Entrapment of algae for wastewater treatment and bioelectricity generation in Microbial fuel cell

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INTRODUCTION

Recently, microbial fuel cells (MFCs) are drawing increasing attention as an effective means for electricity energy recycling from not only carbohydrates [Bullen et al., 2006; You et al., 2006; Park. et al., 2005] but also from complex organic wastewater (Logan et al., 2004; Liu et al., 2004). Since the turn of the century, the research on microbial fuel cells (MFCs) has experienced rapid increases. MFCs are unique in their ability to utilize microorganisms, rather than an enzyme or inorganic molecule, as catalysts for converting the chemical energy of feedstock directly into electricity. Microorganisms such as members of the *Geobacter* family (Bond et al. 2003), *Shewanella putrefaciens* (Kim, 2002), *Rhodoferax ferrireducens* (Chaudhuri, et al., 2003) and *Clostridium butyricum* (Park, et al.,2001) are able to oxidize organic matter by accepting electrons via the electrode to obtain energy for their own growth, and this process gives rise to electricity generation. MFCs often consist of two compartments, anode and cathode, which are often separated by a proton-exchange membrane (PEM). The anode chamber contains microorganisms that oxidize the available substrate (i.e., the electron donor). The anaerobic oxidation is coupled with liberation of electrons which are transported through the cellular respiratory chain ultimately to the anode. Domestic, industrial, and animal waste streams have been used as feedstock for generating electricity in MFCs. It may be explained as:

Anode : $C_6H_{12}O_6$ (electron donor) $+6H_2O \rightarrow 6CO_2 + 24H^+ + 24^{e-}$ (1)

Here, the anode works as an artificial, external electron acceptor for the microorganisms. The electrons travel through a resistor or a device to be powered, generating electricity until reaching the cathode.

Cathode : $6O_2 + 24H^+ + 24^{e-} \rightarrow 12H_2O$ (2)

While the electrons travel through the circuit, the corresponding protons migrate to the cathodic compartment through a proton- exchange membrane to maintain charge neutrality. At the cathode an electron acceptor (e.g., oxygen) is reduced by the electrons via the circuit and the protons via the membrane. The reduction of molecular oxygen is the best choice for the cathodic reaction in microbial fuel cells. The direct and virtually inexhaustible availability of oxygen as well as its positive redox potential are two of the major reasons for the superiority of this element as an electron acceptor. The improvement of the performance of the oxygen reduction at lowest possible costs is one of the most important issues for research and development, since it is often the cathodic reaction that limits the performance fuel cells. Cyanobacteria (blue green algae) and green algae are photosynthetic organisms that play a key role in aquatic ecosystems. In fact, around 40% of the total photosynthesis on earth performed by these micro algae**.** In the same context current work is undertaken to develop bio-cathode. The idea behind this woke is to use the photosynthetic ability of blue green algae for oxygen supply for cathodic reaction of MFC. It will not only reduce the cost of external mechanical oxygen supply but will reduce the chance of diffusion of oxygen into anode

chamber (which should be completely anaerobic) due to non turbulent oxygen production in cathode chamber. In our, knowledge, this is first ever study of immobilization of algae for such a novel application for microbial fuel cells for bioelectricity production and wastewater treatment. Entrapment of algae will reduce the area requirement for the production of more oxygen. It will lead to development of compact cathode of MFC and will reduce the higher internal resistance problem, which is one of the bottlenecks in MFC scale up.

MATERIALS AND METHODS

Blue green algae were collected from a shallow water body from a zoological park, Bhubaneswar. It was further cultured on BG-11 media at room temperature (25^0 C) in plastic tray under continuous illumination with fluorescence light (Philips spiral fluorescence light lamps, 15 W). A 2% (w/v) of sodium alginate was prepared in hot distilled water ($60\ ^0$C). After cooling, 10 g blue green algae (wet weight) was mixed with 50 ml sodium alginate solution (w/v). The mixture was dropped into 0.2M $CaCl_2$ solution with a burette and gentle stirred to avoid aggregation of the beads. The resultant beads of 2-4mm in diameter were cured in 0.2M $CaCl_2$ solution at $4\ ^0$C for to complete gellation (Wu et al.,2007). After keeping them overnight in the $CaCl_2$ solution, the beads were rinsed with distilled water.

Dual chambered MFC was fabricated in the laboratory using cylindrical plastic jar of 500 ml capacity. 450 ml of synthetic wastewater was fed in anode chamber; same volume was fed in cathode chamber. The two chambers were connected through tube and separated by proton exchange membrane (PEM) (Nafion^{TM} 117). PEM was pretreatment by boiling in 30 % H_2O_2 solution, then in deionized water followed by 0.5 M H_2SO_4, then deionized water sequentially each for 1 hour. Graphite plates without any coating were used as electrodes for both anode and cathode. Total projected surface area of anode was 60 cm^2 and for cathode it was 58 cm^2. Distance between electrodes were 6.4 cm. Copper wires were used for connecting electrodes. The anode chamber was equipped with sample port, gas exit port. It was perfectly sealed with epoxy to ensure anaerobic microenvironment. The cathode was remained open to provide aerobic condition. During experimentation whole experimental setup was placed under continuous illumination with fluorescence light (Philips spiral fluorescence light lamps, 15 W) in order to provide light to algal beads for photosynthesis.

A synthetic wastewater containing sucrose as a carbon source was used throughout the study. The composition of the synthetic wastewater used was as; sucrose, 6 g/l; NH_4Cl, 0.5 g/l; KH_2PO_4, 0.2 g/l; K_2HPO_4, 0.2 g/l; $MgCl_2$, 0.25 g/l; $CoCl_2$, 20 mg/l; $ZnCl_2$, 10 mg/l; $CuCl_2$, 10 mg/l; $CaCl_2$, 4 mg/l; $MnCl_2$, 10 mg/l. The anodic chamber was inoculated with marine sludge, which was collected from one of the seacoast of Orissa, India. The inoculum sludge (50 g) was mixed with synthetic wastewater and 450 ml volume of inoculum was added to the anode chamber. The cathode chamber was fed with entrapped algal beads and BG 11 media. The experiment was conducted at room temperature ranging from 25 to $30\ ^0$ C. The voltage and current were measured using a digital multimeter (MASTECH, MAS830 L) and converted to power according to P=VI, where P=power (W), I= current (A), and V=voltage (V). Then current density and power density were also calculated. The influent and effluent characteristics for Chemical oxygen demand (COD), dissolve oxygen (DO) were also done. Figure 1-3 are showing separate algal beads, beads in cathode and whole experimental setup

Figure 1. Entrapped algal bead in cathode (left hand side)

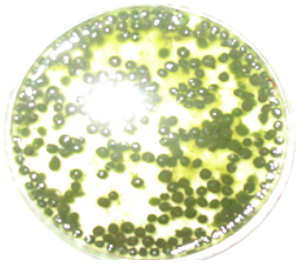

Figure 2. Entrapped algal beads

Figure 3. Experimental setup of microbial fuel cell

RESULTS AND DISCUSSION

Alginate is a linear copolymer of a-l-guluronate (G) and a-dmannuronate(M), which constitutes 10–40% of the dry weight of all species of brown algae (Volesky et al., 2003). Depending on the algal species used for the extraction of alginic acid, its molecular weight as well as its M/G ratio presents great variations. The capability of this copolymer to form stable biodegradable gels in the presence of divalent cations has been known and extensively studied for various application (Grant et al., 1973; Smidsrod et al., 1972). These gelation properties can be attributed to the simultaneous binding of the divalent cations such as Ca^{2+} to different chains of a-l-guluronate blocks (G-blocks) (Veglio et al., 1997). As a result of their configuration, these chains form electronegative cavities, capable of holding the cations via ionic interactions, resulting in cross-linking of the chains into a structure resembling an “egg box” (Grant et al., 1973). Due to its ability to form stable structures, cross-linked alginate has been used for the immobilization of biological material for various purposes, including the immobilisation of material with metal binding properties, such as algae, for the removal of heavy metal from wastewater (Kuyucak et al.,1989).

In the present work blue green algae were entrapped in order to use its fast photosynthetic capacity for novel use in microbial fuel cell. These beads were placed in cathode chamber for constant oxygen supply by photosynthesis. As per authors knowledge, this is the first ever attempt in this direction and which shows very exciting early results. The preliminary investigation shows that entrapped algal beads do constant photosynthesis and maintains the dissolved oxygen concentration

around 4.0 mg/l in cathode solution, which is reasonably good for successful microbial fuel cell. Beside this, present MFC produces Power in the range of 3.97.53 x 10^{-6} W, Power density in the range of 0.238 mW/m^2 and Current density in the range of 1.05 mA/m. 48 % COD reduction was also observed after five days of experimentation.

CONCLUSIONS

The early results of present study indicated that entrapped algae may be utilized for oxygen supply to cathode of MFC. It also indicated the potential of entrapment of algal beads for successful bio-cathode development.

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