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Comparison of oxygen and hypochlorite as cathodic electron acceptor in microbial fuel cells

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HIGHLIGHTS

- Performance of MFC was compared using NaOCl solution and aerated water in cathode.
- NaOCl solution as catholyte demonstrated higher organic matter removal.
- Power produced using NaOCl was 9 times more as compared to aeration in cathode.
- Partial regeneration of HOCl makes it sustainable catholyte than other chemicals.
- Improved Tafel kinetics supports practical use of MFC using NaOCl catholyte.

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ABSTRACT

Effect of oxygen and sodium hypochlorite (NaOCl) as cathodic electron acceptors on performance of a clayware microbial fuel cell (MFC) was evaluated in this study. Maximum power density of 6.57 W/m^3 was obtained with NaOCl as catholyte, which is about 9 times higher than oxygen being used as an electron acceptor. Voltammetry and Tafel analysis further supported the faster reduction kinetics lead to increase in power output and reduction in internal resistance of MFC operated with NaOCl as an electron acceptor. Using NaOCl as catholyte, higher exchange current density of 10.91 and 11.52 mA/m^2 and lower charge transfer resistance of 0.58 and 0.56 kΩ m^2 was observed for anode and cathode, respectively. Higher organic matter removal of about 90% with 25% Coulombic efficiency was achieved using NaOCl as catholyte. Higher internal resistance, lower cathode potential and slow reduction kinetics deteriorated performance of MFC using oxygen as cathodic electron acceptor.

1. Introduction

The conventional wastewater treatment processes can efficiently remove organic pollutants, but operating such system is energy intensive, mainly due to the requirement of aeration and disposal of excess sludge generated in this process. Microbial fuel cells (MFCs) can offer a viable technological alternative to treat wastewater at the same level as traditional aerobic process does, and it carries greater potentials as an electricity generating process (Du et al., 2007; Rabaey and Verstraete, 2005). Application of MFC for wastewater treatment will save considerable cost and energy as compared to activated sludge process. The energy available in organic wastewaters can be harvested in the form of electricity by using MFC to offer simultaneous wastewater treatment.

The major problem associated with the dual chambered MFC is cost involved in aeration while in operation and poor oxygen reduction kinetics demonstrated by non-catalyzed cathodes. Hence, to improve oxygen reduction reaction on cathode, expensive catalyst is required that increases production cost of this device. Theoretically, maximum voltage produced by single chamber MFC with oxygen as an electron acceptor is limited to 1.1 V (Logan, 2008) and thus they cannot be employed directly for practical utility. To overcome this barrier, it may be advantageous to use chemical catholytes having higher reduction potential. Application of such catholytes is possible only in dual chamber MFC configuration.

Oxygen has been widely used as an electron acceptor in most of the MFC research because of its unlimited availability and high standard redox potential. However, oxygen consumption is considered to be the most serious factor to limit the performance of MFC, due to poor oxygen-reducing catalytic activity at the cathode (Gil et al., 2003). Also, the low solubility of oxygen at higher operating temperature limits the availability of electron acceptor

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near electrode–electrolyte interface, which reduces the performance of MFC. In order to eliminate oxygen limitations and to increase power output, various researchers have tested performance of MFCs using different catholyte with high redox potentials such as potassium ferricyanide, dichromate, aerated catholyte (Wei et al., 2012), bleaching powder (Momoh and Naeyor, 2010a,b), persulfate, permanganate, etc. (You et al., 2006; Behera, 2011). The addition of chemical electron acceptor facilitates faster reduction kinetics by overcoming the activation energy barrier, thus minimizing cathodic activation loss. Solubility of oxygen in aqueous medium depends upon the temperature and pressure. Under normal environmental condition, it has limited solubility of 7–9 mg/L; whereas, for other chemical catholytes much higher concentration of oxidant can be maintained and this limitation is not there up to saturation concentration of these chemicals. Hence, chemical catholytes are considered to be useful to enhance the power generation in MFC. As reported, the maximum volumetric power generated during polarization in MFC with ferricyanide, dichromate, permanganate and persulfate were 2.3, 2.2, 3.4 and 7.1 times higher than that obtained with oxygen as cathodic electron acceptor, respectively (Behera, 2011). The byproducts generated from some of them are environmentally harmful which restricts their application for commercialization of the MFC technology.

Hypochlorite can acts as strong oxidant in cathodic chamber than oxygen to enhance power generation from MFC. Use of hypochlorite as a catholyte in MFC could also serve as a disinfectant while treating sewage. In this case, the anode effluent will be admitted to the cathodic chamber alongwith hypochlorite. The maximum theoretical potential difference for hypochlorite as catholyte is about 2.01 V (Mathews, 2002; Momoh and Naeyor, 2010a,b), which is higher than standard redox potential of oxygen (E^o = 1.23 V vs. SHE). Previously, Momoh and Naeyor (2010a,b) performed experiment on use of bleaching powder as catholyte (20 g/L) in MFC with agar-salt bridge inter-connection for treatment of high strength abattoir wastewater. The maximum power density (12.26 mW/m^2) demonstrated by them was very low as compared to other chemical catholyte (Table 1) because of higher internal resistance (4000 ′Ω) generated by this MFC. Also, this study has not considered the kinetic activity of electrodes and consequently their influence on MFCs performance.

Application of polymeric ion exchange membrane increases the overall fabrication cost of MFC as a wastewater treatment process (Li et al., 2011). Ceramic membranes are found to be promising to replace polymeric membranes to reduce the fabrication cost of MFC drastically (Behera et al., 2010a). The MFCs made from such clayware ceramic membranes have demonstrated performance comparable with the MFC made from synthetic polymer membrane (Behera et al., 2010b).

The objective of this research was to evaluate the performance of MFC, made with baked clayware separator, operated using sodium hypochlorite as a catholyte, and comparing it with the performance of MFC using oxygen as a cathodic electron acceptor. In addition, it was aimed to highlight electrochemical activity using Tafel analysis and cyclic voltammetry to monitor activity at the electrodes while using oxygen and hypochlorite as cathodic electron acceptor, and correlate it with performance of MFC.

2. Methods

2.1. MFC construction and operation

The study was carried out in a laboratory MFC with outer cathode chamber volume of 3.5 L made from plastic beaker and inner cylindrical anode chamber with working volume of 1.3 L. Baked clayware cylinder was used for making anode chamber and the wall material of the cylinder itself acted as separator between anodic chamber and cathodic chamber. The MFC was provided with stainless steel wire mesh as an anode having total surface area of 576 cm^2. The cathode was made up of carbon felt (Panex® 35, Zoltek Corporation) with projected surface area of 1428 cm^2. The connections between two electrodes were made with concealed copper wire through an external resistance of 100 Ω.

This MFC was inoculated initially with anaerobic sludge collected from a septic tank bottom. The inoculum sludge was given a heat pre-treatment (heated at 100 °C for 15 min) to suppress growth of methanogens and 60 ml of pretreated sludge was added to the anode chamber along with synthetic feed. Synthetic wastewater was prepared using sodium acetate as a source of carbon having chemical oxygen demand (COD) of about 3000 mg/L. It was made by adding sodium acetate, 3840 mg/L; $NaHCO_3$, 4500 mg/L; NH_4Cl, 954 mg/L; $CaCl_2{\cdot}2H_2O$, 750 mg/L; $MgSO_4{\cdot}7H_2O$, 192 mg/L; K_2HPO_4, 81 mg/L; and KH_2PO_4, 27 mg/L; $FeSO_4{\cdot}6H_2O$, 60.00 mg/L. Trace metals were added as $MnSO_4$, 0.526 mg/L; $ZnSO_4{\cdot}7H_2O$, 0.106 mg/L; H_3BO_3, 0.106 mg/L; $CuSO_4{\cdot}5H_2O$, 4.5 μg/L; $CoCl_2$, 105.2 μg/L; and $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$, 105.2 μg/L (Jadhav and Ghangrekar, 2008).

This MFC was operated under batch mode with two different catholyte conditions, where oxygen and hypochlorite were used as cathodic electron acceptors, successively. In first four feed cycles, tap water was used as catholyte with an aerator (SOBO Aquarium air pump, China) to supply air with an aquarium pump at a rate of 3.5 ml/min. Sodium hypochlorite (NaOCl) solution containing 4% w/v available chlorine was used. Addition of 90 g/L of this NaOCl solution resulted in 1.7 g/L of available chlorine in the cathodic chamber for reduction reaction.

In each operating condition, MFC was operated for four feed cycles with feeding frequency of 5 days each.

Table 1
Performance comparison of MFC with different cathodic electron acceptors.

Electron acceptors	Concentration	OCV (V)	Max. power density (mW/m^2)	References
Oxygen			10.2	You et al. (2006)
Ferricyanide	0.1 M	0.78	40.6	Pandit et al. (2011)
		0.71	0.92	Rangel et al. (2010)
Dichromate		0.56	0.79	Rangel et al. (2010)
		0.76	45.9	Pandit et al. (2011)
Permanganate		1.04	7.29	Rangel et al. (2010)
		1.11	116.2	Pandit et al. (2011)
		1.33	115.6	You et al. (2006)
Persulfate		1.10	101.7	Pandit et al. (2011)
Calcium hypochlorite	20 g/L	1.56	12.26	Momoh and Naeyor (2010a,b)
Oxygen		0.676	17.43	This study
Sodium hypochlorite	90 g/L	1.065	148.4	This study