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Exploitation and optimization of a microbial fuel cell for the treatment of whey wastewater and the power generation

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ABSTRACT

The dairy industry like most other agro-industries generates strong wastewaters with high biological and chemical oxygen demands representing the high organic content. The let out of untreated wastewater may cause serious problems in terms of organic load on the local municipal sewage treatment systems. The study examined the mediator-less microbial fuel cell (MFC) for the treatment of whey wastewater with simultaneous current generation in the presence of *E. coli*. The maximum current generated using whey wastewater was 3.019–6.99 W/m^2/d with a constant resistance of 10 Ω with 0.1 N potassium permanganate as catholyte with carbon and graphite as electrodes respectively. The graphite electrodes were able to produce more current when compared to the carbon electrodes. During the study a biomass concentration of 3.042 g/l with a CO_2 production of 13–20 mg/l as $NaCO_3$ and H_2 production of 20–25 ml/d respectively were obtained. The distance between the electrode and the Proton Exchange Membrane (PEM) and the distance between the electrodes in case of the dual electrodes also played an important role in the power generation. SEM image evidences the bio-film formation on the electrodes that supported the power density and a COD removal of 91–98% was also obtained. This phenomenon could be utilized to design an inexpensive autonomous system consisting of graphite or carbon electrodes, an electrical load and a recordable voltmeter to track energy generation due to *E. coli* fermentations. In the near term, these fuel cells could be utilized as a research tool for metabolic studies where the current response of microbial fuel cells would be extremely useful.

Keywords: Microbial fuel cells; Whey wastewater treatment; Current generation; Hydrogen production

1. Introduction

In the modern world, energy in any form is required for daily needs for the normal human life. Every year the global energy demand increases. Energy output is one of the indicating factors of the countries progress. We are completely dependent on the conventional energy such as coal and oil for a quite long time. These are non-replenishing source of energy and contribute to major part of energy consumption. While petroleum products currently supply much of this demand, the increasing difficulty of sustained supply and the associated problems of pollution and global warming are acting as a major impetus for research into alternative renewable energy technologies. Due to this we are slowly approaching a stage where all the fuels are fast becoming scarce leading to the huge increase in the demand for energy. Oil will not suddenly run out, but it is a finite resource. We must develop energy saving technologies that can stretch oil reserves. Alternative source can also be potential solution to all these problems by taking nature's solution of energy generation. Biological fuel cells offer a potential solution to

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all these problems of energy generation. It is a bio-electrical system which converts biomass into electricity through the metabolic activity of microorganisms. Microorganisms are capable of metabolizing the organic matter to provide them with energy. The waste from industries or sewage water is excellent source of mixed microbial communities [1].

The dairy industry like most other agro-industries generates strong wastewaters characterized by high biological oxygen demand (BOD) and chemical oxygen demand (COD) concentrations representing their high organic content [2,3]. Due to the high concentrations of organic matters these effluents may cause serious problems in terms of organic load on the local municipal sewage treatment systems [4,5]. Efforts to utilize the huge amount of dairy by-products have led to the development of various whey treatment methods. Despite of the different possibilities of whey utilization, approximately half of the whey produced worldwide is discarded without treatment [6]. The dilution of whey by mixing with other wastewater is a method for reducing the instability and low efficiency problems caused by its high organic content. Over the past decades, several cost-effective treatment technologies comprising anaerobic, aerobic and facultative processes have been developed for the treatment of whey. The microbial fuel cell (MFC) is a rapidly developing technology, which promises the benefit of harvesting electricity while biologically treating whey wastewater. Active research is going on in the field of fuel cells for the production and generation of electricity from the harmless renewable sources. One of the greatest advantages of MFCs over hydrogen- and methanol-fuel cells are that a diverse range of organic materials that can be used as fuels [7,8].

During the process of treatment of wastewater, the protons that are transferred to the cathode chamber from anode 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 [9]. Recently, H_2 has emerged as one of the most promising carriers of new energy because it is clean, recyclable and efficient. In addition, H_2 can be used as an important raw material in various chemical industries [10]. However, H_2 is still primarily produced from fossil fuels, such as natural gas, petroleum and coal, through steam reforming or from water through electrolysis and thermo chemical decomposition. These processes are costly and not environment friendly. Therefore, biological H_2 production process with waste degradation, which is favorable for low costs, has been explored by many researchers [11–13,]. The exploitation of wastewater as substrate for H_2 production with concurrent wastewater treatment is an attractive and effective way of tapping energy from renewable resources in a sustainable way. This provides dual environmental benefits, viz., wastewater treatment with simultaneous energy generation [14].

In this communication, experimental data pertaining to the studies carried out on the treatment for whey wastewater using the MFC and biological H_2 and CO_2 production utilizing whey water has been dealt. The system was designed in such a way that the anode and cathode chamber is separated with a proton exchange membrane that allows charge transfer between two electrodes. A wire containing a load connects the two electrodes, but in the laboratory, a resistor is used as the load. Electrons travel from the anode to cathode due to the redox potential difference that exists between their dissimilar liquid solutions. The current produced by an MFC is typically calculated by monitoring the voltage drop across the resistor using a multimeter. Because of its advantageous properties including rapid growth rate and avirulence, *E. Coli* is one of the most frequently used bacterial model in laboratory for degradation studies. This MFC setup could also be used to track *E. Coli* fermentations.

2. Methods

2.1. Microbial fuel cell assembly

The MFC used in the study was constructed using acrylic with two semi-cylindrical chambers. The anode chamber had total working volume of 4000 cm^3 and cathode with 1000 cm^3. 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). Cylindrical carbon electrodes (15.5 cm × 1.5 cm) and rectangular graphite electrodes (length 10 cm, width 1.3 cm and 1 mm thickness) were used as electrodes and were connected using copper wire through an external resistance of 5, 10 and 20 Ω which was in turn connected to a multimeter. The electrodes were placed close to the PEM to avoid the internal resistance. 0.1 N potassium permanganate was used as catholyte. The MFC was working as a non-continuous reactor (Fig. 1).

2.2. 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 overnight at aerated condition to a concentration of 1 OD_{600} and was fed with diluted whey water as anolyte and 0.1 N potassium permanganate was used as a catholyte. The energy and fuel generated at varying resistance was recorded. Then the efficiency of the carbon and graphite electrodes in generating current was compared to know the electron absorbing capacity of the electrode. The difference in the power production with dual electrodes (Two nos of

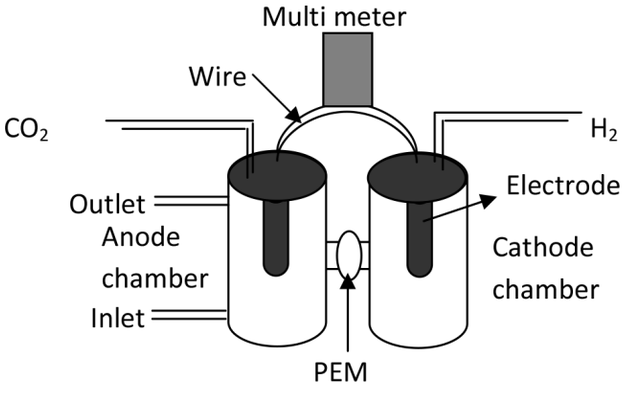

Fig. 1. Microbial fuel cell assembly.

electrodes in Anode chamber) and the distance of the electrode from the PEM was also monitored.

2.3. Analyses of bio-energy, gases generated and degradation rate

A multimeter was used to detect the potential and the current generated regularly in varying time intervals and the power P generated was calculated using the following formula.

Power (P), watts = Current (I), ampere × Voltage (V), voltage

The gases CO_2 and H_2 were monitored using the method described by Tepe and Dodge [15], in the presence of 0.05 N NaOH as absorbent and gas displacement method respectively. Parameters such as COD removal, biomass concentration etc. were monitored as per standard methods [16].

2.4. SEM analysis of the bio-film from anode

Bio-film from anode was removed carefully, was fragmented to fine bits and was washed thoroughly and fixed with 1% formaldehyde and glutaraldehyde. Samples were mounted to an aluminum specimen mount with adhesive and iso-propanol based colloidal graphite paint was applied to the conducting bridges. Then the samples were coated with argon at 13 Pa using gold-palladium powder with the help of a Polaron E-5100 Sputter Coater for 2 min at 2.2 k and was observed in a JEOL JSM-5400 SEM that was operated at 15 kV and the images were digitally captured.

3. Results and discussion

3.1. Optimization of operating conditions and external resistance for a microbial fuel cell with carbon electrode

For optimization and acclimatization the anode compartment of the MFC was fed initially with an influent COD concentration of 250–500 mg/l which reached the outlet port in 13 h and the COD removal was 91 and 95% respectively in the effluent from anode chamber (Table 1). The DO content of the effluent from the anode chamber was found to be 0.6–0.8 mg/l which supported the growth of facultative anaerobes. The CO_2 and H_2 produced in the anode and cathode compartments were collected separately and the overall gas production was 11 mg/ l as $NaCO_3$ and 14–15 ml/d.

The electrons generated in the anode chamber were transferred through the electrodes (anode) and the protons got transferred through the PEM to the cathode chamber which helped in the power generation. As described by Sajana et al [17], there was decrease in the power generation with increase in the external resistance thus an external resistance of 10 Ω was found to work efficiently with a power generation of 0.025–0.04 W/m^2/d than that of 5 and 20 Ω (Fig. 2a and 2b). The power generation with time was found to fluctuate with the decrease and increase in the external resistance.

3.2. Current and gas generation with varying concentrations of substrate with different electrodes

Substrate is a key factor for efficient production of electricity from MFC. Substrate spectrum used for electricity generation ranges in this study ranges from COD concen-

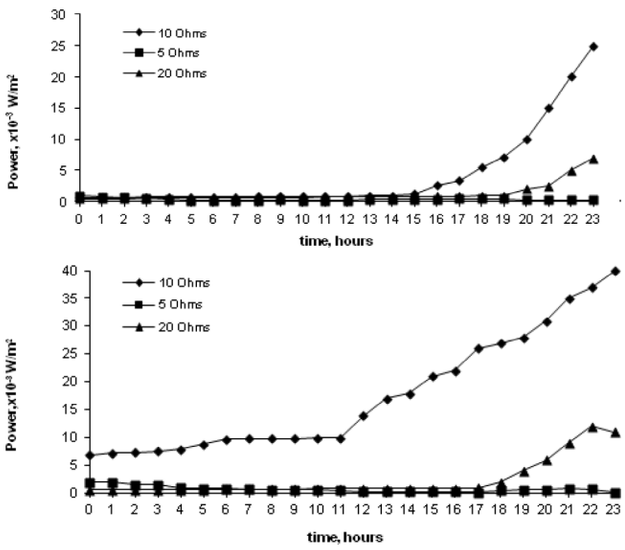

Fig. 2. Difference in external resistance. a) with a whey water of 250 mg/l COD, b) with a whey water of 500 mg/l COD.

Table 1
Characterization of effluent from MFC

Inlet COD, mg/l	Outlet COD, mg/l	Removal, %	Outlet DO, mg/l	CO_2, mg/l as $NaCO_3$		H_2, ml	
				Carbon electrode	Graphite electrode	Carbon electrode	Graphite electrode
250	12.5	91	0.6	11	18	14	20
501	20	95	0.8	11	18	15	20
1010	35	97.7	0.8	13	20	20	20
2002	46	97.7	0.8	13	20	20	25
3000	65	97.8	0.8	13	20	20	25
4050	75	98	0.8	13	20	20	25
5012	80	98.4	0.8	13	20	20	25

tration of 250–5000 mg/l. Anodic materials play an another important role in MFC by affecting the performance of MFCs significantly. Figs. 3 and 4 show the power generated from MFC with varying concentrations of substrate by using carbon and graphite electrodes respectively. As described by Logan et al. [18], the electron absorbance efficiency of the carbon electrode was found to be weaker than that of the graphite electrode, which reflected in the power generation capacity of the system. The carbon electrode was able to generate up to 3.019 W/m^2/d and the graphite electrode was able to produce 6.99 W/m^2/d. Table 1 shows the value of CO_2 and H_2 produced from MFC. The graphite electrodes generated 20 and 25 ml of CO_2 and H_2 per day whereas the carbon electrodes were able to produce 13 and 20 ml respectively. The COD removal efficiency of the system was more than 90% [19,20].

3.3. Effect of the dual electrodes and spacing between the electrodes

The distance between the electrode and the PEM and the distance between the electrodes in case of the dual electrodes also played an important role in the power generation. As shown in Table 2, the system was able to produce a maximum power of 0.025 W/m^2/d with a wastewater COD of 250 mg/l when the electrodes were placed at the distance of 5 cm from the PEM [21]. In case of the dual electrode system, the MFC was able to produce a maximum power when the electrodes were placed at the distance of 5 and 10 cm from the PEM at the anode and 5 cm from the PEM at the cathode, lesser or greater the distance between the electrodes found to affect the current generation due to the limited proton transfer and repulsion among the electrons [22,23].

As shown in Fig 5, when carbon dual electrodes were used, the power generated was accounting to 0.06 W/m^2/d and for the graphite electrode, the power generation accounted to 0.1224 W/m^2/d with a wastewater COD of 250 mg/l [24]. There was tremendous increase in the CO_2 and H_2 production which was about 25–30 ml/d and 30–40 ml/d as discussed by Fang et al [25].

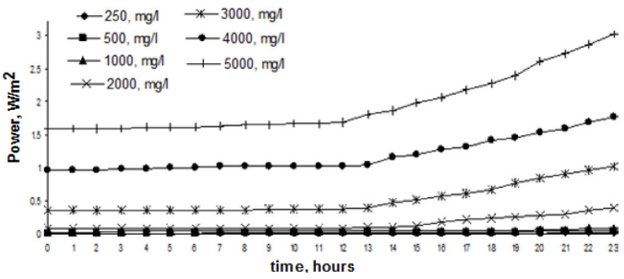

Fig. 3. Power generation with varying concentration of whey water with carbon electrode.

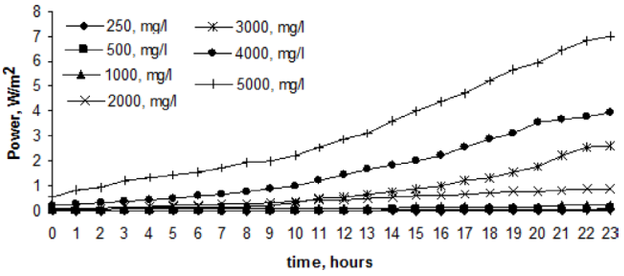

Fig. 4. Power generation with varying concentration of whey water with graphite electrode.

3.4. Bio-mass and Bio-film formation, its effect in current generation

The bio-mass concentration in the MFC increased with the increase in the voltage generation, a maximum of 0.106 OD_{600} was observed in 24 h for *E. coli* with the whey water with a power generation 3.019–6.99 W/m^2/d. A clear layer of granulated sludge was seen at the bottom of the reactor and the effluent was found to have 0.304 OD_{600} after 24 h with a current generation of 6.99 W/m^2/d with that of the 5000 mg/l COD containing whey water. These granules were found to be porous with different fermentative bacteria at the concentration of 3.042 g/l for both the electrodes. A prominent layer of bio-film of 1.5–2 mm thickness was seen to cover both the electrodes and the PEM at the anode compartment to enable the mediator-less electron transfer to the electrodes. The SEM image (Fig. 6a, b) of the bio-film over the surface of both the electrode in the anode chamber also revealed the presence of predominant filamentous fer-

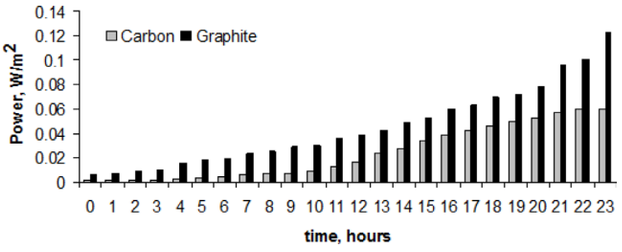

Fig. 5. Comparison of power generation efficiency with carbon and graphite dual electrodes.

Table 2
Power generation with different spacing with single and dual electrodes

Single electrode			Dual electrode		
Anode distance, cm	Cathode distance, cm	Power, W/m^2/d	Anode distance, cm	Cathode distance, cm	Power, W/m^2/d
5	5	0.025	5.5	5	0.01
10	10	0.012	5.10	5	0.06
15	15	0.006	5.15	5	0.03
20	20	0.003	5.20	5	0.02

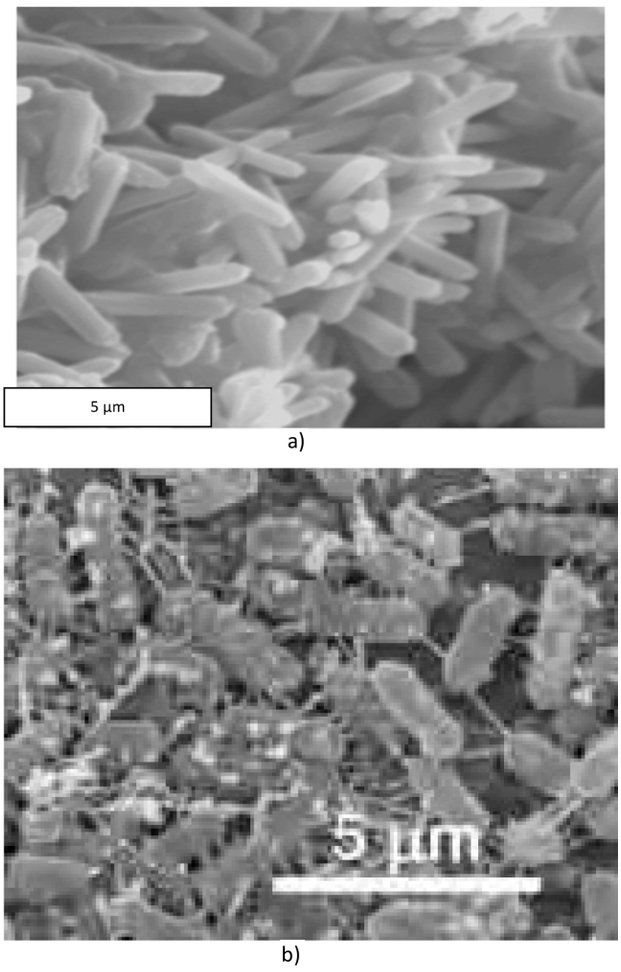

Fig. 6. SEM image of the bio-film from the electrode surface of the anode chamber showing the closely attached filamentous fermentative bacteria enabling the mediator-less electron transfer a) Carbon electrode; b) Graphite electrode.

mentative bacteria that were closely attached to each other enabling the mediator-less electron transfer [26,27].

4. Conclusion

The dual chamber microbial fuel cell inoculated with *E. coli* demonstrated its efficiency in the whey wastewater treatment and in electricity generation. The data presented a direct correlation between voltage output and metabolic phase. In addition to the current generated by the MFC itself, the organism also produces H_2 gas, which may then power a conventional hydrogen fuel cell similarly CO_2 gas can also be stored and used. By consolidating the functions of waste management, renewable power generation, and solvent production, *E. coli* fuel cells have the potential to reduce organic wastes and increase opportunities to convert those wastes to usable energy. Current generation has proven to be reproducible and repeatable and was validated through measurements of COD removal. This phenomenon could be utilized to design an inexpensive autonomous system consisting of carbon or graphite electrodes, an electrical load and a recordable voltmeter to track *E. coli* fermentations. In the near term, these fuel cells could be utilized as a research tool for metabolic studies where the current response of microbial fuel cells would be extremely useful. With continued development, future monitoring systems for bio-production become possible.

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