Utilization of Distillery Wastewater for Electricity Generation Using Microbial Fuel Cell

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Abstract

Energy crises is a serious problem all over the world; there is a need to identify new technologies and renewable resources to fulfill this energy requirements. Due to the increase in awareness environmental problems, that biofuels production is eco-friendly. Ethanol is one of the future fuel that is produced from sugar cane molasses. During distillation of alcohol wastewater also called draw off, this wastewater contains many organic matters, that organic matter can be utilized for power generation. Microbial fuel cell (MFC) is one of the major source of treating wastewater and for electricity generation. This research explores the application of double chamber MFC in generating electricity using distillery wastewater. The different concentration of wastewater has been performed. The maximum current, voltage, BOD, COD, pH and TDS obtained with respect to time. MFC of distillery wastewater showed removal efficiency 69.3% COD, 68.1% BOD and 56.35% TDS with different feed concentration. The current, voltage and power generation in the reactor is 1.28 mA, 0.9 V and 0.304 W/m^2 respectively. This study also deals about the factors like length and concentration of salts in salt bridge that affecting on MFC's efficiency.

Key words Microbial fuel cell; Wastewater; Molasses; Salt Bridge

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INTRODUCTION

Currently, environmental pollution and resource shortage have directly affected human life and development. It is necessary to develop sustainable energy technologies that can promote the world's future economic development. Nowadays wastewater treatment has become a hot topic in environmental problem. Microbial fuel cell (MFC) uses microorganisms to oxidize organic or inorganic matter and directly convert chemical energy into electrical energy (Koeneel et al., 2005; Anand et al., 2013a and 2015). There are plenty of organics in industrial waste water energy (Anand et al., 2013b). MFC has emerged as a promising technology because of its ability to simultaneously treat wastewater and accomplish power generation (Anand, 2015b). In recent years, MFC technology for wastewater treatment and electricity production is still a new and challenging field in the world due to its effectiveness and potential application (Zhuwei et al., 2007; Jiansheng et al., 2011; Anand et al., 2015c). Anaerobic fluidized bed microbial fuel cell is the coupling of the microbial fuel cell technology with the fluidized bed reactor (Abassi et al., 2010). The power density and voltages can be increased when MFCs are stacked in series or in parallel (Abdullah et al., 2012). Individual MFC and electrode material have been widely investigated in the world (Adelaja et al., 2015). The high cost and low voltage has been hampering a systematic scale up of MFC (Anand et al., 2013b). In order to reduce costs of MFC, the cathode catalyst Pt can be reduced to 0.1mg/cm^2. In addition, it has been found that the MFC performance is influenced by many operational parameters, such as temperature, substrate concentration (Muralidharan et al., 2011) and electrode distance (Chi et al., 2015). A new cell configuration, cloth electrode assembly (CEA), was designed by sandwiching the cloth between the anode and the cathode (Dan et al., 2015). Such an MFC configuration greatly reduced the internal resistance, resulting in a power density of 627 Wm^{-3} when operated in fed-batch mode and 1010 Wm^{-3} in continuous-flow mode, which is the highest reported power density for MFCs and more than 15 times higher than those reported for air-cathode MFCs using similar electrode materials (Elakkiya and Matheswaran, 2013). The scale of MFC system must be increased to meet the requirements for large-scale wastewater treatment and bioelectricity production. Capital cost, scalability, modularity and distribution system for MFCs are the most crucial issue. One approach for scale-up is to increase the size of an individual MFC unit (Husen et al., 2014). However, it was reported that the maximum voltage of an air-cathode MFC did not exceed 1.1 V (Ibrahim et al., 2012). MFC scale-up may be more successful when connecting a number of single units together rather than increasing the size of an individual unit (Jia et al., 2010). Thus, the strategy of stack system has been used in MFCs for increasing the power output (Kokabian et al., 2013) showed that one possible way of achieving higher power output from MFCs is connecting multiple small-sized units together either in series or in parallel (Amelia et al., 2015a). But in that time the effect on the microbial electricity generation was as yet unknown (Sharma et al., 2009). In 2008, it was found that based on measured power output from 10 small units; a theoretical projection for 80 small units is approximately 50 times higher than the single MFC (Rismani et al., 2009). In recent years, the research on MFCs has attracted a great deal of interests. But no studies have been published treating wastewater used series and parallel of anaerobic fluidized bed microbial fuel cells (Nishimura et al., 2010). In this work, a MFC was fabricated for investigating the effects of salt bridge, it is length, dia and concentration of salts in salt bride using distillery wastewater. It can provide basic data for the industrial application of MFC.

MATERIALS AND METHODS

Wastewater collection

Wastewater Samples (distillery wastewater, 1L) were collected from UNICOL Distillery Plant Mirpurkhas, Sindh, Pakistan.

Characteristics of distillery wastewater

The characteristics of distillery wastewater are given in Table 1.

Table 1: Characteristics of distillery wastewater

Characteristics	Unit	Sugar Wastewater
Ph	-	4.35
Color		Brownish
Total dissolved solids	(mg/L)	1330
Suspended solids	(mg/L)	1540
BOD5@20ºC	(mg/L)	1040
COD	(mg/L)	4647
Chlorides	(mg/L)	258

Microbial Fuel Cell (MFC)

Double chamber MFC was fabricated for the treatment of distillery wastewater.

Microorganism

Yeast *S.cerevisiae* were purchase from local market with analytical grade. Inoculums of yeast were prepared from following composition with 250 mL medium which contained in g.l-1: glucose, 10; $(NH_4)_2$ HPO_4, 0.64 , and yeast extract 2.5; at pH 5.5 and incubated for 18 hrs on an orbital shaker at 150 rpm at 30°C.

Materials Used for the Fabrication of MFC:

Various materials used for the construction of MFC which are given in Table 2.

Table 2: MFC fabrication prerequisites

Materials	Quantity
PVC bottles (2.5L)	2
PVC pipe (5cm)	1
Copper rods (5×5)	2
Distillery wastewater	1 L
Copper wire	0.5m
Aluminum clips	2
Digital multimeter	1

Functions of the materials used for the fabrication of MFC

Plastic box: It is used to prepare anode chamber. The anode chamber holds the wastewater.

Agar: It is used to prepare agar salt bridge i.e., proton exchange member for keeping the anode and cathode liquid separate. This membrane is permeable so that protons produced at anode can migrate to the cathode.

Pencil leads: These are used as anode and cathode materials.

Copper wire: is used to connect the electrodes to the multimeter which form external circuit.

PVC pipe: holds the agar salt mixture, which is called as agar salt bridge.

Sealant: PVC pipe was connected to the sides of the plastic boxes and sealed with epoxy.

Multimeter: is used to measure the current and voltage.

Fabrication of MFC

Selection of Anode Chamber

Non-reactive, non-conductive and nonbiodegradable plastic box were selected as anode chamber.

Preparation of Agar Salt Bridge

The PVC pipe used in salt bridge construction had dimensions of 5 cm length and 2 cm diameter. Volume 15.7 cm^3 was calculated using the formula $\pi r^2 h$. Salt bridge was prepared using 20 ml of 1M KCl solution and 3% agarose. The solution was first subjected to heat for blending, which in return gave a clear solution of agarose and KCl. the same was poured into the PVC pipe and was kept in the freezer at -4°C for solidification. The solidified salt bridge was attached to the chambers using araldite adhesive which makes them leak proof.

Assembling of electrodes

The graphite rods from pencils have been used as anode and cathode materials. The arrangement of electrodes were done on a plastic pipe in such a way that it looks like a graphite brush. The length and diameter of the graphite rods will be 90 mm and 2 mm respectively. In MFC, there was no cathode chamber. Instead, the graphite rods from pencils have been placed on agar salt bridge and the copper wire was wound on it. This acted as cathode for MFC. The oxygen in air would help in accepting the electrons from anode chamber. Hole was drilled on the top of anode chamber so that plastic pipe containing the graphite rods can pierce through the hole.

Assembling of MFC

MFC reactor was constructed. The assembled electrodes were placed into the anode and cathode chambers, a circular groove was made at the center of plastic box for fitting the PVC pipe containing agar salt then sealed and made air tight. The reactors are checked for water leakage.

Process of bioelectricity generation in MFC

Microbial technology for electricity generation from wastewaters could play role in energy generation and in wastewater treatment. MFC consists of anode and cathode chamber. In Fig.1 represent schematic diagram of MFC. Organic matter oxidized by using microorganisms. In anode chamber anaerobic and in cathode chamber aerobic conditions were maintained (Anand et al., 2010).

Substrate (distillery wastewaters), was put in anode chamber maintained anaerobic conditions, in cathode chamber aerobic condition was maintained with addition of air through fish pump.

In cathode chamber water $C_6N_6FeK_3$ added. Electrodes (copper rods, 6×6) were made for flow of electrons inserted in chambers. *Saccharomyces cerevisiae* sp. is used in anode chamber for degradation of organic matters present in distillery wastewater.

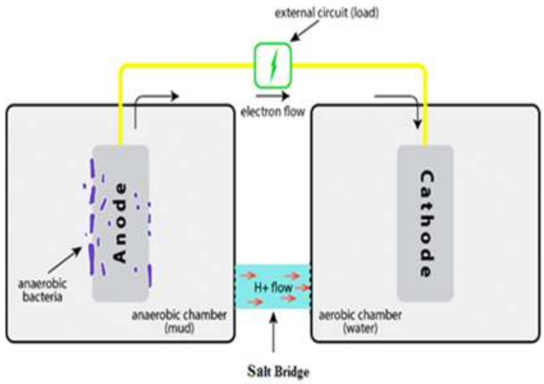

Figure 1: Schematic representation of a MFC

Electron transferred through anode to cathode by external circuit while proton transferred through proton exchange membrane from anode to cathode (Anand, 2015b). Electron transferring could cause of electricity generation (Jiansheng et al., 2011) as shown in Fig. 2.

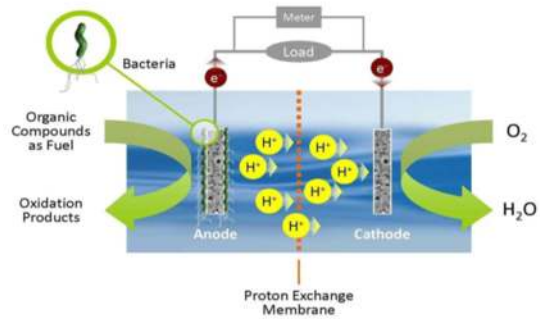

Figure 2: Process of bioelectricity generation in MFC

RESULTS AND DISCUSSION

Waste water samples were collected from distillery for bio-treatment using MFC simultaneously electricity generation. Different parameter for water treatment and electricity generation were under consideration.

Treatment and current generation using various concentrations of sugar wastewater

Sugar wastewater was diluted to get desired feed concentrations. The varied feed concentrations of wastewater were given as the substrate for MFC.

The influent (I),effluent (E) and percent removal (%) of chemical oxygen demand, Total dissolved solids and Biochemical oxygen demand for various feed concentrations are presented in Table 3.

Sugar wastewater showed its potential for COD removal indicating the functions of microbes present in wastewater in metabolizing the carbon source as electron donors. Continuous COD, BOD, TDS removal was observed in MFC. The COD removal efficiency increased from 35% to 69.3%, BOD removal efficiency increased from 34.6% to 68.1% and TDS removal efficiency increased from 25.4% to 56.3% and pH increased from 7.1% to 8.2% randomly, daily pH was brought to neutral for the period 0-28 days. Current increased from 0.11 to 1.28 mA, Voltage increased from 0.1 to 0.9 V as the feed concentration increases from 200 mg COD/L to 1400 mg COD/L.

COD removal efficiency of sugar wastewater for various feed concentrations

Sugar wastewater showed its potential for COD removal indicating the functions of microbes present in wastewater in metabolizing the carbon source as electron donors. It is experimental data that current generation and Cod removal showed relative compatibility. Continuous COD removal was observed in MFC. In MFC, the COD removal efficiency increased from 35% to 69.3% as the feed concentration increase from 200 mg COD/L to 1400 mg COD/L respectively as given in Table 3. The COD removal efficiency improved with the increase in feed concentration. COD efficiency for various feed concentrations has been attained equilibrium after 4-5 days with respect to time.

BOD removal efficiency of sugar wastewater for various feed concentrations

The BOD of Sugar wastewater was reduced in MFC. BOD was analyzed on the first day and final day for each feed concentration. For MFC, the BOD removal efficiency increased from 34.6% to 70.1% as the feed concentration increased from 200 mg COD/L to 1400 mg COD/L respectively as shown in fig 5. BOD efficiency for various feed concentrations has been attained equilibrium after 4-5 days with respect to time.

Total dissolved solids removal efficiency of sugar wastewater for various feed concentrations

During the operation considerable reduction in total dissolved solids increased with increase in feed concentration from 200 mg COD/L to 1400 mg COD/L. The total dissolved solids the BOD removal efficiency increased from 25.4%% to 56.3% as the feed concentration increased from 200 mg COD/L to 1400 mg COD/L respectively as given in Table 3.Total dissolved solids efficiency for various feed concentrations has been attained equilibrium after 4-5 days with respect to time.

Table 3: Treatment efficiency of sugar wastewater and current generation for various feed concentration

Time (Day)	COD (mg/L)			BOD (mg/L)			TDS (mg/L)			pH		Current (mA)	Voltage (V)
	I	E	%	I	E	%	I	E	%	I	E		
0-4	200	127.8	36.1	200	131.6	34.2	423	312.69	26.1	6.8	6.9	0.20	0.16
4-8	400	245.6	38.6	400	252.4	36.9	514	393.40	29.3	6.9	7.1	0.32	0.23
8-12	600	343.8	42.7	600	362.4	39.6	623.2	420.03	32.6	7.1	7.3	0.36	0.36
12-16	800	413.6	48.3	800	456.8	42.9	716.5	452.82	36.8	7.4	7.4	0.49	0.39
16-20	1000	439	56.1	1000	536	46.4	824.9	493.29	40.2	7.6	7.6	0.57	0.42
20-24	1200	487.2	59.4	1200	610	49.1	944.6	542.20	42.6	7.8	7.8	0.62	0.59
24-28	1400	547.4	60.9	1400	693	50.5	1012	545.46	46.1	7.9	7.9	0.73	0.64
28-32	1600	585.6	63.4	1600	710.5	55.6	1196	595.60	50.2	8.0	8.0	0.91	0.83
32-36	1800	631.8	64.9	1800	712	60.4	1202	572.48	52.4	8.1	8.1	1.02	0.97
36-40	2000	694	65.3	2000	718	64.1	1364	622.25	54.4	8.3	8.3	1.26	1.01
40-44	2200	701.8	68.1	2200	720	67.3	1494	648.65	56.6	8.4	8.4	1.40	1.24

pH Variation of Sugar wastewater for Various Feed concentrations in MFC

Sugar wastewater showed its potential for increments of pH. Continuous increment was observed in MFC-1, the pH increased from 7.1 to 8.2 as the feed concentration increased from 200 mg COD/L to 1400 mg COD/L respectively as given in Table 3. The increment of feed concentration showed a positive effect in increment of pH. pH variation for various feed concentrations has been attained equilibrium after 4-5 days with respect to time.

Current and voltage Generation of sugar wastewater for various feed concentrations in MFC

The average value of current and voltage for each feed concentration in MFC is given in the Table 3. The current and voltage showed a gradual increase with respect to increase in feed concentration. The highest average values of current obtained 1.28 mA and 0.9 V. The power produced for 1 m^2 area is watt. Current and voltage generation for various feed concentrations has been attained equilibrium after 4-5 days with respect to time.

Effect of Agrose Concentration on Voltage Generation

Voltage generation from wastewater effected by various agrose concentrations in salt bridge. From 7-12% of agrose concentration were analyzed for voltage generation the maximum voltage (0.67 mV) (Fig. 3) and current generation (0.0642 mA) (Fig.4) occur at 10% agrose concentration using 10 ohm

Effect of salt concentrations on voltage generation

Different salt molar concentrations were used to investigate the effect of varying concentrations of salts from 1-5M of KCl and NaCl. Salt bridge connected two chambers of MFC for proton transferring from anode to cathode. From 1M-5M of salts were used to investigate the optimize range for maximum voltage generation. In Fig. 5 the graph

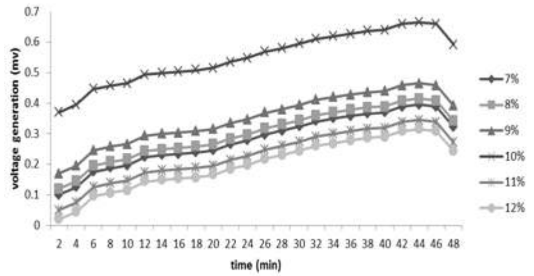

Figure 3: Effect of agarose concentration on voltage generation

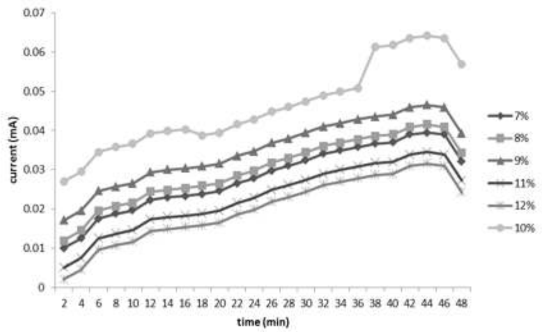

Figure 4: Effect of agarose concentration on current generation

shows relation between voltages generated under different molar concentrations of salts in salt bridge. The maximum voltage generated at 1M KCl and 1M NaCl about 0.67 mV, 0.35 mA respectively (Fig. 5 and 6).

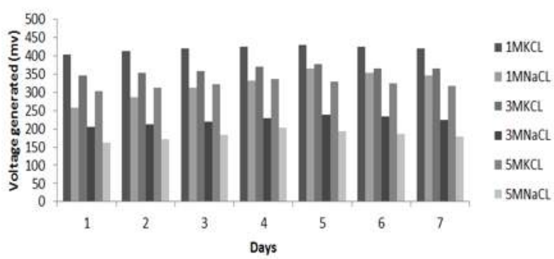

Figure 5: Effect of salt concentrations on voltage generation

Effect of length of salt bridge on current and voltage generation

Salt bridge was used at the place of PEM for transferring protons from anode to cathode chamber. Different lengths of salt bridge were used to identify the optimize length for voltage generation using MFC. The maximum voltage and current generation were observed at 3 cm length of salt bridge that were 0.66 mV, 0.37 mA respectively (Fig. 7 and 8).

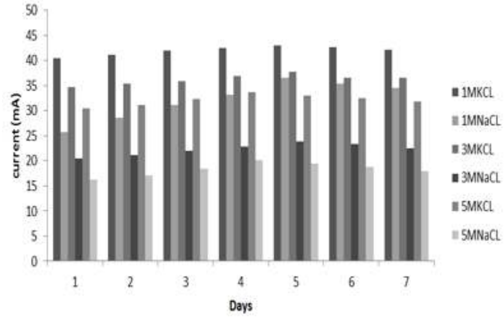

Figure 6: Effect of salt concentrations on current generation

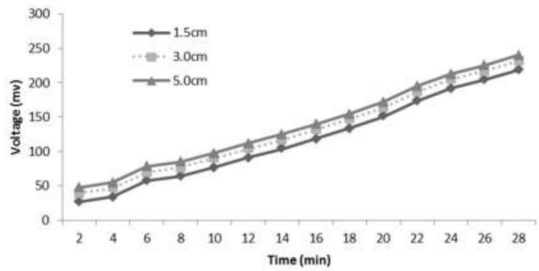

Figure 7: Effect of length of salt bridge on voltage generation

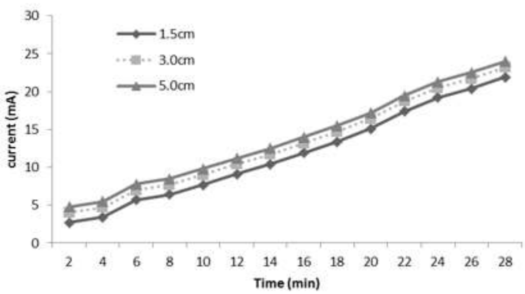

Figure 8: Effect of length of salt bridge on current generation

Effect of dia of salt bridge on electricity and voltage generation

Dia of salt bridge had many advantages regarding proton transferring from anode chamber to cathode chamber for oxidation with air to treat wastewater and continues voltage generation (Anand et al., 2015c).

From 0.1 to 0.2 cm dia were used the maximum voltage and current generation at 0.2 cm dia, that were 0.65 mV, 0.36 mA respectively (Fig. 9 and 10).

Effect of pH on voltage generation

pH is a major factor affecting the activity of most prokaryotes. At optimum PH, microbes perform biological activities of growth and metabolism at the maximum rate. Fig. 4 highlights the point that the

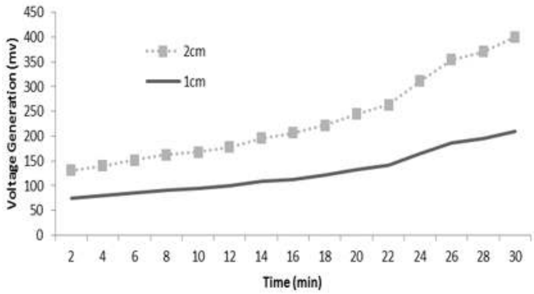

Figure 9: Effect of dia of salt bridge on voltage generation

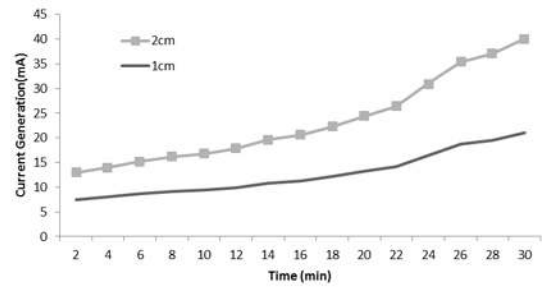

Figure 10: Effect of dia of salt bridge on current generation

highest yield of power was obtained at pH 8.5, when perhaps the enzymes secreted by the microbes would have been in a conducive form of ionic groups on their active sites to function properly. Reportedly, variation in the pH would result in changes in the ionic form of the active sites, which would further change the enzymatic activity leading to the variation in the reaction rate as well (Amelia et al., 2015). The results also suggested that at pH 6 and below, electrochemical and cellulosic activities would likely be lower when compared to the results obtained at higher pH. This might be due to the denaturation of celluloses, proteins or active sites under acidic conditions. This finding was in agreement with that reported by Z. He et al. who observed that neutral pH was suitable for cellulose degraders, as acidic conditions tend to inhibit the growth of the majority of cellulose degrading yeasts (Muralidharan et al., 2011).

Substrate concentration's impact on voltage generation

Different concentration of dairy wastewater were used for measuring maximum power production. MFC had many advantages over utilization of sludge

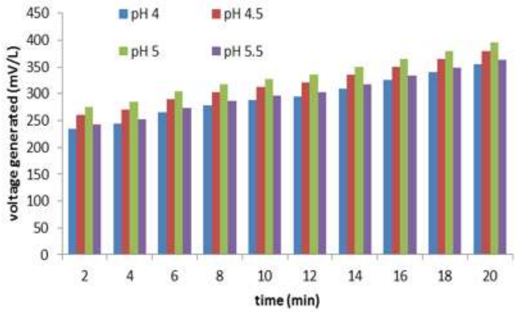

Figure 11: Effect of pH on voltage generation

for power generation, effect of power production using different concentration was considered to investigate optimize condition. In Fig. 12 it is clearly highlighted that 75% dairy wastewater concentration produced maximum power generation as compare to other concentration

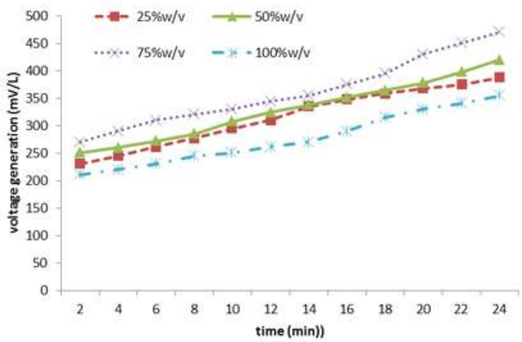

Figure 12: Effect of substrate concentration on voltage generation

CONCLUSION

Due to the rapid depletion and escalation of prices of conventional fossil fuel, the whole world is urgently looking for an alternative source of energy, which is renewable and can be produce in an economical manner. In this context, energy produced from a potential organic biowaste (distillery wastewater) is an attractive option. In the first phase of project work, a MFC was successfully constructed using two 1.5 L bottles, which were operated as cathode and anode chambers. The salt bridge was made using KCl and agarose. Graphite plates were used as electrodes in MFC. In the second phase, experiment was conducted to generate energy from locally available distillery wastewater, which was used as a substrate for MFC. The whole system was connected to desktop multimeter for obtaining précised readings of voltage and current. MFC of distillery wastewater showed removal efficiency 69.3% COD, 68.1% BOD and 56.35 %TDS with different feed concentrations (200-1400 mg COD/L). The current, voltage and power generation in the reactor is 1.28 mA, 0.9 V and 0.304 watts/m^2 respectively. pH was increased randomly from 7.1 to 8.2 with respect to different feed concentration. In the last phase, various effects were analyzed using different length, dia, salt and agrose concentration in salt bridge to investigate the optimize condition for salt bridge. The optimize condition of maximum voltage and current generation were observed at 2 cm dia, 5cm length, 10% agarose concentration and salt concentration of 1M KCl ,1M NaCl about 0.67 mV and 0.0642 mA.. It had been conclude that by varying agarose concentrations, it will resist the proton flow from anode to cathode chamber. Further study to be made for scale up MFC for sustainable development.

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