PalArch's Journal of Archaeology of Egypt / Egyptology

TREATMENT OF WASTEWATER USING MFC

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P. Shanmuganathan , P. Rajasulochana , A. Ramachandra Murthy: Treatment Of Wastewater using Mfc -- Palarch's Journal Of Archaeology Of Egypt/Egyptology 17(9). ISSN 1567-214x

ABSTRACT

Microbial fuel cells are bioelectrochemical system where microrganisms acts as biocatalyst gaining metabolic energy by transferring electrons from an electron donor to an electron acceptor. A mediatorless microbial fuel cell was designed on naturally occurring E.coli in domestic wastewater, which directly transfers electrons with the help of pili and biofilms. Microaerophilic studies helps in steady state of electron transfer and the present study relies on comparing the efficiency of batch and continuous systems. The continuous mode systems were efficient in highest power production than the batch mode with Nafion 1135 as proton exchange system. The maximum voltage reported was 960 mV in domestic wastewater. The COD removal efficiency was found to be around 90% hence enables a better technology for wastewater treatment associated with power generation and biofuel production. Future aspects of MFCs are also discussed.

1. Introduction

India's population is deeply vulnerable to changes in water supply. Especially in urban areas water resources are under significant pressure due to high water demand and complex consumption patterns within a small but highly-densely populated areas. Currently, we are meeting the demands of most of the cities by transporting water from hundreds of kilometres. This is both inefficient and energy intensive. A local level solution is thus essential for sustainable water management. Practices such as reuse of treated wastewater would be of immense significance in achieving water security. Almost 80% of water supply flows back into the ecosystem as wastewater. This can be a critical environmental and health hazard if not treated properly but its proper management could help the water managers in meeting the city's water demand. Currently, India has the capacity to treat approximately 37% of its wastewater, or 22,963 million litres per day (MLD), against a daily sewage generation of approximately 61,754 MLD according to the report of the Central Pollution Control Board. Moreover, most sewage treatment plants do not function at maximum capacity and do not conform to the standards prescribed. On the other side, India's energy sector is one of the most critical components of an infrastructure that affects India's economic growth and therefore is also one of the largest industries in India. The consumption of the energy is directly proportional to the progress of manpower with ever growing population, improvement in the living standard of the humanity and industrialization of the developing countries. The report from Central Electricity Authority says that more than 60 percent of energy demand of India is met by coal thermal power plants (Fig 1). The depletion of natural resources, pollutants emission and green house emission are the main problems associated with thermal power plants. Thus we are in need of the technology by which the problems of both wastewater treatment and energy demand to be solved.

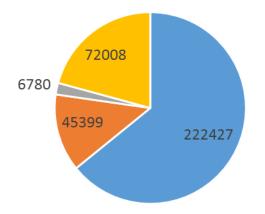


Fig 1. Fuel wise installed capacity (MW)

Sustainable development is possible by (i) constantly maintaining the ecosystems, (ii) more focus on development of biodegradable materials, (iii) environmental friendly manufacturing and disposable methods/processes (Zechendorf, 1999). Another important aspect for sustainable development include global climatic change and waste management. In view of this, production of energy from municipal and industrial waste draws more attention as fossil fuel resources are very limited [Gavrilescu and Chisti, 2005; Venkat Mohan et al., 2007; Li et al., 2014]. In recent years, it is found that using microbial fuel cells, electricity can be generated through the process of anaerobic oxidation [Pant et al., 2013; Patil et al., 2012]. Microbial fuel cells harvest microbially generated energy and provide habitat to their growth and metabolic actions [Logon, 2004]. The main differences of MFCs to the

conventional low temperature fuel cells (direct methanol fuel cell or proton exchange membrane fuel cell) are [Shizas and Bagley, 2004]:

The electrocatalyst is biotic (electroactive bacteria or proteins) at the anode.

The temperature can range between 15 and 45°C, with close to ambient levels as optimum.

Neutral pH working conditions.

Utilisation of complex biomass (often different types of waste or effluent) as anodic substrate.

A promising moderate environmental impact assessed through life cycle analysis.

Table 1 presents typical applications of MFC with defined wastewater substrates (Pandey et al., 2016)

Table 1 Typical applications of MFC with defined wastewater substrates

5. No.	Substrate type	Conc.	Inoculum	Type of MFC	Working volume (1)	Anode	Cathode	OCV Max. (V)	CE%	COD Rem. %	$P_{\rm dmax}$ (mW m ⁻²)
Carbohy HEXOSI	drates: Monosacchario ES	les									
l	p-Glucose	6.7 mM	Mixed bacterial culture	Two chambered	0.012	Carbon cloth	Carbon cloth	0.39	28	≈93	≈2160
2	p-Galactose	6.7 mM	Mixed bacterial culture	Two chambered	0.012	Carbon cloth	Carbon cloth	0.35	23	≈93	≈2090
3	p-Fructose	6.7 mM	Mixed bacterial culture	Two chambered	0.012	Carbon cloth	Carbon cloth	0.31	23	\approx 88	$\approx \! 1810$
1	L-Fucose	6.7 mM	Mixed bacterial culture	Two chambered	0.012	Carbon cloth	Carbon cloth	0.35	34	≈84	≈1760
5	L-Rhamnose	6.7 mM	Mixed bacterial culture	Two chambered	0.012	Carbon cloth	Carbon cloth	0.27	30	≈90	≈1320
5	D-Mannose	6.7 mM	Mixed bacterial culture	Two chambered	0.012	Carbon cloth	Carbon cloth	0.29	25	≈88	≈1240
7	Sucrose	0.1 g l ⁻¹	Anaerobic sludge	Single chambered	NA*	Carbon fiber veil	Carbon cloth	NA	4	94	1.79 W m ⁻³
PENTOS	SES										
3	D-Xylose	8.0 mM	Mixed bacterial culture	Two chambered	0.012	Carbon cloth	Carbon cloth	0.38	31	≈ 95	≈2330
)	D-(-)Arabinose	8.0 mM	Mixed bacterial culture	Two chambered	0.012	Carbon cloth	Carbon cloth	0.26	27	≈93	≈ 2030
10	D-(-)Ribose	8.0 mM	Mixed bacterial culture	Two chambered	0.012	Carbon cloth	Carbon cloth	0.27	30	≈86	≈1520
Sugar d SUGAR	erivatives ACIDS										
1	D-Galacturonic acid	6.7 mM	Mixed bacterial culture	Two chambered	0.012	Carbon cloth	Carbon cloth	0.33	22	≈80	≈1480
12	p-Glucuronic acid	6.7 mM	Mixed bacterial culture	Two chambered	0.012	Carbon cloth	Carbon cloth	0.44	24	≈ 89	≈ 2770
13	D-Gluconic acid	6.7 mM	Mixed bacterial culture	Two chambered	0.012	Carbon cloth	Carbon cloth	0.28	30	≈93	≈2050
Polyalco HEXITO											
14	Galactitol	6.7 mM	Mixed bacterial culture	Single chambered mediatorless	0.012	Carbon cloth	Carbon cloth	0.34	13	≈90	≈2650
15	Mannitol	6.7 mM	Mixed bacterial culture	Single chambered mediatorless	0.012	Carbon cloth	Carbon cloth	0.24	19	≈91	≈1490
16	Sorbitol	6.7 mM	Mixed bacterial culture	Single chambered mediatorless	0.012	Carbon cloth	Carbon cloth	0.26	10	≈71	≈1690
PENTIT											
17	Arabitol	8.0 mM	Mixed bacterial culture	Single chambered mediatorless	0.012	Carbon cloth	Carbon cloth	0.26	25	≈91	≈2030
8	Ribitol	8.0 mM	Mixed bacterial culture	Single chambered	0.012	Carbon cloth	Carbon cloth	0.32	28	≈92	≈2350

Fig. 2 presents a typical layout of a two chambered microbial fuel cell.

A MFC consists of an anode and a cathode separated by a cation specific membrane. Microbes at the anode oxidise the organic substrate, generating protons which pass through the membrane to the cathode, and electrons which pass through the anode to an external circuit to generate a current. The problem is collecting the electrons released by bacteria as they respire. This leads to two types of MFCs: mediator and mediatorless. The mediatorless MFC is the most promising and is the main version used in developments. There are two basic versions of the MFC, the two cell and the single cell. Microbial Fuel Cell (MFC) converts chemical energy to electrical energy during substrate oxidation

with the help of microorganisms (Allen and Bennetto., 1993; Bond and Lovley., 2003; Liu et al., 2004).

Two cell MFC is illustrated in Fig. 2. The cell consists of two compartments, containing the anode and cathode, separated by a permeable membrane. The anode cell contains the substrate (wastewater or organic material) and the anode, which is coated with a surface film of microorganisms. The cathode cell contains the cathode and the electrolyte. Substrate is fed to the anode cell and oxygen to the cathode cell. The anode cell is maintained in and anaerobic state i.e. is kept free of oxygen. The single compartment uses an external air cathode which is separated from the inside of the cell by the membrane (Fig. 3). The air cathode version gives a higher power density than the two chamber version. In practice the MFCs are coupled together in stacks to provide the required voltage.

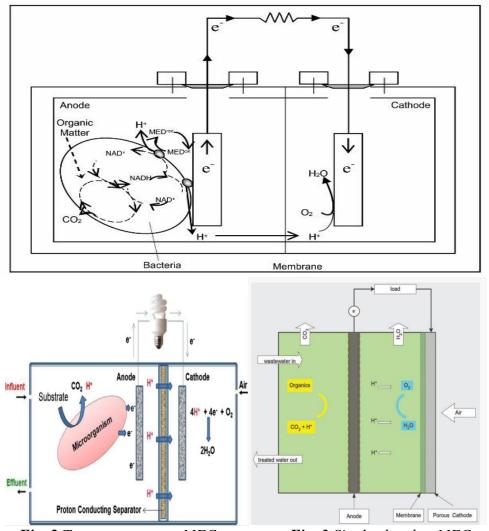


Fig. 2 Two compartment MFC Potassium permanganate is considered the best cathodic electron acceptor with an excellent power density which helps in high electricity generation. Proton exchange membranes play a very important role in the generation of electricity

by transferring the protons generated in the anode chamber to the cathode chamber. During the process of treatment of wastewater, the protons that are transferred to the cathode chamber can be recovered as hydrogen gas by avoiding the passage of oxygen through the cathode. The hydrogen gas produced by microbial fuel cell is relatively of high purity over the other methods used for the production of hydrogen gas (Kim et al., 2008). By avoiding the passage of air through the cathode chamber the possibility of oxygen leakage into anode chamber is prevented (Zhuwei Du et al., 2007). Apart from above mentioned applications, Microbial fuel cells are also used as biosensors and insitu process monitoring and control (Chang et al, 2004,2005). In the present study, waste water samples were collected in the premises of CSIR Lab located in Taramani, Chennai. Investigations were carried out on wastewater using MFC.

2. Construction of microbial fuel cell

The MFC used in the study was constructed using acrylic with two semicylindrical chambers. The anode chamber had total working volume of 4000 cm3 and cathode with 1000 cm3. A bed of poly-insulator beads were added for the biomass growth at the bottom of the reactor. These two compartments were connected using cylindrical tube of 2 cm in diameter which was affixed with a Nafion (1135) – proton exchange membrane (PEM). The anode and cathode chamber had carbon electrodes of 15.5 cm length and a diameter of 1.5 cm and was connected using copper wire through an external resistance of 10 Ω which was in turn connected to a multimeter. The electrodes were placed close to the PEM to avoid the internal resistance. 0.1N potassium permanganate was used as catholyte. The MFC was working as a batch reactor and continuous fed reactor (Figure 4).

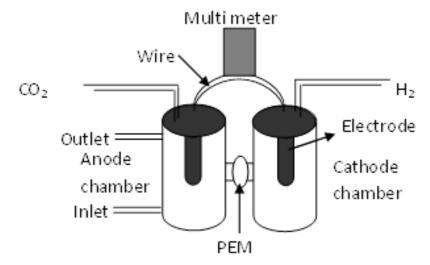


Fig. 4. Typical experimental setup

2.1 Inoculum development and MFC operation

The MFC was immobilized initially with the pure culture of E.coli that was grown in Luria Bertani broth at 37°C for overnight at aerated condition to a

concentration of 1 OD600 and was fed with diluted tannery water as anolyte and 0.1 N potassium permanganate was used as a catholyte.

2.2 Analyses of bio-energy, gases generated and degradation rate

A multimeter was used to detect the electricity and the same was noted at regular intervals. The gases CO2 and H2 were monitored using the method described by Tepe and Dodge, in the presence of 0.05N NaOH as absorbent and gas displacement method respectively. Parameters such as COD and BOD were monitored as per standard methods.

3. Results & Discussion:

Sewage water (raw sewage) collected from sewage treatment of CSIR campus was to the reactor. The acclimation period from batch to continuous mode and to mixed culture was done for 2 days and the readings were noted.

3.1. Effect of Ecoli

The results show that MFC acts as biochemical system generating electrical energy through oxidation of biodegradable organic matter in the presence of fermentative bacteria (Escherichia coli). One of the most active research areas of MFC has been in further development of fuel cells designed to produce power from organic wastes such as sewage. This study dealt with a concept to rely on the microrganisms naturally present in the wastewater that can transfer electrons to the anode. Therefore, Escherichia coli were opted for the study. The choice of microaerophilic studies, with Escherichia coli was beneficial for dual reasons, because it is feasible and the other, it maintains steady state of electron transfer by oxidative metabolic gearing. Bacteria in microaerophilic were adapted to maintain essentially constant turnover of primary energy substrates in response to a wide range of physiological O2. This capacity, oxidative metabolic gearing, allows microaerophilic bacteria to maintain catabolic enzymes, substrates, and cofactors at high steady-state levels. In the present study, constant metabolic activity and organics removal, with electron transfer was found in a steady state.

3.2. Effect of pH

pH of the effluent was reduced slightly than the influent because the bacterial metabolism constantly produces weak acid compounds and maintains their intracelluar pH. As a result, pH was decreased with the electrolyte in anode. The optimal pH for MFC was between 7 and 8. Highest current can be generated between 7 and 8 and the values may be lowered at pH 9. At pH 9, a poor proton transfer takes place at the reduced proton gradient across the membrane.

The decreasing pH in the anode chamber and an increasing pH in the cathode chamber was because proton transport through the Nafion membrane seemed to be slower than both the proton production rate in the anode chamber and the proton consumption rate in the cathode chamber. Protons are equimolarly consumed with electrons in the oxygen reduction reaction in the cathode chamber, thus a pH increase was expected if protons are not supplied through Nafion. However, this periodic buffer replacement evidently reduces the economic viability of MFCs. So catholyte efficiency plays an important factor for operation of MFC. Potassium permanganate was considered to be with high reduction rate potential and cheap.

3.3 Substrate Removal:

The performance of MFC was evaluated by estimating the substrate (C.O.Dr) removal efficiency during operation. It has been found that 90% removal in domestic sewage were recorded in continuous mode. In the batch mode, 76% removal efficiency was recorded (Fig. 5)

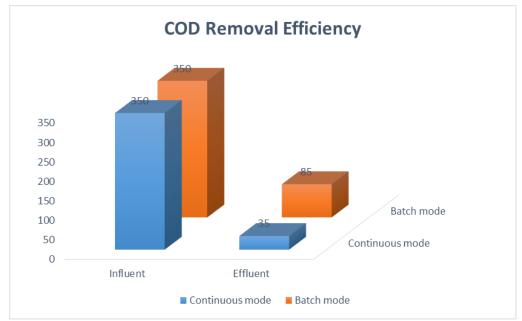


Fig. 5. COD Removal Efficiency

Compared to the batch mode, continuous mode works well with the substrate removal and subsequently the voltage produced was higher than the batch mode system. The decrease in C.O.D concentration indicates effective functioning of mixed microflora with E.coli in metabolizing the carbon source as electron donors in domestic sewage water.

The absorbance of anode electrolyte was monitored with influent and effluent. Initially absorbance for all the effluents was higher and gradually it started to decrease throughout many runs. This was because an organism gets multiplied with the nutrient supplement and biomass concentration decreases. In batch mode, the absorbance was high in the effluent since the biomass, organism, nutrients was mixed up and contribute more optical density.

3.4 Effect of Proton Exchange Membrane

For each electron that was produced, an equivalent proton must be transported to the cathode through the electrolyte to sustain the current. Therefore, proton exchange membranes (PEM) were one of the most important components in MFCs. Nafion membrane has greater efficiency compared to salt bridge. The ratio of PEM surface area to system volume is important for the power output. Hence, the MFC internal resistance decreases with the increase of PEM surface area over a relative range. The oxygen diffusion from cathode to anode was found in Nafion membrane which consumes electrons in the anode compartment, reducing the coulombic yield. The use of mixed cultures may help to minimize the effects of oxygen diffusion into the anode chamber because these bacteria will scavenge any dissolved oxygen, maintaining anaerobic conditions in the anode chamber.

3.5 Effect of biofilm:

Constant C.O.D removal and voltage outputs were considered as indicators for satisfactory formation of biofilms. Biofilm plays essential role in bioelectricity production by electron transfer. A mat of biofilm covered the anodic chamber and it was found covered on the carbon electrode. Due to the presence of high cell density a greater potential for cell-to-cell contact by E.coli, it is possible in biofilms, which helps to stimulate the electron transfer mechanism where anode can resume the role of the solid electron acceptor. The pilus anchored to the periplasmic and/or outer membrane proteins (cytochromes) of the bacteria accept electron transfer beyond the outer surface of the cells (Reguera et al., 2005; Lovley, 2006) and allow the organisms to use an electrode that is not in direct cell contact as its sole electron acceptor (Schroder, 2003). Since E.coli has nanosized pili that may facilitate development of thicker electrochemically active biofilms which allow direct interspecies electron transfers (DET) and removes the need for soluble mediators resulting in higher anode performances (Logan and Regan., 2006; Reguera et al., 2006).

3.6 Voltage and Biogas generation

A steady increase of voltage was observed with continuous mode and a maximum yield of voltage recorded in this study was 960mV by using domestic sewage water as a medium for the seed. Increase in voltage was found with every additional feed and this might be attributed to the adaptation tendency of the inoculted microflora for new environment. During fuel cell operation, carbon di oxide formed in the headspace in anodic chamber was continuously monitored every 24 hours. Since the carbon source increases the metabolic activity of microorganisms, degradation on organic matter was increased subsequently; as a result, more carbon di oxide was formed by carbon di oxide in domestic sewage. There was no difference in the CO2 production with regard to the mode of system used in the reactor.

MFCs operated in continuous mode were more suitable for practical applications than batch MFCs and this study also infers the same, with high voltage production and biogas production. The microbiological conversion of organics into hydrogen was relatively inefficient (15-30% efficiency) and the energy production was low. Normally, biohydrogen formation can be completely suppressed in microbial fuel cells, indicating that the anode is a more energetically feasible electron acceptor than protons, due to a higher overall redox potential (Rabaey et al., 2005 a). In this present study, the hydrogen production was relatively moderate, without using any additional voltage to the cathode chamber and a constant production of 1ml of hydrogen was displaced in both mode of systems.

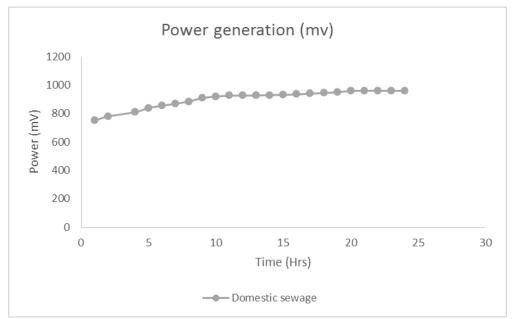


Fig 5. Power Generation in continuous mode

Hence, the study was cost effective and environmentally sound and sustainable due to utilization of wastewater as substrate for in situ power generation along with wastewater treatment, utilizing low cost and non-coated electrodes and mediatorless anode. Normal carbon electrodes were used and the power generation with wastewater could impart a cost effective MFC construction for treating wastewater.

4. Conclusion:

Experimental data demonstrated the feasibility of dual chambered microbial fuel cell in bioelectricity generation and biofuel production from domestic sewage water without using mediator in anode chamber. Designed MFC configuration, adopted operational conditions with carbon electrode, low resistance usage, flow rate of continuous feeding and E.coli with mixed culture showed feasibility of power generation and biofuel production along with wastewater treatment. Substrate degradation was observed with biofuel production in anode chamber and cathode chamber of fuel cell enumerates the functioning of an alternative wastewater treatment from renewable energy.

The environmental emissions of carbon di oxide was arrested and simultaneous recovery of hydrogen as biofuel was major advantage with this study. Hence this green technology of utilizing waste water (renewable energy) for the production of renewable energy (bioelectricity) and biofuels from microaerophilic treatment was feasible, economical and sustainable alternative.

5. Summary

A mediatorless microbial fuel cell was constructed with E.coli as biocatalyst in a two-chambered microbial fuel cell, seperated by a proton exchange membrane. Bacteria converts energy, available in a bioconvertable substrate directly into electricity. The efficiency of proton transfer using nafion membrane was studied with carbon electrodes on potassium permanganate as an electron acceptor. The experimental data evidenced that the 90% C.O.D removal efficiency while treating domestic water. In this study, continuous and batch mode system of working was investigated. It has been found that continuous mode system works to provide maximum power and C.O.D removal than the batch mode. E.coli with its pili and biofilm formation helps in direct and an efficient electron transfer on carbon electrodes. Microaerophilic studies proposed a steady state electron transfer and thus feasible and economical operation than with anaerobic studies. The substrates provided were oxidized and generating electrons and protons. An electron gets transferred to the cathode compartment through an external circuit. Protons transferred in to cathode chamber forms Hydrogen. The off gases of MFC such as CO2 and hydrogen were collected.

Hence, this microbial fuel cell holds a promise towards sustainable energy generation and biofuel production along with wastewater treatment. This type of mediator less MFC emerges, as self-sustaining systems with low cost operation are most feasible and economical. Rapid evolution of MFC technology on many fronts, including reactor designs, selection of materials, renewable substrate utilization, and selection and understanding of biocatalyst has brought it much closer to realize its full potential and application for bioenergy production and simultaneous wastewater treatment.

A mathematical model is required for MFC optimization. The process of MFC should be optimized so that the performance of the fuel cell can be increased. The aspects such as understanding the internal resistance and losses would help the performance of MFC. The focus should be control of overgrowth of non-electrogens in biofilms on electrodes. Computer simulation prototype MFC are required for complete automation and monitoring such as (i) wastewater composition (ii) operational conditions (iii) population dynamics (iv) cell– cell communication (v) molecule–surface interactions and geneexpression profiles of electrode-associated biofilms.

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