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Membrane filtration biocathode microbial fuel cell for nitrogen removal and electricity generation

Guangyi Zhang[a], Hanmin Zhang[a,*], Yanjie Ma[b], Guangen Yuan[a], Fenglin Yang[a], Rong Zhang[a]

[a] Key Laboratory of Industrial Ecology and Environmental Engineering (MOE), School of Environmental Science and Technology, Dalian University of Technology, Linggong Road 2, Dalian 116024, China
[b] Environmental Management College of China, Hebei Road 73, Qinhuangdao 066004, China

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ABSTRACT

Conductive materials with attached biofilms, were used as membrane filtration biocathodes to filter the effluent and supply electrons for denitrification. Stainless steel mesh and carbon felt were employed to fabricate membrane modules, and the two MFC systems were termed as M1 and M2, respectively. High effluent quality was obtained with M1 and M2 in terms of turbidity, COD and ammonium. In M1, no bioelectrochemical denitrification took place, while nitrate decreased from 35.88 ± 4.15 to 27.33 ± 5.32 mg-N/L through the membrane in M2, causing a removal efficiency of $23.3 \pm 6.5\%$ with respect to cathodic nitrate. The denitrification ceased without electricity. The maximum power densities of M1 and M2 were 121 and 1253 mW/m^3, respectively. Micrococcus bacteria and rod-shaped bacteria covered the surface of carbon felt and fewer bacteria were found on stainless steel mesh. According to fluorescence in situ hybridization, the putative bacteria affiliated with *Paracoccus* genus and *Pseudomonas* spp. dominated in the interior biofilm on carbon felt for denitrification. Results demonstrate that the carbon felt system can perform bioelectrochemical denitrification to polish the effluent.

1. Introduction

Microbial fuel cells (MFCs), a promising approach to wastewater treatment, can convert organic substrates contained in wastewaters into electricity [1]. Since nitrate reduction was proved in biocathode MFCs, bioelectrochemical denitrification has attracted increasing attentions [2–4]. Compared to the conventional nitrification/denitrification process for nitrogen removal, bioelectrochemical denitrification can uncouple carbon source and nitrate spatially, making the denitrification an energy-recovering process. The specific MFCs have been established to remove various nitrogen compounds and recover electricity [5–9]. Also, the related processes are well understood in terms of biofilm stratification, microbial communities and analysis of electron fluxes [10–12]. A dual-cathode MFC can carry out successive nitrification and bioelectrochemical denitrification in their respective cathodes [13]. In a rotating biocathode MFC, as much as 25% of nitrogen removal resulted from bioelectrochemical denitrification [14].

MFCs may not be sufficient as a stand-alone wastewater treatment technology to achieve high effluent quality. Membrane bioreactors (MBRs) as a compact treatment technology has several advantages, such as high biomass content for pollutants removal and low effluent turbidity by membrane filtration. More importantly, MBRs provide better retention of slowly growing microorganisms (like nitrifiers, enhancing nitrification) [15]. The idea of combining MFCs with MBRs for wastewater treatment has recently been considered. The systems in which membranes simultaneously functioned as filtration components and cathodes were developed to treat wastewater and recover energy [16–19]. However, previous MFC-MBR studies focused on cathodic oxygen reduction, rather than cathodic denitrification and nitrogen removal. There is little knowledge about the effectiveness of membrane cathode for bioelectrochemical denitrification. Thus, the feasibility of bioelectrochemical denitrification using membrane cathodes as electron donor for nitrogen removal needs to be investigated.

A novel bioreactor combining MFC and MBR was designed. Anode anaerobic chamber primarily removed majority of organic substrates, decreasing the organic load of the next aerobic chamber (i.e. MBR/cathode chamber) and establishing a more suitable environment for nitrifiers. In the cathode, cake layers (biofilm)

* Corresponding author. Tel.: +86 411 84706173; fax: +86 411 84708083.
E-mail addresses: zhanghm@dlut.edu.cn, zhhanmin@126.com (H. Zhang).

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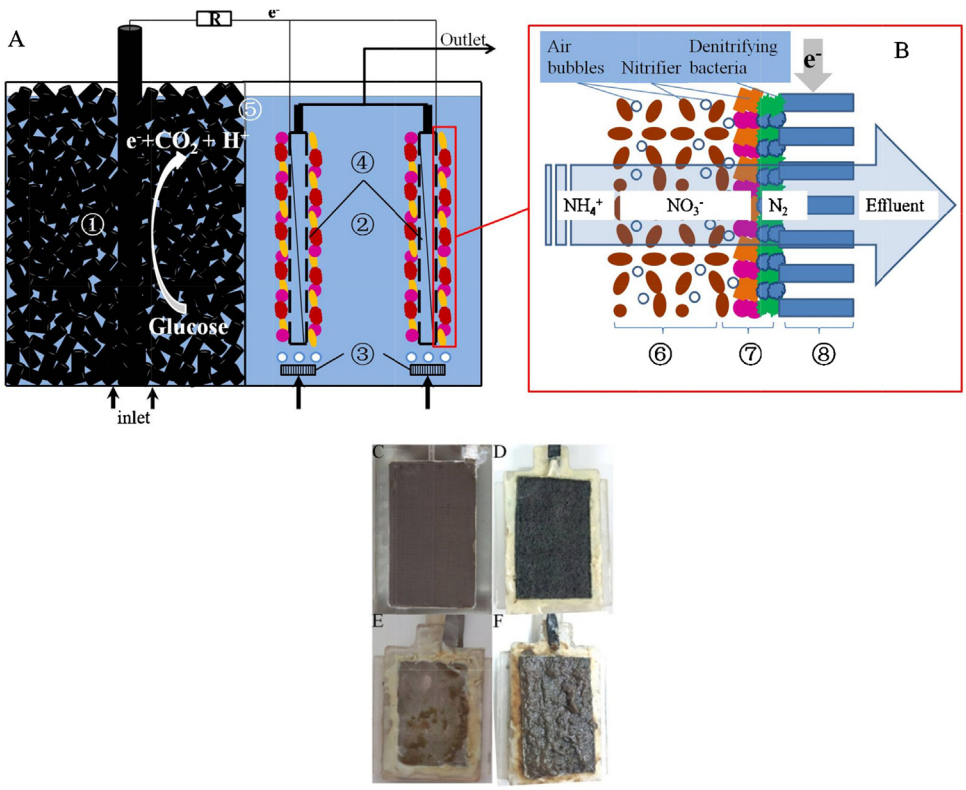

Fig. 1. (A) Schematic of the integrated system, (B) ammonium evolution in the cathode chamber, (C, E) raw/used SS mesh membrane module and (D, F) raw/used carbon felt membrane module. (1) Anodic chamber; (2) cathodic chamber; (3) air diffusers; (4) membrane modules (biocathodes); (5) stainless steel mesh separator; (6) suspended sludge; (7) biofilm; (8) membrane material (stainless steel mesh or carbon felt).

on the membranes simultaneously filtrated the effluent and performed denitrification. The aim of this study was to investigate the feasibility of simultaneous filtration and bioelectrochemical denitrification by employing conductive membrane modules as the cathodes. Two different matrix electrode materials (stainless steel mesh and carbon felt) were investigated in terms of treatment efficiencies of wastewater, electrochemical performances, catalytic behaviors, biofilm morphologies and community structures.

2. Materials and methods

2.1. Construction of MFC reactor

The MFC setup is illustrated in Fig. 1. The total volume of the reactor was 960 mL (16[L] × 12[H] × 5[W]). The reactor was equally divided into two chambers (an anodic anaerobic zone and a cathodic aerobic zone) by a Plexiglas baffle (10 cm high), with a 2 cm gap on the top for completing electrical circuit and mass flow. The anode chamber (480 mL) was filled with granular graphite (3–5 mm diameter) and a graphite rod (8 mm diameter) was used as the electron collector (Sanye Carbon Co.), leaving a net liquid volume of 200 mL. A mm-sized stainless steel mesh (SS mesh) was located at the gap to hold granular graphite. The cathode chamber (480 mL) was constructed like a membrane bioreactor with a net liquid volume of 320 mL. Two gas diffusers were placed at the bottom of cathode chamber. The whole experiment was divided into two stages, stage I (1–93 days) for SS mesh MFC (M1) and stage II (94–143 days) for carbon felt MFC (M2). The used SS mesh was 1000 mesh, corresponding to about 13 μm pore size. In each stage, two membrane modules were installed through the experiments and the effective filtration area of each module membrane was 30 cm^2. The modules were connected with copper wires across an external resistance to receive electrons from the anode. The joints were sealed with superglue to prevent potential corrosion. The MFC was shielded from light to prevent phototrophic reactions.

2.2. Operation conditions

The MFC was operated at a room temperature (20–25 °C) under a continuous feeding regime. Aerobic sludge from the Lingshui Ziguang wastewater treatment plant (Dalian, China) was used to inoculate the MBR (cathode chamber), and the anodic inoculum was taken from another MFC reactor in the laboratory. The feeding medium contained (1 L of tap water): 6 g Na_2HPO_4, 3 g KH_2PO_4, 0.5 g NaCl, 0.1 g $MgSO_4{\cdot}7H_2O$, 0.015 g $CaCl_2$, and 1 mL trace nutrient solution [20]. COD and ammonium were supplied to the medium in the form of glucose and ammonium chloride according to demand. Each feed had a final pH of around 7.1 and a conductivity of around 5 mS/cm. The effluent was pumped out constantly with a fixed membrane flux of 11 L/(m^2 h), resulting in a hydraulic retention time (HRT) of ~9.6 h for the whole system (3.9 h for anode and 5.7 h for cathode, respectively). A pressure sensor was interfaced with the computer for measuring transmembrane pressure (TMP).

2.3. Electrochemical and chemical measurements

The voltages generated in the experiment were collected using a data acquisition system (PISO–813, ICP–DAS) [21]. Power density (P, mW/m^3) was normalized by the liquid volume of the cathodic chamber according to $P = V_{cell}^2/(R_{ex}V_r)$, where V_{cell} (V) was the voltage across the external resistance at a defined time interval, R_{ex} (Ω) the external resistance, and V_r (m^3) the cathodic solution volume. Coulombic efficiencies (CEs) based on COD removal (between the influent and anodic effluent) and/or nitrate reduction (between cathode and the final effluent) were calculated according to the previously described method [22,23]. Following stable power generation, a stepwise change of R_{ex} was performed to obtain polarization and power curves using a three-electrode system. The specific method was: opening circuit for 60 min was initiated, and then the voltage over R_{ex} at 30 min interval per resistor was recorded. Cyclic voltammograms were carried out using a CHI760E electrochemical workstation (CH Instruments, Chenhua Instrument Co., China) at a scan rate of 5 mV/s. At least 2 cycles were performed and the last cycle was shown. $Hg/HgCl_2$ reference electrode (+0.242 V vs. SHE) was employed in all electrochemical tests, mounted in the cathode.

The concentrations of COD and nitrogen compounds were measured according to standard methods [24]. The samples were filtered through a 0.45 μm membrane before analysis. The standard parameters pH, conductivity and dissolved oxygen (DO) were determined potentiometrically with a digital, portable multiline meter (Multi 3430, SET F, WTW, Germany). The diameter of suspended sludge was measured by a Malvern laser particle size analyzer (Mastersizer 2000, UK) and D10 meant the grain size than which 10% of the gains were finer.