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Optimization of a baffled-reactor microbial fuel cell using autotrophic denitrifying bio-cathode for removing nitrogen and recovering electrical energy

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ABSTRACT

Microbial fuel cells (MFCs) gained emerging attention as an eco-friendly pathway for recovering electrical energy and treating wastewater. The electrochemical catalysis of cathodic reactions was one of the important issues for practical application of MFC technology. Here, it was disclosed the performance of a stake up-flow baffled-reactor MFC in which autotrophic denitrifying microorganisms catalyzed the cathodic reactions, reducing nitrate to nitrogen gas. The maximum power produced in this bio-electrochemical system (BES) was $15 \pm 0.4\,W\,m^{-3}$ NCV (net cathode volume) at an optimum cathodic nitrate loading rate (CNLR) of $150\,g\,NO_3^-\text{–N}\,m^{-3}$ NCV d^{-1} using acetate as electron donor. A maximum of $76.5 \pm 0.5\,A\,m^{-3}$ NCV current and $97.7 \pm 1.8\%$ cathodic coulombic efficiency obtained at this CNLR. Autotrophic denitrification achieved on this bio-cathode was $148.3 \pm 1.4\,g\,N\,m^{-3}$ NCV d^{-1} utilizing biological anode. The efficiency of autotrophic denitrification and current generation of this BES was inhibited by the accumulation of denitrifying by-product, nitrite (NO_2^-), at concentrations beyond $3.59 \pm 0.8\,mgNO_2^-\text{–N}\,L^{-1}$ in the cathodic stream. The results demonstrated that this bio-cathode based baffled-reactor MFC had a good potential to eliminate abiotic cathodes and thus, made the system more economical and sustainable alternative for wastewater treatment, nitrogen removal and energy generation.

1. Introduction

In recent years, microbial fuel cell (MFC) has attracted attention as an exciting technology for one-step conversion of biochemical energy into electricity [1–4]. The bacterial biofilm developed on the anode electrode acts as a conductive bio-medium [5]. The conductive bio-medium transfers the produced electrons (e^-) from metabolic reactions carried out inside it into the adjacent electrodes [5]. Due to the difference in redox-potential between the anodic metabolic oxidation and the cathodic chemical reduction, electrons travel from the anode towards the cathode via external resistance. Protons are formed at the anode and dispersed through the membrane to the cathodic surface, where they associate with e^- and O_2 to form H_2O. The continuous movement of electrons and the difference in potential energy between the electrodes generate current and voltage, respectively [6–9].

Electro-chemically active (EA) microbes can produce electrons by their cellular metabolic or extra cellular bio-chemical reactions. The biofilm of EA microbes are utilizing as bio-catalyst on the anode electrode. Therefore, the innovation of biological anode has been recognized as an economical and sustainable process for MFC [4,10,11]. In contrast, the chemicals utilized as a cathode assisting electrolyte in MFC would require continuous regeneration in case of

Abbreviations: MFC, microbial fuel cell; BES, bio-electrochemical system; EA, electro-chemically active; CNLR, cathodic nitrate loading rate; NCV, net cathodic volume; PEM, proton exchange membrane; E′, Redox potential; TCV, total cathodic volume; TAV, total anodic volume; NAV, net anodic volume; HRT, hydraulic retention time; COD, chemical oxygen demand; SS, suspended solid; VSS, volatile suspended solid; TDS, total dissolved solid; TN, total nitrogen; Ac^-, acetate; OCV, open circuit voltage; CE, coulombic efficiency; TOC, total organic carbon; Ac, acetate concentration; R_{int}, internal resistance; R_{ext}, external resistance; P_v, power density; E_{cell}, cell potential generated.

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Table 1
Findings of the recent investigations on denitrifying bio-cathode based MFC.

MFC-Configuration	NCV	max P	E_{cell}	I	OCV	max CE	Denitrification rate	Denitrification efficiency	Anode Substrate	Ref.
	(L)	($W m^{-3}$ NCV)	(V)	($A m^{-3}$ NCV)	(V)	(%)	(g NO_3^-–N m^{-3} NCV d^{-1})	(%)		
Tubular MFC	0.244	8	0.214	35	0.3–0.36	–	146	0.093[a]	NaAc	[16]
Rectangular- reactor MFC: nitrification in external vessel	0.182	34.6 ± 1.1	2.870[a]	99.3 ± 0.4	–	72.2 ± 0.6	345 ± 2	58.9	NaAc	[23]
Rectangular-reactor MFC: nitrification in the cathode chamber	0.2	10.25[a]	0.202	50.73[a]	0.216 (half-cell)	101.7 ± 0.2	175 ± 2[a]	94.1 ± 0.9	NaAc	[24]
Membrane-less MFC	1	0.0712	11.85[a]	0.844	–	152 – 475	186	36.7	NaAc	[25]
Cubical-reactor MFC	0.125	0.19	0.78	0.244[a]	0.63	18.6	–	4.0	NaAc	[7]
Baffled channel plug-flow reactor (Length: Width = 17.25)	0.6	15 ± 0.4	0.21 (6.5 Ω)	53.8 ± 1.6	0.624	97.7 ± 1.7	148.3 ± 1.4	98.6 ± 0.7	NaAc	[Current study]

NCV: Net Cathodic Volume, P: Power, E_{cell}: Cell Potential, I: Current, OCV: Open Circuit Voltage, CE: Coulombic Efficiency, NaAc: Sodium Acetate, a: Calculated values.

ferric iron and hexacyanoferrate [1,12]. Likewise, abiotic catalysts used on cathode were costly in case of platinum, cobalt, rhodium, or manganese [1,6,13,14]. The abiotic catalysts also became fouled by intermediate by-products (such as, sulfide, hardness and alkalinity producing compounds, etc.) resulting from the biological or chemical activity inside the wastewater [15]. That's why, the abovementioned chemical and abiotic cathodes could be unsustainable in the long run because of their replenish behavior and cost. Considering such unsustainability, some recent investigations had been done on bio-cathodes that were using microorganisms as biocatalysts to develop a complete sustainable and affordable MFC system [4,7,16–18]. The investigations on aerobic bio-cathodes in which aqueous O_2 was the final electron acceptor had attracted attention due to its moderate power efficiency compared to that of the chemical assisted cathodes [19,20]. Similar investigations on denitrifying bio-cathodes in which anoxic biofilm retrieved electrons from the cathode of the potentiostat-poised half-cell to reduce nitrate (NO_3^-) to nitrite (NO_2^-) or molecular N_2 [21,22]. However, very few studies were available on the denitrifying bio-cathode based complete MFC system, where biological anode is utilized as an electron contributor for the effective degradation of nitrogenous compounds. The findings of the recent investigations on denitrifying bio-cathode based MFC were summarized in Table 1.

The performance of a denitrifying bio-cathode MFC is measured by its ability to recover electrical energy through the process of biological carbon and nitrogen removal on anode and cathode, respectively. The findings in Table 1 demonstrated that the MFC-reactor configuration had a significant impact on its performance. Further investigation of the MFC-reactor configuration is therefore reasonable. Moreover, the reduction of NO_3^- was advantageous over the reduction of oxygen on bio-cathodes due to (i) comparatively large redox-potential of the pair NO_3^-/N_2 ($E' = +0.74$ V) [26], and (ii) no risk of soaking aqueous O_2 from cathode to anode compartment.

A complete degradation of NO_3^- to N_2 gas by autotrophic denitrifying pathways have been done by four steps evolving NO_2^- anions, nitric oxide (NO) and nitrous oxide (N_2O) gas as intermediates. The step biochemical reactions for the denitrification process was demonstrated in Fig. 1 illustrating the necessary biochemical factors involved in each step, such as, redox-potentials, active enzymes, and responsible genes [17,27].

The first enzyme in the pathway of bio-chemical denitrification was nitrate reductase, which catalyzed the reduction of NO_3^- to NO_2^-. This was a membrane-bound protein formed by molybdenum-iron-sulfur [27]. Both the synthesis and the activity of this enzyme were inhibited by the presence of oxygen in the system. The second enzyme in the denitrification pathway was nitrite reductase, which catalyzed the reduction of NO_2^- to NO gas. This was a periplasmic protein, which had either of the copper containing or the hemi containing molecular structure [27]. Of the four reduction steps, NO_2^- reduction was identified as the rate-limiting step for the biological denitrification in case of wastewater sludge, denitrifying enriched phosphorous removal sludge and sediments [28–30]. This was because of the lowest redox-potential of NO_2^-/NO ($E' = +340$ mV) among the reduction steps of other intermediate compounds (NO_3^-/NO_2^-, $E' = +421$ mV; NO/N_2O, $E' = +1180$ mV; N_2O/N_2, $E' = +1340$ mV) in the bio-chemical denitrification pathways (Fig. 1) [17,27]. However, none of the previous studies has investigated the matter of rate-limiting steps for autotrophic biological nitrogen removal on the cathode of MFC. That's why, one of the important aims of this study was to investigate whether any rate-limiting step involved in this denitrification process. The studies were carried out to (i) demonstrate the performance of an upward flow baffled-reactor MFC using granulated graphite electrode, (ii) find the best cathodic nitrate loading rate (CNLR) on cathode utilizing acetate (Ac^-) containing fluid as an