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APPLICATION OF MICROBIAL FUEL CELL FOR ELECTRICITY GENERATION BY USING UTILIZING DIFFERENT WASTEWATERS

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ABSTRACT

The aim of the present work was to treat the different wastewaters by using Microbial fuel cell (MFC). Wastewater served as an effective substrate for power generation by using microbial fuel cell as they are rich in organic content. In MFC, bacteria were grown under anaerobic conditions. MFC's containing aluminium plates as electrodes using different samples of wastewaters, had been analyzed in the present investigation. It had been observed that aluminium plates gives a maximum of 957 mV after 10 days of operation when used with dairy wastewater, while the cell using vermicompost functioned disappointingly poor to give a maximum of 131 mV as compared to other wastes. In case of distillery waste a maximum of 1240 mV was observed. In this MFC, anode solution was in batch and cathode was in continuous mode of operation under optimum conditions of the operating parameters like pH, oxygen flow rate and substrate concentration.

KEY WORDS: Microbial fuel cell (MFC), Power generation, Distillery effluent, Dairy wastewater, Vermicompost

INTRODUCTION

Distillery producing alcohol from molasses is considered to be one of the most polluting agro-based industries. The effluent discharged from distillery industries has extremely high amounts of organic matter with dark colour and foul odour. The awful colour of distillery waste is due to molasses and charred sugar like caramels, melanoidins and decomposition product like hydroxyl methyl furfural, colloidal nature of caramels and melanoidins. Untreated effluent pollutes water and land when discharged into water bodies and on land. Physico-chemical analysis (pH, CU, COD and BOD) of the effluent showed that most of the parameters are beyond the permissible limit.

Dairy wastewater is classified as nontoxic due to low hazardous chemicals and high amounts of biodegradable organics in comparison to other industrial wastewater. Dairy effluent contains soluble organics, suspended solids, trace organics. All these components contribute largely towards their high biochemical oxygen demand (BOD) and chemical oxygen demand (COD). Dairy wastes are white in colour and usually slightly alkaline in nature and become acidic quite rapidly due to the fermentation of milk sugar to lactic acid. The suspended matter content of milk waste is considerable mainly due to fine curd found in cheese waste. The pollution effect of dairy waste is attributed to the immediate and high oxygen demand. Decomposition of casein leading to the formation of heavy black sludge's and strong butyric acid odours and characterize milk waste pollution (Slavov, 2017). The characteristics of a dairy effluent depend largely on the quantity of milk processed and type of product manufactured. Wastewater treatment has become a big issue.

Currently wastewater treatment plants consume enormous amount of energy to purify water. Microbial fuel cell (MFC) can replace the conventional wastewater treatment plants and the electricity produced from it can be used for running the wastewater plants as well as for supply to households. Its potential also lies in desalination, hydrogen production and biosensors, besides for energy production (Angenent, 2004).

MFC is a type of bio-electrochemical fuel cell, which is divided into two parts: aerobic and anaerobic. Aerobic half is cathode (positively charged), while anaerobic half is anode (negatively charged). The anaerobic chamber contains anaerobic bacteria, which grow in the absence of oxygen to liberate carbon dioxide, protons and electrons (Gong, 2007). The electrons in most cases require mediators to leave the bacterial cell and reach anode. Such type of MFCs are called as mediator MFCs. Examples of mediators are methyl blue, thionines, neutral red *etc.*, which are expensive as well as toxic and hence mediator free MFCs are widely used (Kim, 2008) where the electrons are transferred from the bacterial respiratory enzyme to the electrode directly. Bacterial species like *Geobacter* have *pilli* on their external membrane, which are able to transfer electrons through these *pilli* to anode directly. Hence they do not require any mediator for electron transfer. But recently due to the development of cheaper new methylene blue (NMB), research now has also shifted towards mediator MFCs (Pham, 2004).

The transfer of protons from anodic to cathodic chamber and prevention of oxygen transfer to anodic chamber require semipermeable membrane, which is again expensive to use in MFC. Therefore, salt bridge is used as an alternative for this purpose in the present study (Huang, 2011). One more difficulty in this technology is selection of cheaper electrodes that can be used on large scale. The cathode generally used for best efficiency includes carbon cloth catalyzed by platinum. This makes it very expensive for commercial use. Ferricyanide can also be used in cathode in place of platinum. Extensive research has also been made for selection of anode material. Carbon fiber brush has been found as good anode material as it achieves high surface area, high porosity and efficient electron collection but again it is slightly expensive. To overcome this problem, porous aluminium plates is used in the investigation (Oh, 2010).

In the present study, MFCs were designed by using distillery effluent, dairy wastewater and vermicompost. Comparative efficiency of MFCs was also monitored and effects of parameters on MFC efficiency were optimized.

MATERIAL AND METHODS

Collection of waste samples: Two industrial waste samples namely distillery waste and Dairy waste were collected from Symbaoli (Gajrola, Moradabad), Gazipur dairy farms respectively and kept into the refrigerator for further research.

MFC Using Vermicompost

Vermicompost (0.5 kg) was taken in a 1.5 L container. Water was added to the container to make up the volume. Then sugar solution (0.1%) was added slowly after interval of 2 h. Sugar solution was used as it acts as the source of food for bacterial growth. Moreover, dilute sugar solution did not damage the bacterial cell wall due to osmotic pressure which can happen the case in concentrated sugar solution. Care was taken to avoid formation of air bubbles in the container. Aluminium plates (140 cm^2) with pores of diameter 0.1 cm (approx) were used as anode. Graphite rods extracted from pencil batteries were also tied with the aluminium plate as it helped bacteria to grow on it. This was then connected with copper wires and immersed in the vermicompost. Now the anodic chamber was sealed with epoxy. Cathode compartment was filled with salt solution (200g NaCl/1.5 L water) to make the catholyte conductive. However, high concentration of NaCl could offset the internal resistances produced by the use of salt bridge. Aluminium plate (70 cm^2) with same pore size was immersed, which acted as cathode (Du, 2007).

The cathode and anode compartment were connected with salt bridge. Salt bridge was made by dissolving 6 g agar-agar in 150 mL distilled water. Potassium chloride (4 g) was also added in the warm solution before it hardened. About 20 mL of this solution was used in making the salt bridge. A constant load resistor of 10 K ohm was connected through the circuit. Potential drop was measured across the resistor after particular interval of time using multimeter (Singh, 2017).

MFC Using Dairy Wastewater

The dairy wastewater sample was collected from Ghazipur dairy, New Delhi. This grade of water sample contains bacteria and fungi of mixed strains such as Acaligenes, Flavobacteria and *Bacillus Aspergillus*, *Fusarium* species, etc. The types of anode and cathode used were same as in previous experiment but instead of adding compost to anodic chamber, dairy waste water was used. Hence the cell voltage attained a constant value after 16 h of the experiment, after which sugar solution was added to supplement the bacterial growth. Readings were taken at different time intervals (Singh, 2017).

MFC Using Distillery Wastewater

The Distillery Wastewater contains bacteria of mixed strains. The type of anode and cathode used are same as previous experiment but instead of adding dairy-waste to anodic chamber, distillery wastewater was used. Hence the cell voltage attained a constant value after 16 hours of the experiment after which sugar solution was added to supplement the bacterial growth. Readings were taken at different time intervals.

Analytical Methods

Electrical conductivity (EC) of the effluent was measured using a pocket type digital EC meter (Hanna Instruments Co.) calibrated at 20 °C. The reading was taken in millisiemens. pH of the effluent sample was measured by a pH meter (model PR 8404) using combined glass electrode (Swamy, 2016).

For determining total suspended solids (TSS), 100 mL of the sample was centrifuged at 2000 rpm for 10 min. The supernatant was removed and the residue was washed 3 times by resuspending it in distilled water and recollecting by centrifugation. The residue was finally transferred quantitatively to pre-weighed dish (X_1g). The dish was weighed again after drying at 105 °C (X_2g). TSS was calculated by using the following formula:

$$\text{TSS (ppm)} = \frac{(X_2 - X_1)\times 1000}{\text{mL of sample}}$$

The TDS (total dissolved solids) was calculated as the difference between the total solids (TS) and total suspended solids (TSS), TDS (ppm) = TS (ppm)-TSS (ppm) (Swamy, 2016).

BOD values of samples were monitored by conventional method after 5 days of incubation in MFCs. It proves the fact that MFCs can act as good BOD sensor.

COD was calculated according to the method given by APHA (1989). Colour unit was measured using a spectrophotometer. For colour unit determination, the sample was centrifuged at 1000 rpm for 30 min to remove all the suspended matter. The pH was adjusted to 7.6 with 2 M NaOH [Canadian Paper and Pulp Association (CPPA) standard method] and then used for the measurement of absorbance at 465 nm. The absorbance values were transformed into colour unit (CU) using the following relationship.

$$\text{CU} = 500 \times \frac{A_2}{A_1}$$

Where A_1=Absorbance of 500 CU platinum cobalt standard solution (A_{465} = 0.132) and A_2 = Absorbance of the effluent sample

Electrical Parameters and Measurements

Digital multimeter (T-33) was used to measure the voltage of the current, which was generated during the experiments. After 2h interval, readings were recorded for a maximum of 60h.

RESULTS AND DISCUSSION

Physicochemical analysis of pulp and paper mill effluent (wastewater) was carried by analyzing various parameters, *viz.* pH, TS, TSS, TDS, BOD, COD *etc*, and the results are shown in Table 1. Further, this effluent was used in constructing the MFC.

Table 1. Physicochemical analysis of Dairy Wastewater

Parameters	Mean value
Colour	Dirty white-Greyish and turbid
Odour	Pungent
pH	6.2-7.8
Total dissolved solids (TDS)	2500 ppm
Total Suspended Solids	1000 ppm
Total organic carbon	2250 ppm
Oil and grease	350 ppm
BOD	4350
COD	7500
Phosphorus content	12.5 ppm

In all the three set-up of MFCs, glucose acted as the source of food for the bacterial growth. Anaerobic bacteria were present in anaerobic chamber and decomposed the glucose. As a result, carbon-dioxide, protons and electrons were liberated. This reaction occurred as shown below:

$$C_6H_{12}O_6 + 6H_2O \text{ ® } 6CO_2 + 24H^+ + 24e^-$$

These protons were transferred to the cathode compartment through salt bridge. Moreover, salt bridge prevented oxygen from the cathode compartment to enter the anode compartment. On the other hand, electrons were transferred to the cathode through external circuit connected to a load. The MFCs were continuously monitored during experiment and readings were taken after each 2 hr. Addition of sugar solution in the anolyte of distillery effluent after 12 h resulted in rapid increase in the cell potential. However, in case of vermicompost, the multimeter showed constant reading even after 10 h. Hence sugar solution was added in every 2 h interval, which resulted in an increment in the cell potential by almost 20 mV but only for few min, after which the cell potential again dropped to its previous value. Salt addition in the catholyte of all the three samples result in increase in the cell potential due to increase in conductivity of the catholyte. The maximum voltage of 907 mV was recorded in distillery effluent, whereas it was 516 and 131 mV in case of dairy wastewater and vermicompost, respectively.

The graph for cell voltage v/s time has been plotted, as shown in Fig. 1. The data obtained clearly shows that distillery effluent is best suited for electricity generation as it may contain more number of bacteria than any other sample. The initial increase of current in case of sewage sludge can be attributed to the presence of active population of anaerobic bacteria which quickly utilized easily degradable waste present in wastewater and when these easily degradable substrates were exhausted, the current outputs began to decrease. Meanwhile, degradation of complex components was taken place by which a lower current was still obtained. In case of distillery effluent the output of current increases with time. Distillery effluent contains the mixed strains of bacteria and fungi which may be inactive in beginning but get activated under the experimental conditions and were capable of degrading simple as well as complex components of wastewater with passage of time resulting in increase in current production.

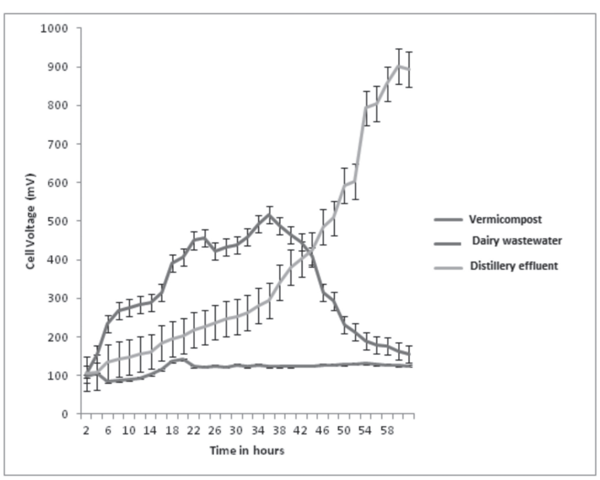

Fig. 1. Study of cell voltage *versus* time for different samples

It was also observed that the voltage was increasing rapidly during day time as compared with night. This can be attributed to the fact that bacterial growth is improved with increasing temperatures. However this growth was limited to temperature around 37 °C. Similarly the readings were also improved slightly on cleaning the cathode plate after certain intervals as it increased effective surface area.

It was also observed that voltage improved by 0.05V to 0.06 V by addition of salt in the cathode chamber and with graphite rods in the anodic chamber. This showed that the bacterial growth was influenced by the presence of graphite. Addition of sugar solution in the anodic chamber also increased the cell potential, since sugar solution acts as food for bacteria. More research is needed to find the optimum level of their concentration.

Factors Affecting Electricity Generation

Impact of Oxygen Flow Rate on Electricity Generation

Impact of oxygen flow rate on voltage generation during working of MFC was examined at different oxygen flow rates from 15 to 60 psi yielding in voltage generation between 0.64 V and 1.09 V respectively (Fig. 2). These results show that voltage

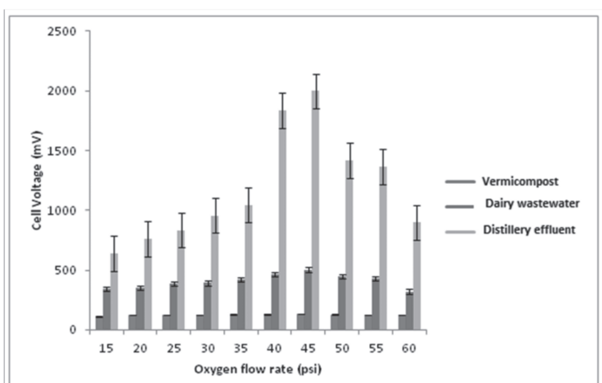

Fig. 2. Effect of Changes in oxygen flow rate on voltage generation

generation was increased as the oxygen flow rate was enhanced and reached at the maximum of around 1.99 V at oxygen flow rate of 45 psi before showing decline afterwards. This decline in the voltage could be attributed to the fact that the higher rate of oxygen flow diffused down air near the vicinity of anode, which probably disturbed the anaerobic microbes living on the anodic surface (Mohan, 2008).

Impact of pH on voltage generation

pH is considered as a significant factor affecting the activity of microbes. Growth and development of microbes was observed maximum at optimum pH. Fig.3 shows the maximum output of voltage was recorded at pH 8.2. The experiments showed that at pH ≤ 5, activities of microbes was minimum as compared with the result recorded at higher pH. This is due to the neutralization of proteins or active sites under acidity (Fang, 2015).

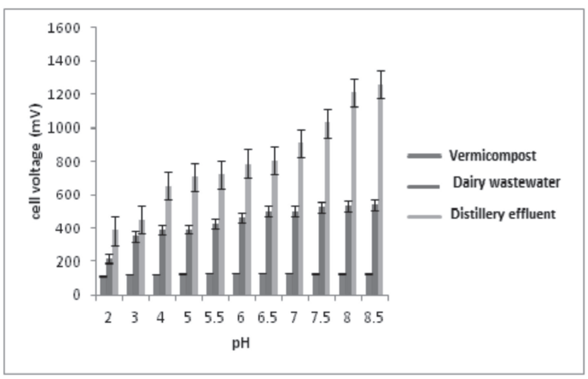

Fig. 3. Effect of changes in pH on voltage generation

Impact of substrate concentration on electricity generation

Power production was observed to increase by increase in the concentration of substrate (Fig. 4). Substrate concentration increased the voltage upto 10% afterward it decreased. This was due to the

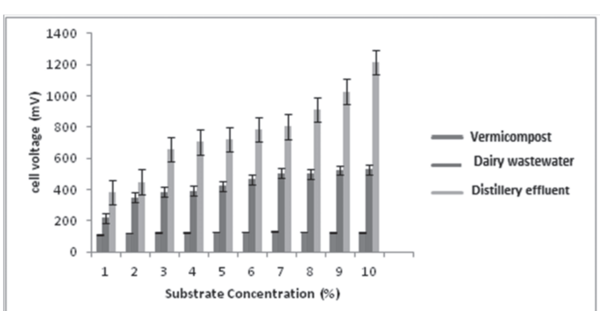

Fig. 4. Effect of changes in substrate concentration on voltage generation

decline in the activity of the microbes owing to various factors such as pH. Decline in the activity of the microbes was probably due to the reduction in the activity of the enzymes due to its specificity to pH. This also indicated that higher concentration of the substrate could actually affect the anode performance considerably resulting in simultaneous lesser power production (Xafenias, 2015).

Reduction of pollution load

Slight increase in pH waste was observed during operation of MFC's with wastewater. There was great reduction in TSS after treatment. The color of water also changed after treatment. TDS values were observed to be increased which may be due to increase in number of microorganism during treatment. It was observed that 96.5% COD, 96.5% BOD and 69.8% TSS was removed after operation of MFCs with distillery effluent as substrate after 60 hours (Fig. 5).

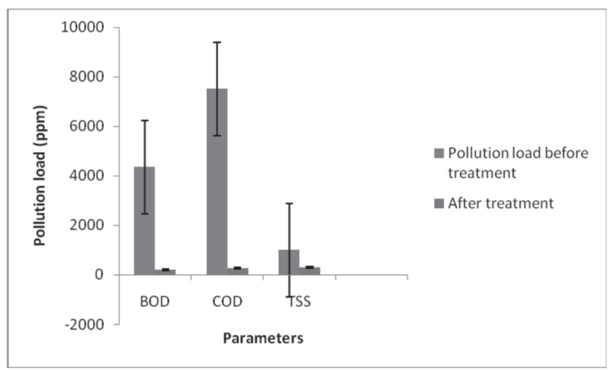

Fig. 5. Pollution load reduction of Distillery effluent by using MFC

During current research the goal of effluent utilization to minimize pollution hazards has been achieved along with power generation by novel microorganisms in MFCs. MFCs containing distillery effluent generated considerable electricity and was also doing well in TSS, BOD and COD removal. The voltage generation in the other two MFC's constructed using Vermicompost and dairy wastewater sludge was quite less as compared to MFC containing wastewaster and therefore their efficiency is also low. The electricity production is very low in vermicompost except distillery effluent since the dairy wastewater contains the mix of several strains of bacteria and fungi which are capable of degrading simple as well as complex components of the waste.

Table 2. Impact of MFC using Dairy Wastewater on pollution load

Parameters	Pollution load before treatment	After treatment
BOD	4350	190
COD	7500	260
TSS	1000	302
TDS	2500	2965

CONCLUSION

The present study evidently showed that distillery effluent generated much more potential than vermicompost and dairy wastewater samples. The same procedure was also able to reduce the pollution load in terms of BOD, COD, TSS and colour. pH, substrate concentration, temperature of surroundings and oxygen flow rate played an important role in deciding the cell potential. Temperature around 37°C was observed most effective for bacterial growth. By improving certain parameters this method can be applied in wastewater treatment plant, which will also help in producing electricity and reducing pollution load as shown in the present investigation. Future research can be suggested for improving the efficiency of microbial fuel cell in context to other industrial effluents.

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