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Electricity generation during wastewater treatment by a microbial fuel cell coupled with constructed wetland

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Abstract: A membrane-less constructed wetland microbial fuel cell (CW-MFC) is constructed and operated under continuous flow with a hydraulic retention time (HRT) of 2 d. Fed with glucose, the CW-MFC generates a stable current density of over 2 A/m^3 with a resistor of 1 kΩ and has a chemical oxygen demand (COD) removal efficiency of more than 90% after the startup of 2 to 3 d. A series of systems with the electrode spacings of 10, 20, 30 and 40 cm are compared. It is found that the container with the electrode spacing of 20 cm gains the highest voltage of 560 mV, the highest power density of 0.149 W/m^3, and the highest Coulombic efficiency of 0.313%. It also has the highest COD removal efficiency of 94.9%. In addition, the dissolved oxygen (DO) concentrations are observed as the lowest level in the middle of all the CW-MFC reactors. The results show that the more COD is removed, the greater power is generated, and the relatively higher Coulombic efficiency will be achieved. The present study indicates that the CW-MFC process can be used as a cost-effective and environmentally friendly wastewater treatment with simultaneous power generation.

Key words: constructed wetland; microbial fuel cell; wastewater treatment; electricity generation; electrode spacing

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A microbial fuel cell (MFC) is a device using microorganisms as biocatalysts to convert chemical energy to electrical energy for direct bio-electricity generation with simultaneous organic pollutants degradation[1-2]. Given the bacteria adaptation of different organic matters and mild working conditions, MFCs are proposed to be potentially applicable to the wastewater treatment coupled with power output[1,3]. The first demonstration of the MFC solely powered a meteorological buoy[4]. Kaku et al.[5] applied an MFC system to electricity generation in a rice paddy field, suggesting that the paddy-field electricity-generation system was an ecological solar cell in which the plant photosynthesis was coupled to the microbial conversion of organic material to electricity.

Constructed wetlands (CWs) rely upon natural microbial, biological, physical and chemical processes to treat wastewater[6]. Due to their low cost, coexistance with an inner aerobic/anaerobic environment, a high specific surface area of the matrix, a long hydraulic retention time (HRT) etc., CWs are considered to be a potential technology in the removal of refractory organic pollutants. Improving the performance of CWs has been a subject of intensive research over the past decades[7].

The purpose of this work is to construct a membraneless constructed wetland microbial fuel cell (CW-MFC), by converting the lower layer matrix of the CW into the MFC anode electrode and reforming the surface of the CW into the MFC air cathode electrode. Attempts have been made to examine the influence of the distance between two electrodes on performance. This investigation will provide helpful insights into the practical operation of CW-MFCs in the field, with respect to improving both pollutant removal and electricity generation efficiency, and the economy of the CW-MFC.

1 Materials and Methods

1.1 Construction of constructed wetland microbial fuel cell

A CW-MFC is made of a polyacrylic plastic cylinder (30 cm in diameter) with the anode at the bottom and the cathode at the top (see Fig. 1). From the bottom upward, there are layers of gravel (a diameter of 3 to 6 mm), granular activated carbon (GAC) (the diameter of 3 to 5 mm, a specific area of 500 to 900 m^2/g and a packing density of 0.45 to 0.55 g/cm) as the anode (depth of 10 cm). The stainless steel mesh (12 mesh) coupled with GAC is used as the cathode (a depth of about 2.5 cm). The volume of the whole container is 35.3 L with a total liquid volume of 12.4 L, while the volume of the anode is 7 L with an anode liquid volume of 2.1 L. The stainless steel mesh is made with a thickness of 0.3 cm and a diameter of 30 cm. *Ipomoea aquatica* is grown through the upper layers as the CW plants. Electrodes are connected to a circuit using titanium wires (1 mm in diameter) passing through the middle of a granule bed with an external resistance of 1 kΩ, and epoxy is used to seal metals exposed to the solution. Nine sampling ports with

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an 8 mm inner diameter are arranged at intervals of 5 cm throughout the height of the reactor.

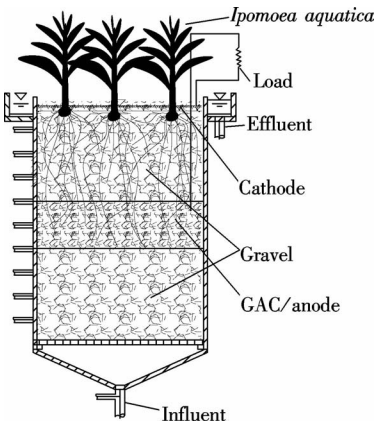

Fig. 1 Schematic diagram of constructed wetland microbial fuel cell system

1.2 System operation

The CW-MFC is inoculated with a 4 L concentrated anaerobic sludge resulting in a mixed liquor suspended solid (MLSS) of 20 g/L and fed with the artificial wastewater (AW)[1] containing glucose (200 mg/L) through a peristaltic pump. The systems are operated in a continuous mode with an inflow of 6.36 mL/min, resulting in a hydraulic retention time of 2 d. The systems are operated for more than 3 months to obtain a stable performance before evaluation under each system working condition.

1.3 Monitoring and calculations

The dissolved oxygen (DO) concentration is monitored by a DO meter (DO-31P, DKK-TOA Co., Japan). COD_{Cr} is determined by the standard methods using chromate as the oxidant [8].

The voltage across the external resistor of 1 kΩ is automatically collected every 10 min using a data acquisition system (USB120816, Hytek Automation, Inc., Shanghai, China). The circuit current is converted from the recorded voltage according to Ohm's law described by Hong et al[9]. The current density is determined based on the wet anode volume. Power ($P = IV$) and Coulombic efficiency are evaluated as previously described[1, 10].

2 Results and Discussion

2.1 System startup and power production

A CW-MFC is constructed to electrochemically enrich active microbes using anaerobic activated sludge as an inoculum with a 20 cm distance between the anode and the cathode. Fig. 2 shows that the current density starts to increase after approximately 20 h. Then, the current constantly increases for 2 to 3 d to reach a maximum current density of over 2 A/m^3 with a 1 kΩ resistor, indicating the realization of the system startup. The current is maintained stably for over half a year under the given conditions, and the initial open circuit potential is about 0.75 V. The effluent COD decreases gradually from over 200 mg/L to less than 20 mg/L during the enrichment and an efficiency of more than 90% is achieved in the end. The results show that the CW-MFC can be used for simultaneous wastewater treatment and power generation.

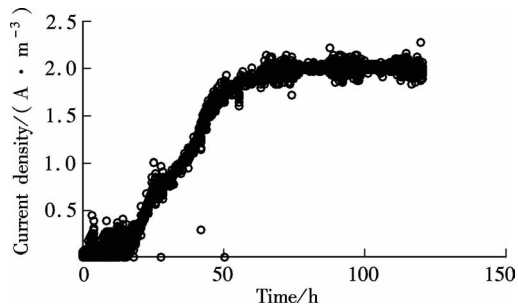

Fig. 2 Startup of a CW-MFC with a 20 cm electrode spacing

2.2 Effect of spacing between the electrodes

The CW-MFCs are operated with a fixed external resistance of 1 kΩ at different distances varying from 10, 20, 30 to 40 cm between the anode and the cathode. Fig. 3 shows that the voltage profile is a function of time under different electrode spacings. The voltage is measured and plotted under the stable operation. The system with an electrode spacing of 20 cm achieves a higher voltage of 560 mV, in comparison to the system with an electrode spacing of 30 cm, which achieves a voltage of 520 mV. The lower voltage is observed at spacings of 10 and 40 cm, recorded as 440 and 420 mV, respectively. As the electrode spacing keeps increasing, electricity generation increases first and then starts to drop. This might be caused by the distribution of DO and the consumption of COD throughout the container.

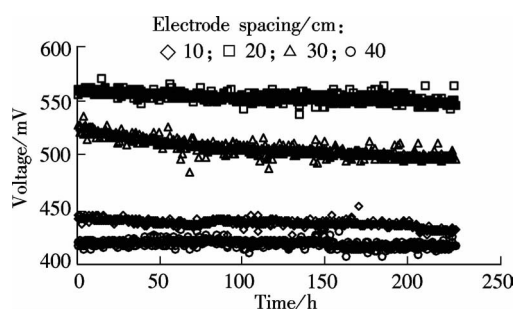

Fig. 3 Effect of electrode spacing between two electrodes on voltage production in the CW-MFCs

As shown in Fig. 4, the DO concentrations are observed along the side of the CW-MFCs from bottom-up with the lowest level in the middle of all the reactors. The system with the 20 cm electrode spacing obtains the lowest DO of 0.425 mg/L in the height of 25 cm where the anode region is located and the highest DO of 4.725 mg/L in the surface where the cathode region is located. In contrast, for

the systems with electrode spacings of 30, 10, and 40 cm, the lowest DO of 0.535, 0.595 and 0.515 mg/L, respectively, are observed in the middle height of each system while the highest DO of 4.465, 4.295 and 3.75 mg/L, respectively, are observed in the corresponding surface cathode region. In addition, the DO in the anode regions are observed to be 0.770 to 1.135, 0.595 to 1.230 and 0.790 to 1.365 mg/L, respectively. Therefore, the system with the electrode spacing of 20 cm gains the most severe anaerobic anode in the lower layer and the most sufficient aerobic cathode region in the surface layer, which is in accordance with the best power generation performance. Oxygen dissolved in the water declines with the height of the reactors due to organic pollutant degradation. However, the oxygen release of the plant rhizosphere coupled with the air diffusion from the surface area can increase the DO concentration in the upper layer where plants are planted. This is demonstrated by the profiles of the DO concentrations. It can be speculated that the DO concentration of both electrodes is one of the important limiting factors, as the anode rejects oxygen for promoting metabolism of the exoelectrogens, whereas the cathode needs dissolved oxygen as the terminal electron acceptor for the reaction of electrons with protons[11-14].

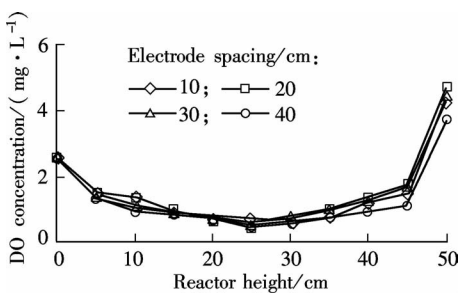

Fig. 4 Effect of electrode spacing between two electrodes on the vertical profile of DO concentration in the CW-MFCs

Tab. 1 shows the power densities, COD removals, and Coulombic efficiencies of the systems. The lowest effluent COD concentration of 11 mg/L, the highest COD removal efficiency of 94.9%, the highest power density of 0.149 W/m^3, and the highest Coulombic efficiency of 0.313% are achieved in the system with a 20 cm electrode spacing. On the other hand, as illustrated in Fig. 5, the COD removal from the bottom to the surface of the reactors for each system decreases two times, one for the bottom section and the other for the anode layer, suggesting that the system gains efficient organic matter degradation and the anode compartment has more remarkable oxidization of organic compounds. High removal in an anode compartment is assumed for the large surface area of the GAC which has high adsorption capacities both for organic compounds removal and microorganism adhesion. In an MFC, microbes on the anode oxidize substrates generating electrons and protons. Electrons are then transferred to the anode which passes through an external circuit producing current. Protons migrate through the electrolyte to the cathode, where they combine with oxygen and electrons to form water [1,11]. Therefore, the more the COD is removed, the greater the power is generated, and the relatively higher Coulombic efficiency may have. The current yield is less than 1% throughout the study, which is much lower than those of common MFCs. This can be explained by the large volume of the container. Also a major part of the electrons available from the fuel oxidation is not recovered as current, as indicated by the Coulombic efficiency, because electrons are consumed at the anode reducing oxygen diffusion from the upper region (see Fig. 4). As shown in Tab. 1, the power density is higher in the system with the electrode spacing of 20 cm than those of the others, implicating that the mass transfer between two electrodes is a limiting factor. It is caused by the resistance of the matrix between two electrodes when proton transfers from the anode to the cathode, and it is also caused by the low bioactivity of the exoelectrogens inhibited by oxygen in the anode as discussed above. In this sense, a CW-MFC should be constructed to place the electrodes at an optimal distance.

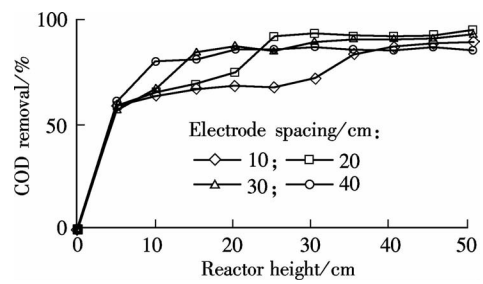

Fig. 5 Effect of electrode spacing between two electrodes on COD removal in the CW-MFCs

Tab. 1 Power outputs of CW-MFCs with different electrode spacings

Electrode spacing/cm	Current generation/mA	Power density/(W·m^{-3})	COD removal/%	Coulombic efficiency/%
10	0.44	0.092	89.6	0.261
20	0.56	0.149	94.9	0.313
30	0.52	0.129	93.3	0.296
40	0.42	0.084	85.4	0.261

2.3 Performing CW-MFC in practical applications

On the basis of this study, the membrane-less air cathode MFC can be well integrated with the constructed wetlands. At the present stage, economic and technological challenges are barriers for the MFC application in wastewater treatment[12,15]. By contrast, the integrated membrane-less CW-MFC has an advantage of low capital and operational costs due to no use of the proton exchange membrane. Although the cost of the CW-MFC cannot be predicted with any certainty, a reasonable mar-

ket price is estimated to be approximately 1 200 yuan/m^2 with 150 yuan/m^2 for gravel, 300 yuan/m^2 for stainless steel mesh, and 750 yuan/m^2 for GAC. The implementation of the CW-MFC can generate electricity during treatment helping to reduce the economic burden of treatment.

3 Conclusion

A membrane-less constructed wetland microbial fuel cell (CW-MFC) is constructed and the influence of spacing between two electrodes on the performance is examined. Using glucose as a substrate, the device generates a stable current density of over 2 A/m^3 connected to a 1 kΩ resistor. A series of systems with electrode spacings of 10, 20, 30 and 40 cm are compared and the system performs best under the spacing of 20 cm. It is found that the more COD is removed, the greater power is generated, and a relatively higher Coulombic efficiency is achieved. Extensive studies are recommended to optimize the operational parameters in lab scale and develop more effective and applicable systems in future engineering studies.

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微生物燃料电池耦合人工湿地处理废水过程中的产电研究

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摘要:构建了一种连续流无膜人工湿地-微生物燃料电池,其水力停留时间为 2 d. 系统以葡萄糖为基质启动 2 ~ 3 d 后,在外接电阻为 1 kΩ 时,其稳定输出电流密度高于 2 A/m^3,同时, COD 去除率大于 90%. 比较了阴阳极间距为 10, 20, 30 和 40 cm 的系统. 当间距为 20 cm 时,系统的产电电压、库仑效率和能量密度皆最高,分别为 560 mV,0.313% 和 0.149 W/m^3,且 COD 去除率也为最高,达到 94.9%. 此外,各系统中的 DO 最低浓度均出现在装置中部. 结果表明,COD 去除率越高,系统产能越高,因而库仑效率也越高. 人工湿地-微生物燃料电池系统作为一种低成本及环境友好的污水处理同步产电技术显示出实际应用潜力.

关键词:人工湿地;微生物燃料电池;废水处理;产电;阴阳极间距

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