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Short communication

Power generation enhancement in novel microbial carbon capture cells with immobilized *Chlorella vulgaris*

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ABSTRACT

With the increasing concerns for global climate change, a sustainable, efficient and renewable energy production from wastewater is imperative. In this study, a novel microbial carbon capture cell (MCC), is constructed for the first time by the introduction of immobilized microalgae (*Chlorella vulgaris*) into the cathode chamber of microbial fuel cells (MFCs) to fulfill the zero discharge of carbon dioxide. This process can achieve an 84.8% COD removal, and simultaneously the maximum power density can reach 2485.35 mW m^{-3} at a current density of 7.9 A m^{-3} and the Coulombic efficiency is 9.40%, which are 88% and 57.7% greater than that with suspended *C. vulgaris*, respectively. These enhancements in performance demonstrate the feasibility of an economical and effective approach for the simultaneous wastewater treatment, electricity generation and biodiesel production from microalgae.

1. Introduction

Microbial fuel cells (MFCs) are promising biological technologies that can treat wastewater with simultaneous electricity recovery [1–3]. More recently, microbial carbon capture cell (MCC) has emerged, which is a new sustainable form of MFCs that the carbon dioxide generated from organic wastewater treatment can be further converted to useful biomass with photosynthetic creature, achieving simultaneous electricity generation, CO_2 sequestration, wastewater treatment and biomass production (e.g., biodiesel) [4–6].

Till now, there are still very few attempts introducing microalgae into the cathode of MFCs to fulfill carbon dioxide reduction and electricity generation [5,6]. And what's more, the microalgae used are all in suspension, thus it is difficult to separate the biomass from the culture media to obtain products of high added value such as biodiesel. Immobilized microalgae can solve the separation problem as well as provide the advantages of high algae cell density, fast reaction speed, strong resistant to hazardous matter, stable and flexible operation [7,8]. With light illumination, the microalgae in the cathode chamber can utilize CO_2 from the anode as carbon source for photosynthesis and produce oxygen, which acts as electron acceptor for electricity generation. Therefore, the application of immobilized microalgae as the supplier of oxygen in MCC might have benefits both on microalgae separation and MFC performance.

In the present study, for the first time, we evaluated the feasibility of using immobilized *Chlorella vulgaris* as the cathode oxygen supplier for electricity generation in a dual-chamber MCC equipped with carbon fiber cloth cathode assembly. To address the advantages, a comparison of electricity generation performance was carried out between the MCCs using immobilized and suspended *C. vulgaris*. Moreover, operations of MCCs in different COD loads and microalgae inoculation concentrations were performed to evaluate the MCCs with immobilized *C. vulgaris*.

2. Experimental

2.1. Preparation of immobilized algae beads and media

C. vulgaris (FACHB 31) was purchased from Freshwater Algae Culture Collection, Institute of Hydrobiology, Chinese Academy of Sciences (Wuhan, China) and grew in a Blue-Green medium (BG11).

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The concentrations of nutrients were (gram per liter of deionized water): 1.5 $NaNO_3$, 0.04 K_2HPO_4, 0.075 $MgSO_4{\cdot}7H_2O$, 0.036 $CaCl_2{\cdot}2H_2O$, 0.006 citric acid, 0.006 ferric ammonium citrate, 0.001 $EDTANa_2$, 0.02 Na_2CO_3 and 1 mL trace metal solution. The trace metal solution consisted of (milligram per liter of deionized water): 2.86 H_3BO_3, 1.86 $MnCl_2{\cdot}4H_2O$, 0.22 $ZnSO_4{\cdot}7H_2O$, 0.39 $Na_2MoO_4{\cdot}2H_2O$, 0.08 $CuSO_4{\cdot}5H_2O$, and 0.05 $Co(NO_3)_2{\cdot}6H_2O$.

The free *C. vulgaris* were cultivated in batch cultures containing BG11 culture medium and maintained under standard conditions in an illuminating incubator with a 12:12 L:D cycle supplied with 1600 lux cool-white fluorescent light illumination, keeping at a constant temperature of 25 ± 1 °C. All the glassware and BG11 culture medium were pretreated by sterilizing method. Immobilized *C. vulgaris* was prepared as previously described [9]. The algae cells in logarithmic growth phase were harvested by centrifugation at 3500 rpm for 10 min. The cell residues were washed with sterilizing deionized water and resuspended in BG11 culture medium to form certain concentrated algal suspension. The algal suspension was then mixed with sodium alginate solution to yield a mixture of algal alginate suspension. This mixture was dropped into calcium chloride solution using a syringe to form uniform algal beads. The algal beads were left in calcium chloride solution certain time for hardening, and then rinsed by deionized water.

2.2. Microbial carbon capture cell design and setup

The MCC was constructed similarly with that in Ref. [5], composed of two identical double-chambers MFCs made of Plexiglas. As shown in Fig. 1, each cell (400 mL) was made by bolting two half circular columns together with a piece of cation exchange membrane (56 cm^2, Ultrex CMI7000, AnkeTech Membrane Separation Engineering & Technology Co., Ltd., China) as the separator. Each chamber had a vent at the top of the reactor. The two vents were connected through a tube. Carbon dioxide generated from wastewater treatment in the anode was piped through the tube into the catholyte for microalgae production via photosynthesis. The anode was made of carbon felt while the cathode was carbon fiber cloth (6 cm × 6 cm, Jilin Carbon Plant, China) containing 0.1 mg cm^{-2} Pt catalyst. The anode chamber was inoculated with anaerobic sludge (TEDA Sewage Treatment Plant, Tianjin) and a 50 mM phosphate buffered nutrient solution (PBS: NH_4Cl 0.31 g L^{-1}, KCl 0.13 g L^{-1}, $NaH_2PO_4{\cdot}2H_2O$ 3.32 g L^{-1}, $Na_2HPO_4{\cdot}12H_2O$ 10.36 g L^{-1}; trace minerals 12.5 ml L^{-1}; vitamins 5 ml L^{-1}) containing 1.0 g L^{-1} glucose as substrate. The external resistance was fixed at 1000 Ω and the anode pH was adjusted to 6.9–7.0 while the cathode pH was 7.20.

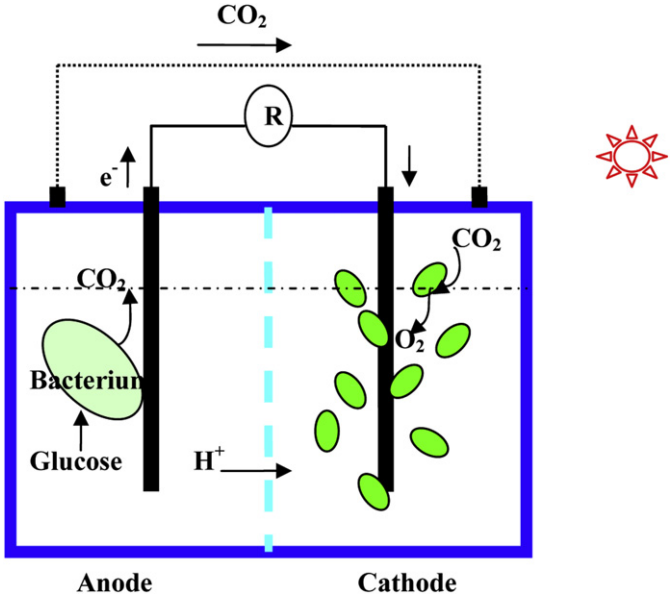

Fig. 1. Schematic illustration of the functional principles of the PAMFC.

2.3. Analysis and calculations

The cell mass of suspended algal was determined by optical density measurements on an UV759 spectrophotometer (Shanghai Precise Scientific Instrument Corporation, Ltd., China) at 683 nm. Optical density was converted to cell number using a previously prepared calibration curve (all cell concentrations were given in cell number). For the immobilized algal, they were pretreated as follows before measurement: immobilized beads were dissolved in sodium citrate solution, and then centrifuged at 3500 rpm for 5 min, and finally the cell residues were resuspended in BG11 culture medium to form certain concentrated algal suspension for the subsequent optical density determination.

Voltage outputs were recorded every 30 min using a data acquisition system (PISO-813, ICPDAS Co., Ltd.). After stable voltage outputs were observed, polarization curves were obtained by

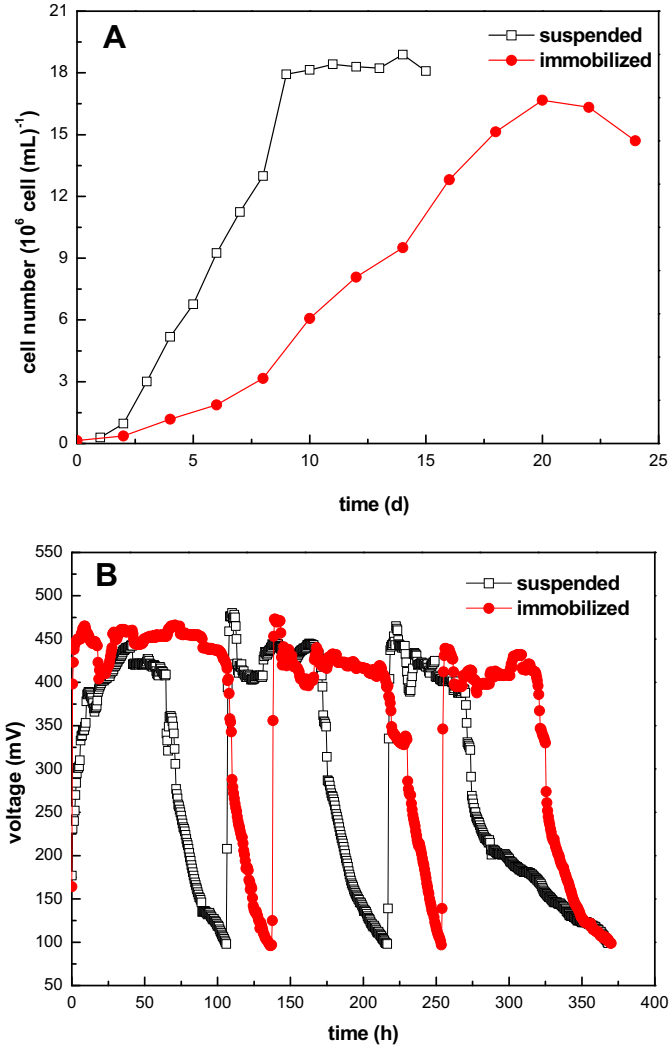

Fig. 2. Growth curves (A) and voltage output (B) in MCCs with immobilized and suspended *C. vulgaris*.

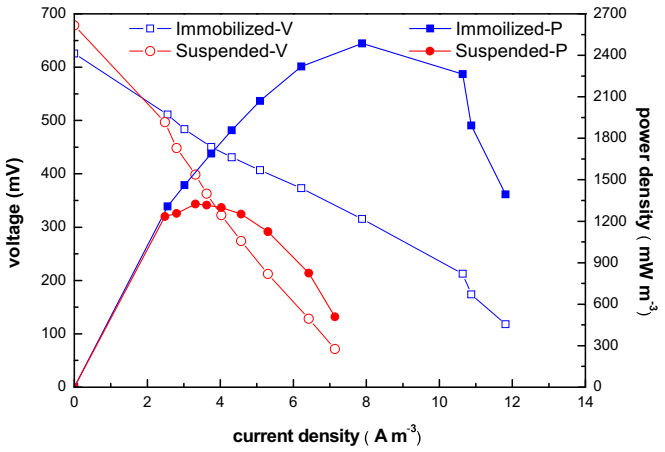

Fig. 3. Polarization and power generation of MCC with immobilized and suspended *C. vulgaris*.

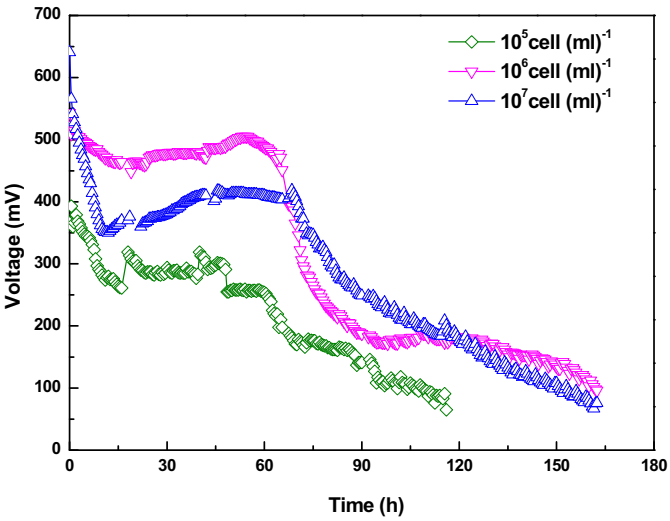

Fig. 4. Effect of initial inoculation concentrations on voltage output.

varying the external resistances from 1000 to 50 Ω. Power density and current density were calculated based on the effective volume of anode chamber. The Coulombic efficiency (CE) was calculated as previously described [10]. The chemical oxygen demand (COD) was measured using the closed reflux spectrophotometric method on a commercial COD detector (HACH, DRB 200, DR/890 Colorimeter, USA).

3. Results and discussion

Fig. 2A shows the growth curves for suspended and immobilized cell of *C. vulgaris*, both following an exponential model. Obviously, the growth rate of the immobilized *C. vulgaris* was slower than that of the suspended. The logarithmic growth phase in suspended culture (7 d) was much shorter than that in the immobilized cell (12 d), suggesting that the immobilized cells can keep the living cells metabolically active as long as possible. This might be one possible reason why the steady voltage output in MCCs with immobilized possessed a much longer period (Fig. 2B), since it benefited to the absorbing and utilizing the carbon dioxide to sustain stable electricity output. It should be noted that the concentration of *C. vulgaris* cells within beads did not show significant differences compared to the suspended cells. For the immobilized *C. vulgaris*, the maximum concentration reached 16.7×10^6 cell $(mL)^{-1}$ after 20 d, while 18.3×10^6 cell $(mL)^{-1}$ for the suspended after 11 d.

When the immobilized and suspended *C. vulgaris* were separately added into the MCCs at a concentration of 1000 mg L^{-1} COD in anode chamber, a steady voltage generation was rapidly achieved (Fig. 2B). It produced a steady voltage 464 mV for a period of 107 h in MCC using immobilized *C. vulgaris*, while 443 mV for 64.5 h in MCC using suspended *C. vulgaris* in the first period. Following this steady output, the voltage generation gradually decreased to 100 mV over a period of 30 h. When the voltage fell to 100 mV, the anode chamber was replaced with the same wastewater (initial COD 1000 mg L^{-1}), and the voltage increased rapidly to the maximum (460 mV). However, the voltage plateau shortened gradually in the following cycles, in average, 83 h plateau period with the immobilized *C. vulgaris* compared to 59 h with the suspended. In the last cycle, the difference on voltage in two systems was weakened, which might be accounted for the alga cells in the suspended system deposited and attached on the cell and reactor wall. In three consecutive cycles, the COD removal efficiencies in MCC with immobilized *C. vulgaris* were all higher than 80%. Thus it could be concluded that the immobilized *C. vulgaris* as the electron acceptor supplier in MCCs was feasible and the electricity generation performance was superior to the suspended accounting for the extended and stable voltage output.

Fig. 3 shows the polarization and power density curves using immobilized and suspended *C. vulgaris* in the cathode of a two-chamber MCC. The maximum power density with immobilized *C. vulgaris* was 2485.35 mW m^{-3}, which was 88% higher than that with suspended (1324.68 mW m^{-3}). As listed in Table 1, the internal resistance with immobilized *C. vulgaris* (165 Ω) accounted for only one-third of that with the suspended (476 Ω). The maximum power density was obviously increased with the decrease of internal resistance, suggesting that ohmic resistance might be the limiting step of the present system. The maximum Coulombic efficiency with immobilized *C. vulgaris* (9.40%) was 57.7% higher than that with the suspended *C. vulgaris* (5.96%). All these results proved that using immobilized *C. vulgaris* in MCC had many advantages over using suspended *C. vulgaris* such as its high power density, high Coulombic efficiency as well as low internal resistance.

In principle, the overall biochemical reactions that occurred at the anode and cathode chamber of MCCs are as follows (using glucose as the sample wastewater):

Anode chamber:

$$C_6H_{12}O_6 + 6H_2O \rightarrow 6CO_2 + 24H^+ + 24e^- \quad (1)$$

Table 1
Comparison of electricity generation and wastewater treatment efficiency with immobilized and suspended *C. vulgaris*.

	Resistance (Ω)	Plateau period (h)	Maximum power density (mW m^{-3})	Maximum voltage (mV)	Coulomb efficiency (%)	COD removal efficiency (%)
Suspended	476	83	1324.68	443	5.96	84.2
Immobilized	165	59	2485.35	464	9.40	84.8

Table 2
The electricity generation and wastewater treatment efficiency at different anodic COD loadings.

COD ($mg\,L^{-1}$)	Period (h)	Maximum voltage (mV)	Total electricity generated (10^5 C)	Power density ($mW\,m^{-3}$)	Coulomb efficiency (%)	COD removal efficiency (%)
500	25	406	0.65	1194.39	6.68	80.2
1000	137	464	1.92	2485.35	9.40	84.8
2000	268.5	470	2.96	2265.03	7.53	81.4

Cathode chamber:

$$nCO_2 + nH_2O \xrightarrow{\text{algae}+h\nu} (CH_2O)_n(\text{biomass}) + nO_2 \quad (2)$$

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \quad (3)$$

Comparably, oxygen can be reduced (Eq. (3)) immediately to achieve electricity generation; the photosynthesis reaction (Eq. (2)) usually becomes the limiting step. According to the two-film theory, mass transfer of CO_2 from the gas phase to the cell phase occurs through different stages; many related studies confirmed that CO_2 transport was mainly controlled by resistance offered by the liquid film [11]. In case of immobilization, *C. vulgaris* was embedding in the matrix, gas production by photosynthesis and respiration promoted the beads floating on the gas–liquid interface, which reduced the liquid-phase mass transfer resistance and was favorable to the adsorption and utilization of CO_2. In contrast, suspended *C. vulgaris* tended to adhere to the wall or deposited at the bottom of the reactor, mass transfer resistance and reactor internal resistance both increased. What's more, some alga grew on the surface of cathode, which might also increase the proton and oxygen mass transfer resistance. These caused the decrease in the efficiency of electricity generation with suspended *C. vulgaris*.

Under the other similar conditions of photosynthesis (e.g., light illumination, temperature), the microalgae inoculation concentrations and COD loads (that means carbon dioxide loads) would be two important factors influencing performance. Fig. 4 shows the effect of microalgae inoculation concentration on the voltage output. After the immobilized *C. vulgaris* beads were added into the cathode chamber, the change of the voltage included three stages: the rapidly increasing and linearly decreasing stage, the stable stage, and the slowly declining stage. During the first stage, there was some dissolved oxygen in fresh culture medium and the immobilized *C. vulgaris* was in adjustment period, the voltage increased rapidly first and then decreased. After 14 ± 2 h, the voltage outputs gradually stabilized at maximum values of 319, 505, 414 mV for the three initial inoculation concentrations, with slight fluctuations. Stable voltage outputs indicated that the immobilized *C. vulgaris* grew well in MCCs. The maximum voltage output with 10^6 cell $(mL)^{-1}$ inoculation concentration was much higher in comparison with the other two inoculation concentrations. In general, the lower initial inoculation density, the lower final cell numbers. Thus the lower inoculation concentration (e.g. 10^5 cell $(mL)^{-1}$) might not produce enough oxygen as electron acceptor, which led to a poor power density. However, a very high inoculation concentration (e.g. 10^7 cell $(mL)^{-1}$) was also not suitable because the larger number of cells at the surface of the beads would cause a greater self-shading effect to the cells inside the beads that limited the cells growth and increased the mass transfer resistance [12,13].

The removal rate of COD in the anode will induce different carbon dioxide generation. Thus the electricity generation and wastewater treatment efficiency at different COD loads (500, 1000, 2000 $mg\,L^{-1}$) were investigated. As shown in Table 2, the COD removal efficiency indicated no considerable difference with the initial COD loading, which was consisted with the report by Tam that the immobilized cells increased the cell retention time within bioreactors and kept higher metabolic activity [14]. The total electricity generated was observed increased with the initial COD loading. This was reasonable since a high CO_2 release would promote the photosynthesis, and thus the generation of oxygen as electron acceptor. However, the power density and Coulombic efficiency did not present positive correlation to the COD loading, and the maximum values obtained at anodic initial COD of 1000 $mg\,L^{-1}$. This fact might be attributed to the adverse effect of microalgae photosynthesis under high carbon dioxide concentration [15]. These results indicated that MCC with immobilized *C. vulgaris* could continuously keep excellent bioactivity for the treatment of wastewater with relative high initial COD loading.

4. Conclusions

The immobilized *C. vulgaris* as the cathode supplier of oxygen was investigated for efficient electricity generation in MCC. The comparison demonstrated that the performance of MCC with immobilized *C. vulgaris* was superior to that suspended. The maximum power density of 2485.35 $mW\,m^{-3}$ generated from the MCC with immobilized *C. vulgaris* could be 88% higher than that (1324.68 $mW\,m^{-3}$) produced from the MCC using the suspended *C. vulgaris*. Meanwhile, the Coulombic efficiency of the MCC with immobilized *C. vulgaris* could reach 9.40%. This work indicated that MCCs with immobilized *C. vulgaris* had the potential to simultaneously produce extended and stable bioelectricity and fulfill wastewater purification.

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References

[1] B.E. Logan, Water Sci. Technol. 52 (2005) 31.
[2] P. Alterman, K. Rabaey, P. Clauwaert, W. Verstraete, Water Sci. Technol. 54 (2008) 9.
[3] M.H. Zhou, M.L. Chi, J.M. Luo, H.H. He, T. Jin, J. Power Sources 196 (2011) 4427.
[4] X.X. Cao, X. Huang, P. Liang, N. Boon, M.Z. Fan, L. Zhang, X.Y. Zhang, Energy Environ. Sci. 2 (2009) 498.
[5] X. Wang, Y.J. Feng, J. Liu, L. He, C. Li, N. Li, N.Q. Ren, Biosens. Bioelectron. 25 (2010) 2639.
[6] P.B.T.B.S. David, T. Hilde, V.M.H. Hubertus, J.N.B. Cees, Appl. Microbiol. Biotechnol. 81 (2008) 659.
[7] J. Jin, L.H. Yang, S.M.N. Chan, T.G. Luan, Y. Li, N.F.Y. Tam, J. Hazard. Mater. 185 (2011) 1582.
[8] L.E. De-Bashan, Y. Bashan, Bioresour. Technol. 101 (2010) 1611.
[9] A. Ruiz-Marin, L.G. Mendoza-Espinosa, T. Stephenson, Bioresour. Technol. 101 (2010) 58.
[10] S. Cheng, H. Liu, B.E. Logan, Environ. Sci. Technol. 40 (2006) 2426.
[11] H. Markl, Biotechnol. Bioeng. 19 (1997) 1851.
[12] P. Chevalier, J. De la Noüe, Biotechnol. Lett. 7 (1985) 3950.
[13] H. Uemoto, H. Saiki, Appl. Environ. Microbiol. 66 (2000) 816.
[14] N.F.Y. Tam, P.S. Lau, Y.S. Wong, Water Sci. Technol. 30 (1994) 369.
[15] S.-Y. Chiu, C.-Y. Kao, T.-Z. Huang, C.-J. Lin, S.-C. Ong, C.-D. Chen, J.-S. Chang, C.-S. Lin, Bioresour. Technol. 102 (2011) 9135.