



# Comparison of anodic metabolisms in bioelectricity production during treatment of dairy wastewater in Microbial Fuel Cell



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## HIGHLIGHTS

- Energy generation from dairy wastewater was investigated using dual chambered MFC.
- Anaerobic metabolism showed higher current efficiency than aerobic metabolism.
- Aerobic metabolism showed higher power generation capacity.
- MFC operate at pH 7 and COD concentration of 1660 mg/L showed better performance.
- MFC operation using a buffer for pH maintenance given better power generation.

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## ABSTRACT

Energy generation from dairy industry wastewater was investigated using a dual chambered Microbial Fuel Cell by aerobic and anaerobic anodic metabolism, operating with initial COD concentration of 1600 mg/L and anolyte pH of 7 produced highest power density of 192, 161 mW/m<sup>2</sup> and volumetric power of 3.2, 2.7 W/m<sup>3</sup> with COD removal efficiency of 91% and 90%, respectively. The columbic efficiency was 3.7-folds lower for aerobic metabolism compared to anaerobic metabolism with 17.17%. Effect of operating parameters such as anolyte pH and COD concentration on MFC performance was also evaluated. Anaerobic metabolism operated with COD concentration of 1600 mg/L and anolyte pH 7 showed best performances. Biofilm formation by inherent microbes of wastewater on anode was visualized by instrumental techniques. Milk processing operation runs almost through the year, hence MFC utilizing dairy industry wastewater would be a sustainable and reliable source of bio-energy generation.

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## 1. Introduction

The rising concern over protection of environment and depleting energy resources has made it inevitable to taken over the waste management system from merely treating the waste to new horizon of recovery of energy from waste (Pant et al., 2009). Microbial Fuel Cell (MFC) a novel method of directly generating electricity from organic matter in wastewater, simultaneously treating waste water solves issues of energy crisis and environmental damage. MFC is a bioelectrochemical system exploiting bacterial oxidation of biodegradable organic matter, to generate electricity. The micro-organism present in anode chamber of fuel cell acts as catalyst to convert chemical energy in wastewater to electrical energy. The microbial metabolism generates electrons (e<sup>-</sup>) and protons (H<sup>+</sup>) by oxidation of organic substrate, which leads to the development of bio-potential. The electrons are transferred to the anode by the bacteria through various mechanisms such as solid conductive

matrix or by electron shuttles. Electrons are then transferred to cathode through external circuit (Rabaey and Verstraete, 2005). The protons in anode chamber pass through the proton exchange membrane into the cathode chamber, where they combine with the electrons and oxygen with the help of mediator to form water. The potential between the respiratory system of bacteria and electron acceptor generates the current and voltage needed to make electricity (Logan, 2007; Rabaey and Verstraete, 2005). Scaled up MFC system consisting of 40 individual cells, generating 4.1 W/m<sup>3</sup> of energy, capable of powering LED panel has been constructed and evaluated by Zhuang et al. (2012). Detailed research on MFC and its scale up would enable efficient conversion of waste to energy.

The pioneering research in MFC was performed using pure substrates. Though usage of pure substrate provided better understanding of the underlying process, the present day researchers are using more unconventional substrates with an aim of exploiting waste biomass or treating wastewater on one hand and improving MFC output on the other. Also MFC using complex substrates nurtures wide range of microbial communities enhancing

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the power generation (Pant et al., 2009). A range of organic wastewater including brewery industry wastewater (Feng et al., 2008), domestic (Min and Logan, 2004), rice mill (Behera et al., 2010), starch processing (Gil et al., 2003), landfill leachate (You et al., 2006), food processing (Oh and Logan, 2005), hospital wastewater (Aelterman et al., 2006), alcohol distillery (Huang et al., 2011), manure sludge waste (Scott and Murano, 2007), meat packing plant wastewater (Heilmann and Logan, 2006), paper recycling wastewater (Huang and Logan, 2008) have been used as substrate in MFC.

In rapidly developing country like India, the industrialization has triggered the recent trend of migration of rural people to urban areas for employment, raising the need of processing milk. The food processing industries have reported that 94.6 million tones of milk processed in the year of 2006–2007 and growing at the rate of 3–4% in India every year. Dairy industry wastewater consists of carbohydrates, proteins and fats, making it complex in nature. For every liter of milk processed, 2–2.5 L of wastewater is produced (Ramasamy et al., 2004). Hence the huge volume of dairy wastewater goes unutilized, pollutes the environment when released without treatment.

Current treatment methods include biological and physiochemical process (Kushwaha et al., 2011). Aerobic procedures are energy intensive increasing the cost of treatment, making it impossible to be implemented on large scales (Wheatley, 1990). Anaerobic treatment approach include production of biogas by Methanogenic bacteria, Inhibition of Methanogenic bacterial growth by long chain fatty acids produced by lipid hydrolysis present in wastewater results in lower biogas yield (Vidal et al., 2000). The presence of Methanogenic bacteria is the cause behind reduced electricity production in MFC, hence inhibition of methanogens growth by long chain fatty acid would prove to have positive influence over power generation in an MFC. The organic nature of wastewater makes it a suitable substrate for MFC operation (Pant et al., 2009).

Gil et al. (2003) has reported that increasing the fuel oxidation and electron transfer in anode compartment enhanced the power generation in MFC using starch processing wastewater. Rate of bio-oxidation can be improved by increasing microbial activity. Venkata Mohan et al. (2008) have studied MFC using synthetic wastewater, state that substrate degradation was higher using aerobic anodic metabolism than anoxic and anaerobic mechanism, which was due to higher substrate oxidation and good biofilm growth on anode surface. Most of the literatures on MFC include usage of inoculum from existing industrial wastewater treatment plants, (Venkata Mohan et al., 2010). These microbes require an initial lag phase to adapt itself to grow in dairy industry wastewater.

Studies have reported that dairy industry wastewater produces relatively lower power in comparison with other wastewater in MFC (Mathuriya and Sharma, 2010; Velasquez-Orta et al., 2011). Main components of dairy wastewater are carbohydrates and proteins. Apart from COD removal, influence of carbohydrates and proteins in power generation of MFC using dairy wastewater as substrate has been studied by Venkata Mohan et al. (2010) and has reported that reduction in carbohydrates and proteins did not show good relation to power generation. Researchers working with dairy industry wastewater have concentrated in improving the configuration of MFC to improve power generation. Mardanpour et al. (2012) tried to improve the power output in MFC using dairy wastewater by increased anode area using spiral anode where high open circuit voltage (OCV) of 810 mV was obtained. Ayyaru and Dharmalingam (2011) studies reveal that using SPEEK membrane in MEA-MFC assembly produced higher power in comparison to Nafion in MFCs treating dairy industry wastewater. The maximum voltage of  $400 \pm 15$  mV was obtained in this system.

In this study, we concentrate on improving power generation by increasing fuel oxidation. The aim of investigation was to improve power production of dual chambered MFC employing plain graphite plate electrodes by varying anodic metabolism (aerobic and anaerobic) by increase rate of fuel oxidation, the native microbes present in the wastewater has been used as inoculum. The influence of operating parameters such as pH and concentration of Chemical Oxygen Demand (COD) in fuel oxidation and power production has been studied.

## 2. Methods

### 2.1. Dairy wastewater and inoculum

Dairy wastewater was collected from milk processing industry near Krishnagiri, Tamil Nadu. The wastewater was stored at 4 °C and brought to room temperature prior to use. The collected wastewater was foul smelling, with characteristically lower COD of 3200–3400 mg/L and pH value near neutral of 7.6.

For aerobic operations, single aerobic bacterial colony was isolated from dairy wastewater by serial dilution (Harley and Prescott, 2002). The isolated colony was maintained in slant cultures. The isolated colony was inoculated to sterilized dairy wastewater, to avoid the influence of other microbes on the MFC performance. Distilled water used in case of dilution was also sterilized. Continuous supply of oxygen was maintained for aerobic metabolism in the anode chamber. For operation of MFC, using anaerobic metabolism the wastewater was purged with nitrogen to remove dissolved oxygen and the anode chamber was completely sealed from external atmosphere. Unsterilized wastewater was used as inoculum for anaerobic metabolism. The anode plate was subjected to scanning electron microscopy (SEM JEOL JSM-6701F) to visualize the bacterial biofilm formed over the graphite plate. The electrode was air dried and thin layer of platinum was coated prior to imaging.

### 2.2. Fuel cell configuration and operation

Dual chambered Microbial Fuel Cell was fabricated using plexi glass material each chamber with total/working volume of 0.35/0.3 L operated in a batch mode. Ferricyanide was used as catholyte. Plain graphite plates ( $6.5 \times 4 \times 0.3$  cm; surface area  $50 \text{ cm}^2$ ) without any coating were used as electrodes. The electrodes were soaked in distilled water for 24 h and placed 1 cm away from the membrane in the MFC. Nafion 117 was used as proton exchange membrane separating the anode and cathode chamber. To increase porosity the Nafion membrane was pre-treated by boiling sequentially in 30%  $\text{H}_2\text{O}_2$ , distilled water pH 7, 0.5 M  $\text{H}_2\text{SO}_4$  and distilled water (Venkata Mohan et al., 2007). Sampling ports were made to collect anolyte at particular intervals. These ports were sealed when anaerobic environment had to be maintained. Connections were made using copper wires.

MFC reactors were operated in fed batch mode and refilled each time when the OCV dropped below 200 mV. No extra inoculum of microbes from previous cycles was added. The MFC were operated at room temperature of  $30 \pm 2$  °C. The effect of COD concentration was studied with dilution of wastewater made using sterilized distilled water.

### 2.3. Analyses and calculations

The cell potential ( $E$  in volts) of the system was measured using a digital multimeter (aplab vc97). The current ( $I$  in ampere) produced from a single MFC is small, so that the current is not measured, but instead it is calculated from the measured voltage

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