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Treatment of Aged Landfill Leachate by a Self-Sustained Microbial Fuel Cell-Microbial Electrolysis Cell System

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Microbial fuel cells (MFCs) can supply power and drive reactions for microbial electrolysis cells (MECs) when they are connected in series. This study designed three different air-cathode single-chamber MFC-MEC systems constructed with aged landfill leachate as the substrate to enhance energy recovery and pollutant removal efficiency. These systems were designated as MFC (S_1), MFC-MEC (S_2) and MFC-MEC-MFC (S_3). Maximum voltage outputs of 146, 421, and 253 mV were obtained from the S_1, S_2 and S_3 systems, respectively. The removal efficiency of COD in the S_2 and S_3 systems was significantly enhanced compared to that of the S_1 system, and the removal rate of ammonia could reach more than 90%. In addition, the degradation of ammonia nitrogen in the S_1 and S_2 systems was consistent with fractal reaction kinetics, providing a theoretical basis for pollutant removal in the future. Therefore, it was demonstrated that the associated system could enhance the performance of electricity generation and thus could be applied to enrich wastewater treatment efficiency as a new and promising approach.

Keywords: microbial fuel cell; microbial electrolysis cell; landfill leachate; chemical oxygen demand; ammonia

1. INTRODUCTION

MFCs include a cathode and anode, similar to conventional batteries. At its core, electrochemically active bacteria attach to the anaerobic anode of the MFC and decompose complex organics into small molecular substances, such as CO_2. Then, the protons are transported to the cathode while the electrons are transmitted to the cathode through an external circuit, and the electron acceptor reacts with the electrons and H^+ to produce water[3]. Various substrates have been widely researched for MFCs, such as landfill leachate[4-6], groundwater[7], lake water[8], paper-recycling wastewater[9] and

distillery wastewater[10]. Landfill leachate mainly contains excessive ammonia nitrogen, complex organic chemicals, heavy metals and other harmful pollutants that are not effectively removed by traditional wastewater treatment methods[11]. Several researchers have researched the feasibility of applying different types of MFCs for leachate removal and simultaneous electricity generation. Hai T. H et al reported that COD and ammonium removal from landfill leachate wastewater were up to 97% and 98%, respectively, with algae cathode MFCs[5]. Jayesh M et al. obtained an open circuit voltage (OCV) of 1.23 V, and it is the highest OCV ever reported for a single MFC system[4]. Furthermore, Yan L et al investigated the treatment effect of advanced landfill leachate by using Fenton oxidation combined with a MFC and indicated that the physicochemical process could connect with the biological process to degrade wastewater[11]. It can be concluded from the above that an MFC can achieve both pollutant treatment and energy recovery and has the advantages of mild reaction conditions, higher energy conversion efficiency and no secondary pollution. However, MFCs are confronted with extreme difficulties, such as large internal resistance, low output power, and no storage of electric energy, which leads to energy waste if not used in time.

A MEC is an anaerobic wastewater treatment that requires an external power supply to overcome thermodynamic obstacles and obtain a high cathodic reaction rate[12, 13]. The energy requirement for a MEC can be supplied by an air-cathode MFC because the theoretical driving voltage of a MEC is quite low. Furthermore, it saves the cost of storing electricity and power loss. The serial connection of a MFC significantly increased the hydrogen production and input voltage of the MEC[14, 15]. Jiang et al achieved sulfide removal and a methane product from CO_2 in a MFC–MEC coupled system[16]. It provided an economical and environmentally friendly technology to accomplish the immobilization of the CO_2 released from waste degradation.

This study aimed to achieve the joint operation of the MFC-MEC system, in which a MFC was used to supply power to a MEC without any external energy consumption. The interaction between the MFC and MEC in the associated system, including its electricity generation performance, the landfill leachate COD and the ammonia removal efficiency was discussed. This work is expected to provide a proof-of-concept demonstration of the MFC-MEC system as a new way to reuse energy and recycle resources of ammonia-rich organic wastewater.

2. EXPERIMENT

2.1 System construction and reagents

In this experiment, 4 air-cathode single-chambered MFCs and 2 MECs were constructed. S_1 was 1#MFC in parallel with 1000 Ω of external resistance, and S_2 was composed of 2#MFC connected with 1#MEC. S_3 consisted of 3#MFC, 4#MFC and 2#MEC, as shown in Fig. 1 (the structures of S_1 and S_2 were the same as those of 3# MFC and 4#MFC connected in series with 2#MEC in Fig. 1, respectively). The effective volumes of the MFC anode chamber and MEC unit were 120 and 18.75 mL, respectively. The anodes of both the MFC and MEC were 4-mm-thick circular carbon felts that measured 4 cm in diameter; the cathode materials were carbon cloth loaded with 10% Pt/C powder[17, 18]. The carbon

felt was pretreated with 10% H_2O_2 at 90 °C for 2 h to remove impurities and then thoroughly rinsed and finally dried for 3 h at 60 °C.

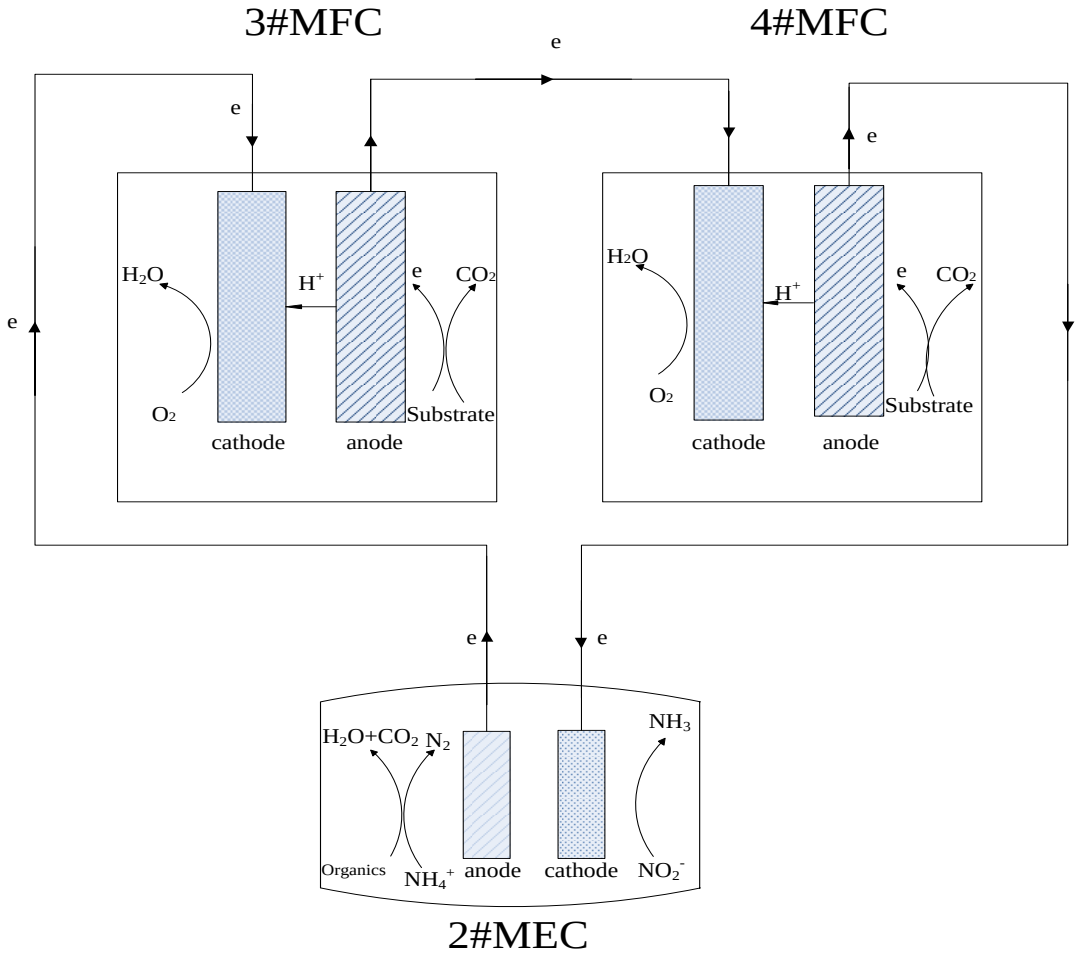

Figure 1. Schematic diagram of the MFC-MEC-MFC system

2.2 Inoculation and operation

First, glucose as nutrients was added to the activated aerobic sludge suspensions and sealed for 24 h. Second, the excess supernatant was removed to produce a 1:1 ratio of sludge to liquid. Then, the aerobic sludge was stirred at a constant temperature of 30 ℃, with the pH controlled at 7~8 during the period. After 15 days of culture, the black and odorous suspension was an active anaerobic sludge.

After that, the suspension of anaerobic sludge was set in a 1:1 ratio with 1 g/L of glucose nutrient solution to form an inoculum, with 12.5 mL/L of minerals and 5 mL/L of vitamins as added nutrition. We replaced the substrate with 1 g/L inoculum and stabilized the power generation for 2~3 cycles when the output voltage was reduced to approximately 50 mV. Then, the MFC substrate was replaced by the landfill leachate with a volume fraction of 50% in the operation stage, and the concentrations of ammonia, COD, nitrate, and nitrogen in the S_1 and S_2 systems were 1308, 1760, 8.33 and 0.16 mg/L, respectively along with a pH value of 8.57. The S_2 and S_3 start-up phase was the same as that of 1#MFC. Due to the self-degradation of landfill leachate, the initial average concentrations of ammonia, COD,

nitrate and nitrogen in the S_3 system were 1385, 1477, 7.56 and 0.19 mg/L, respectively, with a pH value of 9.08 and a conductivity of 25.05 mS/cm.

2.3 Electrochemical analyses, calculations and kinetic analysis of ammonia nitrogen removal

The output voltage (*U*/mV) was collected once every 0.02 s with a computer-aided data acquisition system, and the average value per 10 s was automatically stored[19]. The current (*I*/mA) and current density (I_V / mA·m^{-3}) were calculated by Equations (1) and (2).

$$I = U/R_{ex} \quad (1)$$

$$I_V = U/(V_{An} R_{ex}) \quad (2)$$

Where, U is denoted voltage, R_{ex} is external resistance, and V_{An} is the effective volume of the anode.

The power density (P_V/mW·m^{-3}) refers to the power output per unit area or unit volume of the MFC, and Equation (3) is used for the calculation. The polarization curve shows the linear relationship between output voltage and current density[20, 21]. The main method to change the output voltage is by changing the resistance value of the MFC resistor in parallel[22]. Coulombic efficiency (CE) is defined as the ratio of total amount of charge actually transferred to the anode from the substrate to the maximum possible charge that can be created from the removal of the substrates and is calculated using Equation (4) [10]:

$$P_V = U^2/(V_{An} R) \quad (3)$$

$$CE(\%) = \frac{M_{O_2} \int_0^t Idt}{F \bullet b V_{An} \bullet \Delta COD} \times 100\% \quad (4)$$

Where $M_{O_2}$is molar mass of organics based on oxygen(32 g/mol), F is Faraday constant(96485 C/mol), b(constant 4) represents the number of electrons to be transferred to oxidized per mol organics, and ΔCOD is the changed COD over time.

The organic compound and nitrogen concentrations in the landfill leachate were measured as COD, ammonia, nitrite, and nitrate using the standard methods[23, 24]. The pollutant removal efficiency was calculated using Equation (5):

$$\eta = \left[\frac{C_{in} - C_{out}}{C_{in}}\right] \times 100\% \quad (5)$$

where C_{in} and C_{out} are the influent concentration and effluent concentration.

According to previous studies, the rate equation of ammonia bimolecular and unimolecular reactions do not follow the classical kinetic model[25]. This indicates that the relationship between the rate coefficient k and time can be expressed by Equation (6) [26]:

$$k = k_0 t^{-h} (0 \le h \le 1) \quad (6)$$

where k_0 is the fractal-like rate constant, h is the fractal-like exponent, reflecting whether a system is homogeneous. The h and reaction order X can be calculated by the following Equations (7) and (8)[27],This solution is applicable to any pseudo-monomolecular cluster-limited (percolative) reaction..

$$h = 1 - {}^{D_s}/_2 \quad (7)$$

$$X = 1 + {}^2/_{D_s} \quad (8)$$

where, Ds is fractal spectral dimension, an important parameter to describe the dynamic behavior of fractal structure.

3. RESULTS AND DISCUSSION

3.1. Electricity production performance of the MFC-MEC system

A stable output voltage was generated when the system operated for a long duration (14 days), as shown in Fig. 1. At the start-up period, the aged landfill leachate was rich in organic matter and provided abundant nutrients for the microorganisms. Therefore, the output voltage of S_1~S_3 rose rapidly, with maximum output voltages for S_1, S_2, and S_3 being 146, 421, and 253 mV, respectively. However, with the fast depletion of such easily degradable contents, the voltage swiftly dropped. Then, the refractory organics were further utilized to maintain a slowly declining generation of electricity. The output voltage of S_2 increased by almost 189% when the external resistance was replaced by a MEC. However, the continued increase in the MFC led to a voltage reversal [28], which was mainly caused by the decrease in microbial activity or the lack of fuel [28, 29].

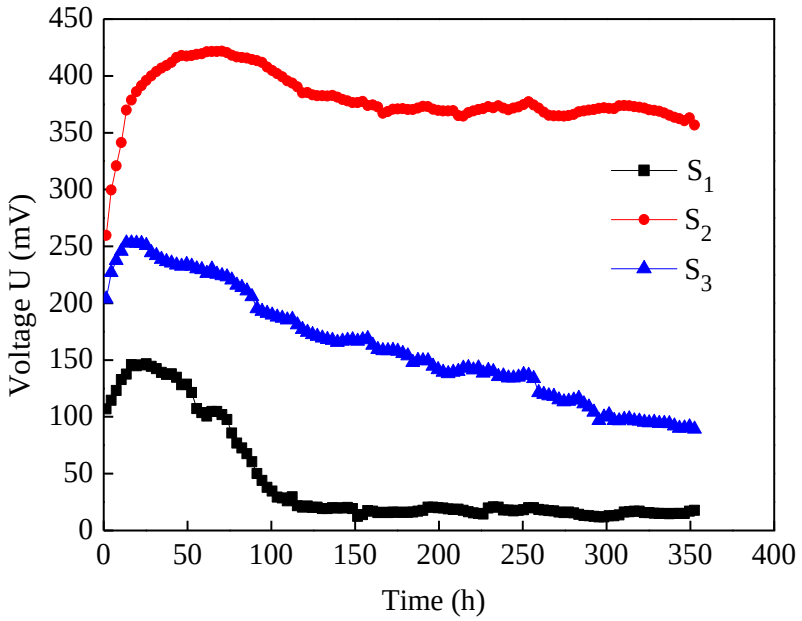

Figure 2. Variation of output voltage in the S_1, S_2 and S_3 systems during operation from 0~352 h

The S_1 and S_2 systems volume power generation were compared along with their polarization curves in Fig. 3 and Fig. 4. The highest power densities of 1#MFC, 2#MFC and 1#MEC were 78.1, 86.4 and 1330.7 mW/m^3, respectively. This demonstrated that landfill leachate could be effectively utilized by microbes for power production and that the MFC could generate enough bioelectricity to power the MEC and serve as the potential external resistance[30]. In addition, the output power of 2#MFC was

much higher than that of 1#MFC, which indicated that the MEC enhanced the activity of electron-transfer bacteria without voltage reversal, further providing the output power at a more practical current density[31].

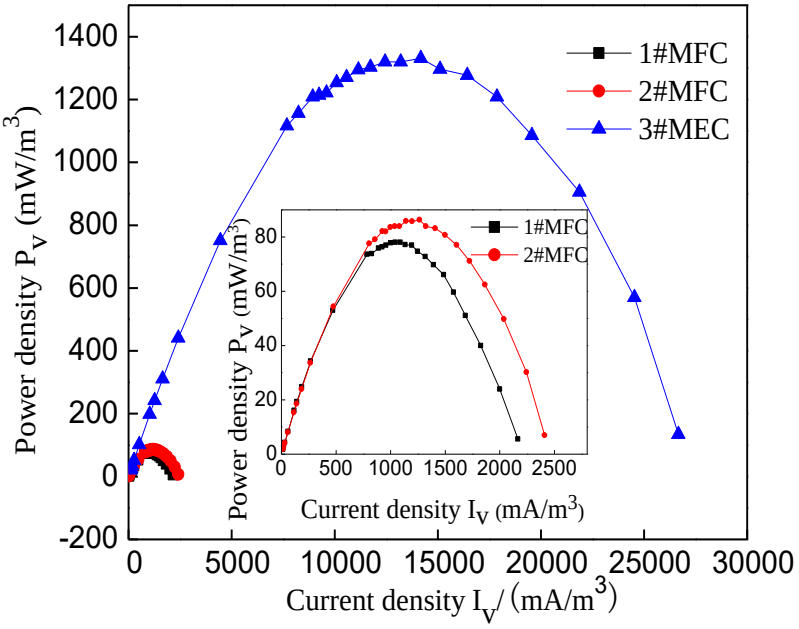

Figure 3. Variation of volume power density in S_1 and S_2 during the voltage stable output period (after 11 days of startup)

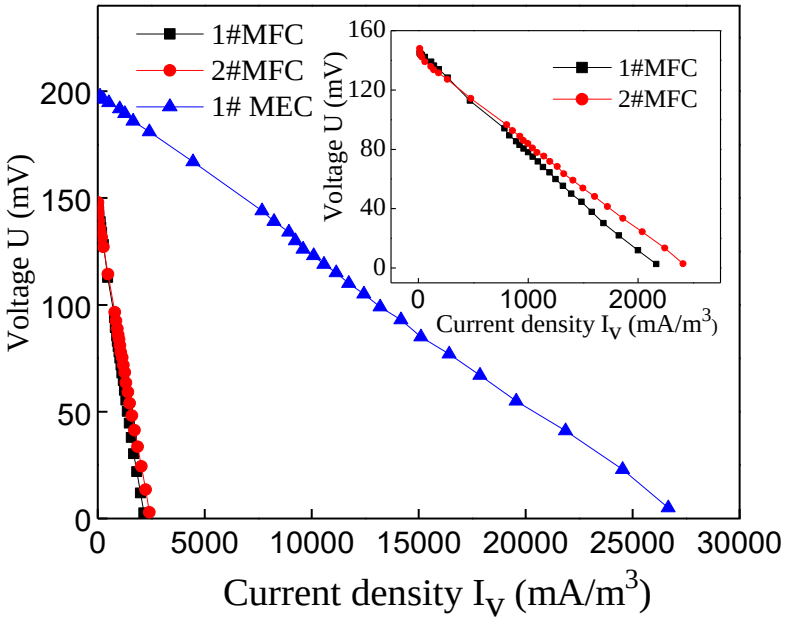

Figure 4. The MFC and MEC Polarization curves of S_1 and S_2 (after 11 days of startup)

After the first cycle of operation, the reactor was fed with aged landfill leachate to investigate the current-voltage characteristics. Polarization curve tests were operated by varying the external

resistance from 100 kΩ to 10 Ω (Fig. 4). Based on the relationship between current density and voltage, the internal resistance (ohmic resistance) of 1#MFC, 2#MFC and 1#MEC were calculated as 564, 492 and 388 Ω, respectively. The results were consistent with those of previous research[15]. This indicated that the internal resistance decreased as a result of ionic strength and electrode spacing [32]. The external resistance of the air-cathode MFC was lower than that of the MEC interior resistance, which resulted in a significant increase in the generation of continuous current. Another reason for the large difference in battery resistance may be that the volume of the MEC was much smaller than that of the MFC. The polarization test proved that the reactors were satisfactory for hydrogen production.

3.2. COD and nitrogen removal performance

COD changes over time are shown in Fig. 5. The COD concentrations of 1~4#MFCs gradually increased in the early operation and decreased rapidly afterwards. The reason for this was that the metabolic rate of the microorganisms was lower than that of the self-fermentation of the anode substrate, and the trend was quite the opposite when the microbes fully adapted to the substrate. Tab. 1 shows that the highest COD removal efficiency was 38.9%, and the 2#MFC, 3#MFC and 4#MFC COD removal rates increased by 36.8%, 198.1%, and 247.9%, respectively, compared with the rates of 1#MFC. The results showed that the MEC in series could work with the MFC to enhance the removal efficiency of COD, especially when two MFCs and a MEC were connected in series.

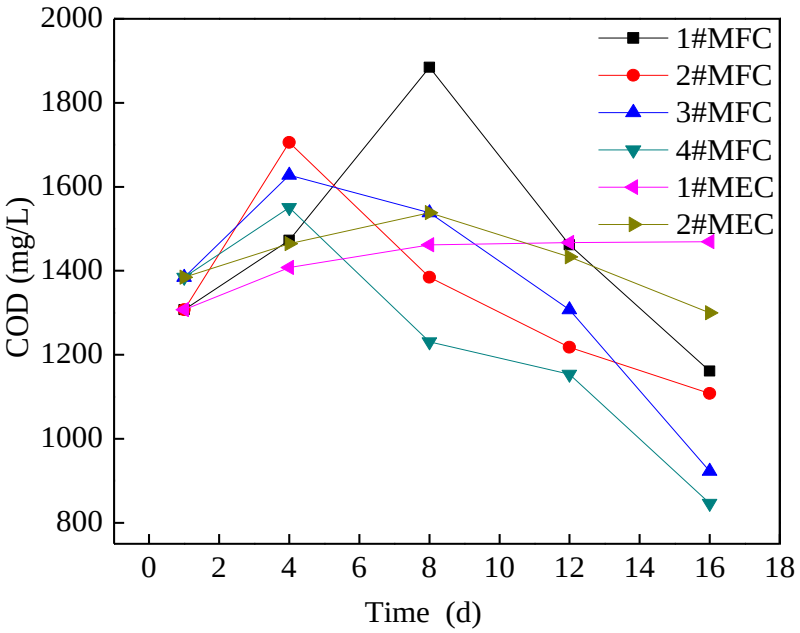

Figure 5. Changes in COD of aged landfill leachate during 16 days of operation

In addition, the removal efficiency of the S_3 system was significantly higher than that of the S_1 and S_2 systems, indicating that the initial COD was positively correlated with COD removal[3]. The overall CE was only 10% for real wastewater in the S_1 system. One of the proposed reasons for the low CE may be the nitrate and sulfate in the real wastewater consuming the electrons. However, the CE

significantly improved in the S_2 and S_3 systems, which indicated that the growth of the exoelectrogenic microorganisms exceeded that of the other microorganisms for substrates, and approximately 40% of the effective electrons in the removed substrate were used for current production [33].

Table 1. Comparison of the COD removal and Coulombic efficiency in several MFCs and MECs of all systems

System	Unit	Removal quantity(mg/L)	Removal Efficiency(%)	Removal Efficiency(%) (compared to 1#MFC)	CE(%)
S_1	1#MFC	146.2	11.2	/	21.2
S_2	2#MFC	200.0	15.3	36.84%	45.3
	1#MEC	-161.5	-12.4	/	/
	3#MFC	461.5	33.3	215.8%	39.8
S_3	4#MFC	538.4	38.9	268.4%	31.3
	2#MEC	84.6	6.11	/	/

It can be calculated from Tab. 2 that the ammonia removal efficiency of a MEC reaches more than 90%, indicating that such aerobic inoculant grew well and was capable of evident biological activity. Thus, the transport of protons from the anode to the cathode became more fluid [34]. The nitrate and nitrite of the six batteries increased to varying degrees, which might be due to the nitrification of NH_4^+ at high concentration and its reaction rate being much faster than that of denitrification, as shown in Equations (9) and (10) [35]. Accordingly, the total inorganic nitrogen removal of the systems was significantly decreased.

$$NH_4^+ + 3/2O_2 = NO_2^- + 2H^+ + H_2O \quad (9)$$

$$NO_2^- + 1/2O_2 = NO_3^- \quad (10)$$

Table 2. Variation of ammonia nitrogen with time during 15 days of operation (all concentration units are mg/L)

System	Unit		Running time (d)				
			1	3	7	11	15
S_1	1#MFC	ammonia	1760	1451	1310	1202	1191
		nitrate	8.33	8.21	7.07	8.04	8.78
		nitrite	0.16	0.18	0.15	0.18	0.19
S_2	2#MFC	ammonia	1760	1379	1276	1163	1121
		nitrate	8.33	5.44	8.96	7.23	6.63
		nitrite	0.16	0.23	0.14	0.22	0.42
	1#MEC	ammonia	1760	1100	257	165	67
		nitrate	8.33	5.02	5.67	4.10	1.32
		nitrite	0.16	0.24	0.30	0.26	0.18

S_3	3#MFC	ammonia	1477	1395	1306	1245	1098
		nitrate	7.56	6.83	6.91	5.45	4.69
		nitrite	0.19	0.25	0.21	0.31	0.27
	4#MFC	ammonia	1477	1384	1297	1153	1115
		nitrate	7.56	7.13	6.68	7.25	7.59
		nitrite	0.19	0.26	0.27	0.31	0.28
	2#MEC	ammonia	1477	986	542	354	135.2
		nitrate	7.56	4.31	3.93	3.25	1.42
		nitrite	0.19	0.22	0.29	0.32	0.20

Without considering the interaction between ammonia and other pollutant degradation in landfill leachate, the rate constant k was calculated based on the concentration variation from 0 to t_n in the process of ammonia nitrogen degradation in Tab. 3. The above result indicated that the degradation of ammonia was a function of time in both systems and thus that the degradation decreased over time. It also showed that the relationship between the rate coefficients of the MFCs over time obeyed Equation (6).

Table 3. Changes in the rate coefficients of ammonia degradation over time during 14 days of operation (k×100/d^{-1})

Unit	Time/d			
	2	6	10	14
1# MFC	9.653	4.924	3.813	2.789
2# MFC	12.198	5.359	4.143	3.222

By using Equation (7) to fit the data in Tab. 4, it can be seen that the correlation coefficient r of the MFCs are above 0.99, and the values of h, Ds, and X are within the range determined by the literature[36]. The results showed that the process of ammonia degradation by MFCs in the systems displayed the characteristics of a fractal kinetic reaction, and the process was not substantially changed after the external resistance was changed to a MEC. In fact, Equation (7) was also able to provide satisfactory simulation of experimental data from other wastewater effect studies.

Table 4. Kinetic parameters of 1#MFC and 2#MFC

Unit	k_0	h	D_s	X	correlation coefficient (r)
1# MFC	0.15	0.62	0.76	3.62	0.9966
2# MFC	0.51	0.68	0.64	4.10	0.9976

3.3. Variations in pH and conductivity during operation

The pH and conductivity in the anode chambers were measured during 16 days of operation (Fig. 6). A low value of pH 9.0 is essential for maintaining the activity of electrogenic microorganisms. From Fig. 6(a), it can be seen that the pH increased in the S_1 and S_2 systems, which result from microbial metabolism generating H^+ and electrons transferring to the cathode to form H_2O. The rate of anode-produced H^+ was higher than that of the cathode consumption when the oxygen was sufficient. The pH values of each unit in the system were similar after treatment, indicating that similar electrochemical reactions were carried out during the reaction process. Combined with the changes in pH, the degradation rate of COD, ammonia, NH_4^+ and others were consumed in large quantities by the reaction with oxygen during the operation of the cell. Therefore, the decrease in ionic concentration in solution led to the decrease in conductivity, as shown in Fig. 6(b).

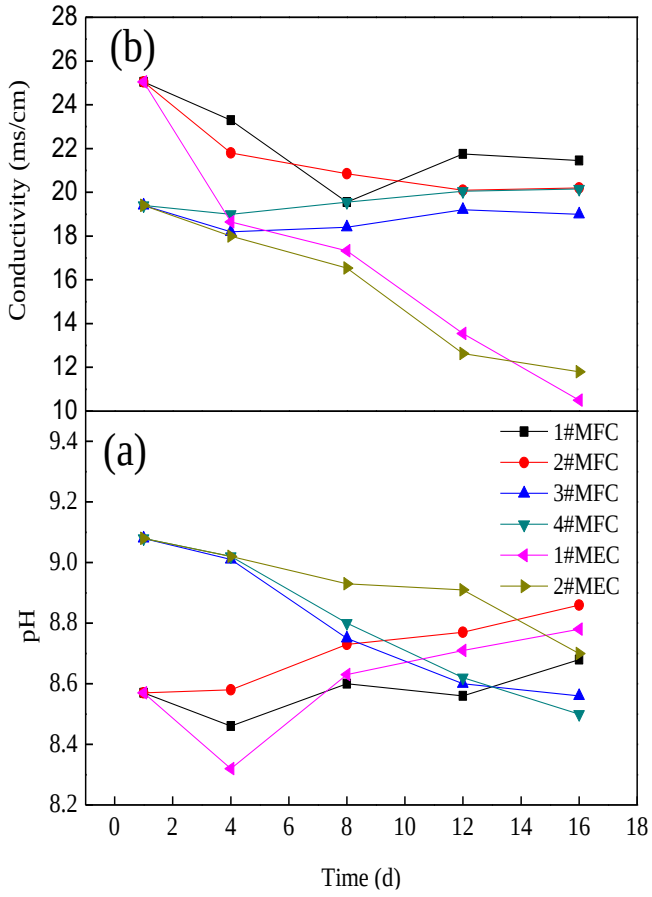

Figure 6. The change in pH with time during 16 days of operation. (b) The change in conductivity with time during 16 days of operation.

4. CONCLUSIONS

In this study, self-sustained MFC-MEC systems were developed for the first time to simultaneously remove pollutants of aged landfill leachate. A high COD and ammonia removal rate of

38.9% and 90% were attained, respectively, and the model kinetic reactions of ammonia could predict the variations of ammonia concentrations in the MFC-MEC system over time. In addition, the results showed that the MFC-MEC system had higher performance (with a voltage of 421 mV and a power density of 1330.7 mW/m^3) than that of independent MFCs.

Overall, it can be concluded that a MFC can be used as a real-time power supply for a variety of electrochemical equipment, such as a MEC, and it is feasible to treat wastewater with MFC-MEC systems. However, a posttreatment process is needed to reduce COD to corresponding standards for discharge, which will continue to be optimized in the next step.

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CONFLICT OF INTEREST
The authors declare that there is no conflict of interest.

References

1. E. Blazquez, D. Gabriel, J. A. Baeza, A. Guisasola, S. Freguia and P. Ledezma. *Sci. Total Environ*., 677 (2019) 175.
2. S. Liang, B. Zhang, J. Shi, T. Wang, L. Zhang, Z. Wang and C. Chen. *Bioelectrochemistry,* 124 (2018) 112.
3. N. Yang, G. Zhan, D. Li, X. Wang, X. He and H. Liu. *Chem. Eng. J*., 356 (2019) 506.
4. J. M. Sonawane, S. B. Adeloju and P. C. Ghosh. *Int. J. Hydrog. Energy,* 42 (2017) 23794.
5. H. T. H. Nguyen, R. Kakarla and B. Min. *Int. J. Hydrog. Energy*, 42 (2017) 29433.
6. S. Puig, M. Serra, M. Coma, M. Cabre, M. Dolors Balaguer and J. Colprim. *J. Hazard. Mater.,* 185 (2011) 763.
7. L. Hao, B. Zhang, C. Tian, Y. Liu, C. Shi, M. Cheng and C. Feng. *J. Power Sources,* 287 (2015) 43.
8. Y. R. He, X. Xiao, W. W. Li, P. J. Cai, S. J. Yuan, F. F. Yan, M. X. He, G. P. Sheng, Z. H. Tong and H. Q. Yu. *Biochem. Eng. J.*, 71 (2013) 57.
9. M. Radha and S. Kanmani. *Curr. Sci.*, 113 (2017) 468.
10. J. M. Sonawane, A. Gupta and P. C. Ghosh. *Int. J. Hydrog. Energy*, 38 (2013) 5106.
11. Y. Li, A. Lu, H. Ding, X. Wang, C. Wang, C. Zeng and Y. Yan. *Electrochem. Commun*., 12 (2010) 944.
12. S.K. Cho, M.E. Lee, W. Lee and Y. Ahn. *Int. J. Hydrog. Energy,* 44 (2019) 2253.
13. Y. H. Jia, J. Y. Choi, J. H. Ryu, C. H. Kim, W. K. Lee, H. T. Tran, R. H. Zhang and D. H. Ahn. *Korean J. Chem. Eng*., 27 (2010) 1854.
14. J. Shen, Y. Sun, L. Hua and J. Yang. *Front. Env. Sci. Eng*., 9 (2015) 1084.
15. M. Sun , G. P. Sheng, L. Zhang, C. R. Xia, Z. X. Mu, X. W. Liu, H. L. Wang, H. Q. Yu, R. Qi ,T. Yu and M. Yang. *Environ. Sci. Technol.*, 42 (2008) 8095.
16. Y. Jiang, M. Su and D. Li. *Appl. Biochem. Biotechnol.*, 172 (2014) 2720..
17. X. A. Walter, C Santoro, J. Greenman and I. Ieropoulos. *Int. J. Hydrog. Energy,* 44(2018)4524.

18. L. Shi, Z. F. Wang, X. L. Chen, G. M. Yang and W. Liu. *Int. J. Electrochem. Sci.*, 14(2019) 7104.
19. T. Catal, S. Yavaser, V. E. Atalay, H. Bermek and S. Ozilhan. *Bioresour. Technol.*, 268 (2018) 116.
20. H.Z. Zhao, Y. Zhang, Y. Y. Chang and Z. S. Li. *J. Power Sources*, 217 (2012) 59.
21. M. A. F. D. Dios, O. Iglesias, E. Bocos, M. Pazos and M. A. Sanromán. *J. Ind. Eng. Chem.*, 20 (2014) 3754.
22. W. Zhao and S. Chen. *Bioresour. Technol. Rep.*, 3 (2018) 185.
23. O. M. Gomaa, S. Fapetu, G. Kyazze and T. Keshavarz. *World J. Microbiol. Biotechnol.*, 33 (2017) 56.
24. C. L. S. Greenberg and A.D.Eaton. Am J Public Health Nations Health, 56(1966)387.
25. C. Xie, L. Xu, T. Peng, K. Chen and J. Zhao. *Chinese Journal of Geochemistry,* 32 (2013) 222.
26. Q. Hu, Y. Xie, C. Feng and Z. Zhang. *Chem. Eng. J.*, 358 (2019) 1471.
27. R. Kopelman. *J. Stat. Phys*., 42 (1986) 185.
28. S. E. Oh and B. E. Logan. *J. Power Sources*, 167 (2007) 11.
29. P. Aelterman, K. Rabaey, H. T. Pham, N. Boon and W. Verstraete. *Environ. Sci. Technol.*, 10 (2006) 3388.
30. G. Zhang, Y. Zhou and F. Yang. *Electrochim. Acta*, (2019).
31. X. Cao, H. Wang, X. Q. Li, Z. Fang and X. N. Li. *Bioresour. Technol.*, 227 (2017) 273.
32. Liu. H, S. A. Cheng and B. E. Logan. *Environ. Sci. Technol*., 14 (2005) 5488.
33. X. Zhang, W. He, L. Ren, J. Stager, P. J. Evans and B. E. Logan, *Bioresour. Technol*, 176 (2015) 23.
34. N. Zhao and I. Angelidaki and Y. Zhang. *Electrochimica Acta*, 281 (2018) 266.
35. X. Zhang, F. Zhu, L. Chen, Q. Zhao and G. Tao. *Bioresour. Technol.*, 146 (2013) 161.
36. R. Kopelman. *Science*, 241(1988) 1620.

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