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Biotechnology Reports

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Evaluation of limiting factors for current density in microbial electrochemical cells (MXCs) treating domestic wastewater



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ARTICLE INFO

Article history:
Received 21 July 2014
Received in revised form 10 September 2014
Accepted 11 September 2014
Available online 20 September 2014

Keywords: Alkalinity Biodegradability Particulates Domestic wastewater Microbial Electrochemical cells

ABSTRACT

This study quantitatively assessed three limiting factors for current density in a microbial electrochemical cell (MXC) treating domestic wastewater: (1) buffer concentration, (2) biodegradability, and (3) particulates. Buffer concentration was not significant for current density in the MXC fed with filtered domestic wastewater (180 mg COD/L). Current density reduced by 67% in the MXC fed with filtered sewage having similar COD concentration to acetate medium, which indicates poor biodegradability of soluble organics in the wastewater. Particulate matters seriously decreased current density down to 76%, probably due to the accumulation of particulates on biofilm anode. Our study quantitatively showed that buffer concentration does not limit current density much, but biodegradability of soluble organics and fermentation rate of particulate matters in domestic wastewater mainly control current density in MXCs.

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1. Introduction

Microbial electrochemical cells (MXCs) that include microbial fuel cells, microbial electrolysis cells, and microbial desalination cells show a promise as sustainable wastewater treatment due to resource recovery (e.g., electric power, H_2 , CH_4 , water, H_2O_2 , etc.). However, substantial energy loss in MXCs would trade off the profits of resource recovery, especially for large scale systems, and hence existing studies did not show clear benefits of MXCs, as compared to other anaerobic biotechnologies (e.g., anaerobic membrane bioreactors) [23]. In wastewater treatment perspectives, MXCs still have significant merit of no aeration requirement. Anode-respiring bacteria (ARB) that oxidize organic wastewater and transfer electrons to the anode in MXCs are anaerobes, which mean that MXCs can treat wastewater without significant oxygen supply. Aeration costs account for 30-50% of operating and maintenance costs in municipal wastewater treatment facilities [33]. For instance, MXCs application to sewage treatment would save \sim \$1.5 billion annually in Canada.

To improve current density is crucial for MXC application to domestic wastewater treatment, since it represents wastewater treatability. Volumetric current density (A/m³ of anode chamber) is equivalent to organic loading rate (kg COD/m³ d), one of the most

important design and operating parameters in wastewater treatment facilities. Organic loading rate typically ranges from 0.9 to 1.2 kg COD/m³ d in activated sludge [24,31], while it depends on the concentration of chemical oxygen demand (COD) in given domestic wastewater. MXCs should produce $\sim 150 \,\text{A/m}^3$ of volumetric current density (equivalent to $\sim 1 \ kg \ COD/m^3 \ d)$ for sewage treatment, while subsequent polishing step seems essential to meet wastewater effluent standards. Lefebvre et al. (2013) [18] reported high current density of 110 A/m³ in an MXC from domestic wastewater, mainly due to high packing density of anodes in a small anode chamber (15 mL of working volume). In comparison, most of literature employing relatively large MXCs has commonly shown small current density from 0.4 to 43 A/m³ for domestic wastewater [1,9,35,36]. Feng et al. [9] recently reported the maximum current density of 0.43 A/m³ in a large-scale MXC (1 m³), despite of using carbon brush anode, which implies the challenge of achieving high current density in large MXCs treating sewage.

There are many parameters that are able to influence current density in MXCs, including microbial community on biofilm anode, pH, temperature, oxygen, separator, cathodic catalysts, biodegradability of substrate, alkalinity, biofilm conductivity and so on [7,8,20,21,26,28,30,34]. Microbial community would show functional redundancy consistently once kinetically-efficient ARB are well proliferated on biofilm anode [1,29]. The limitations in cathodic reaction or ohmic resistance can be alleviated by using better materials or optimizing MXC design [6,20]. However, characteristics of wastewater are uncontrollable factors that can

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substantially affect the substrate-utilization rate of ARB and current density in MXCs [17,27]. When municipal wastewater is compared to acetate medium, there are three key differences: [1] biodegradability, [2] alkalinity, and [3] presence of particulates. Literature have commonly reported that the biodegradability of the wastewater was very poor, as compared to acetate, which seems to account for low current density in sewage-treating MXCs [1,9,36]. However, it is daring to conclude that poor biodegradability of domestic wastewater mainly decreases current density in the MXCs because the other two important factors of alkalinity and particulates can also limit current density in the MXCs. For instance, it is well known that low alkalinity can acidify a part of biofilm anode, which can seriously decrease current density in MXCs [12,34]. Alkalinity concentration in the domestic wastewater, however, is extremely lower than that in the acetate medium having 50–200 mM phosphate buffer [1,11,25].

Particulates are also present in municipal wastewater and they can directly block the formation of ARB biofilm on the anode, reducing current density in MXCs [14,34]. Alternatively, competitive microorganisms (e.g., methanogens) present in particulates can divert substrate electrons to other electron sinks than coulombs [4,28], which can finally dilute ARB biofilm density on the anode and decrease current density and coulombic efficiency in MXCs. There are, however, no studies that quantitatively evaluate the three limiting parameters separately in MXCs treating domestic wastewater, while those factors co-exist in the wastewater.

The goal of this study is to identify a main limiting factor for current density in MXCs treating domestic wastewater. To exclusively assess biodegradability of domestic wastewater, and the effects of alkalinity and particulates on current density, a dual-chamber MXC was operated with acetate medium, and filtered and raw domestic wastewater as alkalinity concentration was varied.

2. Material and methods

2.1. Microbial electrochemical cell (MXC) configuration

A dual chamber microbial electrochemical cell (MXC) was used for this study. Briefly describing MXC design, two cylindrical plexiglass tubes consisted of anode and cathode chambers, and anion exchange membrane was placed between the two chambers. By integrating carbon fibers with a stainless steel current collector, the anode surface area per membrane was increased at $1600\,\mathrm{m^2/m^2}$ approximately, along with electrode distance less than 1 cm. The literature [2] provides detailed information on MXC configuration; current density was expressed per the surface area of the membrane for simplicity in this study.

2.2. Inoculation, feed, and start-up

Recycle activated sludge (RAS) was collected from the Waterloo Wastewater Treatment Plant (Waterloo, Ontario, Canada) to inoculate the MXC. 15 mL of RAS was added to the anode chamber, the chamber was sparged with ultra-pure nitrogen (99.999%) for 20 min, and then acetate medium (25 mM sodium acetate) was fed to the MXC as the electron donor and carbon source. The composition of the acetate medium was (per litre of $18.2\,\mathrm{M}\Omega\,\mathrm{cm}$ MilliQ water) 2050 mg CH₃COONa, 2274 mg KH₂PO₄, 11,678 mg Na₂HPO₄·12H₂O, FeCl₂·2H₂O 3.255 mg, $18.5\,\mathrm{mg}$ Na₂S·9H₂O, 840 mg NaHCO₃, 37 mg NH₄Cl, 25 mg MgCl₂·6H₂O, 6 mg MnCl₂·4H₂O, 0.1 mg CuSO₄·5H₂O, 0.1 mg Na₂WO₄·2H₂O, 0.1 mg NaHSeO₃, 0.01 mg CaCl₂·2H₂O, 0.5 mg ZnCl₂, 0.1 mg AlK(SO₄)₂, 0.1 mg H₃BO₃, 0.1 mg Na₂MoO₄·2H₂O, 0.2 mg NiCl₂, 5 mg EDTA, 1 mg CO (NO₃)₂·6H₂O, 0.2 mg NiCl₂·6H₂O. To mitigate contamination

during experiments the medium was autoclaved and then sparged with the ultra-pure nitrogen for 30 min before being fed to the MXC. Medium pH was constant at 7.5 ± 0.15 .

A reference electrode (Ag/AgCl reference electrode, MF-2052, Bioanalytical System Inc. USA) was placed within \sim 1 cm distant from the anode to fix the anode potential at -0.4 V vs. Ag/AgCl reference electrode using a potentiostat (BioLogic, VSP, Gamble Technologies, Canada). The cathode chamber was filled with tap water in which hydrogen gas is produced. Under this potentiostat mode, cathode potential responds to current density and overpotentials in the MXC [17,35]. The applied voltage (cathode potential-anode potential) was constant at $0.85 \pm 0.5 \, \text{V}$ during the acclimation phase. Electrode potentials and currents were recorded at every 60 s using EC-Lab for windows v 10.23 software in a personal computer connected with the potentiostat. The MXC was mixed at 150 rpm using a multi-position magnetic stirrer (Model 650, VWR International Inc. Canada), and operated in a temperature-controlled room at 25 ± 1 °C. The MXC was run with 25 mM acetate medium in batch mode for over 3 months until steady-state current density $(18 \pm 2 \text{ A/m}^2 \text{ of membrane})$ was achieved. Then, the MXC was operated in continuous mode. Acetate medium or domestic wastewater (filtered and raw) was fed to the MXC at a flow rate of 37.5 mL/h using a cartridge-type peristaltic pump (Master Flex® L/S digital drive, Model 7523-80, Cole-Parmer, Canada) to maintain hydraulic residence time (HRT) of 8 h in the anode chamber.

2.3. Experimental conditions

MXC performance and effluent quality were evaluated with different feed conditions at a fixed HRT of 8h. First, buffer concentration effect was assessed with acetate medium $(2.7 \pm 0.2 \,\text{mM}, 175 \pm 10 \,\text{mg} \,\text{COD/L})$ amended with 50 mM or 5 mM bicarbonate buffer (Run 1 and 2). Then, wastewater biodegradability against acetate medium was investigated at Run 3. To avoid particulate (i.e., SS) effects on current generation and exclusively assess the biodegradability of the wastewater against acetate, the wastewater was filtered and fed to the MXC. Particulates were separated from the wastewater in two filtration steps using glass fiber filters (Fisherbrand glass fiber filter, 1.6 µm, G6, Cat. No. 09-804-55 A) and glass microfiber filters (Whatmann microfiber filter, 1.2 µm, GF/C, Cat. No. 1822-070). The average soluble COD (SCOD) for the domestic wastewater was close to the COD concentration of the acetate medium. Table 1 summarizes the characteristics of the domestic wastewater. At Run 4, buffer effect on current density was re-assessed in the MXC fed with the filtered wastewater having 50 mM bicarbonate buffer. At Run 5, the MXC was operated with the acetate medium having 5 mM bicarbonate buffer to recover current density. After that, SS collected from the wastewater were added to the acetate medium at Run 6. To collect SS, the domestic wastewater was centrifuged at 5000 rpm for 15 min with a centrifuge (Beckman TJ-6 Tabletop Centrifuge, Beckman Coulter Inc. CA, USA). The SS was added to the acetate medium (L) having $230 \pm 28 \text{ mg SS/L}$, which is close

Table 1The characteristics of domestic wastewater.

| Total chemical oxygen demand (TCOD) | $660\pm10mg/L$ |
|---------------------------------------|--------------------------------|
| Soluble chemical oxygen demand (SCOD) | $185\pm20\text{mg/L}$ |
| Total suspended solids (TSS) | $260\pm15mg/L$ |
| Volatile suspended solids (VSS) | $225\pm10mg/L$ |
| Volatile fatty acids (VFAs) | <5 mg COD/L |
| рН | 8 ± 0.05 |
| Alkalinity | $200 \pm 50 mg/L$ as $CaCO_3$ |
| | |

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