Effect of Wastewater Characteristics and Biomass Growth in Cathode Compartment on Performance of Membrane-less Microbial Fuel Cell

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The performance of mediator-less and membrane-less microbial fuel cell (ML-MFC) was evaluated for synthetic wastewater treatment by changing carbon source, alkalinity and total dissolved solids (TDS) concentration in the influent. The ML-MFC, inoculated with pre-heated septic tank sludge, was operated for total 192 days. The chemical oxygen demand (COD) removal efficiency greater than 85% was noticed under different influent characteristics. Higher TDS in the influent, due to sulphate and bicarbonate alkalinity, showed a diminution in power and current density. Built-up of high biomass concentration in the cathode compartment had adverse effect on current and voltage; hence, biomass concentration should be kept under control to get maximum power generation. Close spacing between anode and cathode was considered to be favourable for getting higher power output.

Keywords: Microbial fuel cells; ML-MFC; cathode biofilm; power production; anode surface area; wastewater treatment

The increasing difficulty of sustained supply of fossil fuel and the associated problems of pollution and global warming are acting as major impetus for research of alternative renewable energy technologies [1]. Microbial fuel cell (MFC) offers a possible (and partial) solution to this problem. Although the fuel needed for conventional cells usually is either hydrogen or methanol, some cells which run on other fuels such as wastewater have been developed [2 - 5]. Approaches by which common waste materials and the chemical energy locked within them could be utilized, would offer many benefits. In MFC type fuel cells, the organic contaminants present in the wastewater are oxidized and during this process direct electricity recovery is possible. Thus, simultaneous wastewater treatment and electricity recovery can be achieved. In addition, excess sludge production is very low in MFC, as compared to conventional aerobic wastewater treatment, reducing the cost of further sludge management [6].

A MFC is a device that converts chemical energy to electrical energy with the aid of the catalytic reaction of microorganisms [7]. MFC consists of anode and cathode compartments separated by a cation-specific membrane (proton exchange membrane, PEM). In the anode compartment of MFC, microorganisms oxidize fuel (i.e., organic matter present in the wastewater) generating electrons and protons. Electrons are transferred to the cathode compartment through external circuit, and the protons are transferred to the cathode through the internal membrane. Electrons and protons are consumed in the cathode compartment reducing oxygen to water. Usually oxygen is supplied by aeration in cathode compartment to act as oxidant.

It has recently been shown that certain metal-reducing bacteria, belonging primarily to the family *Geobacteraceae*, can directly transfer electrons to electrodes having electrochemically active redox enzymes, such as cytochromes on their outer membrane [8,9]. These microbial fuel cells do not need mediator for electron transfer to electrodes and are called as mediator-less MFCs. In a mediator-less MFC, the membrane separates the anode from the cathode and functions as an electrolyte that plays the role of an electric insulator and allows protons to move through [10]. Proton transfer through the membrane can be a rate limiting factor, especially with fouling, expected due to presence of suspended solids and soluble contaminants in a large scale wastewater treatment process, requiring replacement. Membranes being expensive may limit acceptance of MFC as a wastewater treatment process.

A membrane-less microbial fuel cell (ML-MFC) was developed [10] and used successfully to enrich electrochemically active microbes that converted organic contaminants to electricity. The chemical oxygen demand (COD) removal rate of 0.526 kg/m^3.day was reported with maximum power production of 1.3 mW/m^2 and current density 6.9 mA/m^2. The present research on MFC is being mainly focused on identifying and enriching electro-chemically active microbes and evaluating performance of MFC using different electrode materials, with or without supplementation of external mediator [7,11 - 13]. Few studies have used mixed culture as inoculum to start MFC, *e.g.*, heat treated soil [14], sulphate enriched anaerobic sewage sludge [15], marine sediments [16], activated sludge [10]. Effectiveness of mixed anaerobic sludge as inoculum needs further investigation. If wastewater treatment efficiency and electricity recovery from the ML-MFC could be enhanced, this device has a greater potential for commercial applications due to less production cost.

When any technology is used for wastewater treatment, it should have capability to handle the variation in the characteristics, which is expected in real wastewaters. Hence, further investigations are necessary to study performance of MFC under different alkalinity and total dissolved solids (TDS) concentration present in the wastewater for organic matter removal, as well as effect of these parameters on electricity production. Thus, the objective of this work was to evaluate performance of mediator-less and membrane-less MFC, inoculated with septic tank sludge, for synthetic wastewater treatment and

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electricity generation under variable alkalinity and TDS concentration. In addition, the aim was to assess the effect of mixed liquor suspended solids (MLSS) growth in the cathode compartment on electricity generation at different distance between electrodes and surface area of the electrodes.

Experimental part

Materials and methods

The schematic diagram of the membrane-less microbial fuel cell used in this study is shown in Fig. 1. The ML-MFC was made of acrylic polymer cylinder with effective height 60 cm and internal diameter 15 cm, having anode compartment (depth 26 cm) at bottom and cathode compartment (depth 26 cm) at top. Glass wool (4 cm depth) and glass beads (4 cm depth) were placed at top of the anode compartment separating anode and cathode. Three graphite electrodes were placed in each anode and cathode compartments. The distances between the respective anode and cathode electrodes were 20 cm, 24 cm, and 28 cm. The total apparent surface area of the three anode electrodes was 210.64 cm^2. The electrodes were connected with copper wire through an external resistance and a multimeter. The ML-MFC was operated at constant external resistance of 100 Ω, including resistance of copper connecting wire, except when the current and voltage were measured under variable external resistance.

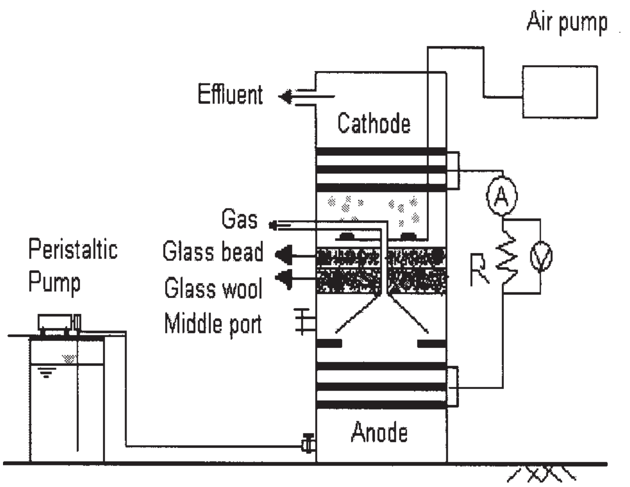

Fig. 1. Scheme of membrane less microbial fuel cell (ML-MFC) used in the study

The wastewater was supplied to the bottom of the anode compartment and the effluent left through the cathode compartment at top.

The wastewater was applied at the rate of 5.011 L/day to the ML-MFC making overall hydraulic retention time (HRT) as 50.78 h. The cathode compartment was aerated at rate of 60 mL/min using an air pump. Synthetic wastewater containing sucrose as a carbon source was used in the study, with the composition shown in table 1. In other experiments, lactose or dextrose were introduced in the wastewater as carbon surces.

The alkalinity achieved by adding sodium bicarbonate (in concentration shown also in table 1) to alter the TDS in the influent under three experiments, no. 1 to 3. In the experiment no. 4, TDS was increased in the feed by supplementing 150 mg/L sodium chloride and 150 mg/L anhydrous sodium sulphate. The *p*H of influent was in the range of 7.2 to 7.6. Sludge collected from septic tank bottom was preheated at 100°C for 15 min to suppress the methanogens, then cooled at room temperature; a volume of 2 L of sludge was added to anode compartment as inoculum. The inoculum had suspended solids (SS) and volatile suspended solids (VSS) concentrations as 40.80 g/L and 11.70 g/L, respectively. No microbial addition was carried out in cathode compartment. The ML-MFC was operated at ambient room temperature varying between 24 and 29 °C.

Influent and effluent characteristics, such as COD, pH, dissolved oxygen (DO), SS, and VSS were monitored according to standard methods [17]. Biochemical oxygen demand (BOD) was determined for three days at 27 °C. Influent and effluent pH was monitored daily and COD was monitored on alternate days. BOD was measured once per week, after achieving steady state conditions in each experimental run. The voltage was measured using a digital multimeter and converted to power according to $P=IV$, where P = power (W), I = current (A), and V = voltage (V). While measuring current and voltage under variable external resistances, the system was allowed to get stable for 5 to 10 min under each external resistance and the values were recorded. The coulombic efficiency was estimated [18].

Results and discussion

The performance of ML-MFC during start-up

After preheates septic tank sludge inoculation, synthetic wastewater was admitted immediately to the ML-MFC. The ML-MFC was operated at influent COD concentration varying between 299 and 328 mg/L during initial start-up,

Table 1

COMPOSITION OF THE SYNTHETIC WASTEWATER

Component	Sucrose	$NaHCO_3$	NH_4Cl	K_2HPO_4	KH_2PO_4	$CaCl_2.2H_2O$	$MgSO_4.7H_2O$
mg/L	312	440 - 1200	95.5	10.5	5.25	63.1	19.2

Metal traces were added as $FeSO_4.7H_2O$ = 10 mg/L, $NiSO_4.6H_2O$ = 0.526 mg/L, $MnSO_4.H_2O$ = 0.526 mg/L, $ZnSO_4.7H_2O$ = 0.106 mg/L, H_3BO_3 = 0.106 mg/L, $CoCl_2.6H_2O$ = 52.6 μg/L, $CuSO_4.5H_2O$ = 4.5 μg/L, and $(NH_4)6Mo_7O_{24}.4H_2O$ = 52.6 μg/L.

Table 2

EVOLUTION OF COD AND BOD REMOVAL FOR ML – MFC WORKING AT 27°C

Days	Influent COD (mg/L)	COD at middle port (mg/L)	Effluent COD (mg/L)	COD removal Efficiency (%)	Influent BOD (mg/L)	Effluent BOD (mg/L)	Effluent DO (mg/L)
0-17	314.66 (±19.9)	196.28 (±40.1)	107.82 (±58.3)	65.40 (±19.7)	ND	ND	4.88 (±0.2)
18-71	324.19 (±9.5)	174.06 (±11.7)	38.03 (±5.85)	88.24 (±1.8)	225.92 (±8.7)	29.6 (±6.4)	4.84 (±0.1)

ND – Not Determined

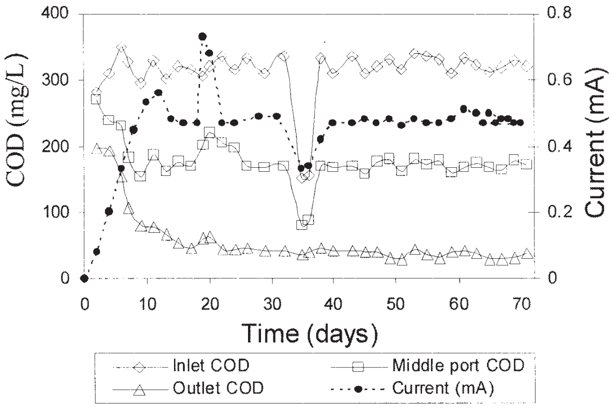

Fig. 2. Removal of organic matter in terms of COD and current production in the ML-MFC. On 19th day lactose (COD = 305 mg/l) and on 20th day dextrose (COD =319 mg/l) were used as carbon source in synthetic feed instead of sucrose. On 35th and 36th day actual sewage (COD = 152 mg/l) was used instead of synthetic feed.

as presented in table 2. The time evolution of COD removal observed for inlet, middle part and outlet of celll is presented in figure 2.

After 17 days of operation, when steady state conditions for COD removal were established, the COD and BOD removal efficiencies were 88.24 % and 86.9 %, respectively. Organic loading rate (OLR) of this ML-MFC with respect to anode chamber was 0.305 kg COD/m^3.day. Under steady state conditions, the average effluent COD was 38.03 mg/L and BOD_3 at 27°C was 29.60 mg/L. The reported COD and BOD values are for unsettled effluent containing average SS and VSS of 37.57 mg/L and 8.29 mg/L, respectively. Of course, using settling tank after ML-MFC further improvement in the effluent quality is expected. The observed COD and BOD removal efficiencies demonstrated the ability of ML-MFC, inoculated with preheated septic tank sludge, as being an effective wastewater treatment process.

As a comparison, at OLR 0.53 kg COD/m^3.day and HRT of one day (24 h), the COD removal efficiency more than 90% was reported in a ML-MFC cell [10]. Also, in the mediator - less MFC, while treating a glucose containing wastewater, with COD 300 mg/L, COD removal efficiency over 90% was reported at very short HRT (1.26 h) and at loading rate of 9.2 kg COD /m^3.day [19]. The overall efficiency obtained by using the ML-MFC in our experiment is in agreement with the values reported in the literature. The COD removal efficiency of anode compartment in the experimented ML-MFC was 46.62%. Thus contribution of anode compartment to overall organic matter removal seems to be lower in this ML-MFC. For single chamber microbial fuel cell treating domestic wastewater it was reported that [20], COD removal increased from 40% at HRT of 3 h to a maximum of 80% at HRT of 33 h. Hence, we consider that further investigations are necessary to enhance organic matter removal in anode chamber for this ML-MFC, as reported for single chamber MFC. Certainly, enhancing anode efficiency will improve overall performance of ML-MFC for both organic matter removal and electricity production.

Effect of change in substrate on electricity generation

For evaluating the effect of change of substrate on the electricity generation, the carbon source in the synthetic wastewater was changed. On 19th day lactose (COD = 305 mg/L) and on 20th day dextrose (COD = 319.54 mg/L) were used as carbon sources instead of sucrose. On 35th and 36th days, raw sewage (COD = 152 mg/L) was used as an influent. The corresponding current production of ML-MFC is also presented in figure 2. In the first 18 days the current was stabilized at cca. 0.5 mA. When lactose and dextrose were used as a substrate, a drop in COD removal efficiency of 80% was observed at similar influent COD concentration. However, the increase in current production was observed for both these substrates the current production being 0.71 mA (in the 19th day) and 0.67 mA (in the 20th day), for lactose and dextrose, respectively.

When sewage was used as an influent, the COD observed removal efficiency was 75.7% and the current production was 0.33 mA (days 35 and 36). The effluent COD concentration was 37 mg/L, a value which was similar to the effluent COD concentration when sucrose containing synthetic feed was used. Variation in the current production under different substrates can be explained on the basis of the half-reaction for these substrates with different proton and electron production. Coulombic efficiency was highest when lactose was used as a substrate; the coulombic efficiencies were 10.43, 10.21, 7.4 and 4.4% for lactose, dextrose, raw sewage and sucrose, respectively, at a constant external resistance of 100Ω.

Performance of ML-MFC at various influent alkalinities and TDS concentrations

The effect of various alkalinities and TDS in the influent on the performance of ML-MFC was also evaluated in our experiments. Under similar influent COD concentration, the ML-MFC was operated at different alkalinity and TDS values as presented in table 3. Based on the performance observations it can be noted that there is no significant effect on COD and BOD removal in the ML-MFC for alkalinity range from 327.04 mg/L to 910.46 mg/L and TDS concentration in the range from 661.57 mg/L to 1109.0 mg/L. When alkalinity to COD ratio was about 1.3

Table 3
PERFORMANCE OF ML-MFC AT DIFFERENT ALKALINITY AND TDS IN THE SYNTHETIC WASTEWATER

Experiment. No.	Days	OLR (kg COD /m3.day)	Alkalinity (mg/L)	TDS (mg/L)	COD (mg/L)			Efficiency (%)	BOD (mg/L)		
					Inlet	Middle	Outlet		Inlet	Middle	Outlet
1	18-71	0.305	417.23 (±26.9)	829.87 (±36.10)	323.10 (±10.71)	175.69 (±15.22)	38.03 (±5.85)	88.24	225.0 (±8.74)	117.68 (±10.70)	29.69 (±7.80)
2	72-114	0.283	910.46 (±25.5)	1109.0 (±37.9)	299.71 (±20.72)	174.28 (±13.64)	42.28 (±5.58)	85.81	211.83 (±7.59)	105.69 (±22.43)	27.45 (±10.4)
3	115-161	0.293	327.04 (±18.8)	661.57 (±21.03)	314.28 (±16.96)	166.88 (±7.73)	42.21 (±2.95)	86.56	225.07 (±8.7)	139.86 (±2.13)	19.88 (±2.48)
4	162-192	0.310	430.60 (±29.5)	1020.65 (±36.95)	328.12 (±20.77)	221.79 (±21.62)	33.13 (±4.55)	89.90	227.06 (±26.4)	140.06 (±5.49)	27.22 (±3.44)

OLR- with respect to anode compartment

Table 4
ELECTRICITY PRODUCTION OBSERVED UNDER DIFFERENT TDS AND ALKALINITY CONCENTRATION

Experiment. No.	Days	OLR (kg COD/ m^3.day)	Alkalinity (mg/L)	TDS (mg/l)	Current (mA)	Voltage (mV)	Resistance (ohm)	Power density (mW/m^2)	Current density (mA/m^2)
1.	18-71	0.305	417.23 (±26.9)	829.87 (±36.01)	0.49 (±0.03)	49.2 (±3.24)	100	1.12 (±0.10)	23.26
2.	72-114	0.283	910.46 (±25.5)	1109.0 (±37.9)	0.36 (±0.02)	38.13 (±2.42)	100	0.67 (±0.09)	17.09
3.	115-161	0.297	327.04 (± 18.8)	661.57 (±21.03)	0.52 (±0.04)	53.91 (±4.91)	100	1.38 (±0.23)	24.69
4.	162-192	0.310	430.60 (±29.5)	1020.65 (±36.95)	0.36 (±0.07)	39.30 (±7.29)	100	0.705 (±0.23)	17.09

OLR- with respect to anode compartment

(experiments no. 1 and 4) the overall COD removal was slightly higher than 88.24% and 89.90%, respectively, than comparing to other experiments with lowest or highest value of alkalinity to COD ratio (3.04 in experiment no. 2 and 1.04 in experiment no. 3) in the influent.

Under lower values of TDS in the influent, contribution of anode compartment for COD removal was higher. For example, the COD removal from anode compartment was maximum (46.9%) in experiment no. 3, having the lowest TDS and alkalinity. Addition of sodium sulphate in the feed has deteriorated the COD reduction in anode compartment, leading in experiment no. 4 to the lowest value, as 32.40%. The diminution in removal efficiency in anode compartment could be due to electro-reduction of sulphate ion to sulphide in this compartment, increasing COD of the sample collected at top of anode compartment. Although, the re-oxidation of sulphide ion to sulphate is reported to occur in anode compartment [21], a higher COD value at effluent end of anode compartment does not support, at least complete, re-oxidation of sulphide ion in the experimented ML-MFC.

Electricity production during start-up

A slow increase in current was observed as being direct depending on operation time frame during MFC start-up. From figure 2 it can be seen that the ML-MFC took two weeks to produce stable current. At the constant external load of 100Ω, the current production in ML-MFC reached the maximum value of 0.56 mA on 11^{th} day and dropped to 0.48 mA on 15^{th} day with fairly constant current production on later days. The open circuit voltage of 0.5 V was observed, with closed circuit voltage drop across the resistance as 43 mV. Similar slow increase in current for first two weeks after inoculation was reported earlier, while treating synthetic wastewater in a ML-MFC inoculated with electrochemically activated sludge [10]. In this report, a rapid increase in current for next 2 weeks was reported with maximum current production as 2 mA. The open circuit potential reported was 0.8 V, during enrichment process at HRT of 6.7 days. The current production observed in present experiment was lower than the value reported, probably due to use of anaerobic sludge as inoculum rather than the electrochemically active sludge.

Electricity production under different influent TDS concentrations

The effect of influent TDS concentration on electricity generation was also evaluated. Electricity production observed in ML-MFC at different influent TDS concentration is presented in table 4. In experiment no. 1, 2, and 3, the TDS concentration was altered by addition of sodium bicarbonate where as under experiment no. 4, sodium chloride and sodium sulphate were added in extra amount apart from regular feed composition. With increase in influent TDS concentration, a decrease in current production was observed. Thus, the current density was less when TDS concentration was greater than 1000 mg/L, than at lower TDS concentrations (table 4). Also, the power density increased from 0.67 mW/m^2 to 1.38 mW/m^2, when influent TDS was decreased from 1109 mg/L to 661.57 mg/L, in experiments no. 2 and 3, respectively. The coulombic efficiency was observed to be inversely proportional to influent TDS concentration. For higher TDS, the coulombic efficiency was lower and, *vice versa*, varying between 4.4% (experiment no. 2) and 5.37% (experiment no. 3). Thus, high TDS concentration, due to presence of bicarbonate alkalinity, had adverse effect on electricity production and this may be one of the limiting parameters in ML-MFC.

Comparing the electricity generation under similar influent alkalinity but with an increase in TDS due to sulphate and chloride addition (experiment no. 1 and 4), and with usual TDS concentration in experiment no. 4, it was observed that all electrical parameters (current, voltage, and power density) decreased. The decrease in electricity production under this experiment might be due to higher concentration of sulphate ion in the influent. In this regard, it was reported [6] that, if the electron acceptor is sulphate, the potential difference decreases. On the contrary, other researchers [15] have described a microbial fuel cell, with sulphate enriched sewage sludge as the biocatalyst, and reported that the power output of the cell, when fuelled by glucose, could be increased by a factor of five by the simple addition of sulphate. However, in the present the diminution reduction in power output was observed with increase in sulphate concentration in the feed; this probably proceeds because of use of non-sulphate enriched inoculum.

Sodium chloride is generally used as electrolyte to improve the mass transfer of charged particles [7]. Addition of NaCl to the cathode compartment is reported to increase current [10]. However, such increase in current was not observed when NaCl was supplemented in the synthetic wastewater, in experiment no. 4. Thus, at similar alkalinity, an increase in TDS due to sodium sulphate and sodium chloride showed a diminution in power and current density.

Effect on electricity production of MLSS concentration in cathode compartment

In the cathode compartment, no sludge was added during start-up. Owing to low COD removal in the anode chamber (about 50%) a substantial COD fraction from the influent was entering into cathode compartment. During a continuous aeration in the cathode compartment, at a flow rate of 60 mL/min, the built-up of aerobic microorganisms was observed. After few days from start-up, when sufficient microbial growth occurred in the cathode compartment, a considerable decrease of COD was observed in this compartment. Due to biodegradation, further built-up in concentration of mixed liquor suspended

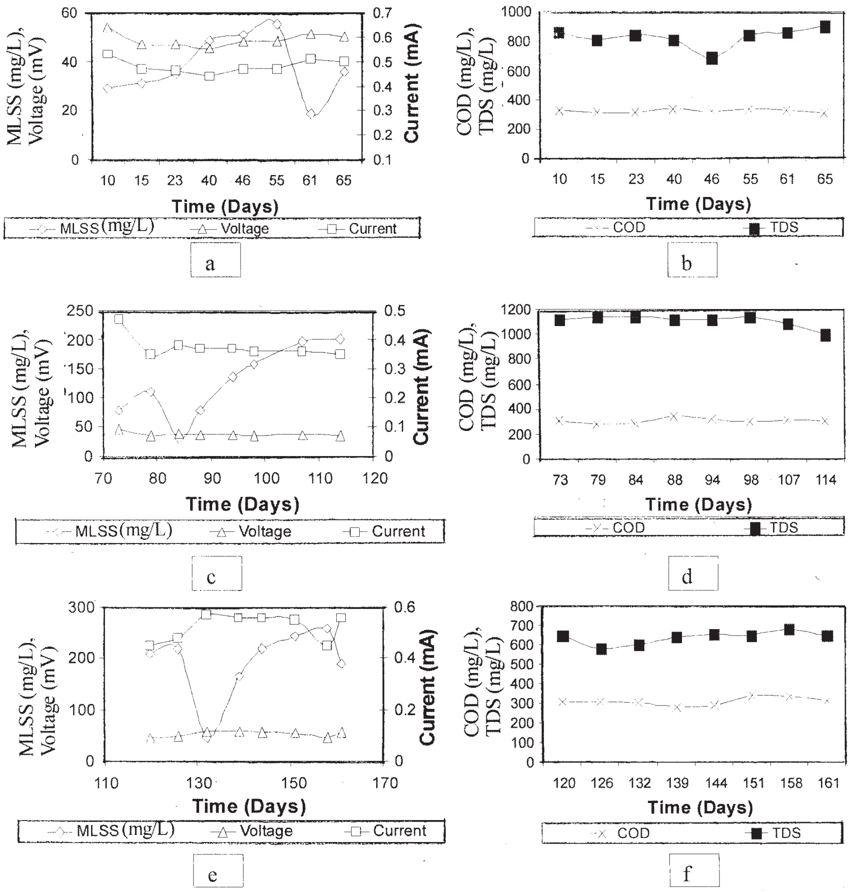

Fig. 3. Current production in ML-MFC under different MLSS concentration in the cathode compartment and influent COD and TDS. (a and b – for experiment no.1; c and d – for experiment. no. 2; e and f – for experiment no. 3)

solids (MLSS) was observed, although no measures were adopted to retain biomass inside the cathode compartment. During this period the increase in biofilm growth on cathode was also visible, and on 65th day of cell working the biofilm thickness observed on cathode was about 1 mm. The maximum concentration of MLSS observed was 258.79 mg/L on 158th day. Typical effect of MLSS concentration in the cathode compartment on electricity production is presented in figure 3. To separate the effect of influent TDS and COD concentration on current production, these values for corresponding days are also illustrated in the figure.

When very high concentration of MLSS was observed in cathode compartment, the contents were drained out to reduce the amount of MLSS. During this process, a change in electricity production was noticed. Thus, the voltage and current production observed at different MLSS concentration in cathode compartment was evaluated. With increase in biomass concentration in cathode compartment, a decrease in current production was observed. Hence, after certain interval the cathode compartment of ML-MFC was drained off. After draining of cathode compartment, current production was increased, as shown in figure 3 (a, c, and e).

This ML-MFC was operated up to 192 days and during this period cathode compartment was drained four times (consecutive experiments, no. 1-4), when current production was decreased. For example, when MLSS concentration was increased from 29.01 mg/L to 55.32 mg/L (experiment no. 1), the current production dropped from 0.53 mA to 0.47 mA, respectively (fig. 3 a). When sludge from the cathode compartment was drained, the SS concentration was reduced to 18.56 mg/L and current production increased to 0.51 mA. Similar trend was observed in other experiments as shown in figure 3(c) and figure 3(e) for experiment no. 2 and 3, respectively.

With fluctuations in MLSS concentration in cathode compartment, little variation in voltage was observed. With increase in MLSS concentration, voltage across the resistance decreased and *vice versa*. For example, at maximum MLSS concentration (258.79 mg/L) the voltage across the resistance observed was 46 mV and for lower MLSS concentration (190 mg/L) after draining, the voltage across the resistance increased to 56 mV (fig. 3 e). These results indicate the optimum range of MLSS concentration in cathode compartment in order to favour maximum power output of a biocathode and organic matter removal from the ML-MFC. The effect of limited variation in the influent TDS concentration was not significant. The current production mainly varied inversely proportional with MLSS concentration.

Effect of electrode distance and surface area on current and power density. Effect of different MLSS in the cathode compartment

The current, voltage, power density and current density were measured using different distances between anode and cathode and different surface area of anode. The results obtained were at variable external resistance before and after draining of cathode compartment and are presented in figures 4(a) and 4(b), respectively. Before draining of cathode compartment, the MLSS concentration was 258.29 mg/L, and after draining the MLSS concentration was 190 mg/L. After draining of cathode compartment, an increase in electricity production was observed in the ML-MFC. For the same wastewater COD concentration and flow rate, at higher MLSS concentration in cathode compartment, the maximum current production at variable external resistance was 0.33 mA

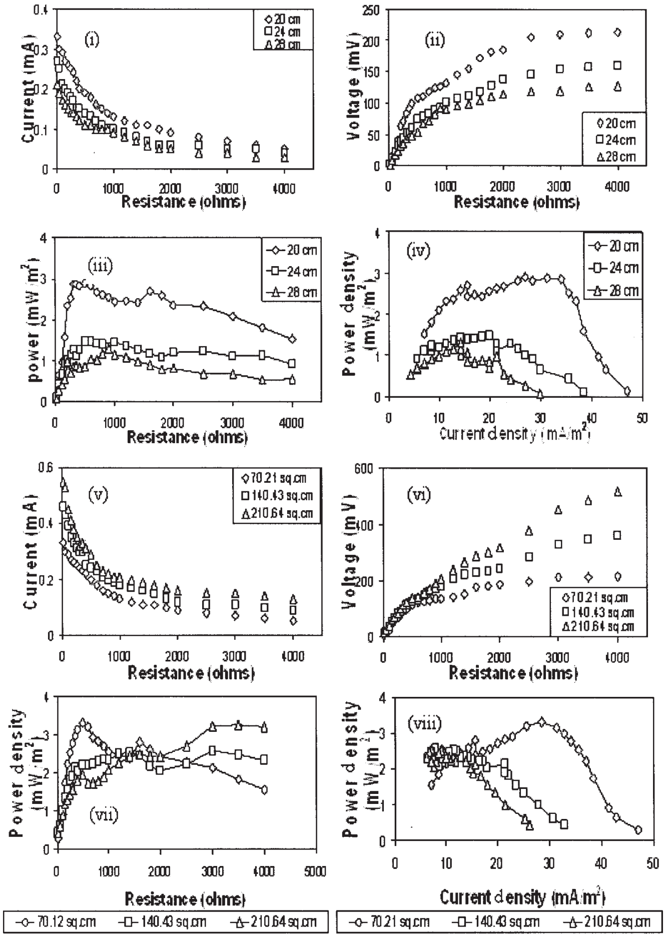

Fig. 4(a). Electricity production observed before draining the cathode compartment (Expt. No.3, MLSS = 258.79 mg/L, TDS = 659 mg/L, COD = 287.66 mg/L). (i) to (iii) Current, voltage, and power density observed under variable resistance, respectively, at different distance between the electrodes. (iv) Polarization curve at different distance between the electrodes.
(v) to (vii) Current, voltage, and power density observed under variable resistance, respectively, under different anode surface area. (viii) Polarization curve under different anode surface area

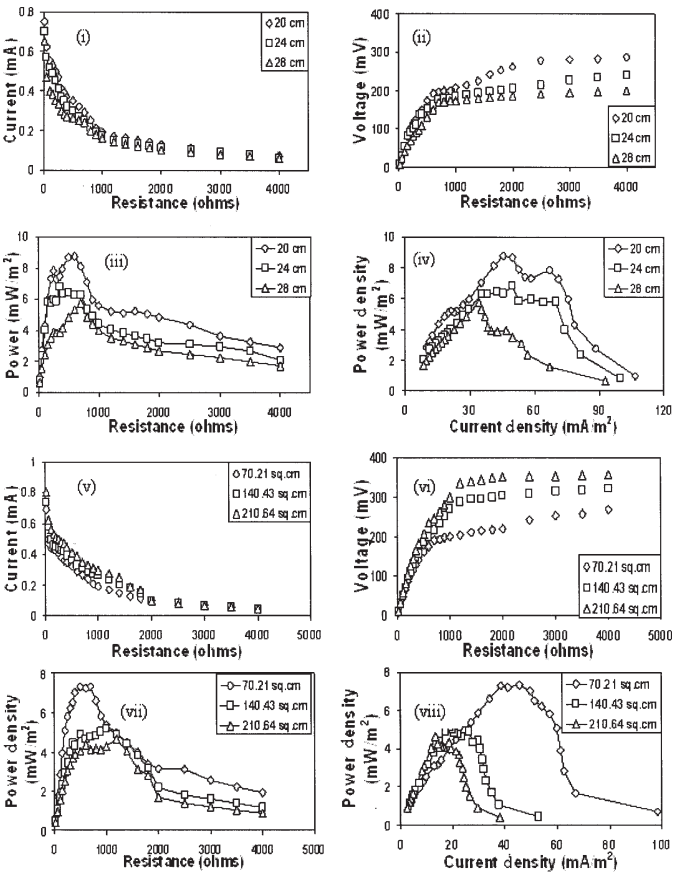

Fig. 4(b). Electricity production observed after draining the cathode compartment (Expt. No.3, MLSS = 190 mg/L, TDS = 634 mg/L, COD = 310.3 mg/L). (i) to (iii) Current, voltage, and power density observed under variable resistance, respectively, at different distance between the electrodes. (iv) Polarization curve at different distance between the electrodes. (v) to (vii) Current, voltage, and power density observed under variable resistance, respectively, under different anode surface area. (viii) Polarization curve under different anode surface area.

(fig. 4 a (i)), whereas at lower MLSS it was 0.75 mA (fig. 4 b (i)).

Similarly, the maximum voltage was 214 mV at higher MLSS, whereas at lower MLSS after draining it was about 280 mV. The increase in power output was significant after reducing MLSS concentration. With reduction in MLSS from 258 mg/L to 190 mg/L, the maximum power density increased from 2.9 mW/m^2 (fig. 4 a (iv)) to 8.75 mW/m^2 (fig. 4 b (iv)), respectively.

It is evident from the figures 4 a and 4 b, that the effect of surface area of anode is more pronounced at higher MLSS concentration. For example, at external resistance of 3000 Ω, the difference between voltage using single pair electrodes and three pair electrodes, was 239 mV at higher MLSS (fig. 4 a(vi)), whereas this difference was 101 mV at lower MLSS (fig. 4 b(vi)). Provision of additional surface area of electrode was favourable for obtaining higher voltage under higher MLSS concentration in the cathode compartment. Also, the difference between current and voltage obtained under 24 cm and 28 cm distance between the electrodes was more pronounced under higher MLSS concentration in the cathode compartment.

From the polarization graphs at two different MLSS concentrations in cathode compartment, it is obvious that the maximum current density is higher for lower MLSS concentration. Thus, it indicates that lower MLSS concentration in cathode is favourable for higher electricity production and this might be due to reduction in internal resistance in MFC. Also, the dissolved oxygen DO might be limiting factor in the cathode compartment under higher MLSS concentration. Higher amount of DO might have been used for biochemical oxidation at higher biomass concentration and sufficient oxygen might not be available for oxidation of proton in cathode compartment. In this conditions, the MLSS is one of the limiting factors for electricity production in ML-MFC.

The electricity production of ML-MFC was evaluated at higher TDS concentration and lower MLSS concentration in the cathode compartment (fig. 5).

Comparing figure 4 (b) and figure 5, with increase in TDS concentration, when single pair electrodes were used, the current was similar to the observed one at lower TDS, for all respective distances between anode and cathode. Little improvement in voltage was observed at higher TDS concentration values in the influent (fig. 5), which might have occurred due to lower MLSS in the cathode compartment. However, a decrease in power density was observed with increase in TDS concentration in the influent even with reduction in MLSS concentration. At higher influent TDS, with increase in surface area of anode (fig. 5), increase in voltage was recorded as compared to lower

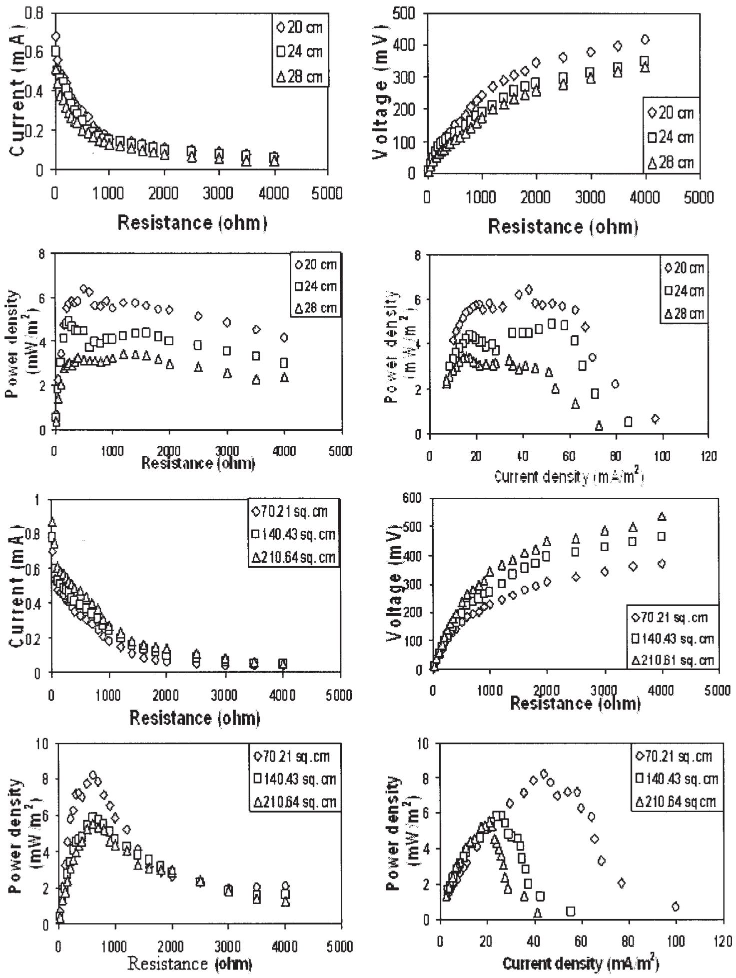

Fig. 5. Effect of TDS on current production in ML-MFC at different distance between the electrodes and surface area of the electrodes. (Experiment no.4, MLSS = 96.82 mg/L, TDS = 1020 mg/L, COD = 329.66 mg/L, OLR = 0.31 kg COD/m^3.d)

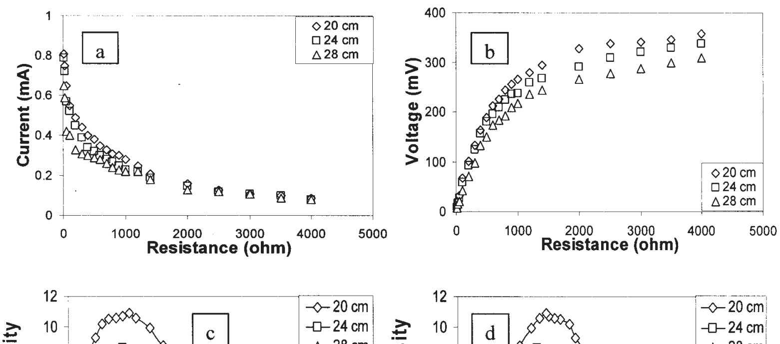

Fig. 6. Current (a), voltages (b), power density (c) and current density (d) observed in ML-MFC at different external resistance and for different spacing between the anode and cathode electrode under experiment no.1. (MLSS 35.62 mg/L in cathode compartment)

influent TDS (fig. 4 b). Also, with reduction in MLSS in cathode compartment and increase in TDS concentration, when higher surface area of electrode was used, marginal increase in power density was evidenced. Thus, it can be said that by decreasing the MLSS concentration in the cathode compartment and increasing the influent TDS concentration, it did not show significant effect in improving power density although value of voltage drop across the resistance increased.

Effect of anoxic biomass formation in cathode compartment

During operation of ML-MFC it was observed that some biomass was moved from anode to cathode compartment due to upward flow conditions. Development of anoxic condition at the lower portion of the cathode compartment also might have occurred due to settlement of bio-mass from the cathode compartment itself, and subsequent development of anoxic conditions due to oxygen limitations. Under such situation, the lower electrode in the cathode compartment was touching the anoxic biomass and a decrease in current production was observed. The current production was dropped to 0.15 mA from 0.52 mA, when cathode was surrounded with black sludge from bottom (experiment no. 3). When the third pair electrodes were taken out from the circuit, improvement in current production to 0.49 mA was observed. The entry of anoxic biomass in cathode

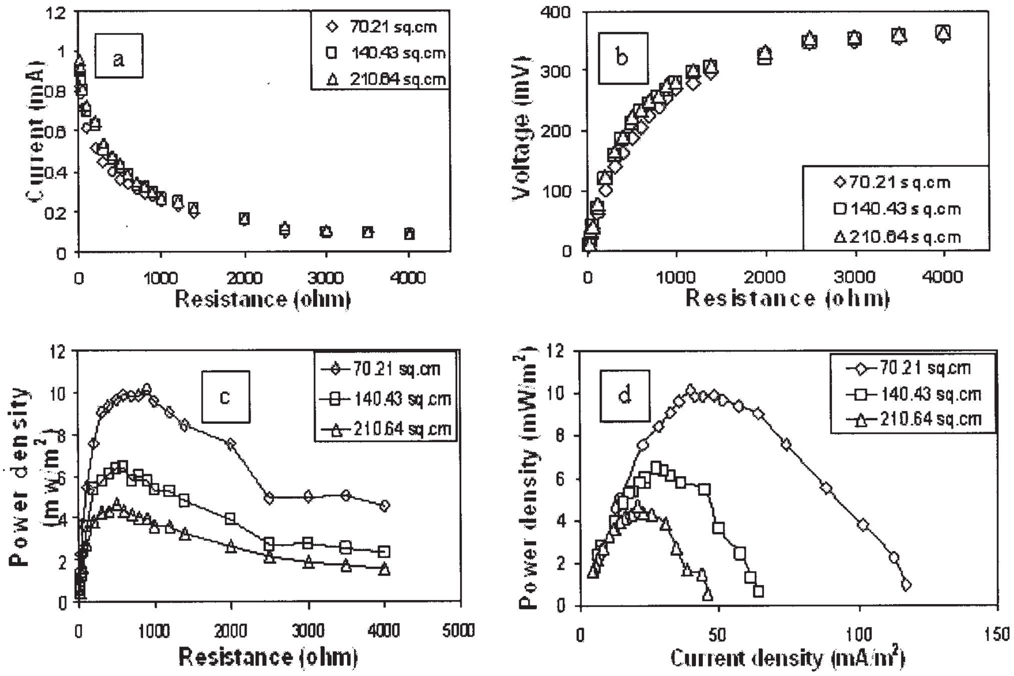

Fig. 7. Current (a), voltages (b), power density (c) and current density (d) observed in ML-MFC at different external resistance and for different surface area of anode electrode. (MLSS 35.62 mg/L in cathode compartment)

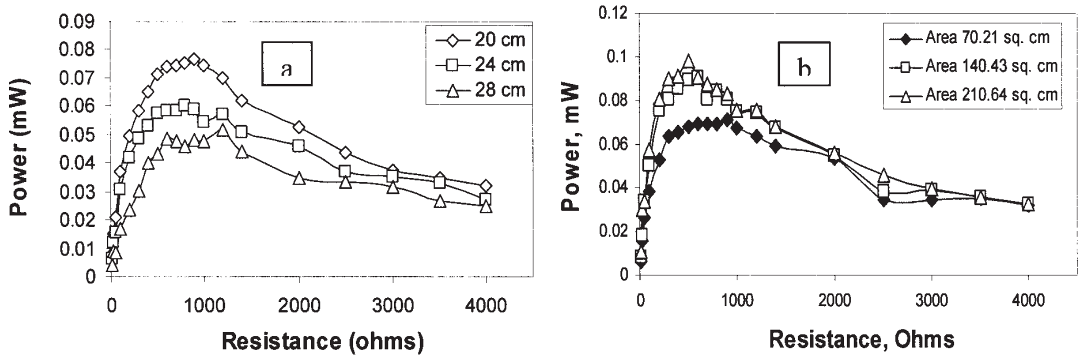

Fig. 8. Effect of electrode distance and surface area on absolute power production (a) Power production under variable resistance for different distance between the electrodes; (b) power production under variable resistance at different surface area of anode

compartment was eliminating dis-similarity of liquid in two compartments and as a consequence, the drop in current production resulted.

Effect of distance between anode and cathode on power density

The voltage and current delivered by the cell were measured under different external resistances and for different spacing between the anode and cathode electrodes, under experiment no. 1. As figures 6 shows, both these parameters increase with decrease in the distance between the electrodes.

The higest power density of 10.89 mW/m² was observed for 20 cm distance between the electrodes, when the external resistance was ranging between 800 and 1000 Ω; this power density was observed at current density of 42.72 mA/m². The results suggest that the mass transfer between electrodes, probably reducing proton transfer from anode to the cathode, could be the limiting factor. Hence, the ML-MFC should be constructed to place the electrodes as close as possible, keeping the internal resistance high enough to avoid an electrical leak [10]. Although, the power density observed was less than the recently reported values for MFC using membrane [2,13], it is higher than the power density reported for MFC without using membrane [10,18].

Effect of electrode surface area on power density

The effect of anode surface area on power density was evaluated in ML-MFC by applying variable resistance. Out of the three electrodes provided in the anode chamber single, two and three electrodes (surface area 70.21 cm², 140.43 cm² and 210.64 cm², respectively) were connected to the circuit to evaluate this effect. According to figure 7, with increase in area of anode, decrease in power density was observed. This means that in our reactor, the area of anode electrode is used less efficiently than those of smaller reactors used as BOD sensors [22].

In the experimented ML-MFC, when area of anode was 70.21 cm², 140.43 cm² and 210.64 cm², the maximum power density observed was 10.13 mW/m², 6.45 mW/m² and 4.66 mW/m², respectively, the corresponding current density being was 39.88 mA/m², 27.77 mA/m² and 20.89 mA/m², respectively. With increase in external resistance, power density increased up to certain resistance and then decreased. The results show that to reach the maximum power density the favourable external resistance observed was 900, 600 and 500Ω for the above experiments with single, two or three electrodes, respectively. This indicates that, with increase in surface area of anode, internal resistance of ML-MFC decreases. When resistance was increased more than the respective value for that anode area, power density decreased. This means that external resistance is also among the factors that control the flow of electrons in the system. Because in our ML-MFC total area of the electrodes was not utilized efficiently, hence power production was not proportional to the area of anode. It was [23] stated that as area of anode electrode was doubled, the power density was increased from 12 mW/ m^2 to 13.4 mW/m^2, also indicating a less power than is expected when second pair electrode was added.

By discussing the total power production measured under variable external resistance at different distances between the electrodes and electrode surface area (experiment no. 1), we noticed that the net power production was higher when the electrodes were placed closely. The highest power production was observed at 20 cm distance between the electrodes and its value was 0.077 mW at external resistance 900 ohms (fig. 8 a). When the distance between the electrodes was reduced from 28 cm to 20 cm, the power was increased by 48 %.

As figure 8(b) indicates, the use of third pair electrodes had less effect on production of power as compared to using two electrodes. The increase in power production was observed by 28.6%, when two electrodes were used as anode instead of single electrode. Although, area of anode was multiplied twice and three times, the increase in net power (mW) was 28.6% and 40% only, a fact which indicates that power generation was limited by a factor other than anode surface area. Probably, the limitation could occur from the electron transfer from microorganism cell to the anode due to the presence of a less number of electrochemically active microbes and absence of external mediator. Thus, the power production did not increase in the same ratio as by addition of anode surface area.

Conclusions

We have demonstrated that the preheated septic tank sludge can be used as inoculum to initiate microbial fuel cells. Under different influent alkalinity to COD ratio (1.04 to 3.04) in the influent, COD removal efficiency of membrane-less microbial fuel cell ranged between 85.8 and 89.9%. Lower alkalinity to COD ratio in the influent increases contribution of anode compartment for COD removal. Increase in TDS due to addition of sulphate has adverse effect on COD reduction in anode compartment. The current production and coulombic efficiency of ML-MFC vary with the type of carbon source in wastewater. At similar influent COD concentration, both higher alkalinity and TDS have adverse effect on electricity generation and decrease current and voltage.

For maximum power output from the ML-MFC, lower MLSS concentration in the cathode compartment is favourable. With increase in MLSS concentration in cathode compartment, current and voltage across the resistance decrease.

The net power production is higher when the anode and cathode are placed closely. The highest power density of 10.89 mW/m^2 was observed when the electrodes were placed close at a distance of 20 cm. The power production did not increase in the same ratio as by addition of anode surface area.

However, in this ML-MFC, the contribution of anode compartment for overall COD removal remained low (less than 50%). Hence, further investigations are paying attention on increasing the organic matter removal in anode compartment to enhance the electricity generation.

Acknowledgements: The financial support provided to carry out this research by IIT Kharagpur, India under ISIRD scheme is duly acknowledged.

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Manuscript received: 17.02.2009