Bioelectric Activity of Microbial Fuel Cell during Treatment of Old Corrugated Containerboard Discharges

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The bioelectric activity of two lab scale microbial fuel cell (MFC) designs, MFCI (1,500 cm^3) and MFCII (12,000 cm^3) were examined using old corrugated containerboard (OCC) discharge for simultaneous effective treatment with greater power production. The decrease of MFC internal resistance (MFC-R_{in}) resulted in increased generated power output. The different parameters used in MFC included electrode conducting area (ECA), cathodic redox solution (CRS), MFC volume capacity, and MFCs connections. The generated current densities (CD) and power densities output (PD) at variables of external resistances (R_{ex}) that ranged from 10 Ω to 20,000 Ω were calculated to estimate the MFC-R_{in}. In MFCI, using potassium ferri-cyanide as CRS, the change of ECA from 16 cm^2 to 64 cm^2 decreased the MFCI-R_{in} from 130 Ω to 110 Ω, and it was further decreased to 65 Ω when manganese dioxide was used as the CRS. Using R_{ex} 100 Ω, MFCII exhibited lower R_{in} 18.46%, enhanced voltage 37.5%, and greater chemical oxygen demand removal 4.77% compared with MFCI. Series and parallel connections between four MFCI increased the generated PD by 286% and 258%, respectively, compared with that obtained by single MFCI.

Keywords: Microbial fuel cell; Bio-electric energy; Pulp and paper effluent

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INTRODUCTION

Water and energy are two major concerns in global environmental protection. The size of the pulp and paper industries is increasing, and they generate high liquid effluent discharges with different characteristics. A main discharge in paper industries is old corrugated containerboard (OCC), which is widely used as recycled OCC fibers. This effluent has different chemical properties depending on the pulping process, rate of recycling, and contaminant contents. The most general characteristics of these discharges are color, pH, alkaloids, dissolved salts, suspended solids, lignin, cellulose, organic acids, soluble small fibers, fillers, coatings, plastic materials, wet strength agent, and halogenated organics (Du and He 2002). The re-use of pulp and paper liquid discharges is an important operating task because of its high water and chemical contents (Han 2003). Traditional treatment processes include alkali recovery (Ai *et al.* 2003), acid precipitation (Chen *et al.* 2002; Zhang 2003), ultrasonic treatment (Zhou *et al.* 2002), combustion (Yin *et al*. 2004), coagulation (Guo and Wang 2003; Xiong *et al.* 2004), chemical oxidation with ozone and photo-catalysis (Wu 1999), floatation (Zhang *et al.* 2002; Liu *et al.* 2002), flocculation (Lu *et al.* 2000), filtering (Yue 1997), membrane separation (Tang and He 2003), and electrochemical separation (Wang and Wang 2000; Jian and Wang 2002). Most of these techniques are either expensive or insufficient for organic elimination to match with environmental pollution control.

Aerobic or anaerobic biological treatment is an effective way for organic consumption needed for microbial survival and proliferation. The anaerobic biological techniques include: up-flow anaerobic sludge blanket (UASB), anaerobic filter bed method, anaerobic moving bed method, anaerobic expanded bed method, anaerobic rotating disc method, and anaerobic microbial fuel cell method (Bal and Dhagat 2001). Microbial fuel cell (MFC) treatment technology is advantageous for its environmental friendliness, economic return, and organic disposal especially for high organic loads discharges (Li and Li 2001).

The use of MFC for generating power density (PD) and achieving high organic removal rate from OCC discharges represent a new perspective technique in advanced research areas. Optimizations of MFC, which is required to magnify power output, include continuous development of biochemical reactions (Qiao *et al.* 2004; Ahmad *et al.* 2013). The biochemical oxidation and reduction reactions are described as follows.

$$C_6H_{12}O_6 + 6H_2O \rightarrow 6CO_2 + 24H^+ + 24e^- \quad \textit{General anodic reaction}$$

$$6O_2 + 24H^+ + 24e^- \rightarrow 12H_2O \quad \textit{General cathodic reaction}$$

Oxygen, ferric cyanide, and manganese dioxide are the most common cathodic redox solutions (CRS) in the cathode cell part and are characterized by their effective reduction reactions. Oxygen has limited activity due to low solubility, so the uses of ferric cyanide and manganese dioxide have better activities as of their independency on the solubility (Rhoads *et al.* 2005). Cathodic reactions are described as follows.

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \quad \textit{Oxygen as CRS}$$

$$[Fe(CN)_6]^{-3} + e^- \rightarrow [Fe(CN)_6]^{-4} \quad \textit{Ferric cyanide as CRS}$$

$$MnO_2 + H_2O_2 + 2H^+ \rightarrow Mn^{+2} + 2H_2O + O_2 \quad \textit{Manganese dioxide as CRS}$$

$$Mn^{+2} + 2H_2O_2 \leftrightarrow Mn(OH)_2 + 2H^+ \quad \textit{Manganese dioxide as CRS}$$

$$Mn(OH)_2 + H_2O_2 \rightarrow MnO_2 + 2H_2O \quad \textit{Manganese dioxide as CRS}$$

$$MnO_2 + 4H^+ + 2e^- \rightarrow Mn^{+2} + 2H_2O \quad \textit{Manganese dioxide as CRS}$$

MFC can produce greater power output by modifying factors that can generate and receive high electron numbers leading to lower MFC-R_{in} (Logan 2004). The challenge is to study the bio-electrochemical behavior of MFC through definite key factors attributed to enhance performance by decreasing the MFC-R_{in}. OCC discharge was used as the anodic organic substrate. By using an R_{ex} ranging from 10 Ω to 20,000 Ω in two MFCs lab-scale batch models, MFCI (1500 cm^3) and MFCII (12000 cm^3), the MFC-R_{in} was calculated. The key variable parameters were the electrode conducting area (ECA), cathodic redox solutions (CRS), and MFC volume capacity. This study also focused on the increase of power generation efficiencies through four MFCI connections in both series and parallel states. This study also estimated the organic consumption efficiencies in both studied MFC models.

EXPERIMENTAL

Analytical Equipment

A 5B-6 spectrophotometer was used for rapid determination of chemical oxygen demand (COD) at a λ value of 610 nm (Lian-hua Technology Ltd., Lanzhou, China). A computer multi-function voltage digital data acquisition collector card was used for online measurements of the MFC voltages (MPS-010602, Qichuang Mofei Electronic Technology Co., Ltd., Beijing, China).

Anaerobic Biofilm and OCC Collection

Anaerobic microbial biofilm samples were collected from an anaerobic reactor (Sun Paper Ltd., Shandong, China). Anaerobic biofilm was activated using basic nutrient media, including 5 g/L of glucose, 5 g/L of peptone, 1.5 g/L of beef extract, 1.5 g/L of yeast extract, and 100 g/L of granular activated carbon (GAC) (Mahmoud *et al.* 2018). This was incubated at 30 °C for 90 d under anaerobic conditions. Samples of OCC effluents were collected from Sun Paper Ltd. (Shandong, China), analyzed within 8 h, and stored at 4 °C for use. The physio-chemical analysis of both biofilm and OCC effluent are listed in Table 1.

Table 1. Physico-Chemical Analysis for Biofilm and OCC Samples

Item	OCC	Biofilm	Item	OCC	Biofilm
Color	Yellow	Black	Alkalinity (mg/L)	1300	105
pH	6.9	6.1	COD (mg/L)	6000	69700
Temperature (°C)	20	28	BOD (mg/L)	2400	41300
TSS (mg/L)	2841	45770	TDS (mg/L)	5690	420

MFC Operation Setup

Two methyl methacrylate MFC lab-scale designs, MFCI (1500 cm^3) and MFCII (12000 cm^3), were used. Each one consists of two cell-parts separated by a cationic exchanger membrane. Variable external resistances (R_{ex}) that ranged from 10 Ω to 20,000 Ω were used for each MFC operation study. Carbon cloth was used as a conducting electrode. In the cathode cell-part, two cathodic redox solutions were used: 50 mmol/L of $K_3[Fe(CN)_6]$-K_2HPO_4 and 0.2% manganese dioxide dissolved in sulfuric acid and hydrogen peroxide (30 %). In the anode cell-part, the pH was adjustment to a pH of 6.0 to 6.5 and the anaerobic biofilm was added to the OCC effluent by ratio 1:3 with mixed liquor suspended solids (MLSS) concentration of around 5000 mg/L (Mahmoud *et al.* 2018). The MFCs anaerobic conditions were controlled by supplying an adequate nitrogen gas capacity of 0.5 L/min. Online assessments of various parameters such as the obtained voltages, pH, DO, MLSS, TSS, COD, and BOD were monitored regularly under different hydraulic retention times (HRT).

Analytical Methods

All MFCs tests measurements were analyzed in triplicate according to the procedures described in the standard method (APHA 2005). The removal percentage was calculated as follows,

$$Removal\ (\%) = 100 \times \frac{C_0 - C_e}{C_0} \quad (1)$$

where C_0 and C_e are initial and final concentrations (mg/L), respectively.

The power density (W. m^{-2}), current density (A. m^{-2}), and MFC resistance (Ω) were calculated by Eqs. 2, 3, and 4, respectively,

$$Power\ density\ = \frac{U^2}{A \cdot R} \tag{2}$$

$$Current\ density\ = \frac{U}{A \cdot R} \tag{3}$$

$$R = \frac{U}{A \cdot Current\ density} \tag{4}$$

where U is the voltage output (V), R is the total resistance (Ω) used, and A is the electrode area (m^2).

Each MFC-R_{in} was achieved by plotting the current density against power density at different external resistances (R_{ex}) that ranged from 10 Ω to 20,000 Ω.

RESULTS AND DISCUSSION

Microbial fuel cell technology can be an affordable, reliable, clean source of energy and alternatives to waste disposal. To achieve high organic elimination and supplementary power generation, two MFCs lab scale designs, MFCI (1500 cm^3) and MFCII (12000 cm^3), were operated by feeding of enriched anaerobic microbial biomass with GAC and OCC effluent in the anode cell-part. The role of GAC is to increase electron transfer mechanism (Mahmoud *et al*. 2018). As the MFC generated power output depends on different induced reactions, this study focused on the change of the electrode conducting area (ECA), cathodic redox solutions (CRS), MFC volume capacity, and MFCs connections in both series and parallel states.

Electrode conducting area (ECA) is one of the most important reasons for electron transfer mechanisms in both MFC cell-parts that affect the MFC-R_{in}. In MFCI lab design, MFCIa and MFCIb potassium ferri-cyanide were used as a CRS with ECA of 16 cm^2 and 64 cm^2, respectively. Results showed that there was an increase in the voltage output and a decrease in the R_{in} due to the increase of the electron transfer mechanisms. The achieved MFCIa-R_{in} was 130Ω, while the MFCIb-R_{in} was 110Ω. By using R_{ex} 100Ω, results represented a significant increase in the obtained voltage from 0.185 V to 0.361 V, while a decrease in the generated power density was observed from 214.85 mW.m^{-2} to 203.84 mW.m^{-2} for both MFCIa and MFCIb, respectively, as drawn in Fig. 1. The increase of the obtained voltage resulted from the decrease of MFC-R_{in}, while the decrease of PD was due to increase of the electrode surface area (Shima 2017).

The cathode redox solutions (CRS) are of great importance in MFC power generation in which reduction reaction and attraction of electrons takes place. In MFCI lab design, MFCIc manganese dioxide was used as CRS with ECA of 64 cm^2. Results showed increase in power output and decrease of R_{in}. The achieved MFCIc-R_{in} was 65 Ω. By using 100 Ω R_{ex}, the obtained voltage was 0.480 V, the generated PD was 360.73 mW.m^{-2}, and the obtained CD was 0.751 A.m^{-2}, as shown in Fig. 2. This could be explained by high activity of electrons attracting and the high protons reducing activity (Rhoads *et al.* 2005; Li *et al.* 2010; Passos *et al.* 2016; Mahmoud *et al.* 2018).

To study the effect of MFC volume capacity on the MFC power output, MFC-R_{in} and organic removal at different hydraulic retention time (HRT), scale-up process takes place. In the MFCII lab design, manganese dioxide was used as CRS with ECA of 256 cm^2. Results showed significant increase in both current output and organic removal by increasing the MFC volume capacity, as drawn in Fig. 2. The MFCII-R_{in} was 53 Ω. By using R_{ex} 100 Ω, the obtained voltage was 0.660 V, the generated PD was 169.99 $mW.m^{-2}$, and the obtained CD was 0.258 $A.m^{-2}$. The decreases of both PD and CD by increasing MFC volume capacity are due to the reverse correlation with the electrode area (Passos *et al.* 2016; Mahmoud *et al.* 2018).

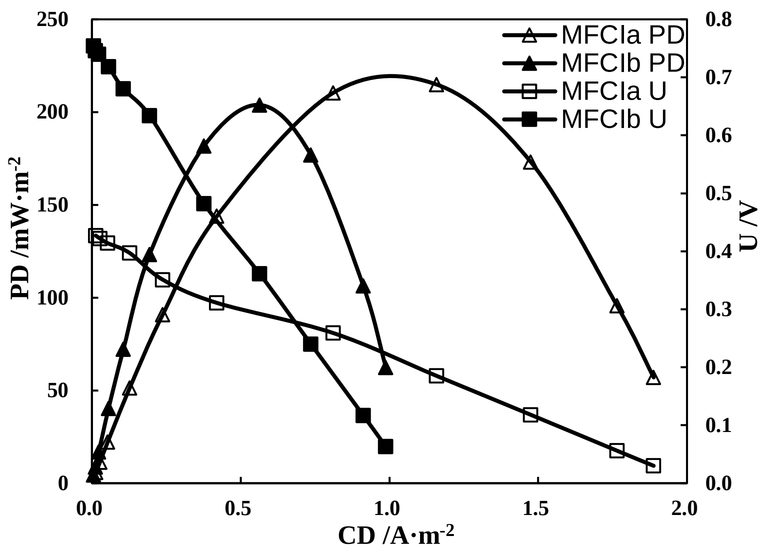

Fig. 1. Power output of MFCIa and MFCIb

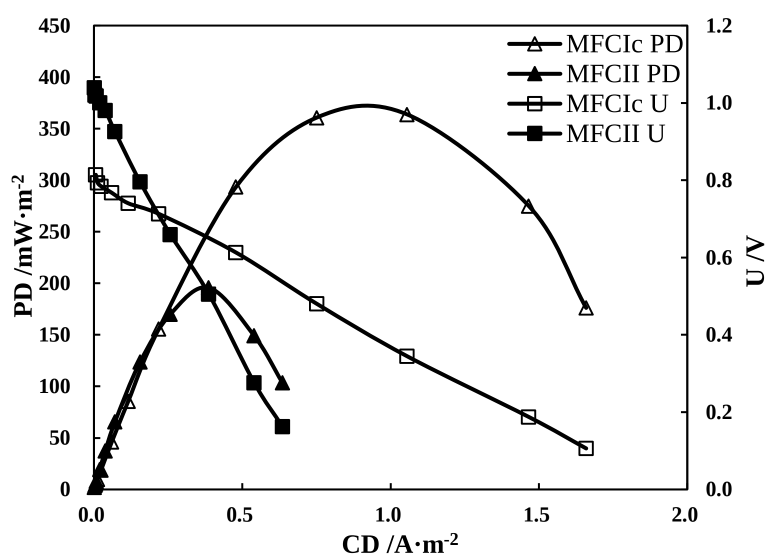

Fig. 2. Power output of MFCIc and MFCII

For organic waste removal represented in the OCC chemical oxygen demand (COD) removal, it was noticed that the MFC consuming efficiency had proportional correlation with MFCs scale-up in both operational retention time and removal percentages. The results showed that the consumption of COD reached 88% and 92.2%

after 8 d of operating MFCIc and MFCII, respectively, as shown in Fig. 3.

The rate of anaerobic granulation was expressed by the rate of biological growth in relation with the organic ratio (F/M) and formation of MLSS (Guo *et al.* 2017). The initial F/M ratio [COD/SS] for both MFCIc and MFCII was 1.2. The MFCII exhibited higher growth rate or sludge loading rate in the mixed liquor suspended solids (MLSS) in a shorter time of operation than MFCIc, as shown in Fig. 4. The F/M ratio highly decreased in case of MFCII with an effective start-up than MFCIc at the same time of operation, and this could be explained by extra competition between the anaerobic microbes and organic COD in case of MFCII.

The limitation of the F/M ratio along with retention time of operation for both MFCs, indicated that the OCC effluent had limited biodegradability, as the BOD/COD ratios that were in range from 0.25 to 0.43 (Durgesh and Akshay 2013; Yazdi *et al.* 2015).

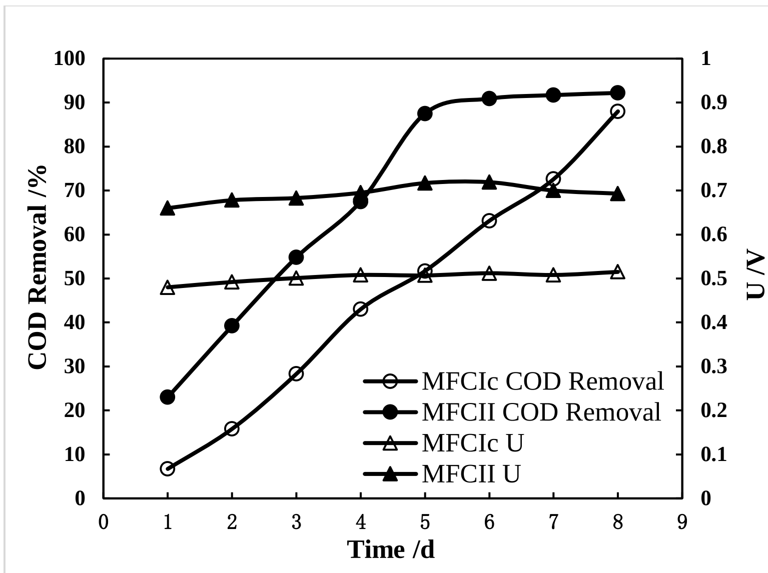

Fig. 3. Voltage output and COD removal of both MFCIc and MFCII

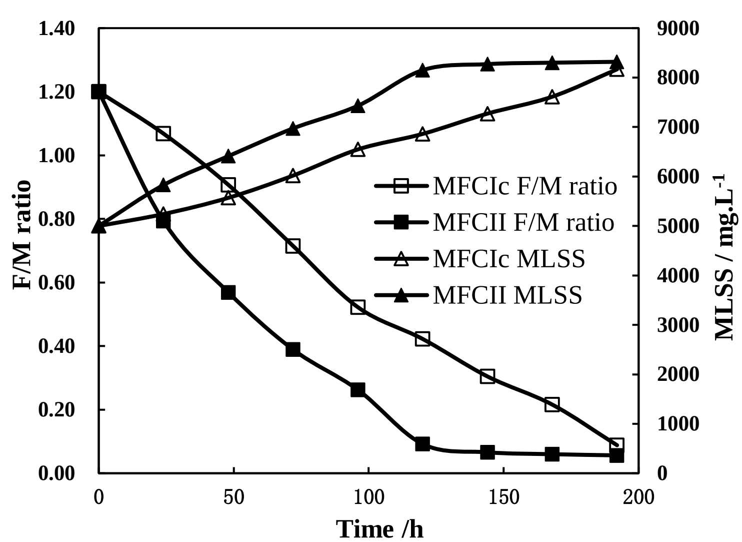

Fig. 4. F/M ratio and MLSS of both MFCIc and MFCII

The connections between four MFCIcs on the current production were studied in both series and parallel connections as shown in Fig. 5. In the series connection, the obtained voltage increased from 0.815 V to 3.14 V and the PD increased from 378 to 1461 for single and four connections of MFCIcs, respectively. In the parallel connections, there was no noticeable increase in the obtained voltages, while the PD increased from 378 mW.m^{-2} to 1355 mW.m^{-2} for both single and four connections of MFCIcs, respectively (Passos *et al.* 2016; Mahmoud *et al.* 2018).

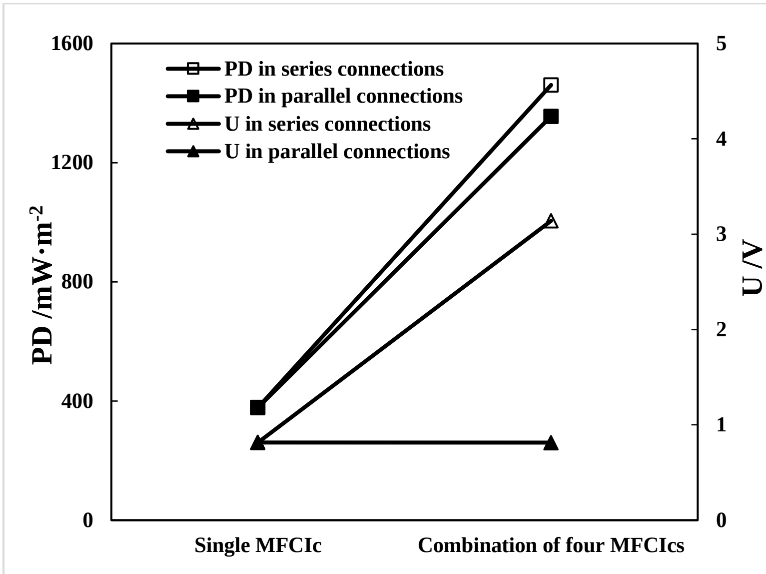

Fig. 5. The power output for both single and connections of four MFCIcs in series and parallel states

CONCLUSIONS

1. This study focused on microbial fuel cell (MFC) innovation and development using old corrugated container (OCC) effluent as bio-resources for sustainable energy production along with effective organic removal performance.
2. For high MFC performance, lower internal resistance (MFC-R_{in}) should be achieved through increasing the electrode areas, using manganese dioxide as the cathodic redox solution (CRS), increasing the MFC volume capacity.
3. For high power generation, multiple MFCs connections should be connected either in series or in parallel states.
4. The decrease of MFC-R_{in} that results in accelerating the start-up time, which decreases the power losses and is better for power production.

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REFERENCES CITED

Ahmad, F., Atiyeh, M. N., Pereira, B., and Stephanopoulos, G. N. (2013). "A review of cellulosic microbial fuel cells: Performance and challenges," *Biomass and Bioenergy* 56, 179-188. DOI: 10.1016/j.biombioe.2013.04.006.

American Public Health Association (APHA) (2005). "Standard methods for the examination of water and wastewater," American Public Health Association, American Water Works Association, and Water Environment Federation, Washington, DC.

Ai, T., Dong, X., Jiang, Z., Ai, D., and Wang, X. (2003). "The direct production of calcium carbonate black liquor alkali recovery in new technology," *Paper and Paper* (4), 59-60.

Bal, A. S., and Dhagat, N. N. (2001). "Upflow anaerobic sludge blanket reactor--a review," *Indian J Environ Health* 43(2), 1-82.

Chen, J., Tang, H., Zhang, G., and Dong, J. (2002). "Of black liquor resource utilization," *Journal of Northwest Institute of Light Industry* 20(6), 78-80.

Durgesh, S. S., and Akshay, K. (2013). "Electricity generation in microbial fuel cell by the decomposition of organic slurry using *E. coli*," *VSRD International Journal of Technical and Non-Technical Research* 4(11), 245- 250.

Du, Z., and He, L. (2002). "In addition to wheat straw black liquor alkali recovery silicon studied," *Gansu Environmental Research and Monitoring* 15(3), 153-155.

Guo, J., and Wang, J. (2003). "Slag composite coagulant treatment of black liquor," *Industrial Water Treatment* 23(11), 50-52.

Guo, N., Zhang, J., Xie, H., Tan, L., Luo, J., Tao, Z., and Wang, S. (2017). "Effects of the food-to-microorganism (F/M) ratio on N_2O emissions in aerobic granular sludge sequencing batch airlift reactors," *Water* 9(7), 477. DOI: 10.3390/w9070477.

Han, B. (2003). "Hydrolysis- Aerobic process pulp gray water," *Pollution Control Technology* 16(4), 97-98.

Jian, J., and Wang, J. (2002). "SBR coagulation and sedimentation treatment pulp gray water," *Engineering Design and Research* 4, 14-16.

Li, H., and Li, X. (2001). "Immobilized microbial treatment of paper mill bleaching effluent," *Industrial Water and Wastewater* 32 (5), 19-22.

Li, X., Hu, B., Suib, S., Lei, Y., and Li, B. (2010). "Manganese dioxide as a new cathode catalyst in microbial fuel cells (MFC)," *Journal of Power Sources* 195(9), 2586-2591. DOI: 10.1016/j.jpowsour.2009.10.084.

Liu, Q., Liu, W., Zhang, C., Li, J., Tian, J., Zhan, H., and He, B. (2002). "Application of PEO/PFR dual flocculation system to handle paper-making white water," *Heilongjiang Paper* 30(2), 23-24.

Logan, B. E. (2004). "Peer Reviewed: Extracting hydrogen electricity from renewable resources," *Environmental Science and Technology* 38(9), 160A-167A. DOI: 10.1021/es040468s.

Lu, X., Ma, Y., Wang, R., and Shi, G. (2000). "Flocculation study on white water," *Industrial Water Treatment* 20(5), 33-35.

Mahmoud, M. S., Wen, B., Su, Z., Fan, S., and Zhang, Y. (2018). "Parameters Influencing Power Generation in Eco-friendly Microbial Fuel Cells," *Paper and Biomaterials (PBM)* 3(1), 10-16.

Passos, V. F., Aquino, N. S., Andrade, A. R., and Reginatto, V. (2016). "Energy generation in a microbial fuel cell using anaerobic sludge from a wastewater treatment plant," *Scientia Agricola* 73(5), 424-428. DOI: 10.1590/0103-9016-2015-0194.

Qiao, Q., Chen, M., and Chen, Z. (2004). "Breeding predominant bacteria chlorine bleaching wastewater treatment research," *China Paper Sinica* 19(1), 53-56.

Rhoads, A., Beyenal, H., and Lewandowski, Z. M. (2005). "Microbial fuel cell using anaerobic respiration as an anodic reaction and biomineralized manganese as a cathodic reactant," *Environmental Science and Technology* 39(12), 4666-4671. DOI: 10.1021/es048386r.

Shima, F. (2017). "Microbial fuel cells and their applications in electricity generating and wastewater treatment," *International Scholarly and Scientific Research & Innovation* 11(3), 203-207.

Tang, G., and He, B. (2003). "China's papermaking white water reuse status and countermeasures," *Guangxi Light Industry* (6), 7-10.

Wang, Y., and Wang, S. (2000). "On the electrochemical-flocculation papermaking wastewater treatment," *Heilongjiang Environmental Bulletin* 24(2), 23-24.

Wu, S. (1999). "Advanced chemical oxidation process in pulp and wastewater treatment applications," *Chinese Paper* 18(5), 43-49.

Xiong, Z., Yuan, H. S., and Liu, X. (2004). "Iron clay coagulation treatment of black liquor applied research," *Journal of Nanhua University* 18(2), 17-19.

Yazdi, H., Alzate-Gaviria, L., and Ren Z. J. (2015). "Pluggable microbial fuel cell stacks for septic wastewater treatment and electricity production," *Bioresource Technology* 180, 258-263. DOI: 10.1016/j.biortech.2014.12.100.

Yin, G., Ning, C., and Fu, X. (2004). "The use of red mud and paper black liquor combustion-supporting agent development of bulk coal desulfurization," *Environmental Engineering* 22(2), 57-59.

Yue, C. (1997). "Microfiltration machine in paper-making in an integrated approach to the use of white water," *Zhejiang Paper* (1), 44-47.

Zhang, G., Gu, L., and Ping, H. (2002). "Preparation of cationic modified starch flocculant flocculation and its role in white water," *Journal of Northwest Institute of Light Industry* 20(3), 42-44.

Zhang, Y. (2003). "Analysis of paper mill waste water sub-processing technology," *Shanxi Architecture* 29(4), 254-255.

Zhou, S., Wu, X., Huang, W., and Lu, X. (2002). "Ultrasonic degradation of black liquor in a preliminary study," *Industrial Water Treatment* 22(10), 26-29.

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