ISSN 1063-455X, Journal of Water Chemistry and Technology, 2019, Vol. 41, No. 1, pp. 13–20. © Allerton Press, Inc., 2019.

PHYSICAL CHEMISTRY
OF WATER TREATMENT PROCESSES

Microbial Fuel Cell Using UASB as Anode and Effects of Hydrogen Peroxide on Treatment Efficiency[1]

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Received May 10, 2016
Revised October 21, 2016
Accepted October 27, 2018

Abstract—Dual chambered continuous up-flow microbial fuel cell (MFC) was used to check the effect of controlled temperature and addition of different hydrogen peroxide (H_2O_2) doses on bioelectricity production. MFC-1 and MFC-2 showed 77 and 89% of COD removal efficiency, respectively, while same amount 13.4% of coulombic efficiency under continuous operation mode were produced by both reactors. Oxygenation of cathode chambers of both MFC with 5 mL of H_2O_2 resulted in higher values of potential difference and current, 1100 mV and 0.6 mA in MFC-1 and 674 mV and 0.32 mA in MFC-2. Higher power density of 166 Pd·cm^{-2} was produced by reactor 1 than 75 Pd·cm^{-2} from reactor 2. Result showed that control temperature of 35°C had lowered down the bioelectricity production while increased the COD removal. The use of H_2O_2 for oxygenation was found to improve the voltage and current production and stability of MFC.

DOI: 10.3103/S1063455X1901003X

Keywords: coulombic efficiency, voltage, power density, salt bridge, waste water, COD.

INTRODUCTION

One of the main sources of many industrial contaminations is the wastewater produced by industries which must be treated in order to achieving local effluent discharge standards [1]. Treated water is considered as an essential part of the freshwater sustainability and resulted water is considered as a fresh water resource instead of a waste [2]. Bioelectricity generation during wastewater treatment can be a great achievement by its dual benefits of wastewater treatment and green energy production [3]. The microbial fuel cell (MFC) has been used for treating wastewater since 1991. Many researchers around the world still are working to enhance the consistent electricity generation from MFC [4].

Aerobic wastewater treatment has high energy consumption therefore, priority of industrial sector is, a cost effective and reliable wastewater treatment option, which can be an anaerobic system [3]. Up-flow anaerobic sludge blanket (UASB) reactor, an energy conservative biotechnology, is one of the best anaerobic digesters used for wastewater treatment [5]. MFC is a bio-electrochemical device that converts chemical energy, present in chemical bonds of organic compounds [6] to electrical energy with the help of microorganisms under anaerobic conditions. It can utilize wastewater for the generation of electricity [7, 8].

The conventional MFC is a two chamber system, consisting of anaerobic anode and aerobic cathode, which are separated by a proton exchange membrane (PEM) or salt bridge. MFC is half biological, because only the anode side consists of electrochemically-active microorganisms, while the cathode is abiotic. Actually, microorganisms motivate the degradation of organic materials to release electrons and act as biocatalysts. Electrons are shifted towards the cathode side via an external electric circuit and protons travel toward cathode chamber through salt bridge. At cathode, electrons and protons combine in the presence of oxygen to form water [9].

In UASB-MFC, two chambers with anode and cathode are used for bioelectricity production and flow of electrons is measured in between. Different compositions of salt bridge and membranes were used for transferring protons from anode to cathode. The movement of electrons through external circuit, forms the current

[1] The text was submitted by the authors in English.

[10]. The important factor for electricity generation in MFC was to keep oxygen or electron acceptor separated from microorganisms, which was an important part of MFC designing [11]. A key factor in the successful performance of cathode chamber of MFC is oxidation. Mostly aeration pump was used to provide oxygen, which consumed a large amount of energy and oxidation with $K_2Cr_2O_7$ contributed to huge operating cost in wastewater treatment [12, 13]. Because of its high oxygen content (50%), $H_2O_2$was also used in biological treatment where high levels of oxygen was required [14]. In this study UASB reactor was modified and converted into MFC for SN solution degradation and acted as anaerobic chamber attached to aerobic cathode chamber through salt bridge. H_2O_2 was used as a source of oxygen to react with protons which passed through salt bridge. The aims and objectives of this study were to check the effect of H_2O_2, controlled temperature and glucose concentration in synthetic wastewater for electricity production and COD reduction from UASB-MFC.

EXPERIMENTAL

Experiment was carried out in two separate up-flow MFC made up of acrylic transparent materials. Each reactor consisted of 4 L capacity anaerobic anodic compartments and 4 L aerobic cathodic compartments, all operational parameters of MFC are given in Table 1. The total height of the reactor was 40 cm, and the distance between the anode and cathode was 12 cm. Up-to 50 % volume of anode compartment of the MFC reactor was inoculated with homogenized anaerobic sludge and SN solution was used as fuel at a flow rate of 0.42 $L{\cdot}d^{-1}$ (see Table 1). Reactor was operated in an up-flow mode with all influent feeding at the base and effluent was collected from the top of the reactor. Five carbon rods were used as anode, made from waste batteries carbon, each with a length of 55.17 mm and a diameter of 8.02 mm and were spaced 2 mm apart. Area of single carbon rod was 2.78 cm^2 and total area of anode assembly was 13.9 cm^2.

Table 1. MFC reactor operating parameters

Parameter		MFC-1	MFC-2
Temperature	°C	20–30	35
Volume of reactor	L	4	4
Flow rate	$L{\cdot}d^{-1}$	0.8	0.8
Concentration of influent	mg $COD{\cdot}L^{-1}$	400–800	400–800
Mass loading rate	g $COD{\cdot}L^{-1}{\cdot}h^{-1}$	0.042–0.094	0.042–0.094
Hydraulic loading rate	$L{\cdot}L^{-1}{\cdot}day^{-1}$	0.105	0.105
Hydraulic retention time	day	5	5

Hollow aluminum rods were used as cathode in aerobic chamber. Each set of cathode consisted of 5 aluminum rods, with a diameter of 9 mm and a length of 15 mm. These aluminum rods were connected together through copper wire and were spaced 2 mm apart. Area of single aluminum rod was 1.35 cm^2 and total area of cathode assembly was 6.75 cm^2. In cathode chamber, 35% H_2O_2 with different amount from 0.5 to 5 mL was added as source of oxygen to react with proton. Separate aerobic cathode chamber was connected to anaerobic anode chamber through 9 cm long salt bridge. Salt bridge was used as protons exchange system prepared in electrically and chemically flexible plastic pipe with 3 cm internal and 3.5 cm external diameter, having groves on its surface; purpose of selecting wavy pipe was to pack agar tightly and to stop water penetration through salt bridge. This pipe was insulated to reduce the effect of temperature (35°C) on the PEM in MFC-2.There was a possibility that without insulation, PEM might shrink inside the pipe and cause exchange between the aerobic and anaerobic compartment (Fig. 1).

Salt bridge was prepared by mixing 3% agar in 100 mL 1M KCl solution [15]. 1 M KCl solution was prepared by mixing 74.55 g KCl in 1000 mL distilled water. MFC-1 operated at room temperature and MFC-2 immersed in water bath, operated at controlled temperature of 35°C.

Three different concentrations 300; 500 and 1000 $mg{\cdot}L^{-1}$of synthetic wastewater were prepared to feed anode chamber of both MFC to provide a desirable growth substrate for microorganisms. Synthetic wastewater consisted of three components, glucose, trace elements and microelements solution. MFC were operated in a continuous mode with a same retention time of 5 days.

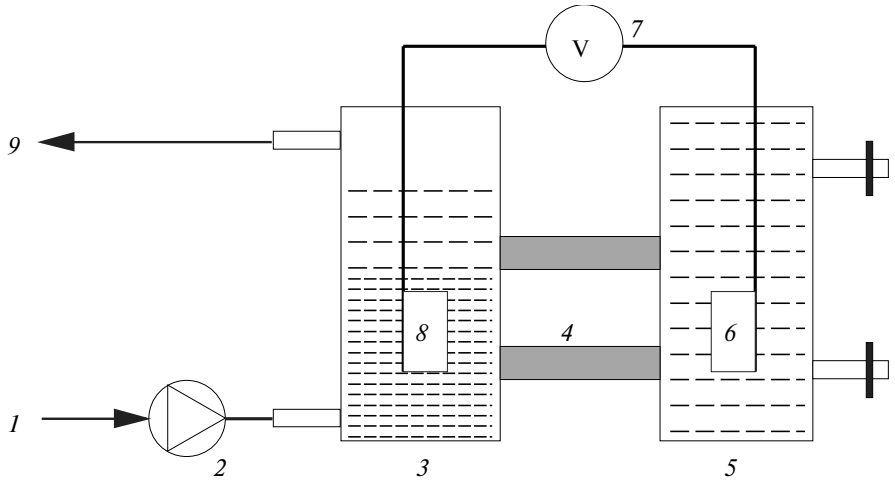


Fig. 1. Up-flow microbial fuel cell set up: *1*—influent, *2*—peristaltic pump, *3*—anaerobic sludge, *4*—salt bridge, *5*—aerobic part, *6*—cathode rods, *7*—voltmeter, *8*—anode rod, *9*—effluent.

To see the effect of glucose dosage on bioelectricity production from UASB-MFC, different parameters were tested. COD was measured using closed reflux method, by standard methods for the examination of water and wastewater [16]. The potential difference and current were measured using a multimeter and readings of volts and amperes were recorded after every hour from 8 am to 7 pm. The calculations were carried out for external resistances in ohm (Ω). Temperature, pH, conductivity and TDS were measured by Wagtech multi-meter.

Coulombic efficiency (E_c) of the both MFC was evaluated using the measurements of glucose and degradation intermediates in the anodic compartment. The E_c was calculated using the ratio of total Coulombs obtained in the present study (C_p) to the theoretical amount (C_{max}) available from complete substrate oxidation [17]:

$$E_c = \frac{C_p}{C_{max}} \times 100\,;\; C_p = I \cdot t\,;\; C_{max} = \frac{FbSV}{MV},$$

where t—time of stable voltage output, s; I—current, A; F—Faraday's constant's 96,485 C·moL^{-1} of electrons; b—available mole of electrons for removal per mol of substrate; S—COD concentration, g·L^{-1}; V—volume, L; MW—molecular weight of organic source (glucose).

RESULTS AND DISCUSSION

The pH of MFC-1 and MFC-2 was observed from 7.2–8.4 during whole operation. The effluent pH of MFC remained higher than the influent pH until day 12 and, after 12th day, it dropped very sharply and remained below the influent value on day 15, due to fermentation of glucose to acetate. Glucose served as a better carbon source for active biomass, which was easily biodegradable to form acetate. On day 25 and 29, MFC-2 pH dropped to 7 while MFC-1 pH remained 8.5 (see Fig. 1). It was because MFC-2 temperature was about 35°C and MFC-1 temperature was below 25°C hence, high temperature favors the fermentation of glucose to acetate, alcohol and CO_2 which dropped the pH [17].

The synthetic wastewater had COD range of 300 to 1000 mg·L^{-1} was treated anaerobically under room temperature in MFC-1 and a constant temperature of 35°C was adjusted for MFC-2. During the initial 4 days, the substrate uptake was lower due to insufficient active biomass and effluent COD was high due to washing out of dead biomass and solids from unsettled sludge. From the 4th day, substrate uptake increased and reached a maximum level on the 11th day where MFC-2 effluent COD was below 100 mg·L^{-1}. During 18 days, both MFC were fed with COD ranges from 300–500 mg·L^{-1} and both reactors reached to maximum efficiency of 86% on 12th day. From 19th day, COD load was doubled in the range 800–1000 mg·L^{-1} and an increase in COD removal till day 25th was observed in MFC-2 i.e. 88% (Fig. 2) and remained same in reactor 2. Finally on 31st day, it decreased to 77% and increased 89% from MFC-1 and MFC-2, respectively.

Higher COD removal from MFC-2 was attributed to the control temperature of 35°C which enhanced the biodegradation [18] of synthetic waste water (Table 2).

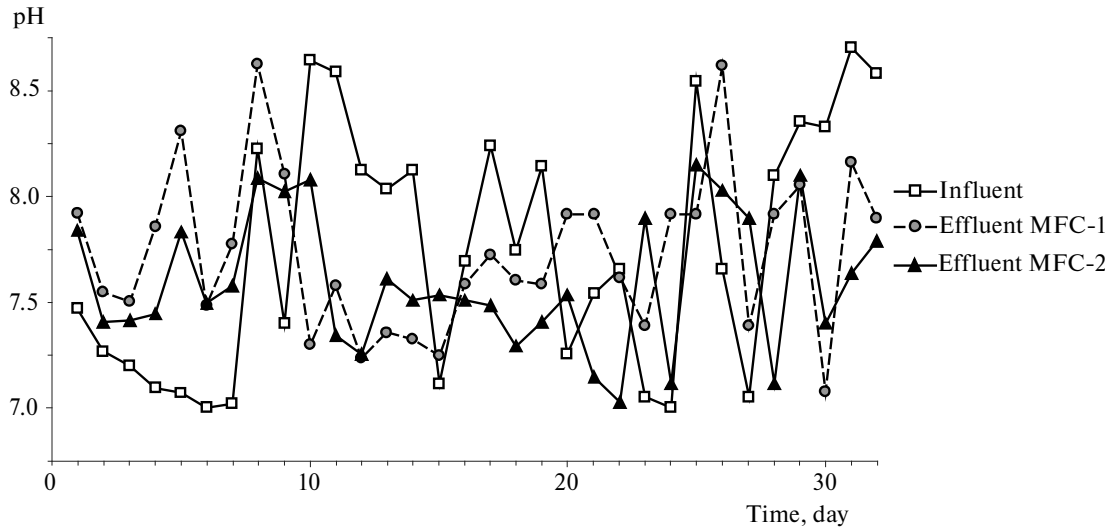


Fig. 2. The pH changes of influent in MFC-1 and MFC-2 during 31 days of treatment.

Table 2. Synthetic wastewater treatment efficiency of MFC-1 and MFC-2

Parameter		Influent	MFC-1	MFC-2
Temperature	°C	23 ± 0.3	Room	35 ± 0.3
pH	–	6.5 ± 0.42	7.89 ± 0.035	7.79 ± 0.08
EC	μS	393 ± 4.35	612 ± 12.09	618 ± 34
TDS	$mg \cdot L^{-1}$	205 ± 2	320 ± 3.46	307 ± 10.59
COD		900 ± 13.13	203 ± 5.85	96 ± 13.52
TSS		0.0210	0.12	0.21
VSS		0.001	0.0312	0.0297

Another study showed 95% COD removal efficiency when active biomass was increased with only glucose as substrate [19] and it was only 54% when antibiotic factory wastewater was treated in UASB reactor with hydraulic retention time of 33.7 h and organic loading rate of 10.81 kg COD/m^3·day [20]. In the present study, maximum COD removal was 89% and if it was kept operating further for few more days, it could have reached 95% (Fig. 3). Macro- and micronutrients were present in wastewater to contribute in the synthesis of protein and new cell growth. Addition of nutrients helped to increase the active biomass. Higher active biomass results in higher COD removal rate because COD is the useful measurement of chemical oxidation by chemoorganotrophs [17].

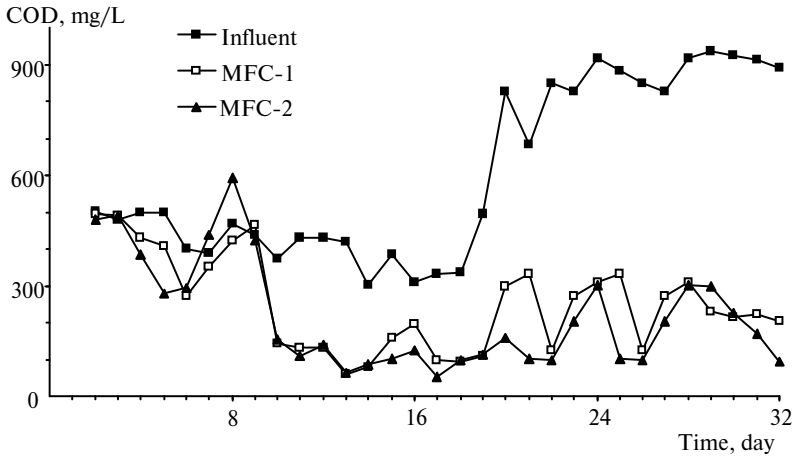


Fig. 3. The COD removal efficiency of influent in MFC-1 and MFC-2 during 31 days of treatment.

In the cathode compartment, H_2O_2 was dissociated and oxygen free radicals reacted with protons received through PEM from anode chamber and developed potential to move electrons to cathode through external circuit.

In MFC-1, the influence of H_2O_2 on electricity production in cathode chamber was noted as, when 0.5 to 1 mL H_2O_2 was added, 623 mV of potential difference and 0.287 mA of current was produced. On further addition of H_2O_2 from 2–4 mL; power generation decreased from 723 to 465 mV and 0.3 to 0.1 mA. Highest values of 1100 mV and 0.6 mA were observed when 5 mL of H_2O_2 was added, which became stable later on around 850–900 mV and 0.52–0.57 mA (Fig. 4). It was same with the maximum voltage of 890 mV, which was generated when vegetable oil industries discharge was treated with columbic efficiency of 5184.7 C [21]. Significant positive correlation were found between different parameters as $r = 0.75$, $n = 16$ existed between amount of H_2O_2 and voltage, $r = 0.7$, $n = 16$ were found between amount of H_2O_2 and current, $r = 0.69$, $n = 16$ between $H_2O_2$and power density. Similar study showing successful application of H_2O_2 for bioreactor oxygenation has been demonstrated in [22].

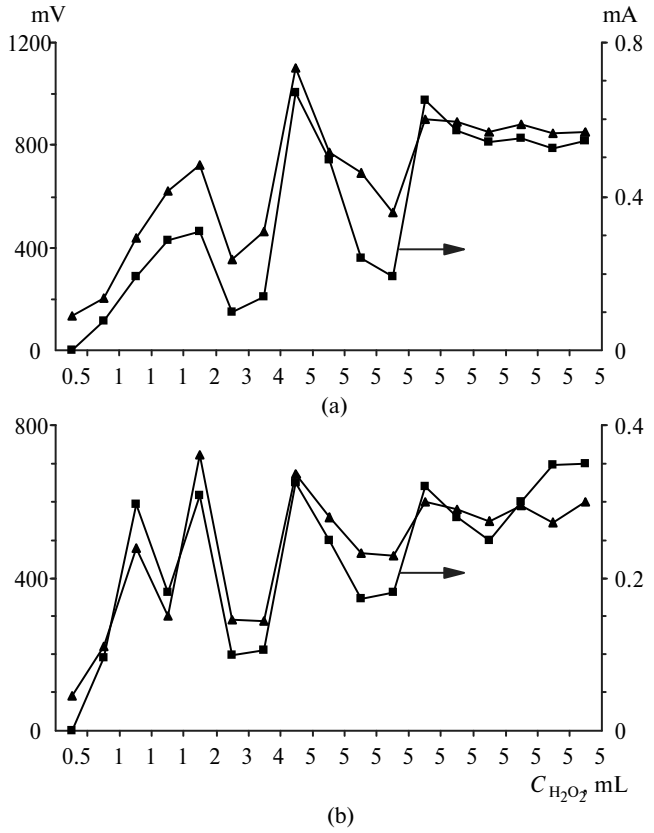


Fig. 4. MFC-1 (a) and MFC-2 (b): different volumes of H_2O_2 and its effect on voltage and current production.

In MFC-2, similar pattern but lower values of voltage and current were observed as compared to MFC-1 (Table 3). At 0.5–1 mL of H_2O_2, 90–480 mV and 0.29 mA were observed which gradualy increased at 2 mL of H_2O_2 but during 3–4 mL of H_2O_2 addition, values became lower from 723 to 287 mV and 0.3 to 0.1 mA. On 5 mL of H_2O_2 voltage and current again reached to 674 mV and 0.32 mA and remained stable at 550–600 mV and 0.25–0.35 mA, respectively (see Fig. 4). Significant positive correlation were found as, $r = 0.62$ existed between amounts of H_2O_2 and voltage, $r = 0.52$ between amounts of H_2O_2 and current while $r = 0.5$ between H_2O_2 and power density. These correlation values were lower than MFC-1 which means that H_2O_2 under controlled temperature of 35°C produced less electricity while authors [18] found that the control temperature had no significant effects on power production.

H_2O_2 was added from 2nd day (39 h) to 7th day (162 h), during synthetic wastewater treatment of 32 days. Voltage generation was recorded every hour (during day time) throughout the week. Electricity generation in both MFC increased gradually with time and stabilized.

Table 3. Electrostatic comparison of MFC-1 and MFC-2

Parameter		MFC-1	MFC-2
Coulombic efficiency	E_c	13.43	13.43
Volts	mV	850	600
Current	mA	0.545	0.348
Power density	$Pd \cdot cm^{-2}$	166	75
Temperature	°C	28	35
Resistance	mΩ	1559.63	1714.28
Volts stability*	mV	800–900	500–600

*1.25 mL $H_2O_2 \cdot L^{-1}$ was added in cathode chamber.

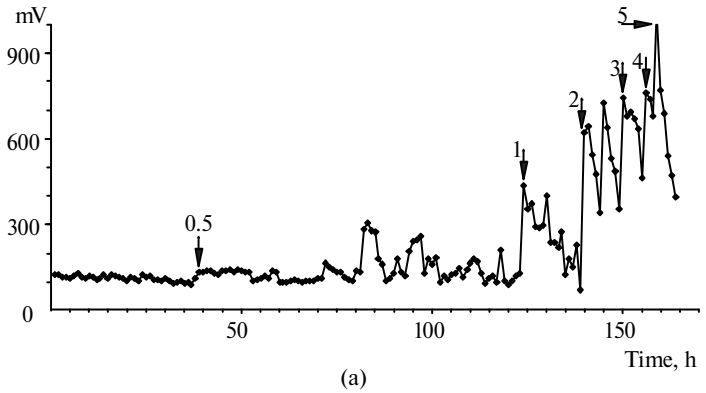
In MFC-1, 0.5 mL of 35% H_2O_2 was injected into the cathodic chamber resulted in rapid increased of voltage to 136 mV at 39 h while in MFC-2 it reached 90 mV. After addition of 1mL H_2O_2, voltage raised to 437 and 480 mV on day 5th (124 h) in MFC-1 and MFC-2, respectively. This voltage kept rising and achieved 723 mV on 6th day (145 h) with 2 mL H_2O_2 dose in both reactors. During 150 to 160 h, 3–5 mL addition of H_2O_2 raised voltage from 741–770 mV in MFC-1 which was higher than 525–558 mV in MFC-2. This result indicated that H_2O_2 can be used to supply good source of electron acceptor to transfer protons through salt bridge.

The decline of voltage from 71–357 during 125–139 h might be due to extensive slime layer formation throughout the cathode rods surface as explained in [23]. Therefore, cathode surface was cleaned repeatedly several times with a soft brush to removed the film than an immediate voltage increased was observed to 450 mV. It was observed previously that biofilm and chemical scale formation on the cathode revealed undesirable effects on the power generation due to decrease in oxygen diffusion and exposed cathode surface area [24].

Since biomass growth on the cathode surface limited oxygen transfer, bulk oxygen concentration had to be increased above 8 $mg \cdot L^{-1}$ in order to provide sufficient influx of oxygen to the cathode. A proportional increase in power production was observed when the H_2O_2 load was changed from 1 to 5 $mL \cdot day^{-1}$. MFC-1 showed high and stable power production while MFC-2 showed lower voltage production (Fig. 5). It means that anaerobic metabolism was better at temperature about 25 to 28°C, which were favorable for microbial growth and membrane permeability, resulting in higher output [25].

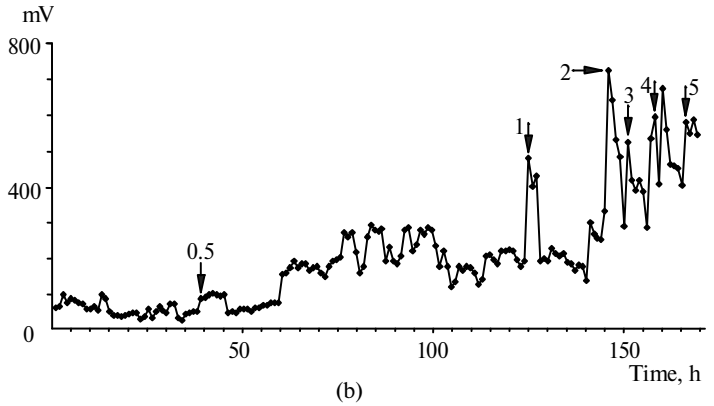
From MFC-1 one volt of potential difference was utilized to turn on the LED light. Threshold minimum voltage for the white LED was 1.5 V. A software Multisim was used to simulate the voltage shortage to turn "on" the LED (Fig. 6).

A physical setup was developed to restrain voltage of 0.5 V from DC battery (0.8 V) and 1 V from MFC. These two energy sources were added up together to reach 1.5 V at terminal. Remaining 0.3 V was utilized in other current limiting resistances in the circuit.



(a)

Fig. 5. Voltage produced during waste water treatment of 32 days, different doses of H_2O_2, mL (as shown by arrows) were added from second day (39 h) to 7th day (162 h). a—MFC-1; b—MFC-2.



(b)

Fig. 5. (Contd.)

The maximum potential difference of 316 mV was recorded in MFC-1 operating with COD concentration of 300 mg·L^{-1} with synthetic solution of glucose. MFC-1 operating with COD concentration of 500–1000 mg·L^{-1} resulted in reduction of voltage to 136 mV, which might be due to substrate mediated inhibition of microbial growth. Organic fouling of the salt bridge was found to be very high on the anode side in both MFC operating with COD concentration of 1000 mg·L^{-1} which could be the reason for poor performance in power production at high COD [26].

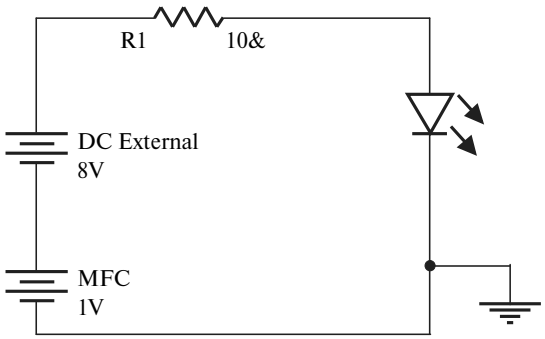


Fig. 6. Circuit diagram of voltage produced by MFC with DC battery to turn on LED light, R1 is the resistor.

CONCLUSIONS

The up-flow two-compartment MFC reactors used in this study carried out biodegradation of synthetic wastewater, which provided a free source of carbon for biological power generation. The use of H_2O_2 for oxygenation appeared to lower the oxygen limitation problem. In addition, control temperature of 35°C had lowered down power generation but improved the COD removal percentage.

ACKNOWLEDGMENTS

The grant received from COMSATS Research Grant Program (CRGP).

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