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Enhanced performance of microbial fuel cell at low substrate concentrations by adsorptive anode

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ABSTRACT

In this study, a microbial fuel cell (MFC) with granular activated carbon packed anode (GAC-MFC) is developed and compared with a MFC with granular graphite packed anode (GG-MFC), to evaluate the adsorptive effect of the granular activated carbon anode on MFC's performance. The current output of GAC-MFC (11.1 mA, 18.1 mA and 21.6 mA) is much higher than that of GG-MFC (4.87 mA, 12.5 mA and 17.9 mA) at low substrate COD concentrations (~50, ~100 and ~200 mg/L) when a low external resistance (20 Ω) and high circulation flow rate (20 mL/min) are applied. The half-saturation constant (K_s) of GAC-MFC is about half as much as that of GG-MFC, suggesting that GAC-MFC has more affinity for anode substrate and deliver better kinetic performance than GG-MFC. Internal resistance distribution shows that mass diffusion resistance of GAC-MFC is at least 50% lower than that of GG-MFC when the substrate COD is ~50 mg/L, indicating that the adsorptive effect of granular activated carbon packed anode helps to effectively facilitate mass transfer at low COD concentrations. Otherwise, the substrates adsorbed on GAC surface also serve to buffer the impact of COD concentration plummeting in bulk solution.

1. Introduction

Microbial fuel cell (MFC) utilizes bacteria as catalyst to degrade organic materials in water and in-situ converts the chemical energy into electricity [1,2]. The potential prospect to recover energy in the process of wastewater treatment makes MFC a promising technology of both economic and environmental benefits [3–5]. Typical domestic wastewater contains tremendous amount of potential energy (~1.23 kWh/m^3) in the form of biodegradable organic materials, which can be more efficiently captured by MFCs than other anaerobic treatment technologies [6]. However, the concentration of organic matter in domestic wastewater is usually much lower than that in normal anode medium of laboratorial MFCs [7,8]. Especially in rainy regions, the chemical oxygen demand (COD) concentration of influent domestic wastewater being under 200 mg/L is normally encountered [9]. Mass transfer in anode chamber will be greatly attenuated by such low substrate concentration, leading to a severely-restrained MFC performance for energy recovery from domestic wastewater. Enhancing turbulence of bulk solution on anode surface, such as stirring electrolyte or increasing solution flow rate is normally employed to improve mass transfer in laboratorial MFC research. Mass-transfer favored electrode configurations like the fluidized bed anode or the flow-through anode were also introduced to MFC and proved feasible to reinforce substrate transport throughout the whole anode structure [10,11]. More recently, transient-state operation mode of MFC, in comparison with steady-state mode, was performed to improve mass transfer within and near electrode biofilms by lowering the energy barrier for ion migration [12]. However, these methods usually require energy-consuming operations or additional automatic-control accessories. The efficiencies and costs of these methods should be re-examined when the MFC is applied to treat large amount of domestic wastewater with low COD concentration at municipal wastewater treatment plants.

Biological granular activated carbon (BGAC) filter bed has been widely used to deal with the effluent of sewage plant or drinking water source over the past few decades [13]. Due to the adsorptive capacity of granular activated carbon (GAC), BGAC is capable of efficiently removing trace organic pollutants such as pharmaceuticals and personal care products, or endocrine disruptor compounds in water [13–15]. Researches also revealed that the biofilm grew on GAC particles, compared with that on non-adsorbing medias such as glass bead and sand, showed a much higher biodegradation rate towards these low concentration pollutants [13,16,17]. These facts suggest that employing GAC packed bed as MFC anode may be an effective way to promote MFC's performance by enhancing anode mass transfer when treating low COD

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concentration of influent domestic wastewater. GAC packed anode in previous MFC studies and research interests were mostly focused on its high surface area for bacteria adhesion and relatively low capital cost [18–21]. However, the possible adsorptive benefit of GAC packed bed anode on MFC performance has not yet been specifically noticed, especially when the substrate concentration was relatively low.

In this study, GAC and granular graphite (GG) were respectively packed in the anode chamber of MFC, designated as GAC-MFC and GG-MFC. To reveal the adsorptive effect of GAC packed anode on MFC's electricity production, the stable output current of two MFCs were compared at different COD concentrations with various external resistances and circulation flow rates. During this process, half-saturation constant (K_s) was obtained from Monod equation fitting to reflect the bacteria's affinity for substrate and the kinetic biodegradation performance. The composition of internal resistance, including ohmic resistance, charge transfer resistance and mass diffusion resistance, were further studied to demonstrate the main intrinsic factor resulting in the different performance between two MFCs.

2. Experimental

2.1. Preparation of anode materials and MFC construction

GAC (2∼3 mm in diameter, 4∼6 in length, Beijing Chunqiudingsheng Environmental Science and Technology Co. Ltd. China) and GG (2∼3 mm in diameter, 4∼6 mm in length, Sanye Carbon Co., Ltd China) were both washed for 24 h in 20% HCl solution to remove organic matter from the surface and then washed with deionized water for an hour.

Two-chamber rectangle MFCs were constructed in the experiment. The anode and cathode chamber had the same volume of 100 mL (2 cm thickness, 50 cm^2 cross section) and were separated by a cation exchange membrane (CMI-7000, Membranes International, USA). Two MFCs' anodes were filled with GAC and the other two were filled with GG. The void fraction of GAC and GG packed anode were 51% and 53%, and the bulk density of them were 700 kg/m^3 and 1130 kg/m^3, respectively. Two pieces of titanium mesh were respectively placed on the cation exchange membrane and blind plate in the anode chamber as current collectors. In order to minimize the influence of cathode performance on MFCs so as to better highlight the effect of different anodes, potassium ferricyanide was used as chemical cathode since it had little overpotential and could deliver a stable and paralleled performance among all MFCs in the experiment. Five graphite felt cubes ($1 \times 2 \times 4$ cm) were stacked in the cathode chamber as electrode material to increase reaction area. A graphite rod with a diameter of 6 mm was inserted through graphite felt cubes to provide external contact. Prior to use, graphite rods and graphite felt cubes were treated with 2 M HCl for 24 h and then rinsed with deionized water to remove impurities. A saturated calomel electrode (SCE, 0.242 V vs. standard hydrogen electrode (SHE), Leici, China) was inserted into anode chamber as the reference electrode.

2.2. Anolyte and catholyte

The anolyte was prepared by dissolving 0.06 ∼1.1 g CH_3COONa and 0.31 g NH_4Cl in 1.0 L phosphate buffer solution (KH_2PO_4: 4.4 g/L, $K_2HPO_4 \cdot 3H_2O$: 3.4 g/L) pH = 6.8–7.0. The conductivity of the anolyte remained 8.14∼8.92 ms/cm throughout the experiment. The catholyte contained 16.46 g/L potassium ferricyanide in the same phosphate buffer solution (PBS). The anolyte of all MFCs were circulated from the same 5 L reservoir to ensure all MFCs operated at a parallel and stable COD concentration, while all catholyte were circulated from the same 2 L reservoir. All the solutions above were pre-deoxidized by nitrogen-stripping before used, and were recirculated by a peristaltic pump (BT100-1L, Baoding Longer Precision Pump Co., Ltd. China) to achieve well-mixed conditions in the anode and cathode chambers.

2.3. MFCs start-up and operation

The MFCs were inoculated with mixed bacterial cultures collected from an MFC operated in our laboratory for over 1 year using sodium acetate as carbon source. During start-up period, the MFCs were operated in fed-batch mode with anolyte containing 1.1 g/L sodium acetate (COD ≈ 800 mg/L). The external resistance was set at 1000 Ω. Anolyte and catholyte were renewed every 3 days. All MFCs were considered to successfully start up until stable cell potential was repeatedly produced for 3 consecutive batch cycles.

After start-up, sodium acetate concentration in anolyte was varied from 1.1 to 0.06 g/L with corresponding COD concentration ranging from ∼800 to ∼50 mg/L to examine the electric current generation as a function of substrate COD concentrations. At each COD concentration, different external resistances (100 Ω, 50 Ω, 30 Ω, and 20 Ω) and different circulation flow rate (2 and 20 mL/min) were applied to test the electricity generation performance of GAC-MFC and GG-MFC. Both MFCs ran at each external resistance and circulation flow rate for at least 2 weeks until the maximum current output remained unchanged for 2 cycles, so as to ensure all MFC anodes reached adsorption equilibrium status and delivered a stable current output at a certain COD concentration. Afterward, the anolyte in anodes and external reservoir were entirely pumped out and refilled with a lower COD concentration anolyte for the next COD period operation as described above. In order to maintain the stability of COD concentration during each COD period, anolyte in all MFCs and the reservoir was refreshed every 24 h. Polarization tests were conducted once the output cell potential stabilized at each COD concentration. Biomass and electrochemical impedance spectroscopy (EIS) analysis were performed when MFCs ran stably at the COD concentration of ∼800 and ∼50 mg/L.

In order to evaluate the stability of current generation in GAC-MFC and GG-MFC, influent COD concentration perturbation test was conducted. When all MFCs presented stable output cell potential with 100 Ω external resistance at ∼800 mg/L COD concentration at 20 mL/min of circulation flow rate, the original anolyte medium in the 5 L reservoir was immediately substituted by a similar PBS except that sodium acetate was replaced by KCl to keep an identical anolyte conductivity. All MFCs were then switched to continuous inflow mode. The responses of output cell potential and effluent COD concentration over time in GAC-MFC and GG-MFC were monitored. All MFCs operated at an ambient temperature of 25 ± 1.5 °C in all of the above experiments.

2.4. Analysis and calculation

The cell potential (U, mV) across the external resistor (R, Ω) was recorded every 1 min using a data acquisition system (DAQ2213, ADLINK, China). The electric current (I, mA) was calculated according to ohm's law: *I&9552;U/R*. The current data in the figures were calculated from the average of current output of two parallel MFC reactors.

Electric current (I, mA) was modeled as a function of substrate concentration (S, mg/L) using a Monod-type equation [22,23]:

$$I = \frac{I_{max} S}{K_S + S} \quad (1)$$

Where I_{max} is the maximum electric current (mA) and K_s is the half-saturation constant (mg/L).