Nanocomposite Electrode Microbial Fuel Cell: A Promising Technology for Enhanced Power Generation from Yamuna Water

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Abstract: ***Microbial Fuel Cell (MFC) is a promising and a futuristic technology for generating electrical energy from anaerobic fermentation of organic and inorganic matter present in the waste water. The performance of MFCs are dependent on various factors like the type of proton exchange system, the type of electrodes, the use of mediators and nitrogen gas sparging. MFCs for waste water treatment incur high cost of components which is a major barrier in commercializing the fuel cells. In this study we examined several parameters which could affect MFC operation. Anode performance and proton exchange membranes are important factors in deciding the efficiency of MFCs for large scale applications. Highly efficient Ni-coated carbon cloth electrodes that are electrometrically and biologically stable were synthesized at a much lower cost by chemical vapour deposition. These nanocomposite electrodes led to almost tenfold increase in the columbic efficiency as compared to the conventional electrodes. The use of the salt bridge which attributes to the higher internal resistance was replaced by the Nafion membrane leading to an increase in the current output. The rate of electron transport from the substrate to the anode by the bacterias showed a significant increase in the power generation by the use of redox mediator like Methylene blue. Thus, our current study demonstrates that using Yamuna water with nanocomposite electrodes in MFCs is a promising technology for the enhanced production of bioenergy.***

Keywords: MFC, Nanocomposite electrodes, Chemical vapour deposition, Mediators, Methylene blue, Nafion membrane, Yamuna water.

1. Introduction

Microbial Fuel Cell (MFC) harnesses the metabolism of micro organisms converting their chemical energy into electrical energy. The power generation in MFC is of great interest as this technology may provide a new method to offset wastewater treatment plant operating costs and less sludge production. The approach will be helpful in waste water treatment as well is in a clean and sustainable energy (Lovely, 2006). The MFC that uses waste water as fuel can produce electrical power and reduce the Biological Oxygen Demand (BOD) loading of the waste water simultaneously (Rahimnejad et al, 2012 and TerHeijne, 2006).

Anode performance is an important factor in deciding the efficiency of MFC for large scale applications. It is central to various bio-electrochemical reactions and helps to mediate electron transfer to the electrode from exo-electrogens (Lovely, 2006 and Liu 2011). Hence it is important to improve the material and design of the anode to enhance the MFC output. Increased surface area, high electrical conductivity, chemical stability and sustainability of its properties with time are some of the important criteria which can influence the performance of MFC (Mohanakrishna *et al*, 2012).

Many forms of carbon based materials with modifications have been studied viz., carbon cloth (Cheng, 2006), carbon paper (Min and Logan 2004), carbon felt (Liu, 2005) and carbon foam (Choudhuri and Lovely, 2003). The available surface of the anode can be clogged by the microbial growth thus hindering the diffusion of the substrate and transport of the electrons. New strategies have been developed to improve the conductivity of the anode. It has been investigated that carbon based anodes modified with polymers (Scott, 2007 and Jiang, 2009), carbon nanotubes (Tsai, 2009) and new composite anodes (Qiao *et al*, 2008 and Zou, 2008) are being used to enhance the electron transport from the microbes to the electrodes. The process of thermal annealing helped in the synthesis of nanoparticles of Ni, Pd and Fe. Fe catalyzed multi-walled carbon nanotubes (MWCTs) were synthesized through chemical vapour deposition. Significant increase in power density was observed with these nanomodified electrodes (Schellar *et al*, 2009).

The second most important component in MFCs is the proton conducting material. These proton bridges allow protons to transport to the cathode and physically separate the anode and cathode compartments. The different materials which can be utilized as proton conductors include salt bridges, Ultrex membranes, and fluoropolymer-containing cation exchange material like Nafion (Bond and Lovely, 2003).The problems associated with salt bridge as a conducting material is its high internal resistance which lowers the coulombic efficiency of the MFC. In comparison, Nafion exchange membrane is a better proton exchanger, as it provides high ionic conductivity (Min *et al* 2005). The substrate plays a significant role in the amount of electrons being generated in a fuel cell. Some substrates are capable of producing a higher columbic yield as compared to some of the more common sugars used. Glucose is reported as the most commonly used substrate for bacterial culture (Rabaey, 2003).

To improve the power generation in MFCs the understanding of charge transport between microbes and electrode interface plays a pivotal role (Du Z., 2007). Electron transport from substrate to electrodes in MFCs can be explained by two mechanisms (1) The direct transfer of electrons from the outer cell membrane to the electrode (Kim *et al*, 2002), (2) The transfer of electrons through mediators or shuttles (Uwe Schroder, 2011).There are various soluble chemical compounds which act as mediators of electron transportation between microbes and the anode. The different dye molecules like Methylene blue (Zhou *et al*, 2007), Methyl orange, Methyl red, Bromocresol green (Taskan *et al*, 2014) and Neutral red (Park *et al*, 2000) have also been used as an electron mediator.

In this study, we have examined several factors that could affect MFC performance: electrode composition (conventional and nanocomposite electrodes), proton conducting material (salt bridge and Nafion membrane) and the effect of Methylene blue as a mediator.

2. Materials and Methods

2.1 Sampling of water from River Yamuna

Water samples were collected in sterilized bottles from Nizamuddin Bridge from the Yamuna River in Delhi. While sampling, care was taken to collect the sample from the middle of the river, in order to rule out water contamination due to human settlements on the banks.

2.2 Physico-chemical analysis of Yamuna water

The water was processed immediately post collection, to ensure that the water profile is not affected by storage. The various parameters like pH, Dissolved Oxygen (DO) and Biological Oxygen Demand (BOD) and Chemical Oxygen Demand (COD) were estimated using pH meters and titrimetric methods (APHA, 2005).

2.3 Construction of MFC using conventional electrodes with salt bridge/Nafion membrane as proton exchanger

The dual chamber microbial fuel cell was constructed as follows: Separate cathode and anode chambers were constructed and sealed after the addition of the required sample. The anaerobic conditions in the anode chamber were maintained by sparging with nitrogen. A salt bridge was created using 10% agar and 5% NaCl. Alternatively, Nafion®117 membrane (Sigma) was used as a proton exchanger. The conventional electrodes were prepared using carbon cloth. Substrate of glucose (3g/L) was added to the anode chamber containing 500 ml of Yamuna water. Methylene blue (300µM) was used as a mediator as per the requirement of set-up. The electricity generated was measured using a multimeter (Sanwa CD770) at a regular interval of 2 hrs for 36 hours.

2.4 Microbial fuel cell construction using nanofabricated electrodes and Nafion membrane as proton exchanger

The microbial fuel cell was then modified for enhanced power generation. Nano modification of the conventional carbon cloth electrode was performed. Chemical Vapor Deposition followed by thermo-annealing of nickel (Ni) was carried out by placing the nickel-coated electrode in a quartz tube and heated in a furnace at a temperature of 800-1000°C. These electrodes were then used for electricity generation using 500 ml of Yamuna water, with glucose as a substrate (3g/L). Methylene blue (300µM) was used as a mediator as per requirement of the set-up. Nafion membrane was used as the proton exchange membrane to separate anode and cathode chambers. The electricity generated was measured using a multimeter (Sanwa CD770) at a regular interval of 2 hrs for 36 hours.

3. Results

3.1 Bioelectricity generated in MFC using salt bridge and Nafion membrane as proton exchanger

Yamuna water was used as inoculum in the dual chambered MFC to generate electricity. The traditional salt bridge proton exchanger generated electricity ranging from 0.4-0.62 V over a period of 36 hrs, with the highest output at 12hrs. The use of a Nafion proton exchange membrane led to the generation of electricity ranging from 0.6-1.22 V over the same period of time, with the highest output at 14hrs (Table 1). These were then analyzed and compared for a better understanding of the importance of proton exchangers in microbial fuel cells (Fig. 1& 2).

Table 1: Potential difference generated at the conventional electrodes using different proton bridges, in the presence and absence of mediators

Time (hrs)	Potential Difference (Volts)			
	Conventional electrodes (salt bridge)		Conventional electrodes (Nafion)	
	Without Mediator	With mediator	Without mediator	With mediator
0	0.4	0.5	0.6	0.8
2	0.44	0.53	0.68	0.84
4	0.48	0.55	0.7	0.89
6	0.52	0.58	0.74	0.93
8	0.58	0.61	0.79	0.96
10	0.6	0.62	0.83	1.1
12	0.62	0.65	0.94	1.5
14	0.62	0.68	1.22	1.8
16	0.56	0.71	1	2.1
18	0.53	0.7	0.97	2
20	0.51	0.68	0.9	1.7
22	0.5	0.66	0.86	1.5
24	0.47	0.63	0.82	1.1
26	0.45	0.61	0.78	0.97
28	0.43	0.59	0.75	0.94
30	0.42	0.56	0.72	0.92
32	0.41	0.54	0.66	0.88
34	0.4	0.52	0.62	0.85
36	0.38	0.49	0.57	0.81

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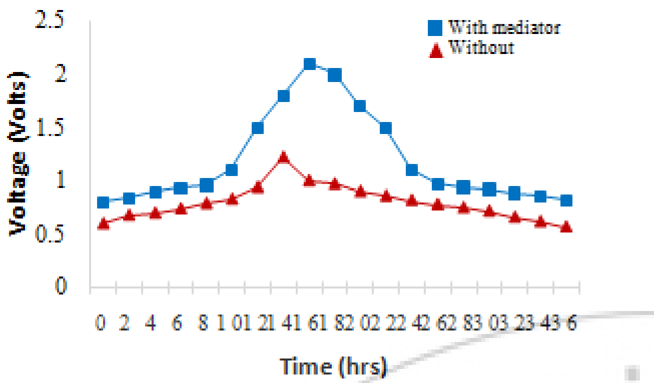

Figure 1: The generation of power in MFC the salt Bridge, using conventional electrodes in the presence and absence of mediators. Yamuna water was used as a source of electricity using conventional electrodes. Addition of Methylene blue as a mediator led to increased power generation (maximum of 0.71 Volts was generated in the presence of mediator as compared to 0.62 Volts in the absence of mediator).

3.2 Bioelectricity generatedin MFC using the mediator Methylene blue

The effect of the mediator Methylene blue on the generation of power in double chambered MFC system was studied. The use of conventional electrodes in the presence of Methylene blue (300µM) using Salt bridge showed the generation of electricity ranging from 0.5-0.71 V over a period of 36 hrs (Fig. 1& 2).

Fig. 2 Power generation in the MFC with Nafion membrane, using conventional electrodes in the presence and absence of mediators. Yamuna water was used as a source of electricity using conventional carbon cloth electrodes. Addition of Methylene blue as a mediator led to increased power generation (maximum of 2.1 Volts was generated in the presence of mediator as compared to 1.0 Volts in the absence of mediator).

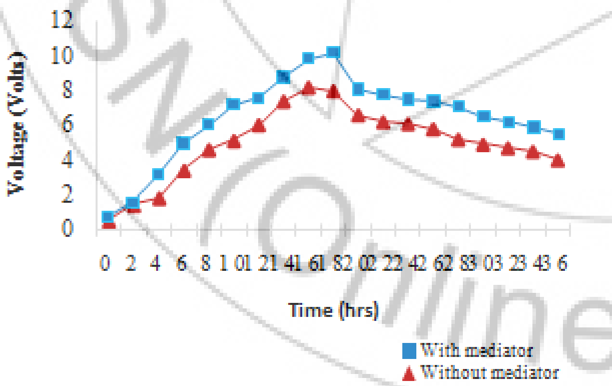

Figure 3: Power generation in the MFC with Nafion membrane, using nanofabricated electrodes in the presence and absence of mediators. Yamuna water was used as a source of electricity. Addition of Methyelene blue as a mediator led to increased power generation (maximum of 10.2 Volts was generated in the presence of mediator as compared to 8.2 Volts in the absence of mediator).

The highest output of electricity was observed at 16hrs. Upon the use of Nafion proton exchange membrane with conventional electrodes in the presence of Methylene blue electricity generated ranged from 0.8-2.1 V for the same time period, with the highest power output recorded at 16hrs (Fig. 2). The use of nanocomposite electrodes in the presence of Methylene blue led to the generation of electricity ranging from 0.8-10.2 V over 36hr time period, where the highest output of power was recorded at 18hrs (Fig. 3). These results were further analyzed in order to understand the contribution of external mediators in the generation of bioelectricity in MFCs (Fig 4).

3.3 Bioelectricity generated using nanocomposite and conventional electrodes

The conventional carbon cloth electrodes of the MFC were improved upon by Ni coating of the carbon cloth, thus fabricating a secondary microporous structure. These nanocomposite electrodes showed the generation of electricity ranging from 0.5-8.2 V over a period of 36 hrs, with the maximum output recorded at 16hrs (Fig. 5). In comparison, theconventional electrodes showed electric current production ranging from 0.4-0.62 V, with the maximum output recorded at

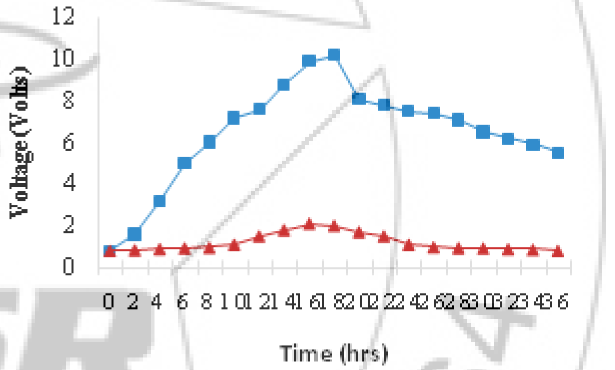

Figure 4: Comparison of the performance of the MFCs with Nafion membrane, using different electrodes in the presence of mediators. The presence of mediators has been observed to further accentuate the efficiency of the nanofabricated electrodes in comparison to the conventional electrodes (maximum of 10.2 Volts was generated using the improved anodes as compared to 2.1 Volts by using conventional electrodes) in the presence of a mediator.

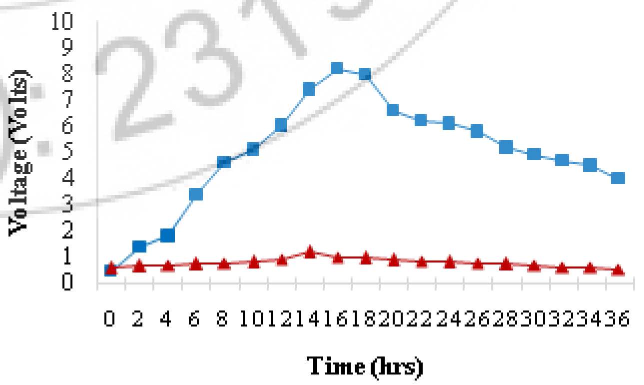

Figure 4: A comparison of the performance of the MFCs with Nafion membrane, using different electrodes in the absence of mediators. The use of nanofabricated electrodes

highly enhance the power generated by the MFC as compared to the conventional electrodes (maximum of 8.2 Volts was generated using the improved anodes as compared to 1.0 Volts by using conventional electrodes) in the absence of a mediator.

12 hrs (Fig. 1). The trend in the power generation by nanocomposite electrode in MFC using Nafion membrane in presence and absence of mediators was further analyzed (Table 2).

Table 2: Potential difference generated at the conventional electrodes and nanomodified electrodes in the presence and absence of mediators. (CE -Conventional electrodes; NE- Nanocomposite electrodes)

Time (hrs)	*Potential Difference (Volts)*			
	Without mediator		*With mediator*	
	CE	*NE*	*CE*	*NE*
0	0.6	0.5	0.8	0.8
2	0.68	1.4	0.84	1.6
4	0.7	1.82	0.89	3.2
6	0.74	3.4	0.93	5
8	0.79	4.6	0.96	6.04
10	0.83	5.12	1.1	7.2
12	0.94	6.04	1.5	7.6
14	1.22	7.4	1.8	8.8
16	1	8.2	2.1	9.9
18	0.97	8	2	10.2
20	0.9	6.6	1.7	8.11
22	0.86	6.2	1.5	7.8
24	0.82	6.1	1.1	7.5
26	0.78	5.8	0.97	7.4
28	0.75	5.2	0.94	7.1
30	0.72	4.9	0.92	6.5
32	0.66	4.7	0.88	6.2
34	0.62	4.5	0.85	5.9
36	0.57	4	0.81	5.5

3. Discussion and Conclusion

The Yamuna water has a consortium of microbes which include *Lactobacillus plantarum, L. casei, Streptococcus lactis, Rhodopseudomonaspalustris, Rhodobactersphaeroides, S. cerevisiae, Candida utilis, Streptomyces albus, S. griseus, Aspergillus* and *Mucorhiemalis* (Shrivastava et al, 2012). These microbes assist in the generation of power in the MFC in the present study.

Carbon cloth, carbon paper and carbon black are widely used as anode in MFCs because of their good conductivity, non corrosivity and stability in microbial inoculums. However the power generated by these conventional electrodes in MFC can be improved upon by modifying the anodes. Since the structure of the supporting material of anode coating can affect the performance of MFC to a large extent, therefore in the present study modified nanocomposite electrodes have been employed. Ni coated carbon cloth electrodes impressively outperform the conventional carbon cloth electrodes owing to the formation of microscale porous structure which provide more surface area with active functional groups for the transfer of electrons. In the current study approximately ten fold increase (8.2 Volts using nanocomposite electrodes and 1.0 Volt using conventional electrodes) in power generation was observed upon the use of nanocomposite electrodes in comparison with the conventional electrodes. This suggests that the modified Ni coated nanocomposite anode substantially increase the power generation and is a promising anodic material for the fabrication of MFCs.

In a dual chambered MFC system, the internal resistance which is a function of proton exchange system plays a critical role in the power production. A comparative study of the power output in MFC with salt bridge and Nafion membrane as proton exchanger was carried out. The low power output (0.62 Volts) with salt bridge is credited to the higher internal resistance of the salt bridge system. The better performance of MFC with Nafion membrane (1.22 Volts) is attributed to excellent proton conductivity and selective ion permeability.

As mediators play a key role in power generation, the performance of MFC using nanocomposite / conventional anode electrodes was investigated with and without mediator (Methylene blue). In the case of nanocomposite electrodes, an increase in power output was observed (10.2 Volts with mediator & 8.2 Volts without mediator). A similar trend was observed in the case of conventional electrodes (2.1 Volts with mediator & 1.22 Volts without mediator). This increase in potential difference can be explained by the diffusion of redox active Methylene blue that shuttles the electrons between the microbes and the electrodes (Fig. 5). However, the increase in power output was not found to be significant on addition of mediators. This may be due to the presence of metal ions like sulphates, ferric and nitrate in the Yamuna water which act as natural mediators in electron transport from the microbes to the electrodes.

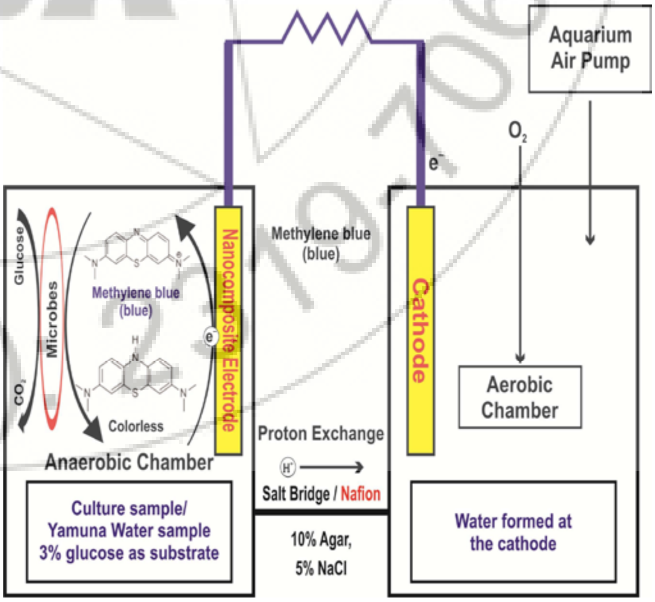

Figure 5: Schematic representation of a dual chamber microbial fuel cell assembly consisting of nanocomposite electrode. Methylene blue used as redox mediator for enhanced power generation.

In our previous work, we had utilized conventional components for the construction of MFC which had led to a low output of electricity; the highest being 0.62 Volts (Malik et al, 2014). Modifications of the traditional electrodes in the current study, in the form of nanocomposite electrodes has led to approximately 10 fold increase in the generation of electricity (8.2 Volts). Thus, our work provides a new platform for designing cost effective and improved electrodes with the aid of nanocomposite material. These electrodes provide a suitable environment for microbes to maintain their electrochemical activity and generation of power. The ability of MFCs to use complex organic materials allows the use of Yamuna water as fuel. Hence the modified MFC constructed are capable of removing pollutants while simultaneously enhancing electrical energy. The robustness of MFCs and their application in bioremediation make it a viable option for energy harvesting.

4. Future Plans

Through our current study we have shown that the water of the river Yamuna is an excellent source for the generation of electricity. The present Ni-coated nanocomposite electrode in the MFC has given an immense increase in power generation. In future the optimization of the mediator concentration, variation of substrates and proton exchange membrane will be carried out to make it more cost effective and sustainable MFC. We have currently taken low volumes of inoculum (Yamuna water), the use of higher volume of sample can be tested for increased efficiency of the MFC. Further optimization studies are being carried out to significantly enhance the power density generated.

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