Effect of Initial Organic Load and Fe^{3+} Concentration on the Electricity Generation and COD Removal in Membrane less Microbial Fuel Cell

Ravi Shankar, Prasenjit Mondal, and Shri Chand

Abstract- The present work deals with the simultaneous generation of electricity and removal of organic load from synthetic wastewater containing glucose and glutamic acid. The effect of initial COD and Fe^{3+} concentration on the generation of current density and voltage has been studied. Although, the amount of COD removed increases with increase in the initial COD value from 500 mg/l to 2500 mg/l, the maximum generation of current density (19 mA/m^2) and voltage (14.8 mV), after 7 days of operation, is achieved at the initial COD value of 1500 mg/l. Difference in the anodic and cathodic pH has also been observed maximum (~1) at the initial COD value of 1500 mg/l. Concentration of Fe^{3+} increases the current density and voltage generation. Addition of optimum concentration of Fe^{3+} (10 mg/l) in the solution produces current density of ~ 600 mA/m^2 and voltage of ~ 321 mV, after 3-4 days of operation, respectively. The present process seems to have maximum current density and voltage generation capacity in comparison to some recently reported literatures and is able to reduce COD value below permissible limit with the initial COD value d 1250 mg/l.

Keywords- Current density, MFC, salt bridge, voltage

I. Introduction

MICROBIAL fuel cell (MFC) is an instrument, which converts chemical energy of a wide range of organic solutions and wastewater to electrical energy with the catalytic activity of microorganisms [1]. Oxidation of organics in wastewater by micro organism in anaerobic condition generates free electrons and H+ cation in the anodic chamber (as equation 1)

$$C_xH_YO_z + H_2O \rightarrow mCO_2 + nH^+ + ne^- \qquad (1)$$

Anodic and cathodic chambers are externally connected through an external circuit, which helps the transfer of electron generated in anodic chamber to cathodic chamber. Internally these chambers are connected either by a membrane or a salt bridge in case of membrane less MFC, through which the transfer of H^+ ion from anodic to cathodic chamber takes place. Selective transport of H^+ through the membrane shows better efficiency of the MFC with comparison to its transport through salt bridge [2]. In the cathodic chamber the electron and H+ combines in presence of oxidant (air) and produces water as per the equation 2

$$4H^+ + 4e^- \rightarrow 2H_2O \qquad (2)$$

Ravi Shankar, Prasenjit Mondal and Shri Chand, Department of Chemical Engineering, Indian Institute of Technology Roorkee, Roorkee-247667, Uttaranchal, India, Corresponding Author. Tel: +91-1332-285181, Fax: +91-1332-276535; Corresponding authors email: mondal2001@gmail.com

The efficiency of a MFC depends on various factors such as initial organic load (COD), concentration of microbial mass in anodic solution, pH, temperature, material of electrodes, presence of trace metals etc. [3]. Like organic compounds, the trace metals are also required for the growth of microorganism. They can also stimulate oxidation of organic substrate by their reduction depending upon the solution pH [4, 5, 6, and 7]. However, higher concentration of metal ions may affect the bacterial sustainability. Thus, an optimum concentration of metals may increase the performance of MFC effectively. Further, the electron transfer coefficient from anodic solution to anode and coefficient of H^+ transfer from anodic to cathodic chamber may differ to some extent which may raise the difference in pH between the anodic and cathodic solutions [8].

Although, hydrogen transport membrane improves efficiency of power generation, it also increases the cost of process including operation and maintenance cost and thus efforts are on to improve the efficiency of membrane less MFC [9, 10]. Both batch [2] and column [5, 11] study are reported in some literature on the membrane less MFC, however, the efficiency of the MFC in these study are not much. In batch study mainly the effect of salt concentration in the salt bridge on the performance of the MFC has been reported [9, 10]. Most of these studies are conducted with fixed initial organic load in lower range (<1000 ppm). Further, there is hardly any literature available on the effect of heavy metals on the performance of MFC and the variation on pH difference between anodic and cathodic solutions.

In present study the effect of initial organic load and concentration of Fe^{3+} on the current and voltage generation in batch scale double chamber MFC has been studied. The variation of pH difference between anodic and cathodic solution with the variation in initial organic load has also been studied. The performance of the present MFC has also been compared with the performance of some other recently reported MFC.

II. Materials and methods

All the chemicals, purchased from S.D. Fine-Chem. Limited, India and HiMedia Laboratories Pvt. Ltd., were of Analytical grade (AR) and solutions were prepared by Milli-Q water (Q-H2O, Millipore Corp. with resistivity of18.2M©cm). Plastic bottles for MFC construction were purchased from local market Roorkee. Carbon rod for electrode, aquarium pumpfor aeration and multimeter (KROS-S, DT830D, Digital Multimeter) for voltage and current measurement were purchased from Punjab Traders, Science market, Ambala cant, Haryana. Microorganisms of activated sludge (MW-AS), collected from municipal sewage *treatment plant*, Jagjitpur Haridwar, was used.

Each litre artificial wastewater were prepared by mixing eqimolar amount of glucose and glutamic acid, 50 ml of 1M phosphate buffer (pH-7) and 10 ml trace mineral solution. The composition of trace mineral salt solution was $(NH_4)_2SO_4$, 0.56 g; $MgSO_4{\cdot}7H_2O$, 0.20 g; $CaCl_2$, 15 mg; $FeCl_3{\cdot}6H_2O$, 1 mg; $MnSO_4{\cdot}H_2O$, 20 mg; $NaHCO_3$, 0.42 g [5]. Stock solution of Fe^{3+} was prepared by dissolving ferric chloride ($FeCl_3$) in demonized water.

Batch scale MFC was made with two plastic bottles each of volume 160 ml (7 cm height, 6.4cm diameter), which were connected by salt bridge as shown in Fig. 1 The salt bridge was built with a plastic tube of internal diameter of 2 cm and length of 5 cm and was filled with 10 % agar media and 3M NaCl solution sterilized at 121^{O}C and 15psi pressure for 15 minute. Graphite rod 10 cm length and 1.5 cm diameter was used as electrode in both the chambers. External connections were made with copper wire and aquarium pump was used to provide constant flow of air (90-100 ml/min) to the cathodic chamber.

To conduct experiments each 150 ml waste water sample, after sterilization, was taken in anodic chamber and was purged with CO_2 gas to reduce the dissolved oxygen and mixed with 5 ml MW-AS as a bacterial source. Concentration of glucose and glutamic acid in the solution was varied from 500 mg/l to 2500 mg/l. The pH in anodic chamber was maintained at 7 ± 0.2.The cathodic chamber was filled with tap water at IIT Roorkee (pH-6.7, conductivity - 725 µS/cm). Temperature was maintained at 35 ± 1^{O}C and continuous air (oxidant) was blown in the cathodic chamber with peristaltic pump at flow rate of 90-100 ml/min. The voltage and current was measured by millimeter (5 times per day) and average generated current and voltage was reported. After operation of 17 days the pH difference between cathodic and anodic chamber, final COD and metal concentrations were measured. COD was analyze by COD analyzer (SN 09/17443 LOVIBOND Spectrophotometer) and metal concentration was determined by using AAS model - Avanta M, GBC Scientific Equipment Pvt Ltd.

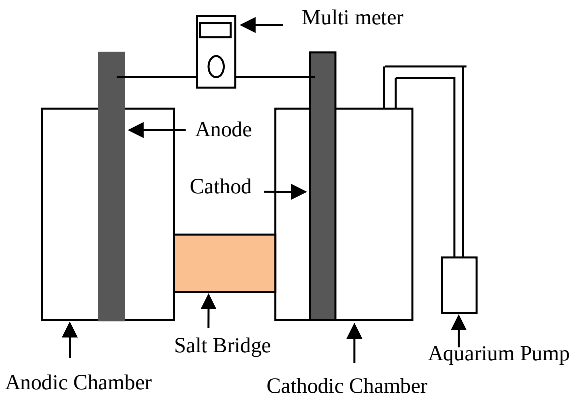


Fig. 1 Schematic diagram of Microbial Fuel Cell (MFC)

III. Results and Discussion

A. *Effect of initial organic load (COD) on current and voltage generation*

The effect of initial organic load (COD) on current and voltage generation in MFC is shown in Fig. 2(a) and 2(b) respectively.

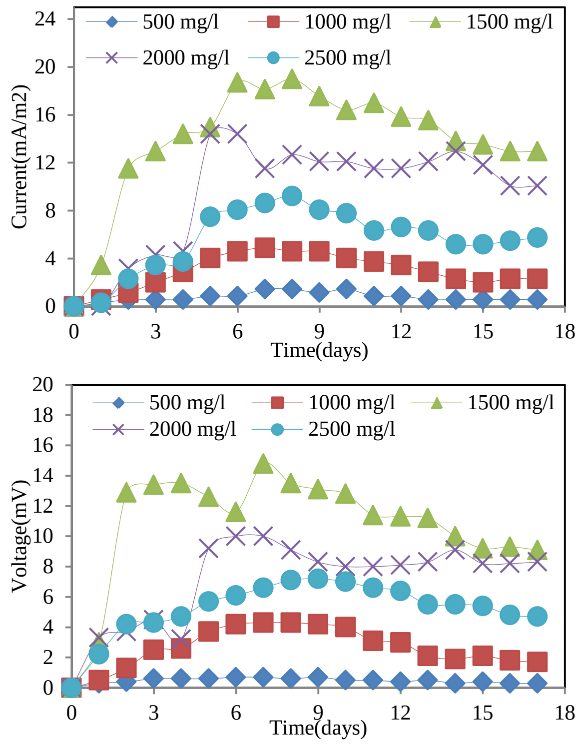


Fig. 2 Effect of Initial substrate concentration on MFC performance at Initial pH 7±0.2 and initial temperature 35±1 OC - (a) Current density generation (b) Voltage generation

From Fig. 2(a) and 2(b) it is evident that for all the initial concentration of COD both current and voltage generation increase with increase in time and become almost stable after around 5-6 days of operation. This is because of the adaptation of microbes in new environment. From Fig. 2(a) and 2(b) it is also noteworthy that the initial COD concentration of around 1500 mg/l gives maximum voltage and current density.

Current generation in microbial fuel cell depends upon the number of free electron generated in the anodic chamber and its transport from bulk phase to the anode. The generation of free electron is directly proportional to the amount of glucose and glutamic acid oxidized in the anodic chamber, where as the transport of electron from bulk phase of anodic chamber to the anode is dependent on various factors such as biomass density, composition of the solution etc. Increase in biomass concentration increases the free electron generation however, may resist transfer of electron from bulk phase to the anode. Due to these two opposite phenomena in the present case the optimum current and voltage generation is achieved at the initial COD value of 1500 mg/l. From Table 1 it can be noted that the biomass concentration increases with the increase in initial COD value from 500 mg/l to 2500 mg/l and amount of COD removal (in mg/l) also increases from 440 mg/l to 1800 mg/l. However, the current and voltage generation is higher

TABLE I
BIOMASS FORMATION AND METAL REMOVAL BY MUNICIPAL WASTEWATER ACTIVATED SLUDGE (MW-AS)

	Initial concentration, COD, (mg/l)					Initial COD-1500 mg/l, Fe^{3+} concentration(mg/l)						
Condition	500	1000	1500	2000	2500	3	6	10	20	40	80	100
B.M. (mg/l)	136	170	193	196	212	188	161	151	128	105	80	51
COD removed (mg/l)	440	860	1260	1500	1800	1260	1240	1180	1140	1100	1198	1200
M.R (mg/l)	-	-	-	-	-	2.73	5.22	8.7	15.2	23.2	25.6	28

B.M. = Bio-mass, M.R.=Metal removed

at the initial COD value of 1500 mg/l with comparison to the initial COD value of 2000 mg/l or 2500 mg/l.

At the initial COD value of 1500 mg/l the current density and voltage after 17 days of operation was observed as 13 mA/m^2 and 9.1 mV respectively. Whereas, the maximum current density (19 mA/m^2) and voltage (14.8 mV) generations was achieved after ~7 days of operation of MFC.

The removal of COD and the variation of pH difference between anodic and cathodic chamber with variation in initial COD values are shown in Fig. 3. From Fig. 3 it is noticeable that the % COD removal after 17 days of operation of the MFC decreases with increase in initial COD value however, the amount of COD removed (mg/l) increases from initial COD concentration of 500 mg/l to 2500 mg/l as evident from Table 1. Since the biomass concentration increases with the increase in initial COD the removal of COD also increases although the % removal of COD decreases.

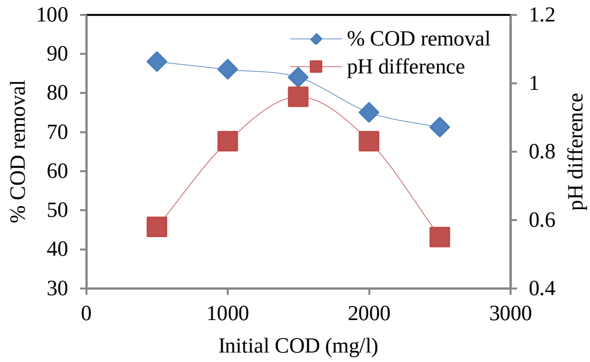


Fig. 3 Removal of % COD and difference in pH ($pH_{Cathodic}$ - pH_{Anodic}) with different initial substrate concentration after 17 days of operation of MFC.

After 17 days of operation ~ 84 % of the COD is removed when initial COD value is 1500 mg/l. Further, it is interesting to note that the pH difference between anodic and cathodic chamber varies within 0.5 to 1.0 under these experimental conditions. At lower and higher initial COD values, the difference is less whereas it is maximum (~1) at the initial COD value of around 1500 mg/l. At lower COD value the electron and H^+ generation is less and thus the pH difference is less. At higher COD value both electron and H+ generations are high, however, the resistance towards the transport of these moieties may increase due to high biomass concentration in the bulk phase and decrease in trace metal concentration [15]. Comparing SEM (Fig. 4) of the anode before and after application in MFC, it seems that hardly any microbial layer is formed on the surface of the anode due to its application in MFC. This observation supports the presence of microbial biomass in the bulk phase.

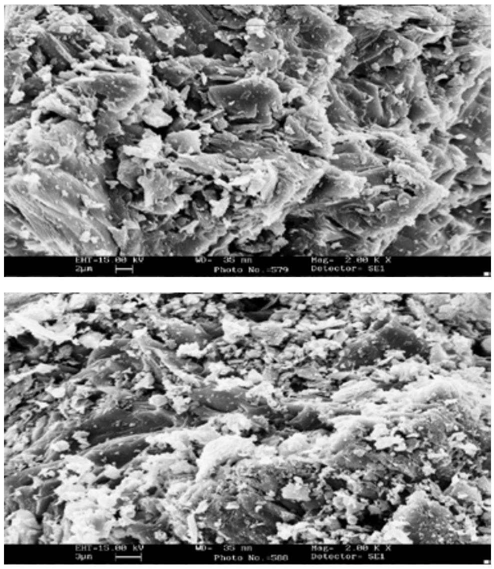


Fig. 4 SEM of anode (carbon electrode) (a) before and (b) after use

B. *Effect of Iron (Fe3+) concentration*

The effect of Iron (Fe^{3+}) on current and voltage generation in MFC is shown in Fig. 5(a) and 5(b) respectively. From Fig. 5 (a) and (b) it is evident that both current and voltage generation initially increase with increase in Fe^{3+} concentration and produce maximum current and voltage at Fe^{3+} concentration of 10 mg/l and decreases thereafter. Further, for the first three days of operation the current and voltage generation is less and within 3 to 17 days of operation the current and voltage generation prevails at the value of ~ 316 mA/m^2 and ~210 mV respectively or more. The maximum current density (~600 mA/m^2) and voltage (~321 mV) generation is achieved after 3-4 days of operation. The initial less production of current and voltage is due to the adaptation of microbes in the new atmosphere as discussed in section 3.1. It seems that above the Fe^{3+} concentration of 10 mg/l, the bacterial sustainability is affected which is clear from the less biomass generation above Fe^{3+} concentration > 10 mg/l as shown in Table 1.

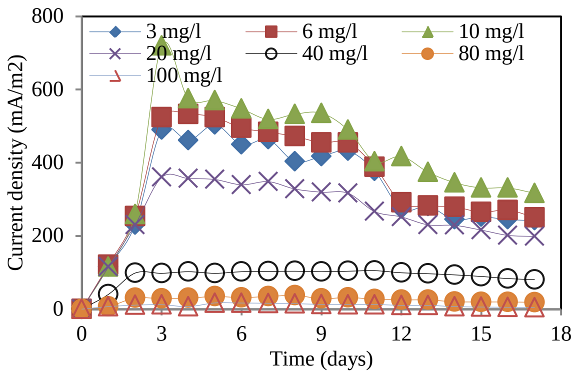
The increase in current and voltage generation due to the presence of Fe^{3+} ion is due to the high electron releasing tendency of Fe^{3+} in the solution under the experimental condition [4]. Under the operating condition at pH 7 ± 0.2, the Fe^{3+} exists predominantly as $Fe(OH)^{2+}$, $Fe(OH)^{2+}$ and Fe^{2+} .

TABLE II
COMPETITIVE STUDY OF MEMBRANE LESS MICROBIAL FUEL CELL

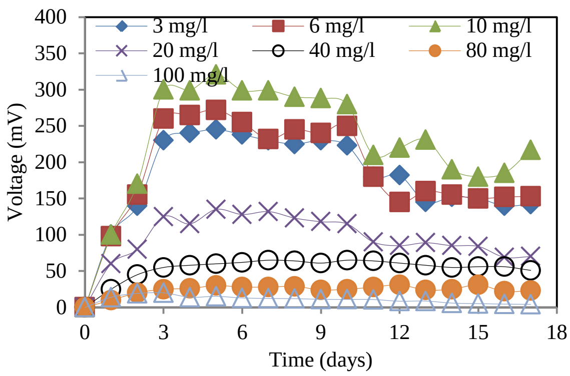
S N	Type of MFC	Substrate	Proton transport	Microbes	Max^{m}Power	% Removal**	References	
1	Continuous flow MFC	Sucrose	None		10.9 mW/m^2	88% COD, 87% BOD	[12]	
2	Continuous flow MFC		None	G. sulfurreducence	24.33 mW/m^3	90.45 % COD	[13]	
3	Continuous flow MFC	Acetate	None		30mW/m2	75.9% SDE	[14]	
4	Dual-chambered MFC		Salt bridge	G. metallireducens	2.2 mW/m^2		[2]	
5	Dual-chambered MFC	G*	Salt bridge	Culture from cow dung	16.02 mW/m^2	88.41% COD	[10]	
6	Dual-chambered MFC	G*	Membrane	G. metallireducens	40±1 mW/m^2		[2]	
				Wastewater incc	38 ±1mW/m^2			
7	Dual-chambered MFC	G and GA*	Salt bridge	Sewage activate sludge bacteria	0.268 mW/m^2	84% COD	No metals	Present study
					155 mW/m^2	79% COD	With Fe^{3+}	

*SDE:Substrate degradation efficiency , CE: Charge efficiency, G: Glucose, GA: Glutamic acid
**Power density (P) = Current density (A)×Voltage

Thus, the trivalent Fe^{3+} added to the solution is reduced to divalent moieties in significant amount generates additional electron. As the current and voltage generation is directly related to the flow of electron, in the present case the addition of Fe^{3+} improves the current density (~37 times) and voltage (~21 times) generation after 7 days of operation. The COD removal, after 17 days of operation, is ~79%. The performance of the present MFC is compared in Table 2.



(a)



(b)

Fig. 5 Effect of Iron (Fe^{3+}) concentration on MFC performance at Initial COD 1500 mg/l and initial temperature 35 ^{O}C - (a) Current density generation (b) Voltage generation

Although the MFC reported in the above literatures are different it is not so easy to compare the performance of these MFC, however, from Table 2 it is noteworthy that the present process generates highest power density amongst all the reported literature as mentioned in Table 2. From Table 1 it is also evident that the COD concentration in the treated water in presence of 10 mg/l Fe^{3+} is ~ 320 mg/l which is slightly more than the standard value (250 mg/l). Thus, this process can be able to generate treated water as per standard when the initial COD concentration is less than 1250 mg/l.

III. CONCLUSIONS

From the above discussions the following conclusions are made:

- Under the operating conditions, with the crease in initial COD value both the biomass concentration and removed amount of COD increases. However, optimum generation of current density (~19 mA/m^2) and voltage (~14.8 mV) is achieved, after 7 days of operation, at the initial COD value of 1500 mg/l.
- Fe^{3+} increases the current and voltage generation and under optimum concentration of Fe^{3+} (10 mg/l), the current density and voltage generation capacity of the MFC improves significantly.
- pH difference between anodic and cathodic solution varies with the initial COD values and at the initial COD value of 1500 mg/l this difference is maximum (~1).
- The present process seems to have capacity to reduce the COD value below the permissible limit if the initial COD value d 1500 mg/l.

REFERENCES

[1] R. M. Allen and H. P. Bennetto, "Microbial fuel cells: electricity production from carbohydrates," Applied Biochemistry and Biotechnology, Vol. 39 (1993), No. 40, pp.27-49.
[2] B. Min, S. Cheng and B. E. Logan, "Electricity generation using membrane and salt bridge microbial fuel cells," Water Research,Vol.39(2005), pp.1675–1686.
[3] A. E. Franks and K. P. Nevin, "Microbial Fuel Cells, A Current Review," Energies, Vol. 3 (2010), pp. 899-919.
[4] G. S. Timmins and M. J. Davies, "Biological Free Radicals, Electron Paramagnetic Resonance," Vol. 16 (1998) @ The Royal Society of Chemistry.
[5] J. K. Jang, T. H. Pham, I. S. Chang, K. H. Kang, H. Moon, K. S. Cho and B. H. Kim, "Construction and operation of a novel mediator- and membrane-less microbial fuel cell," Process Biochemistry, Vol.39(2004), pp. 1007–1012.
[6] L. T. Angenent and S. Sung, "Development of anaerobic migratingblanket reactor (AMBR), a novel anaerobic treatment system," Water Resources, Vol.35 (2001), pp. 1739-1747.
[7] B. E. Logan, C. Murano, K. Scott, N. D. Gray and I. M. Head, "Electricity generation from cysteine in a microbial fuel cell," Water Research, Vol. 39(2005), pp. 942–952.
[8] A. Muralidharan, O. A. Babu, K. Nirmalraman, and M. Ramya, "Impact of Salt Concentration on Electricity Production in Microbial Hydrogen Based Salt Bridge Fuel Cells," Indian Journal of

Fundamental and Applied Life Sciences,Vol. 1(April – June 2011), No. 2, ISSN: 2231-634, pp. 178-184.

[9] T. H. J. A. Sleutels, H. V. M. Hamelersa, R. A. Rozendal and C. J. N. Buisman, "Ion transport resistance in Microbial Electrolysis Cells with anion and cation exchange membranes," international journal of hydrogen energy, Vol. 34(2009), pp. 3612 – 3620.

[10] S. Sevda and T. R. Sreekrishnan, "Effect of salt concentration and mediators in salt bridge microbial fuel cell for electricity generation from synthetic wastewater," Journal of Environmental Science and Health, Part A, Vol.47 (2012), pp. 878–886.

[11] Y. Lee and N. Nirmalakhandan, "Electricity production in membrane-less microbial fuel cell fed with livestock organic solid waste," Bioresource Technology, Vol. 102(2011) ,pp. 5831–5835.

[12] M. M. Ghangrekar and V. B. Shinde, "Performance of membrane-less microbial fuel cell treating wastewater and effect of electrode distance and area on electricity production," Bioresource Technology, Vol. xxx (2006), pp. xxx–xxx.

[13] D. Fangzhou, X. Beizhen, D. Wenbo, J. Boyang, D. Kun, and L. Hong, "Continuous flowing membrane less microbial fuel cells with separated electrode chambers," Bioresource Technology, Vol. 102(2011),pp. 8914–8920.

[14] H. Wang, S. C. Jiang, Y. Wang and B. Xiao, "Substrate removal and electricity generation in a membrane-less microbial fuel cell for biological treatment of wastewater," Bioresource Technology,Vol. 138 (2013), pp. 109–116.

[15] T. A. Hughes and N. F. Gray, "Removal of Metals and Acidity from Acid Mine Drainage Using Municipal Wastewater and Activated Sludge," Mine Water Environment, 2013, doi: 10.1007/s10230-013-0218-8.