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Studies on Sustainable Power Estimation from Local Waste Waters Using Microbial Fuel Cells

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Abstract*: Eco system is deteriorating day by day due to Industrial effluents. The effluents are containing toxic chemicals which are inturn polluting ground drinking water and creating new diseases. Treatment methods for these Industrial effluents are becoming more costly. The Present study is aimed and focused at decreasing the toxicity of Industrial waters and the target is Reduction, Recycle and Reuse (RRR) using Microbial Fuel Cell. Microbial Fuel Cell experiments were carried out in batch operations for Appughar waste water using Bakers yeast (saccharomyces cerevisiae organism) in order to increase oxygen levels and decrease toxicity. The parameters studied are design of MFC, NaCl concentration, Agar concentration, fructose dosage, pH, COD, BOD, DO, TSS, TDS, Sulphates, Chlorides and Power generation. The results produced have high oxygen levels and change of pH is appreciable from 7.8 to 7.0. COD, BOD and DO have changed from 1050 to 450 ppm, 560 to 220 ppm and 2.5 to 4.2 ppm.

***Keywords:* MFC, pH, TSS, TDS, COD, BOD and DO**

I. INTRODUCTION

The search for alternate potential energy sources is also on high demand using green synthesis **[01]**. The dissemination of energy sources has created havoc in the field of energy engineering **[02]**. Among different pollution's Water Pollution is of acute importance as it causes malfunctioning to human body. Eradication of water pollution is done by many methods but only inexpensive methods must be oftenly used to prevent water pollution and try to reuse the waster again. Microbial fuel cells (MFCs) have been of prime importance for the recent studies because they represent a potential green. The necessity of microbial fuel cells is the effluent water treatment and simultaneous transfer of electrons for the production of power. The method of MFC is widely varied from different concentrations of salt bridge to different electrodes as they change the intensity and enhances the treatment process **[03–07]**. The MFCs are mainly driven by redox potential differences between anodic and cathodic environments, and they do not require complicated manipulation of reactants or reaction conditions. There are two limitations to the application of MFCs under field conditions: a conductive aqueous environment and presence of organic matter as a fuel source. A well conductive aqueous environment consists of electrolytes which are crucial to transport the positive charge from the anode to the cathode in MFC reactions. Cathodes floating on the water surface will freely accept the electron via external circuits and positive charge through the water, using oxygen in the air as the electron acceptor. The effect of microbial activity on the change of Oxygen levels in wastewater treatment has been intensely studied in the present experimentation. The present experiment had involved the electrodes like copper, volume capacity of 1.25 lit (bottles capacity-1.5 lit), 3 mM NaCl salt bridge concentration and saccharomyces cerevisiae organism (Bakers yeast). The aim of the experiment is to reduce the COD and BOD levels and increase the DO levels in the locally available waste water and decrease the TSS and TDS levels along with chlorides and sulphates.

II. EXPERIMENTAL PROCEDURE

Characterization of waste water samples include the following

A. Estimation of TSS

Pipette out 50 ml of waste water into a funnel with a previously weighed Whattman No. 1 filter paper and filter. The filter paper is dried in an oven maintained at 105(+/-) 5^0C and weighed again.

B. Estimation of TDS

The filtrate is obtained previously is taken into a weighed china dish and heated on a burner till the water is evaporated. When the water is about to be completely evaporated, the china dish is heated for 1hr in an oven maintained at 105 (+/-) 5^0C.The china dish is taken out, collected and weighed.

C. Estimation of BOD

1) *Preparation of dilution water:* Water is aerated by passing compressed air through a diffusion tube until it is completely saturated. Take about 5 ml of the sample and dilute it to 300 ml with dilution water. The diluted sample is taken in two bottles filled up to the neck. The dissolved oxygen in one bottle is determined immediately and in the other bottle after five days of incubation.

D. Determination of dissolved oxygen (DO)

A known amount of sample water (say 250 ml) is taken in a stoppered bottle avoiding contact with air.

Add 0.2 ml $MnSO_4$ solution to it by means of a pipette, dipping the end well below the surface of water. Also add 2 ml of alkaline iodide-azide solution to it. Stopper the bottle and shake thoroughly. Allow the brown precipitates of $MnO(OH)_2$ formed, to settle down. When some portion of the liquid below the stoppered is clear, add 2ml of concentrated H_2SO_4 with the help of a pipette. Stopper and mix till the precipitate is completely dissolved. The characteristic brown colour of iodine is produced. Transfer 100 ml of the above solution in a 250 ml flask with a pipette. Titrate the liberated I_2 with standardized sodium thiosulphate solution until the sample solution becomes pale yellow. Add 2 ml of starch solution, the solution will turn blue. Continue titration till the blue colour disappears.

E. Estimation of COD

Take reflux flask an add to it 0.4gms of H_2SO_4 and 20 ml of sample.(If required dilute to suitable degree) Mix well. Add 10 ml of 0.25N, $K_2Cr_2O_7$. Drop some pumice stone and slowly add 30 ml of Conc.H_2SO_4- $AgSO_4$ reagent. Mix the contents thoroughly and connect the flask to condenser. Reflux for 2 hours. Cool and wash down the condensers. Dilute the mixture to 150 ml by adding distilled water. Add 3 drops of Ferroin indicator and titrate with N/10 Ferrous ammonium sulphate solution, till the color changes from green to wine red. Note the end point. Perform the same procedure with 'Blank' using distilled water instead of the sample.

F. Estimation of Sulphates

Take 150 ml sample in beaker and make it acidic with HCl. Heat the solution to boiling point and add to it Barium chloride solution, slowly with stirring. Add this till precipitation is complete. Digest the precipitate to 90^oC for 2 hours. Filter out the solution through filter paper. Wash the precipitate with warm distilled water, till wash water is free from chloride by using $AgNo_3$ solution, till there is no colour change. Dry the filter paper and precipitate to 750 ^0C in muffle furnace for 30 minutes. Cool and weigh the precipitate with crucible.

G. Estimation of Chlorides

Take 50 ml of sample in a conical flask, to this add 3 drops of $K_2Cr_2O_7$ indicator. And take $AgNo_3$ solution in a burette. Titrate, the sample with $AgNo_3$ solution then it colour changes to yellowish to reddish brown precipitate.

The experimental work was carried out to reduce the parameters like pH, TSS, TDS, BOD, COD, Sulphides and Chlorides. Microbial Fuel Cell is used for the treatment of waste water sample continuously for a span of 45 days taking samples at regular intervals of 24 hours.

H. Microbial Fuel cell using a Salt bridge

Dual chambered MFC was constructed using air-tight plastic bottles of 1.5 liter volume each (anode and cathode chamber). A side opening of 1 cm radius was made at a height of 12.5 cm from the bottom of the bottle (approximately at the centre) on each bottle and was connected with a PVC pipe (length=34, 29, 24, 19 and 14 cm; diameter = 2 cm).

Fig. 1 Microbial Fuel Cell for the treatment of Waste water

Agar of 5 g along with 7 g of sodium chloride (NaCl) salt was prepared by heating it in a water-bath of 100 ml and the molten agar was allowed to cool down and poured into the PVC pipe and sealed at one end using plastic cap and cello-tape. The agar was left undisturbed to solidify. The PVC pipe containing the salt-agar mixture was fixed between the two bottles using epoxy material and behaved like the salt-bridge assisting in the proton transfer mechanism during the MFC operation. Copper rods (height= 12cm; diameter = 0.75 cm) were used as electrodes. The distance between the two electrodes was maintained at distance of 25, 20, 15, 10 and 5 cm in the MFC setup. Copper wires were used to connect the electrodes to the circuit. An external resistance (R) of 10, 47, 220 and 500 Ω were connected and the readings were measured using a digital multimeter. Constructed salt bridge MFC is shown in Fig. 1. The collected sample was analyzed using standard methods in order to monitor the biodegradation process taking place inside the MFC. Many parameters are used to determine waste water performance. In this study the parameters analyzed were pH, TSS, TDS, BOD, COD, DO, Chlorides and Sulphates to evaluate efficiency of the MFC. The waste water sample is analyzed for every 24 hours and its various parameters are evaluated. During the operation, voltage is also checked by using a multimeter.

III. RESULTS AND DISCUSSION

The Experiment is divided into two parts consisting of preliminary runs and final runs. Preliminary runs comprises of estimating minimum standards to design and set up the equipment for running microbial fuel cell. The parameters studied in preliminary runs are Effect of Salt Bridge Concentration and salt bridge distance and Effect of food source for the development of organism & its dosage. The final runs comprises for 45 day experimental procedure for dual chamber process (Effect of Microbial Fuel Cell) for the degradation of quality of waste water & power production.

Fig. 2 Microbial Fuel Cell Setup

A. Preliminary Runs

1) *Effect of salt bridge concentration and salt bridge distance*: A Cost criterion is vital in energy production plants. The present study clearly showed that the effect of salt bridge concentration is highly important in analyzing the efficiency of microbial fuel cell at a low cost. Molar concentration of salt is crucial as the transfer of protons through the salt bridge is facilitated by the dissociated ions in it. The present experiments (Fig. 3) revealed that, with an increase in molar concentration the current increases. Ideal results were obtained for salt bridge fabricated using 3 M Nacl as it produced 0.22 Volts of maximum current.

Fig. 3 Variation of Salt Bridge Distance

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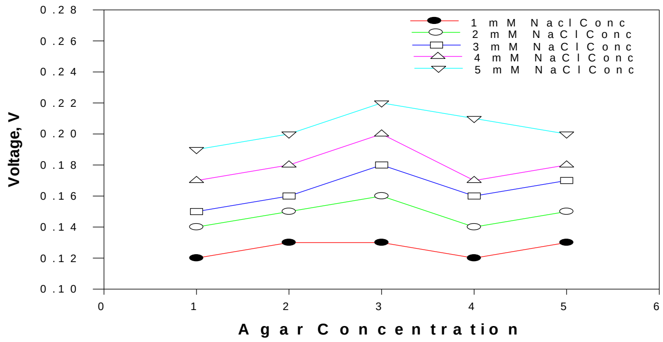

Fig. 4 Effect of Agar concentration for varying voltage

B. Effect of fructose dosage on the potential generated

The present parameter is aimed to study the effect of different dosages (1–10 g/L) of fructose on potential. Voltage generated in the MFC compartment was regularly checked over a period of 24 h. As the dosage of fructose increased from 1 to 7 g/L, the voltage increased and beyond 7 g/L dosage, there is no change or increase in the voltage. A considerable increase in voltage from 0.09 V to 0.16 V was observed and further increase in fructose dosages did not increase the voltage production. Thus, 7 g/l of fructose was considered as the optimal dosage for further MFC studies.

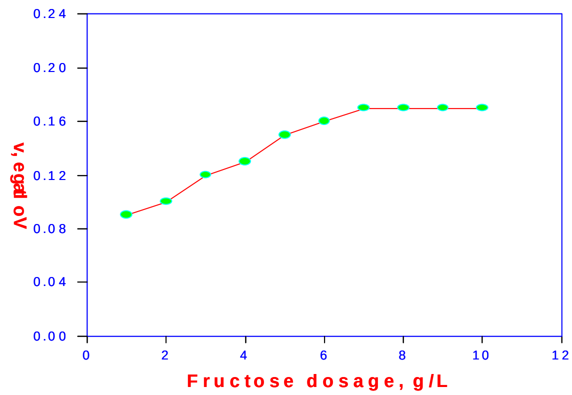

Fig. 5 Effect of fructose dosage

C. Waste water characteristics

Waste water for the present study was procured from Appughar premises, Visakhapatnam. The waste water was collected and stored in 20 lit cans and utilized for the experimental studies. Experimental set up was established and Samples were then examined to find out their ratios and different parameters. The values of various parameters like pH, color, temperature, Dissolved oxygen, COD, BOD, TSS, TDS, Chlorides and Sulphates before the treatment of sample are shown in Table 1.

Table 1: Characteristics of Combination of Appughar waste water

S.NO	Parameter	Untreated waste water
1.	Colour	Light Brown
2.	Temperature	32^0C
3.	pH	7.8
4.	Dissolved Oxygen	2.5
5.	BOD	560
6.	COD	1050
7.	TSS	900
8.	TDS	800
9.	Chlorides	70
10.	Sulphates	70

D. Effect of Microbial Fuel Cells

Appughar waste water was collected for the purpose of Microbial Fuel Cells. In this process, two bottles, one having the waste water sample (Anode) and the other containing the distilled water is taken (Cathode). Copper electrodes are dipped into each bottle and a salt bridge is attached between two bottles through which flow of electrons takes place. Moreover, an aerator is also placed in the bottle having distilled water. During the treatment, samples were tested at constant intervals of 24 hours to determine its various parameters i.e. pH, Total Suspended Solids, Total Dissolved Solids, Chemical Oxygen Demand, Biological Oxygen Demand, Sulphates and chlorides. In the present experimentation, the value of COD has reduced from 1050 mg/L to 450 mg/L. Besides reducing the toxicity MFC also produces Voltage. The voltage produced is checked by connecting electrodes to the Multimeter.
Effect of MFC on various parameters is as follows

E. Effect of pH

pH of the waste water sample was determined using pH meter. The variation of pH of the sample taken at regular intervals of 24 hours is presented in the Fig 6. Results show that pH of the waste water has decreased. The addition of fructose, which serves as food to microorganisms, is responsible for the acidic nature of the waste water sample. pH was decreased from 7.8 to 7.0, which is in the permissible levels of BIS standards [08–17].

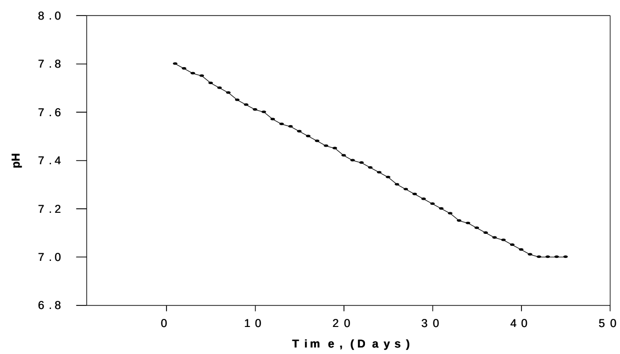

Fig. 6 Variation of pH with Time

F. Effect of Dissolved Oxygen

Fish and other aquatic animals depend on dissolved oxygen (the oxygen present in water) to live. The amount of dissolved oxygen in streams is dependent on the water temperature, the quantity of sediment in the stream, the amount of oxygen taken out of the system by respiring and decaying organisms, and the amount of oxygen put back into the system by photosynthesizing plants, stream flow, and aeration. Dissolved oxygen is measured in milligrams per liter (mg/l) or parts per million (ppm). The variation of Dissolved oxygen with time is depicted in Fig 7. Results showed that dissolved oxygen increased from 2.5 mg/L to 4.2 mg/L. The reason for increase in the Dissolved oxygen of waste water sample is due to decrease in the levels of BOD and COD in the waste water sample and aeration [18–27].

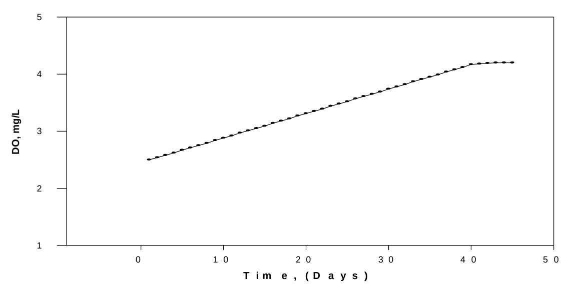

Fig. 7.Variation of Dissolved oxygen with time

C. Effect of Biochemical oxygen demand (BOD)

BOD is a measure of the amount of oxygen that organism will consume while decomposing organic matter under aerobic conditions. The effect of Microbial Fuel Cell on BOD of the waste water sample is illustrated in the below Fig 8. Results showed that BOD has decreased from an initial value of 560 mg/L to a final of 220 mg/L. The decrease in BOD is due to continuous aeration and the action of sludge [28–37].

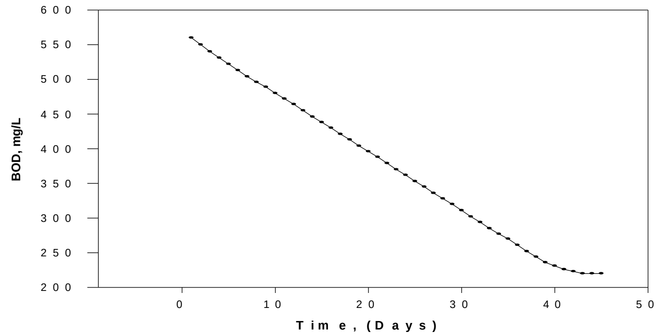

Fig. 8.Variation of BOD with time

D. Effect of Chemical oxygen demand (COD)

COD does not differentiate between biologically available and inert organic matter, and it is a measure of the total quantity of oxygen required to oxidize all organic material into carbon dioxide and water. During operation, MFC was continuously monitored for waste (as COD) removal to enumerate the potential of fuel cell to act as wastewater treatment unit. COD of the waste water sample at different time intervals are presented in the below Fig 9. Results shown that COD of the waste water has decreased from an initial of 1050 mg/L to 450 mg/L because the organisms in the waste water have grown and degraded the organic matter in waste water sample. The waste water showed its potential for COD removal indicating the function of microbes present in wastewaters in metabolizing the carbon source as electron donors [38–47].

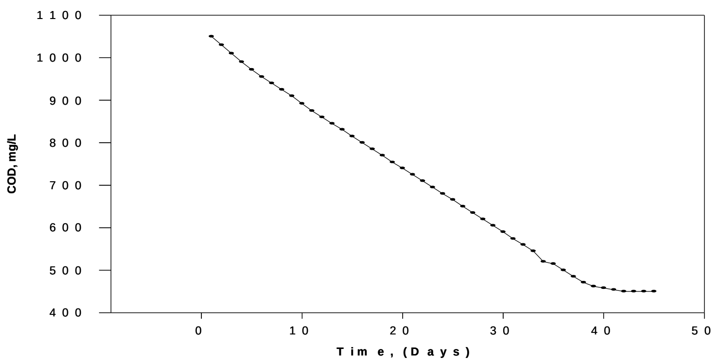

Fig. 9. Variation of COD with time

E. Effect of total dissolved solids

Total dissolved solids (TDS) comprise inorganic salts (principally calcium, magnesium, potassium, sodium, bicarbonates, chlorides, and sulfates) and some small amounts of organic matter that are dissolved in water. Present Microbial Fuel Cell (MFC) showed its potential for Total Dissolved Solids removal. The effect of MFC on total dissolved solids of the waste water sample at regular intervals is presented in the Fig 10. Experimental data indicated that dissolved solids were decreased continuously during the 24 hrs operation for 45 days. The TDS of the waste water sample has decreased from 800 mg/L to 320 mg/L. The TDS removal rate is affected by many factors, such as salt solution volume, wastewater volume, microbial oxidation and oxygen reduction [48–57].

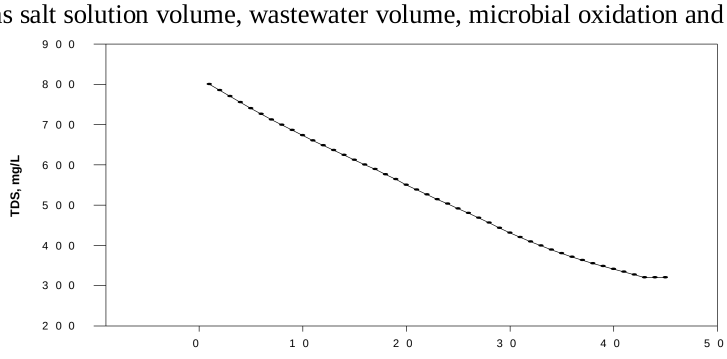

Fig.10. Variation of TDS with Time

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F. Effect of total suspended solids

TSS is the solid materials, including organic and inorganic, that are suspended in the water. The Experimental data shows that the amount of TSS in the sample has decreased with the elapse of time from 900 mg/L to 400 mg/L (Fig. 11). The low TSS concentration in the MFC reactor can be attributed to two reasons. First, the MFC is a biofilm based system, and the accumulation of biomass mainly resides on the electrode except of occasional biofilm falloff, so the suspended solid is low. Another reason is due to the low cell yield of the anoxic to anaerobic microorganisms in the MFC compared to the activated sludge [58–67].

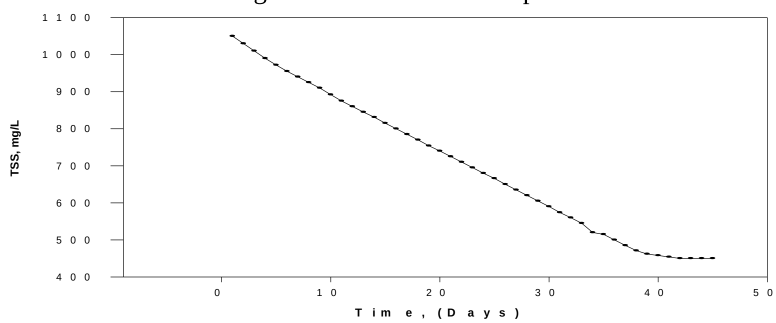

Fig. 11. Variation of TSS with Time

G. Effect of chlorides

Chlorides are widely distributed as salts of calcium, sodium and potassium in water and waste water. In potable water, the salty taste produced by chloride concentrations is variable and dependent on the chemical composition of water. The major taste producing salts in water are sodium chloride and calcium chloride. The effect of MFC on chlorides of the waste water sample is presented in Fig 12. The experimental data shows that chlorides content has decreased from 70 mg/L to 50 mg/L. The removal of chlorides in the sample may be attributed to the availability of biodegradable substrate in wastewater sample leading to competitive inhibition **[68–77]**.

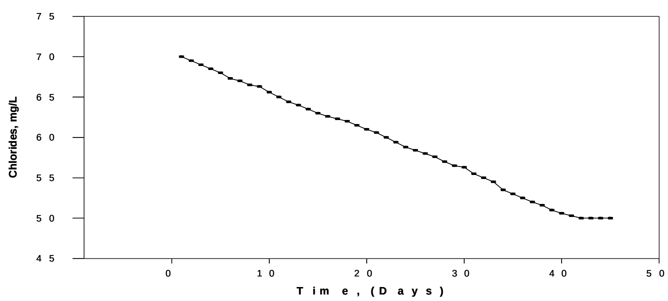

Fig. 12.Variation of Chlorides with Time

H. Effect of sulphates

Sulphate is one of the major cation occurring in natural water. Sulphate being a stable, highly oxidized, soluble form of sulphur and which is generally present in natural surface and ground waters. The effect of MFC on Sulphates is shown in Fig 13. Results clearly show decrease in sulphates from 70 mg/L to 40 mg/L. These results indicate that the saccharomyces cerevisiae cells in biofilm efficiently converted sulphate to sulfide in biofilm. sulfide with low redox potential could be oxidized by sulfide oxidizing yeast with the energy from decomposition of organic matters.

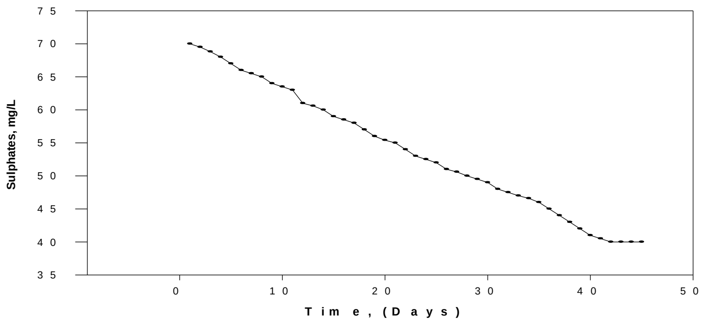

Fig.13.Variation of Sulphates with Time

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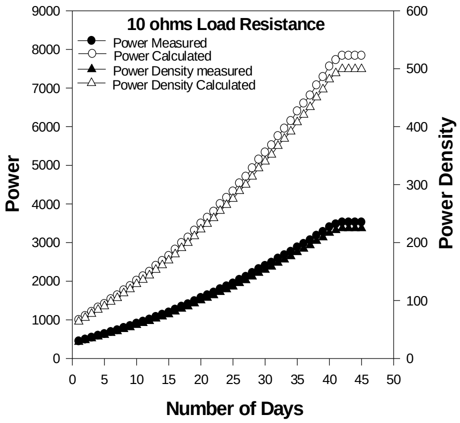
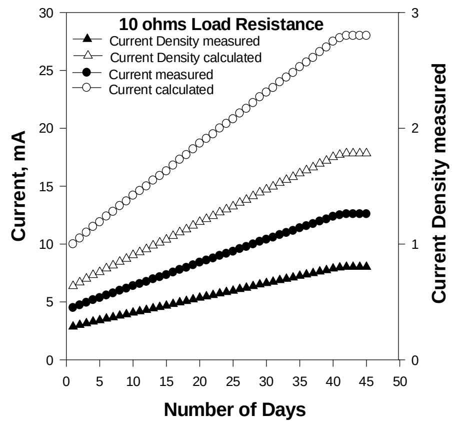
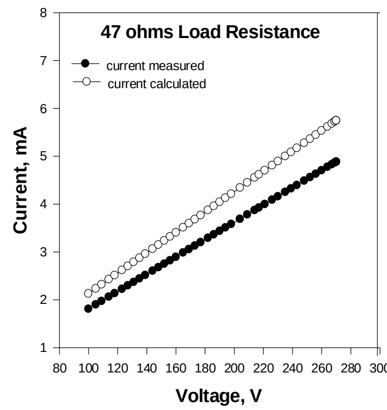
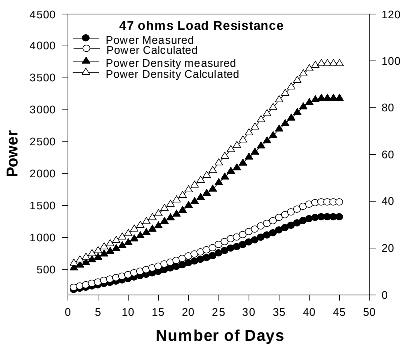
I. *Effect of Resistor*

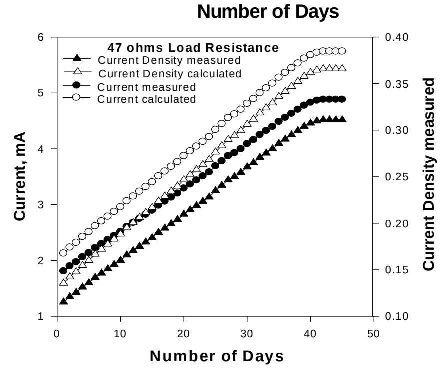
Power yield was calculated as a function of external resistance. The power yield was varied and observed for MFC operated under 10 Ω, 47 Ω, 220 Ω and 500 Ω respectively. Even at higher current densities, the power yield was very low, which demonstrated that the majority of the substrate was not utilized for current generation. This behaviour was perhaps due to competition for electron donor between electrogenic organism and fermentative and anaerobically respiring organisms for electron donor during the initial period of anode colonisation. These observations agree qualitatively with model results showing that an increased external resistance favours the anaerobic microorganisms. This is explainable by the fact that the high resistance leads to less current and decreased electron transfer rate to anode, leading to less energy generation for the electrogenic microorganisms – hence, their reduced growth rate. A functionally stable anode biofilm harbouring electrogenic microorganisms was required for maximum current/power generation. In other studies, it was observed that functionally stable biofilms develop on anodes when the biofilm was grown for several weeks under constant polarization. Mediators are artificial compounds or produced by the microorganism itself. Some microorganisms produce nanowires to transmit electrons directly without using any mediator but other organisms need to add artificial electron shuttle into anode chamber. MFC was connected in series to an external load and the maximum current output was obtained at 10 Ω rather than 500 Ω. The current output was obtained with external load of 10 Ω for every day was more advanced and updated than with 500 Ω (Figures below).

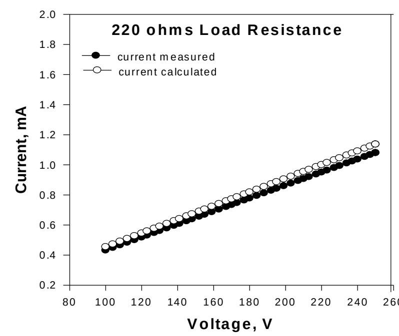


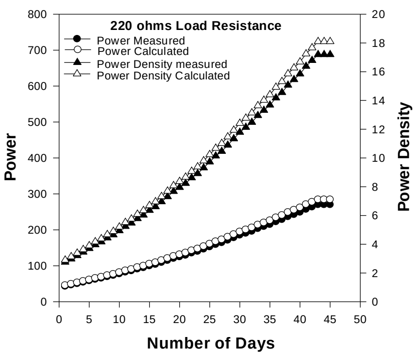


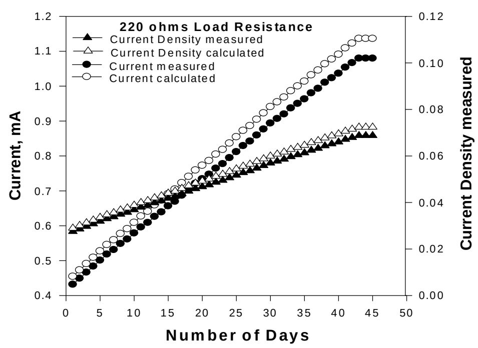


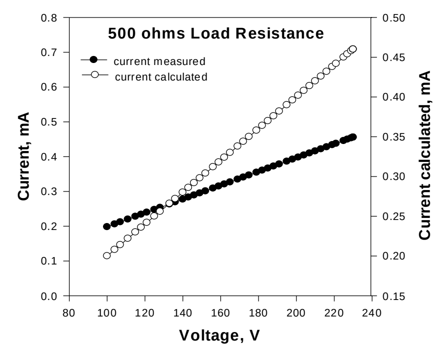


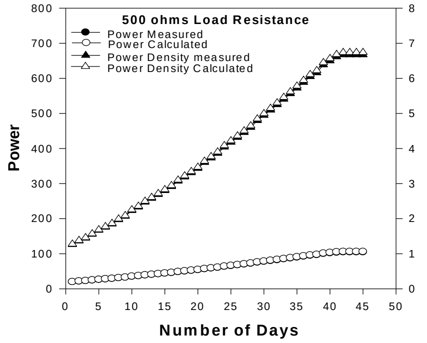


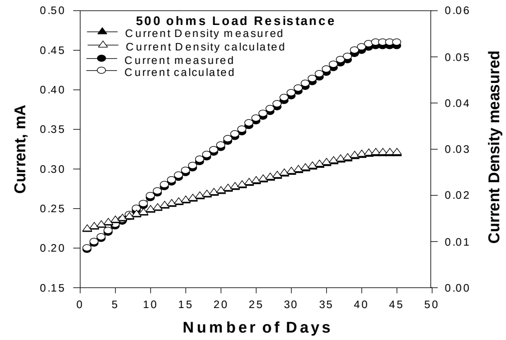












IV. CONCLUSIONS

The focus of the present study was to review biological method involved in the treatment of waste water. In this study, Microbial Fuel Cell was selected to improve the waste water quality and generate electricity. The amount of pH, COD, BOD, TSS, TDS, Sulphates and Chlorides are decreased when compared to initial characteristics of Appughar waste water. The MFC was effective, cheaper, easy to maintain and does not require any paid workers. They undoubtedly have potential in terms of energy recovery during wastewater treatment. It was observed that the basic principle guiding for the removal of toxicity and the production of electricity is the availability of bio-degradable compounds present in the waste water sample. The COD removal denotes the function of microbes, present in wastewaters in metabolizing the carbon source as electron donors. It was observed that MFC has succeeded in achieving the COD removal efficiency of 57.14%. Reduction in the pH was observed from 7.8 to 7.0 in a span of 45 days. BOD also was reduced from 560 to 220 mg/L. Results indicated that maximum power density of 3528 $\mu W/cm^2$ and maximum current density of 0.80255 mA/cm^2 were observed every day of MFC operation and were stable for 45 days. These results clearly indicate that bakers yeast can be successfully employed for electricity generation using MFC Technology.

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