Bioelectricity Generation and Pollutant Reduction from Fishery Wastewater using Dual Chamber MFC and Paddy Plant MFC

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Abstract - *Microbial Fuel Cells (MFCs) have gained a lot of attention recently as a mode of converting organic matter into electricity. In this study, MFC that generates bioelectricity by biodegradation of fisheries wastewater is developed. This study also investigated the potential for bioelectricity production by paddy plant, in Plant Microbial Fuel Cells (PMFC). Three types of MFCs have been developed. They are namely dual chamber microbial fuel cell, double chamber paddy plant microbial fuel cell and single chamber paddy plant microbial fuel cell. Dual chamber microbial fuel cell and double chamber paddy plant microbial fuel cell setup along with preparation of salt bridge. The single chamber plant microbial fuel cell was developed without the separating membrane. Fisheries wastewater (especially squid ink) was used as substrate for generating bioelectricity. The effluent parameters such as BOD, COD, Nitrogen and Phosphorous were evaluated. Bioelectricity was monitored over a period of 60 days. The double chamber paddy plant microbial fuel cell shows better results in terms of bioelectricity generation as well as pollutant reduction. The peak voltage generated in double chamber paddy plant microbial fuel cell was around 194 mV across 1000 Ω on corresponding wastewater volume of 2.5 liter. The maximum power obtained was 37.636mW. Proportionately around 103 W of power can be produced from an overall wastewater volume of 7000 liter from the industry in weekly basis, which can be efficiently utilized for lightening the bulbs and other appliances in the treatment plant. The maximum COD removal efficiency achieved by double chamber paddy plant microbial fuel cell was 58% and the maximum BOD removal efficiency was 76%. Considerable reduction in the nitrogen and phosphorous concentration was also observed.*

Key Words: Bioelectricity, Dual chamber microbial fuel cell, Plant microbial fuel cell

1. INTRODUCTION

Microbial fuel cells (MFCs) are bio-electrochemical transducers that convert microbial reducing power (generated by the metabolism of microorganisms) into electrical energy. They are an alternative to conventional methods of generating electricity for small scale applications. Reduction and recycling of waste are very serious problems all over the world due to the limitation of final disposal sites. Microbial fuel cell (MFC) technologies represent the newest approach for generating electricity from biomass using microorganisms. They use the available substrates from renewable sources and convert them into harmless by-products with simultaneous production of electricity. Typically MFCs convert the organics or pollutants into bioelectricity and the reaction is mediated by microbes. Industrial wastewater treatment is one of the great worldwide challenging environmental issues. Many advanced technologies are being developed in order to get pollutant free environment and also to reuse the wastewater for any other purpose in the form of renewable energy. Microbial fuel cell is one of the promising technologies for simultaneous treatment of wastewater and to obtain sustainable energy in the form of electricity efficiently. Developments in MFCs have expanded its applications owing to its distinctive benefits in treatment of wastewater and electricity generation by employing mild operative condition, greater bioenergy productivity and lesser generation of sludge. Generally, MFCs configured with dual chambers including (anaerobic) anode and (aerobic) cathode. Anode can be employed to receive the electrons from microbes that were migrated to an electron acceptor via cathode. The reactions happen under anoxic conditions. Movement of microbes in the direction of the electrodes causes micro colonization and subsequently resulted in strong development of biofilm. This microbial biofilm acts as biocatalyst to degrade the substrate and subsequent production of many electrons and protons in MFCs.

Similar to most processing industries, fish processing operations produce wastewater, which contains active organic contaminating organisms in soluble, colloidal and particulate form. Squid ink, also known as cephalopod ink, is a dark ink produced by squid. The ink contains many compounds, including melanin, acetate, enzymes, polysaccharides, catecholamines (hormones), metals like cadmium, lead, and copper, as well as amino acids, such as glutamate, taurine, alanine, leucine, and aspartic acid. The main compound in squid ink is melanin, which is the pigment responsible for the ink's dark colour.

1.1 Plant Microbial Fuel Cell

The plant-MFC aims to transform solar radiation into green electricity in a clean and efficient manner by integrating the roots of a living plant in the anode compartment of a microbial fuel cell. The plant-MFC is based on two proven processes, rhizo deposition of organic compounds by living plants and electricity generation from organic compounds in the microbial fuel cell. The living plant is photosynthesizing in its leaves whereby solar energy is used to fix carbon dioxide in the form of carbohydrates. Depending on plant species, age, and environmental conditions up to 60% of the net fixed carbon can be transferred from its leaves to the roots. The plant root system produces and releases different types of organic compounds into the soil. Rhizodeposits contain carbon and a part of this carbon can be utilized by micro-organisms in the rhizosphere, which can lead to mutually beneficial interactions between plants and micro-organisms. Bacteria, for example, can positively interact with plant roots by forming protective biofilms or by producing antibiotics as biocontrols against potential pathogens. Since the largest fraction of rhizodeposits are small molecules they are efficiently synthesized by the plant and efficiently metabolized by bacteria. In the plant-MFC, the principal idea is that plant rhizodeposits will be utilized as substrates by the bacteria to generate electricity in the microbial fuel cell [3].

1.2 Dual Chamber Microbial Fuel Cell

According to how electrons are transferred from the bacteria to the anode, MFCs can be classified into two types: mediator and mediator-less MFCs. Dual chamber microbial cells can be of a variety of shapes such as U-shape with cathode in one arm of the tube and anode being in the different arm. Both the electrodes are separated by ion selective membrane such as proton alternate membrane that approves solely protons to pass by through it and now not to the solutions and microbes itself. The other common design of twin chamber MFC use simple H- fashioned meeting with anode in one face and cathode on the other, each separated by way of proton alternate membrane [3].

1.3 Single Chamber Microbial Fuel Cell

Single chambered MFC are basic anode compartment where there is no complete cathode compartment and may not contain proton trade films. Permeable cathodes shape one side of the mass of the cathode chamber using oxygen from air and letting protons diffuse through them. They are very easy proportional up than the two fold chambered Fuel Cells and hence have discovered broad use and research interests recently. The anodes are ordinary carbon terminal yet the cathodes are either permeable carbon terminals or PEM fortified with adaptable carbon fabric anodes. Advantage of single chamber MFC is the reduced set up costs.

2. METHODOLOGY

2.1 Characteristics of Fishery Wastewater

The fisheries wastewater was obtained from the fish processing industry situated in Ayikkara harbour (Kannur district,Kerala). The collected wastewater was stored at 4°C in refrigerators prior to use and analysis. Cephalopods (squid) processing wastewater (mainly squid ink) has been used for analysis. The initial characteristics of the wastewater are tabulated in Table 1.

Table -1: Initial Characteristics

Parameters	Value
BOD	1200 mg/L
COD	2250 mg/L
Total Nitrogen	28 mg/L
Total Phosphorus	19 mg/L

2.2 Cultivation of Paddy Plants

Plant microbial fuel cells have been developed using paddy plants. The seed variety is IR8. IR8 is a high yielding semi dwarf rice variety. The average height of such variety is 90cm to 95cm and having a maturation period of 130 days whereas the maturation period for other traditional varieties are 160 days. The locally available nutrient rich paddy soil is used for the cultivation of paddy plants. Seeds were soaked in water for less than 12 hours and is then covered with cotton cloth for next 48 hours. Germination was done in polypropylene buckets filled with paddy soil and potting mix at equal proportion. The depth of mixture was 15cm. One plant microbial fuel cell received 20 rice plants.

Fig -1: Cultivation of paddy plants

2.3 Microbial Fuel Cell Design and Setup

A dual chamber MFC was constructed, anode and cathode chamber was made up from Polypropylene (PP) containers. The dimension of container was suitably chosen. The height of container is 270mm with a diameter of 180mm. For anaerobic condition cap of container was closed and for aerobic either open or aerated using aquarium air pump with air diffuser. The anode chamber is filled with substrate and cathode chamber is filled with potassium ferricyanide solution ($K_3Fe(CN)_6$) and phosphate buffer solution. The MFC reactor was separated into anode and cathode chambers by salt bridge. The CPVC pipe containing the salt agar mixture was fixed between the two containers and behaved like the salt-bridge assisting in the proton transfer mechanism during the MFC operation. Carbon rods were used as anode and cathode (electrodes) of Dual chamber MFC. The height of the electrode was 140 mm and diameter 10mm. Copper wire was winded on carbon rod to collect and transfer electrons sufficiently. Electrodes were positioned at the centre of each chamber. The electrodes were connected to external resistance (R) 1000 Ω using a digital multi meter were recorded. The acclimatization phase is set up for 3 days. Normally, the inoculums took 24–72 hours to get acclimatize and to utilize substrate for current generation. Figure 2 shows a constructed dual chamber MFC.

Fig -2: Dual chamber MFC

In a double chamber paddy plant MFC, the anode chamber is planted with 20 paddy plants and is filled with substrate and cathode chamber is filled with potassium ferri cyanide ($K_3Fe(CN)_6$) and phosphate buffer solution. .The size of chamber is 180mm diameter with a height of 350mm. The MFC reactor was separated into anode and cathode chambers by Salt Bridge. The placement of electrodes is important because an operation under aerobic conditions can result in the occurrences of voltage reversal and low electricity production Anode was positioned 5cm bellow the soil surface where as cathode positioned at the centre of cathode. Working volume of the chamber is 2.5L.

Fig -3: Double chamber PMFC (after 20 days)

Fig -4: Double chamber PMFC (after 40 days)

Fig -5: Double chamber PMFC (after 60 days)

Single chambered MFC consisting of basic anode compartment where there is no complete cathode compartment and may not contain proton trade films. The size of chamber is 180mm diameter with a height of 350mm.The electrodes are carbon electrode with 10mm diameter and 140mm height. The container consist of 20 paddy plants. In order to create anaerobic conditions the anode placed 5 cm below the soil. The cathode is placed just above the soil surface. The distance between cathode and anode electrode is 5 cm. Figure 6 shows a single chamber MFC. The electrodes were connected to external resistance(R) 1000 Ω using a digital multimeter.

Fig -6: Single chamber PMFC

2.4 Experimental Analysis

The set of experiments was carried out for a period of 60 days (february to march) under the standard photoperiod of 16-h-light/8-h-dark. The minimum temperature was 27 ± 2 °C during the day and 20 ± 2 °C at night. The voltage across the resister was monitored by the digital multi meter every day at 11 am. Electrode output was measured in volts (V) against time. The current in Amperes (A) was calculated using Ohm's law,

$$I = V/R$$

where V is the measured voltage in volts (V) and R is the known value of the external load resistor in Ohms(1000 ohm). From this it is possible to calculate the power output P in watts (W) of the MFCs by taking the product of the voltage and current. Power density and current density are calculated with the help of anode surface area. Normally, the anode area is taken as the electrode area.

The amount of pollutant reduction (Chemical oxygen Demand, Biological oxygen Demand, Nitrogen, Phosphorus) were determined at 10 days interval up to a period of 50 days. Standard methods are used for laboratory analysis. The pollutant removal efficiencies are calculated.

3. RESULTS AND DISCUSSIONS

3.1 Bioelectricity Monitoring

In dual chamber microbial fuel cell the primary voltage obtained was 65 mV. At day 49, peak voltage obtained and it was 146 mV. After 49 days, the voltage produced is decreased. The maximum power density obtained from the MFC is 0.468 mW/cm^2 . The cell voltage of double chamber plant-MFC increased steadily from day 2 and reached maximum of 194mV at day 52. This corresponds to a current generation of 0.194 mA. The maximal achieved electrical power production was 0.827 mW/cm^2 . In single chamber plant microbial fuel cell the primary voltage obtained was 86 mV. At day 39, peak voltage is obtained. The peak voltage was 149 mV. After 39 days, the voltage produced is declined. The maximum power density obtained from the MFC was 0.488 mW/cm^2.

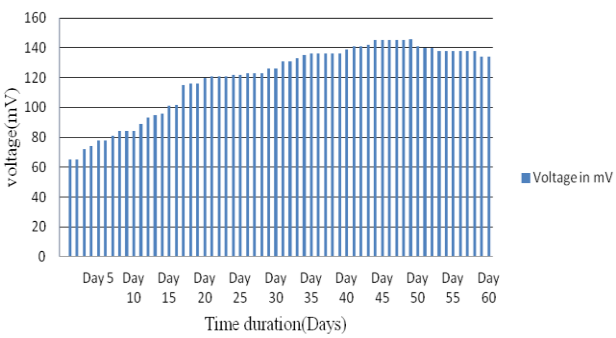

Chart -1: Voltage measured vs Time in MFC

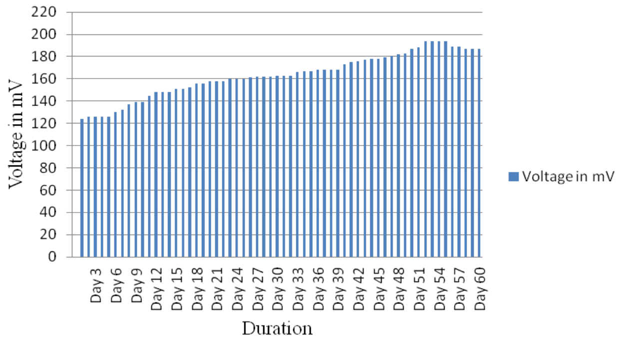

Chart -2: Voltage measured vs Time in Double PMFC

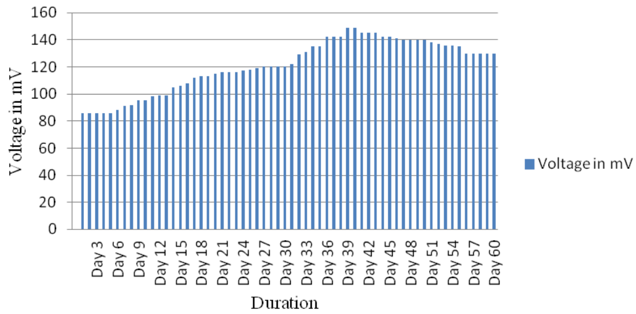

Chart -3: Voltage measured vs Time in Single PMFC

In a dual chamber microbial fuel cell the anodic chamber contains organic substrates that are metabolized by microbes for growth and energy production while generating electron and proton. As time passes the amount of organic substrates available for microbes will get reduced due to the continuous consumption. Also the reduction in ferricyanide concentration (catholyte) due to evaporation loss effects the bioelectricity production. As a result of this a decline trend in the amount of voltage generation is observed after fifty days.

The absence of a good electron acceptor such as ferricyanide causes lack of current production in single chamber PMFC. However the availability of good amount of rizodeposit compensates the absence of electron acceptor and produces current. After 39 days , the voltage produced is declined. The difference might be caused by the relatively lower substrate concentration. MFC without the salt bridge produces bring down current generation because of expanded dispersion of oxygen into the anode. Also, high groupings of hydrogen gas without oxygen in a solitary chamber MFC favors the development of methanogens which can bring down hydrogen recuperations and debase the gas. In this manner, single chamber MFC experiences low general proficiency. The disadvantage of single chamber MFC is the low efficiency generally because of diffusion of oxygen into anode i.e. consumption of oxygen by the bacteria.

It was found that microbial fuel cells produced best power density at double chamber paddy plant microbial fuel cell. These high-power densities were reached within 2 weeks. Large peaks seen at the beginning of the experiment were associated with the amount of organic source accumulated , it can be hypothesized that power output of a PMFC declines near the end of the life cycle. The highest currents were recorded at the seedling and tillering stages in the paddy PMFC. A possible explanation could be high microbial activities and more exudates at early stages or higher photosynthetic compounds utilized by the plants for fruit formation, rendering less to the root at latter stages. Thus, plants can generate more current at a vegetative stage rather than a reproductive stage. A significant decline in power density in last stage of experiment suggests that most of the easily degradable carbon contained in the soil had been converted to other compounds releasing free electrons to produce electricity. The inadequate supply of nutrients to the electrogenic microbes due to thickened biofilm and insufficient proton transfer to the cathode chamber (loss of mass transfer and diffusion limitations) might be the reason for decreased voltage output and current density at the last stage of experiment. Also the power decline in PMFCs could have resulted from the lower availability of rhizodeposits. Also the reduction in ferricyanide concentration (catholyte) due to evaporation loss effects the bioelectricity production by decreasing the capacity to accept electrons from anode chamber. The variable output power density with elapsed time in all of the system is illustrated in chart 5. The dual chambered paddy plant microbial fuel cell achieved highest voltage during the experiments i.e 194 mV. Until 60 day of monitoring an increasing –decreasing trend of output voltage were observed in the MFCs. However, among 35-55 days were obtained the highest peaks of voltages in all experiments, after 55 days the voltage decreasing trend was observed. The variability of the output voltage may be explained for the environmental and experimental conditions during the MFCs operation, such as nutrients availability from wastewater, contribution of inorganic and trace elements from soil, selection and development of the microbial community, and average environmental temperature. It was observed that the voltage values were higher in MFC with paddies than MFC without paddy. The general trend of voltage generation was that it increased gradually in the initial stage before becoming constant and finally it started to decrease when the rice plants were ready to be harvested. Chart 4 illustrates the voltage generation in three systems at ten days interval up to sixty days. A significant voltage production is obtained from double chamber paddy plant MFC than the other two systems.

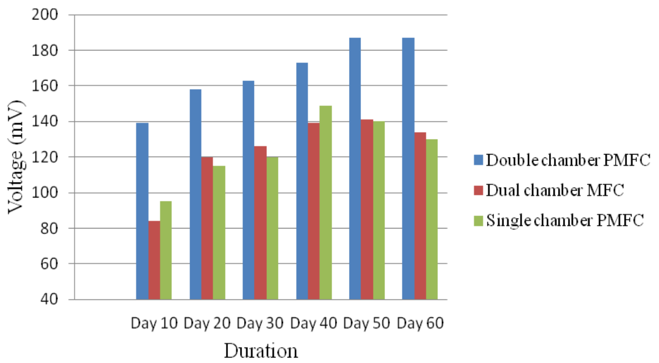

Chart -4: Voltage generation of three systems

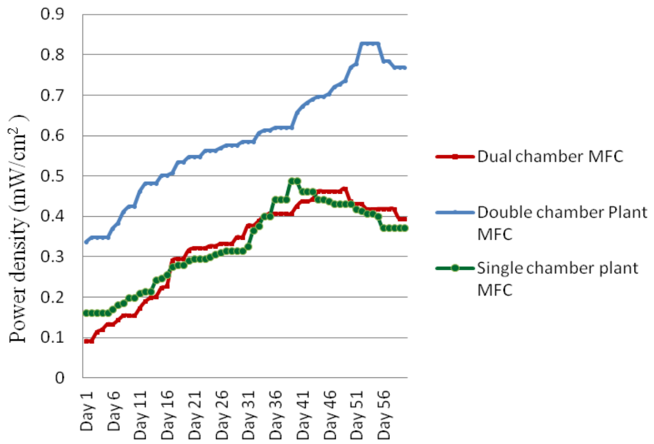

Chart -5: Power density of three systems

3.2 Effluent Parameters during Power Generation

The microbial fuel cell performance regarding the organic matter degradation is demonstrated by COD removal, BOD removal and nutrient removal. Fisheries wastewater characterized after obtaining from processing industry consisted of considerable amounts of pollutants, nitrates and phosphates which need remediation prior to its discharge into the environment. Relatively higher pollutant reduction observed with paddy plant microbial fuel cell than dual chamber microbial fuel cell is attributed to the efficiency of rhizodeposits. Roots of plant could decrease the clogging caused by the rapid growth of biofilm, which was beneficial to the diffusion of protons produced by electrochemically active bacteria. In addition, root exudates consisted of carbohydrates and amino acids, which could be used as the carbon resource to generate electrons. All the MFCs showed stable contaminant treatment performance.

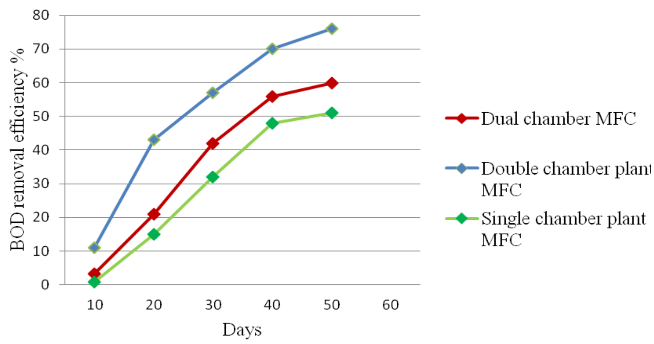

Chart -6: Variation of BOD removal efficiencies of 3 systems

At 10 days the BOD removal efficiency given by ordinary dual chamber microbial fuel cell and single chamber plant microbial fuel cell was very much less than that of double chamber plant microbial fuel cell. The double chambered paddy plant microbial fuel cell gave more than 50% BOD removal efficiency within 4-5 weeks of experiment. In a mediator free paddy plant microbial fuel cell less BOD removal efficiencies were obtained. The bacterial population in the dense biofilm may play a major role in treating the wastewater by achieving higher BOD removal efficiency.

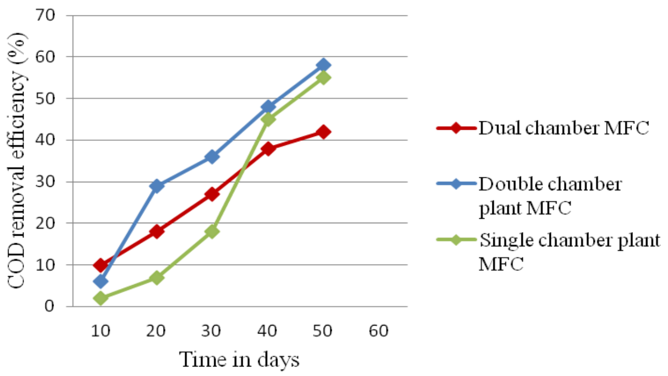

Chart -7: Variation of COD removal efficiencies of 3 systems

The considerable Chemical Oxygen Demand (COD) removal efficiency ranged between 42%, 58% and 55% in dual chamber microbial fuel cell, double chamber plant microbial fuel cell and single chamber plant microbial fuel cell respectively. At the beginning of the experiment double chamber plant microbial fuel gave 6% removal efficiency only. But at the end double chamber plant microbial fuel cell achieved a removal efficiency of 58%. The single chamber paddy plant microbial fuel cell also observed with more than 50% COD removal efficiency. The ordinary dual chamber microbial achieved 42% removal efficiency.

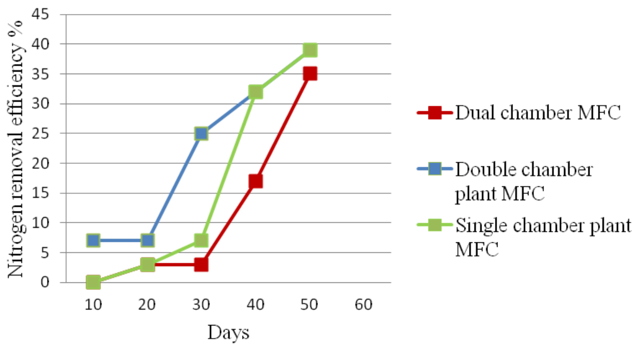

Chart -8: Variation of nitrogen removal efficiencies of 3 systems

The highest nitrogen removal at 39% was exhibited in double chamber plant microbial fuel cell and single chamber plant microbial fuel cell. At 10 days the nitrogen removal efficiency given by ordinary dual chamber microbial fuel cell and single chamber plant microbial fuel cell was zero. The double chambered paddy plant microbial fuel cell gave higher removal efficiency during experiment. There was a sharp increase in removal efficiency in day 30-40 in the single chamber paddy plant microbial fuel cell. The variation in nitrogen removal efficiency is shown in the graph (chart 8). Higher nitrogen removal was observed with plant microbial fuel cells(39%) than the ordinary dual chamber microbial fuel cell(35%).

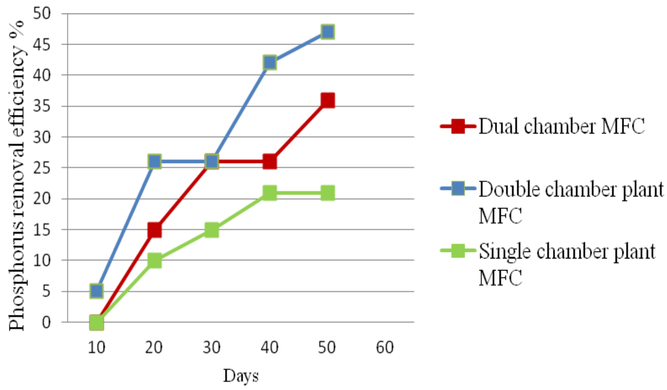

Chart -9: Variation of phosphorous removal efficiencies of 3 systems

The phosphorous removal efficiencies are plotted in chart 9. At the initial period of experiment the removal efficiencies were remained same or low. This could be attributed to the reduced contact time between the inoculum microorganism and wastewater. But at the last stage of experiment the removal efficiencies are increased. The paddy plant microbial fuel cell obtained a maximum phosphorous removal efficiency of 47%.

3.3 Effect of Fishery Wastewater Treatment and Power Generation on Plant Growth

Paddy plants grew well until the end of the experiment. It was observed that the growth of the rice plant showed gradual speed during the first 2 weeks. After that a dramatic increase of the length was observed from weeks 4–9 for all cases. In principle, when plants get older, rhizodeposition decreases. Hence, it can be hypothesized that power output of a PMFC declines near the end of the life cycle. The highest currents were recorded at the seedling and tillering stages in the paddy PMFC. Plants can generate more current at a vegetative stage rather than a reproductive stage. The length of the rice plants at planting was around 10 cm, but within 60 days it grew to around 60-80 cm. The final size of the rice was quite similar with the final size of the rice plants in a real paddy field. Thus it was seen that the additional electricity generation and wastewater treatment did not have any bad influence on the growth of the rice plants.

3.4 Estimation of overall Power Production

From the experiments the maximum output power was obtained from a double chamber paddy plant microbial fuel cell. The working volume of the anode chamber was 2.5L. 0.037 W of power was obtained from this small volume of wastewater. As per the records of this fishery industry, an average of 7000 liters of wastewater has been discharged to the outlet on weekly basis. Proportionately around 103 W of power can be generated from this wastewater volume. Even though it is not a large power generation, still there are possibilities of efficiently utilizing this power for lightening the LED bulbs, tube light and such other appliances. The wastewater is treated simultaneously with the production of bioelectricity. So the implementation of microbial fuel cell in fish processing plants is beneficial.

4. CONCLUSIONS

In the present study, the three different types of microbial fuel cells continuously produce electricity during its 60 days of operation. The microbial fuel cell performance regarding the organic matter degradation is demonstrated by COD removal, BOD removal and nutrient removal. A higher COD, BOD and nutrient removal of fishery wastewater was accomplished with power production through MFC revealed simultaneous substrate degradation with continuous power production in an effective manner. The power density became very much higher when paddy plant microbial fuel cells were used.

- The peak voltage generated in double chamber paddy plant MFC was around 194 mV. The maximum voltage obtained from ordinary dual chamber MFC and single chamber paddy plant MFC was 146mV and 149mV respectively.
- The BOD removal efficiencies in dual chamber MFC was 60%, double chamber paddy plant MFC was 76% and single chamber paddy plant MFC was 51%.
- The COD removal efficiencies in dual chamber MFC was 42% and single chamber paddy plant MFC was 55% . The maximum COD removal efficiency achieved by double chamber paddy plant MFC was 58%
- The nitrogen removal efficiencies in dual chamber MFC was 35%, and double chamber paddy plant MFC and single chamber paddy plant MFC was 39%.
- The phosphorous removal efficiencies in dual chamber MFC was 36%, double chamber paddy plant MFC was 47% and single chamber paddy plant MFC was 21% .

In terms of bioelectricity generation and pollutant reduction, paddy plant microbial fuel cell showed better performance than the ordinary MFCs. It was seen that the additional electricity generation and treatment did not have any effects on the growth of the rice plants. Around 103 W of power can be produced from the overall wastewater from the industry in weekly basis, which can be efficiently used for lightening the bulbs and other such appliances in the treatment plant. Although the energy that could be captured from wastewater is not enough to power a city, it is large enough to someday power a treatment plant. Therefore, it can be concluded that treating fishery wastewater through paddy plant MFC is an attractive alternative and applicable for both wastewater treatment and energy recovery at lab scale.

Significance & Future Perspectives of the Study

The present study utilizing fishery wastewater as substrate and paddy plants is the most effective way for organics removal and sustainable energy production at lab scale. However many scientific, economic and technical challenges must still be addressed for obtaining its complete efficiency at large scale. Therefore, MFC must be designed in a way to overcome these limitations and making its implementation in an economically feasible and eco friendly manner. To attain this aim effectively, research should be attentive on exploring highly proficient and cheap electrode materials, investigation on microbial metabolism and methane production and its scale up feasibility. Keeping vitality of plants along with a stable power output and preventing the electrode materials from deteriorating over time are two major challenges for long term operation of PMFCs. In this context, choosing a suitable plant along with long lasting inexpensive electrode materials that resist fouling may be an important aspect.

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