electrocatalysts. *Electrochim. Acta* 2009; **54(20)**: 4704–4711.
[18] Song C, Zhang J. Electrocatalytic Oxygen Reduction Reaction. PEM Fuel Cell Electrocatalyst and Catalyst Layers. *Fundamentals and Applications* 2008.
[19] Singh R, Awasthi R, Sharma C. Review : An Overview of Recent Development of Platinum- Based Cathode Materials for Direct Methanol Fuel Cells. *Int. J. Electrochem. Sci.* 2014; **9**: 5607–5639.
[20] Lu M, Kharkwal S, Ng HY, Li SFY. Carbon nanotube supported MnO_2 catalyst for oxygen reduction reaction and their applications in microbial fuel cells. *Biosens. Bioelectron.* 2011; **26(12)**: 4728–4732.
[21] Yang X, Zhou W, Su Y, Zhu Y, Jiang H, Shen J, Li C. Activated nitrogen-doped carbon nanofibers with hierarchical pore as efficient oxygen reduction reaction catalyst for microbial fuel cells. *J. Power Sources* 2014; **266**: 36–42.
[22] Lima FHB, Calegaro ML, Ticianelli EA. Investigations of the catalytic properties of manganese oxides for the oxygen reduction reaction in alkaline media. *J. Electroanal. Chem.* 2006; **590(2)**: 152–160.
[23] Morris JM, Jin S, Wang J, Zhu C, Urynowicz MA. Lead dioxide as an alternative catalyst to platinum in microbial fuel cells. *Electrochem. Commun.* 2007; **9**: 1730–1734.
[24] Thorseth MA, Tornow CE, Tse ECM, Gewirth AA. Cu complexes that catalyze the oxygen reduction reaction. *Coord. Chem. Rev.* 2013; **257(1)**: 130–139.
[25] Wang L, Liang P, Zhang J, Huang X. Activity and stability of pyrolyzed iron ethylenediaminetetraacetic acid as cathode catalyst in microbial fuel cells. *Bioresour. Technol.* 2011; **102(8)**: 5093–5097.
[26] Nallathambi V, Lee J-W, Kumaraguru SP, Wu G, Popov BN. Development of high performance carbon composite catalyst for oxygen reduction reaction in PEM Proton Exchange Membrane fuel cells. *J. Power Sources* 2008; **183(1)**: 34–42.
[27] Trogadas P, Fuller TF, Strasser P. Carbon as catalyst and support for electrochemical energy conversion. *Carbon* 2014; **75**: 5–42.
[28] Zhang X, Xia X, Ivanov I, Huang X, Logan BE. Enhanced activated carbon cathode performance for microbial fuel cell by blending carbon black. *Environ. Sci. Technol.* 2014; **48(3)**: 2075–2081.
[29] Lv Y, Li H, Xie Y, Li S, Li J, Xing Y, Song Y. Facile synthesis and electrochemical properties of MnO_2/carbon nanotubes. *Particuology* 2013; 2–6.
[30] Mu B, Zhang W, Shao S, Wang A. Glycol assisted synthesis of graphene-MnO_2-polyaniline ternary composites for high performance supercapacitor electrodes. Phys. Chem. Chem. Phys. 2014; **16(17)**: 7872–7880.
[31] Zhang Y, Hu Y, Li S, Sun J, Hou B. Manganese dioxide-coated carbon nanotubes as an improved cathodic catalyst for oxygen reduction in a microbial fuel cell. *J. Power Sources* 2011; **196(22)**: 9284–9289.
[32] Zhou C, Wang H, Peng F, Liang J, Yu H, Yang J. MnO_2/CNT supported Pt and PtRu nanocatalysts for direct methanol fuel cells. *Langmuir* 2009; **25(13)**: 7711–7717.
[33] Gupta VK, Saleh TA. Synthesis of Carbon Nanotube-Metal Oxides Composites; Adsorption and Photo-degradation. Carbon Nanotubes-From Research to Applications 2011.
[34] Liew KB, Wan Daud WR, Ghasemi M, Loh KS, Ismail M, Lim SS, Leong JX. Manganese oxide/functionalised carbon nanotubes nanocomposite as catalyst for oxygen reduction reaction in microbial fuel cell. . *Int. J. Hydrogen Energy* 2015; 1–8.
[35] Xia H, Wang Y, Lin J, Lu L. Hydrothermal synthesis of MnO_2/CNT nanocomposite with a CNT core/porous MnO_2 sheath hierarchy architecture for supercapacitors. *Nanoscale. Res. Lett.* 2012; **7**: 1-10.
[36] Khilari S, Pandit S, Das D, Pradhan D. Manganese cobaltite/polypyrrole nanocomposite-based air-cathode for sustainable power generation in the single-chambered microbial fuel cells. *Biosens. Bioelectron.* 2014; **54**: 534–540.