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Bio-electrochemical treatment of distillery wastewater in microbial fuel cell facilitating decolorization and desalination along with power generation

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ABSTRACT

Microbial fuel cell (MFC; open-air cathode) was evaluated as bio-electrochemical treatment system for distillery wastewater during bioelectricity generation. MFC was operated at three substrate loading conditions in fed-batch mode under acidophilic (pH 6) condition using anaerobic consortia as anodic-biocatalyst. Current visualized marked improvement with increase in substrate load without any process inhibition (2.12–2.48 mA). Apart from electricity generation, MFC documented efficient treatment of distillery wastewater and illustrated its function as an integrated wastewater treatment system by simultaneously removing multiple pollutants. Fuel cell operation yielded enhanced substrate degradation (COD, 72.84%) compared to the fermentation process (~29.5% improvement). Interestingly due to treatment in MFC, considerable reduction in color (31.67%) of distillery wastewater was also observed as against color intensification normally observed due to re-polymerization in corresponding anaerobic process. Good reduction in total dissolved solids (TDS, 23.96%) was also noticed due to fuel cell operation, which is generally not amenable in biological treatment. The simultaneous removal of multiple pollutants observed in distillery wastewater might be attributed to the biologically catalyzed electrochemical reactions occurring in the anodic chamber of MFC mediated by anaerobic substrate metabolism.

1. Introduction

Production of renewable energy from the treatment of wastewater has been attracting worldwide interest [1–6]. In this direction, bioelectricity generation through microbial fuel cells (MFC) is gaining importance in the research fraternity. MFC is a hybrid bio-electrochemical device which generates electrical energy through the oxidation of organic matter catalyzed by bacteria (biocatalyst) under mild operating conditions (ambient temperature and pressure) [7,8]. MFC facilitates direct conversion of chemical energy present in the waste to electricity during treatment of wastewater. During operation bio-electrochemical reactions catalyzed in anodic chamber which leading to trigger parallel/multiple reactions like bio-chemical, physical, physicochemical, electrochemical and oxidation (cohesively termed as bio-electrochemical reactions) as a result of substrate metabolic activity [9–12]. The feasibility of integrating multiple process in anodic chamber might also have positive influence on the overall wastewater treatment efficiency. Even though considerable literature is available on MFC as power generator, specific work pertaining to its function as bio-electrochemical treatment is very few. Sulphur pollutant removal [13–16], denitrification [17,18], perchlorate reduction [19], chlorinated organic compounds reduction [20,21], pyridine degradation [22], chromium removal [23] and enhanced substrate reduction [10] were reported in this direction. MFC requires considerable research inputs encompassing multi-disciplinary approach to substantiate the basic mechanism and to optimize the experimental conditions pertaining to wastewater treatment. If optimized and understood well this process may be a good replacement for the conventional biological and electrochemical wastewater treatment unit operations. Therefore, an attempt was made in this communication to enumerate the role of single chambered MFC as a viable bio-electrochemical treatment system for treating distillery wastewater apart from the power generation. Distillery wastewater generated in the form of spent wash or spillage is one of

Abbreviations: AB, acidogenic bacteria; *C*, charge (C); C_D, current density (mA/m^2); COD, chemical oxygen demand (mg/l); C_S, COD/carbohydrate/turbidity concentration in outlet of MFC; C_{SO}, COD/carbohydrate/turbidity concentration in feed to MFC; CV, cyclic voltammetry; DAO, direct anodic oxidation; e$^-$, electron; emf, electro motive force (V); ETP, effluent treatment plant; $E_{o,anodic}$, anodic potential; H$^+$, proton; *I*, current (mA); IO, indirect oxidation; MA, methanogenic archaea; MFC, microbial fuel cell; OCV, open circuit voltage (V); OL, organic/substrate loading (kg COD/m^3); OM, organic matter/substrate; *P*, power (mW); P_D, power density (mW/m^2); PEM, proton exchange membrane; RDAP, relative decrease in anodic potential (%); RE, reference electrode (Ag/AgCl); SD, substrate degradation (kg COD_R/m^3); SPY, specific power yield (W/kg COD_R); TDS, total dissolved solids (mg/l); *V*, voltage (V); VFA, volatile fatty acids (mg/l); VPP, volumetric power production (mW/m^3); VSS, volatile suspended solids (mg/l); ξ_{COD}, COD removal efficiency (%); $\xi_{Turbidity}$, turbidity removal efficiency (%); $\xi_{Carbohydrate}$, carbohydrate removal efficiency (%); ξ_{Color}, color removal efficiency (%).

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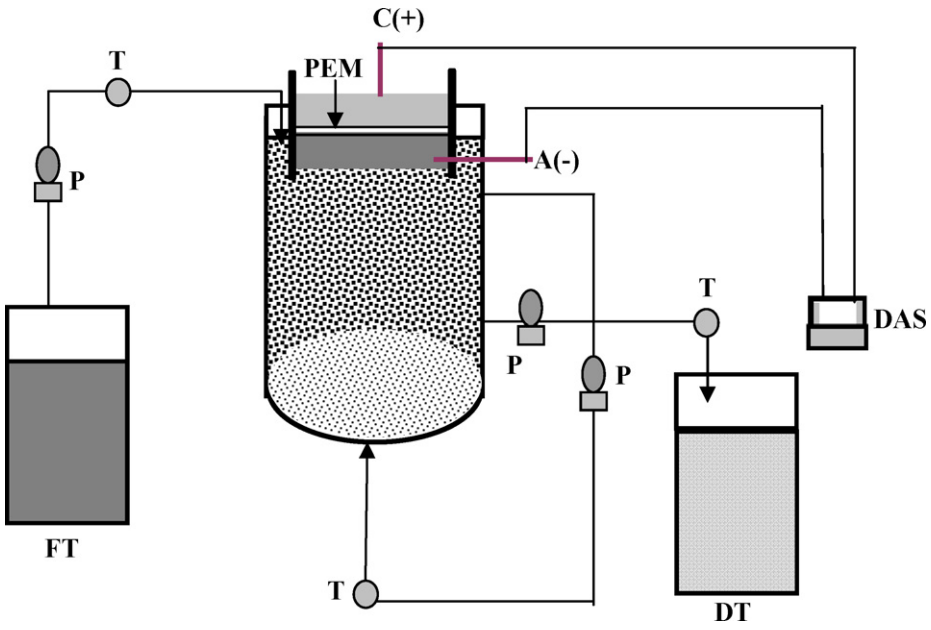

Fig. 1. Schematic details of microbial fuel cell treating distillery wastewater [FT, feeding tank; DT, decant tank; T, pre-programmed timer; P, peristaltic pump; A(−), anode; C(+), cathode; PEM, proton exchange membrane; DAS, data acquisition system].

the most complex and strongest industrial effluents. Molasses-based distilleries generate 8–15 l of wastewater for every liter of the alcohol produced [24,25] and characteristically associated with high organic load and salts concentrations along with persistently dark-brown color. Process was evaluated based on the simultaneous removal of organic matter, color and TDS in concurrence with power output.

2. Experimental details

2.1. MFC construction

MFC was designed and fabricated in the laboratory using 'perspex' material to have single chamber with a total/working volume of 0.50 l having open-air cathode to operate in fed-batch (up-flow) mode under anaerobic microenvironment (Fig. 1). Plain graphite plates (5 cm × 5 cm; 10 mm thick; surface area 70 cm^2) without coating were used as electrodes. Pre-treated NAFION-117 (Sigma–Aldrich) was used as proton exchange membrane (PEM) sandwiched between electrodes [8]. Top portion of the cathode was exposed to air while bottom portion was fixed to PEM and exposed to wastewater. Anode was fixed below PEM-cathode assembly over the liquid layer where the bottom surface was submerged in the wastewater. Copper wires were used to provide connection after sealing with epoxy sealant. Provisions were made in the design for sampling inlet and outlet ports.

2.2. Operation

Mixed consortia of anaerobic origin after selectively enriched for AB [5] was used as biocatalyst. Anodic chamber was inoculated with enriched mixed consortia (3.6 g VSS/l) through distillery wastewater (0.5 l) and performance was evaluated at three different substrate loading conditions (OL; 3.6, 7.85 and 16.2 kg COD/m^3) (Table 1). Prior to feeding, pH of the wastewater was adjusted to 6.0 ± 0.1 to sustain the activity of AB and to suppress the activity of MA present in the mixed culture. MFC was operated in the fed-batch (up-flow) mode at room temperature (29 ± 2 °C). Anolyte was circulated continuously at a rate of 100 ml/min using peristaltic pump in order to prevent the substrate gradient. Voltage drop was considered as an indicator for changing the feed. Before changing the feed, inoculum was allowed to settle down (30 min) and exhausted wastewater (0.4 l) was replaced with fresh wastewater under anaerobic condition. The settled biomass (0.1 l) was used for subsequent operations. Feeding, decanting, and recirculation operations were performed using pre-programmed timer and peristaltic pumps.

2.3. Process monitoring

Open circuit voltage (OCV) and current (I; measured in series at 100 Ω) were recorded on auto-range digital multi-meter. Power (mW) was derived from $P = IV$ equation. Power density (P_D) (mW/m^2) and current density (C_D) (mA/m^2) were calculated with the function of anodic surface area (m^2). Power yield (W/kg COD_R) was obtained by relating power with the amount of COD removed. Volumetric power production (mW/m^3) was calculated based on the liquid volume of the anode. Electrochemical behavior of the mixed consortia was studied employing cyclic voltammetry (CV) using potentiostat–galvanostat system (Autolab, PGSTAT12, Eco-chemie) by applying a potential ramp at a scan rate of 10 mV/s over the voltage range from +0.6 to −0.6 V. All electrochemical assays were performed using mixed consortia in the whole cell form in wastewater (electrolyte) using anode and cathode of MFC as working and counter electrodes respectively against saturated Ag/AgCl(S) RE. Polarization behavior of MFC was evaluated in the range of 100 Ω to 30 kΩ. Cell potentials (anode and cathode) were

Table 1
Characteristics of distillery wastewater used as substrate.

S. No.	Characteristics	Value
1.	pH	4.21
2.	COD	82.20 g/l
3.	TDS	21.60 g/l
4.	VFA	1.94 g/l
5.	SS	1.10 g/l
6.	Color	1,20,000 Hazen units
7.	Total alkalinity	4.00 g/l
8.	Chlorides	4.10 g/l
9.	Sulfates	0.10 g/l

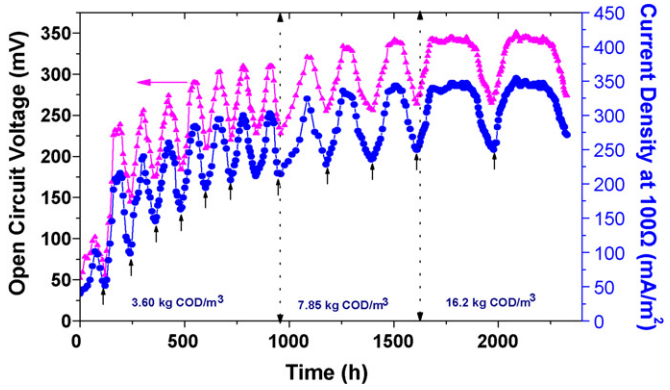

Fig. 2. Voltage (open circuit) and current density (100 Ω external resistor) generation pattern during the operation of MFC with distillery wastewater as substrate at three organic loading rates.

measured against RE. MFC performance with respect to treatment efficiency was monitored by analyzing COD, TDS, color and pH according to the Standard Methods [26].

3. Results and discussion

3.1. Power generation

The experimental data illustrated the function of MFC as power generator by utilizing distillery-based wastewater as substrate (Fig. 2). The organic fraction present in wastewater gets metabolized in the presence of biocatalyst (mixed consortia) and generates electrons (e^-) and protons (H^+) through redox reactions, which results in development of bio-potential (biological mediated voltage) facilitating power generation. Improvement in power output was observed with every feeding event. Stabilization in OCV was observed after 5th cycle of operation. Maximum OCV (310 mV) and current (2.12 mA at 100 Ω (series)) were registered during 8th cycle of operation at 3.6 kg COD/m^3. Not much variation in OCV and current was noticed during MFC operation at higher substrate loading conditions (342 mV; 2.4 mA at 100 Ω (series) at 7.8 kg COD/m^3; 351 mV; 2.48 mA at 100 Ω (series) at 16.2 kg COD/m^3). However, increase in carbon load showed positive influence on the power output. Especially operating system at higher organic load illustrated relatively good power generation for extended period of time. At 3.6 kg COD/m^3, stable performance was recorded up to 120 h of operation, while at 7.8 kg COD/m^3 and 16.2 kg COD/m^3 the time of stable operation extended to 216 and 360 h, respectively. This might be attributed to the availability of additional substrate due to higher load for metabolic reaction. Maximum volumetric power production was observed at 16.2 kg COD/m^3 (1.74 W/m^3) followed by 7.8 kg COD/m^3 (1.64 W/m^3) and 3.6 kg COD/m^3 (1.31 W/m^3) (Table 2).

3.2. Bio-electrochemical treatment

3.2.1. Substrate degradation

MFC operation visualized effective wastewater treatment apart from power generation (Fig. 3a; Table 2). Enhanced substrate (COD) reduction was observed along with simultaneous color and TDS removal. COD removal efficiency varied between 33.33% and 72.84% during MFC operation. The carbon fraction of wastewater functioned as an electron donor in the metabolic process resulting in substrate degradation in concurrence with the power generation. Good reduction in COD enumerates the effective function of mixed microflora in treating distillery wastewater. Low substrate degradation was observed at 3.6 kg COD/m^3 [ξ_{COD}, 33.33%; substrate degradation (SD), 1.2 kg COD/m^3] during initial phase of operation which gradually improved with every additional feeding event and almost stabilized after 6th cycle of operation [ξ_{COD}, 56.67%; SD, 2.04 kg COD/m^3). Generally, wastewater from alcoholic fermentation process is associated with high organic (COD) load which pose serious problem on the ETP performance. MFC operation showed good substrate removal efficiency at higher substrate load conditions [ξ_{COD}, 71.34%; SD, 5.6 kg COD/m^3 at 7.8 kg COD/m^3; ξ_{COD}, 72.84%; SD, 11.8 kg COD/m^3 at 16.2 kg COD/m^3]. MFC documented enhanced substrate degradation efficiency (ξ_{COD}, 72.84%; SD, 11.8 kg COD_R/m^3) compared to the dark-fermentation process studied with the same wastewater [ξ_{COD}, 56.25%; SD, 7.36 kg COD_R/m^3] operated under similar conditions (Table 3) [27]. Maximum specific power yield (SPY) of 0.322 W/kg COD_R was observed with 3.6 kg COD/m^3 operation compared to 7.8 kg COD/m^3 (0.147 W/kg COD_R) and 16.2 kg COD/m^3 (0.074 W/kg COD_R) operations (Fig. 3b).

About 29.5% improvement in substrate degradation was noticed due to integration of electrodes in dark-fermentation process (MFC system; generating bioelectricity) compared to the dark-fermentation process (biofilm reactor without electrode assembly; generating biohydrogen). Distillery wastewater showed higher substrate degradation efficiency compared to designed synthetic wastewater and chemical wastewater evaluated under similar operating conditions in same MFC configuration (Table 3). Enhancement in substrate degradation was also reported in MFC (dual chambered) during composite chemical wastewater treatment at higher substrate loading condition [10] contrary to the conventional anaerobic treatment process (Table 4). The observed improvement in substrate degradation during MFC operation might be attributed to the bio-electrochemical catalyzed phenomena as explained by two mechanisms viz., (a) direct anodic oxidation (DAO) where the pollutants are adsorbed on the anode surface and get degraded by the anodic electron transfer reactions [28]; (b) indirect oxidation (IO) mediated by the oxidants like chlorine dioxide, hypochlorite, hydroxyl radicals, ozone and hydrogen peroxide formed electrochemically on the anode surface which oxidize the organic matter [29]. These reactions are primarily instigated/catalyzed by bio-electrochemical reactions mediated by substrate oxidation. Initially, substrate gets oxidized during DAO process which facilitates formation of primary oxidant species. Primary oxidants formed on the anode surface further react on the anode and yields secondary oxidants which manifest IO process. The oxidants produced through IO process will have significant influence on the organic removal efficiency. Hydroxyl radicals will be formed due to splitting of water molecule in the presence of

Table 2
Consolidated experimental output pertaining to the MFC operation at three substrate loading conditions with distillery wastewater.

Output parameters	Substrate loading condition (kg COD/m^3)		
	3.60	7.85	16.20
ξ_{COD} (%)	56.67	71.32	72.84
SD (kg COD_R/m^3)	2.04	5.60	11.80
ξ_{Color} (%)	20.00	31.67	22.92
ξ_{TDS} (%)	18.75	20.13	23.96
OCV (max, V)	0.310	0.342	0.351
Current (max, mA)	2.12	2.40	2.48
Current density (mA/m^2)	302.86	342.86	354.29
Power density (mW/m^2)	93.89	117.26	124.35
Sustainable resistance (kΩ)/sustainable power density (mW/m^2)	13.5/0.707	18.0/0.484	18.0/0.501
Volumetric power yield (W/m^3)	1.31	1.64	1.74
SPY (Max; W/kg COD_R)	0.322	0.147	0.074

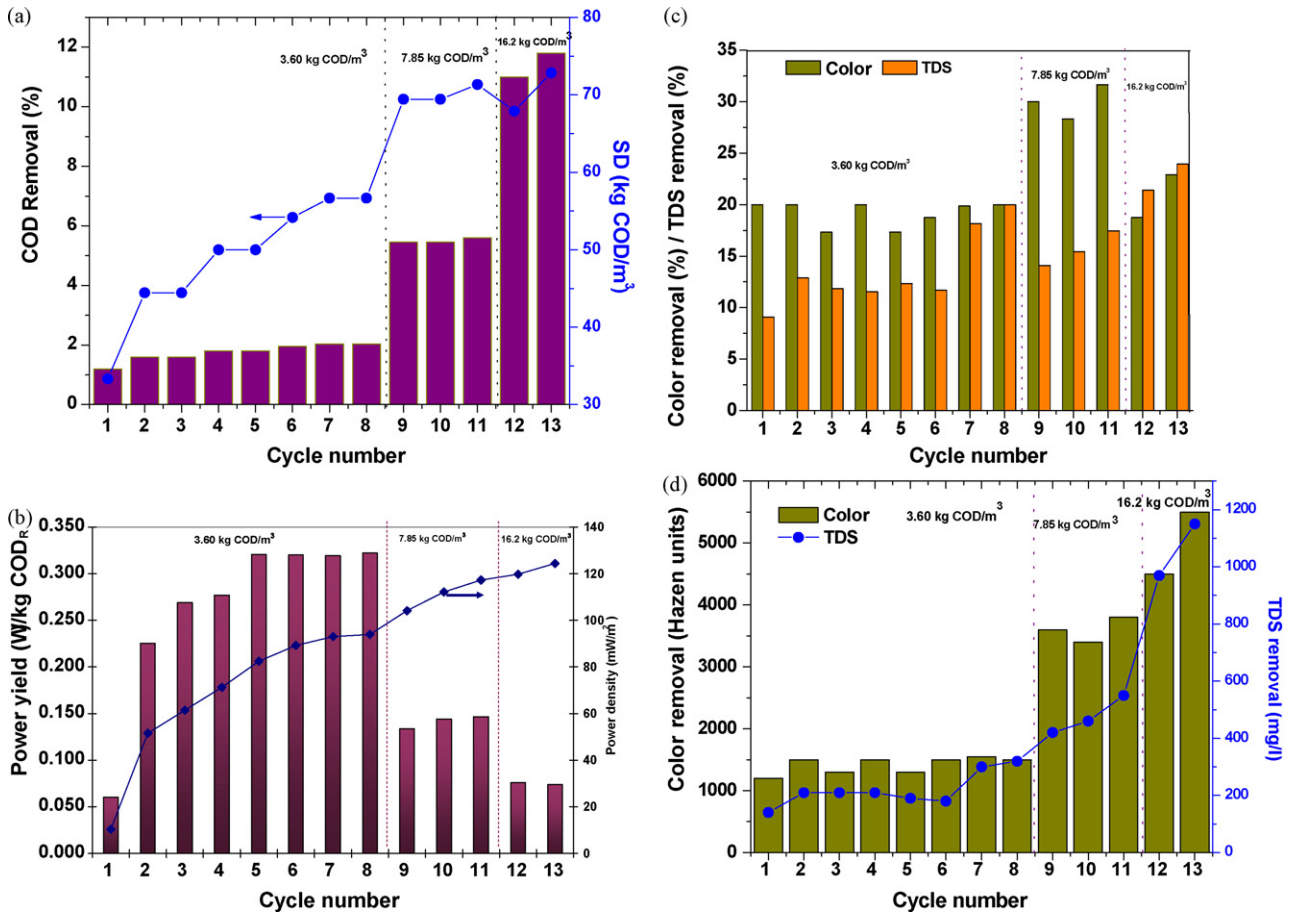

Fig. 3. MFC performance as bio-electrochemical system during treatment of distillery wastewater with the function of 13 cycles of operation at three organic loadings. (a) COD removal efficiency (%) and substrate degradation. (b) Power yield and maximum power density. (c) Color removal efficiency (%) and TDS removal efficiency (%). (d) Color removal and TDS removal efficiency.

bio-potential and these radicals are absorbed on to the anode surface which then oxidizes the organic matter and also produces hydrogen peroxide [29]. This phenomenon enumerates the positive role of incorporating electrode-membrane assembly in bioreactors towards efficient substrate removal.

3.2.2. Desalination

Distillery-based wastewater characteristically contains higher concentration of salts (4800 mg TDS/l). During MFC operation good reduction in TDS concentration was also observed (Fig. 3d; Table 2), which is not generally amenable in biological treatment. During the initial stage of cycle operation relatively less amount of TDS removal [ξ_{TDS}, 9.09% (140 mg TDS/l)] was observed which improved in subsequent cycle operations and almost stabilized after 7th cycle [ξ_{TDS}, 18.13% (290 mg TDS/l)]. At higher substrate load conditions also TDS removal persisted with improved performance. At 7.8 kg COD/m^3 operation, maximum TDS removal [ξ_{TDS}, 20.13% (600 mg TDS/l)] was registered during the 11th cycle. Improvement in TDS removal efficiency [ξ_{TDS}, 23.96% (1150 mg TDS/l) during 13th cycle] was observed at next higher load (16.2 kg COD/m^3) along with current. Transfer of ionic species will happen during MFC operation in proportion to the current generated by anodic bacteria by utilizing distillery wastewater. The observed scaling on the air cathode supports this phenomenon. Removal of salts present in chemical wastewater was reported in dual chambered MFCs operated with diverse catholytes [10]. Cao et al. [30] also reported desalination phenomena in three chambered MFC from synthetic wastewater and called as microbial desalination cell (MDC).

3.2.3. Decolorization

Distillery-based wastewater is generally associated with dark-brown color. Presence of melanoidins imparts this persistent color (pigmented) to wastewater [31,32]. Maillard reaction of sugars/carbohydrates with proteins (amino groups), caramels and furfurals contribute to the formation of melanoidins majorly [33]. The presence of olefinic linkages and conjugated enamines contributes to the chromophores structure in the melanoidin [34] and the conjugated C-C double bonds in the structure are responsible for the deep brown color [33]. The molecular weight of melanoidins

Table 3
Performance of open-air cathode MFC with various types of wastewaters.

Type of wastewater	Operating pH	OCV (mV)	Current (mA)	Power (mW)	CD (mA/m^2)	PD (mW/m^2)	ξ_{COD} (%)	References
Designed synthetic wastewater	6.0	308	0.93	0.29	111.29	8.89	43.06	[8]
	7.0	291	0.82	0.24	98.13	7.69	43.78	[8]
Chemical wastewater	6.0	329	1.28	0.42	182.86	60.16	66.07	[5]
Molasses-based wastewater	6.0	351	2.48	0.87	354.29	124.35	72.84	This study

Table 4
Comparison of treatment efficiency of MFC with the function of anaerobic treatment.

Process	Reactor	Wastewater	Operating pH	Substrate load (kg COD/m^3)	ξ_{COD} (%)	SD (kg COD_R/m^3)	Color removal (%)	TDS removal (%)	References
Biohydrogen production	Biofilm reactor	Distillery based	7.0	12.0	69.68	6.40	–	–	[27]
			6.0	12.0	56.25	5.40	–	–	
Bioelectricity generation	Dual chambered microbial fuel cell (MFC) with ferrocyanide cathode	Composite chemical based	6.0	18.6	68.28	12.79	31.00	51.00	[10]
	Dual chambered microbial fuel cell (MFC) with aerated cathode	Composite chemical based	6.0	18.6	66.13	12.29	31.00	51.00	
Bioelectricity generation	Single chamber microbial fuel cell (MFC) with open-air cathode	Distillery based	6.0	3.60	56.67	2.04	20.0	18.75	This study
			6.0	7.85	71.34	5.60	31.67	20.13	
			6.0	16.2	72.84	11.80	22.92	23.96	

ranges from 5000 to 40,000 and is generally hard to remove by the conventional treatment methods. The color also gets intensified due to re-polymerization of the compound during the anaerobic process [1]. Significant reduction in color was noticed during MFC operation irrespective of the loading conditions (Fig. 3c). Maximum color removal was observed at 16.2 kg COD/m^3 (5500 Hazen units; ξ_{Color}, 22.92%) followed by 7.8 kg COD/m^3 [3800 Hazen units; ξ_{Color}, 31.67%] and 3.6 kg COD/m^3 [1550 Hazen units; ξ_{Color}, 20.01%]. Color removal efficiency was found to depend on the color intensity of the feed. Color removal observed from distillery-based wastewater might be attributed due to the possibility of biologically catalyzed electrochemical oxidation during MFC operation [10]. MFC mimicked the function of a conventional electrochemical cell normally used for color removal purpose. Color removal showed good correlation with COD removal efficiency [R^2 - 0.9346] than with current [R^2 - 0.4684] indicating its association with substrate removal rather than current generation. In presence of salts, formation of active chlorine-based oxidants were observed in electrochemical system which decolorizes highly colored dye [35,36]. Melanoidins are reported to be oxidized into volatile acetic acids and amino acids by the cleavage of C-CO and C-C bonds in the presence of H_2O_2 [34]. Electro-oxidation showed to enhance process efficiency in the presence of H_2O_2 and NaCl with respect to COD (16%), color (7%) and TDS (12.5%) removal [37]. Electro-coagulation employing activated areca nut carbon was studied to treat distillery wastewater (TDS, 55.8%, chlorides, 21.8%, sulphates, 90.3% [38]. Possibility of chlorohydroxyl radical formation on the anode surface in presence of NaCl was also reported [28,29] which might also helps in oxidation of organic matter.

3.3. Characterization of MFC performance

3.3.1. Polarization behavior

Polarization behavior of MFC at three loadings was recorded during stable phase of operation. Polarization curve was plotted against potential and power density at different resistances (100 Ω to 30 kΩ) to visualize current densities in concurrence with the experimental variations studied (Fig. 4a). Under low resistances the fuel cell circuit allows more e^- flow compared to higher resistances and reduces the H^+ present at the cathode. This results in potential drop especially at lower resistances in spite of higher P_D. Current generation showed decreasing trend with increase in the resistance which is in concurrence with the literature reported earlier [5]. At 30 kΩ resistance less current generation (<1 mA) was recorded during three organic loads. Rapid stabilization of voltage was also observed at higher resistances (30 kΩ). However, relatively high potential drop was observed at low resistances. Effective e^- discharge observed at lower resistances might be the probable reason for higher potential drop and slow stabilization of the voltage at lower resistances. Substrate metabolism was observed to be more at lower resistances, where microbes donate e^- to the anode which is discharged in closed circuit [8]. At lower resistances, the e^- move more easily through the circuit than at higher resistance, oxidizing e^- carriers released by the microbes. Higher oxidation by microbes is expected with high ratio of oxidized e^- carriers at a low resistance. The point at which maximum P_D was observed on the polarization curve against voltage and CD is generally considered as cell design point (voltage change region) of that particular fuel cell system [39]. Effective performance with respect to power output can be obtained on the right side of the cell design point. In the case of 16.2 kg COD/m^3, cell design point was observed at 300 Ω resistance with respect to P_D (55.3 mW/m^2). MFC with 16.2 kg COD/m^3 can be operated effectively below 300 Ω resistances with stable performance. The corresponding power densities were observed at 200 Ω, and 100 Ω were 48.47 mW/m^2, and 46.06 mW/m^2, respectively. In the case of 7.8 kg COD/m^3 also,

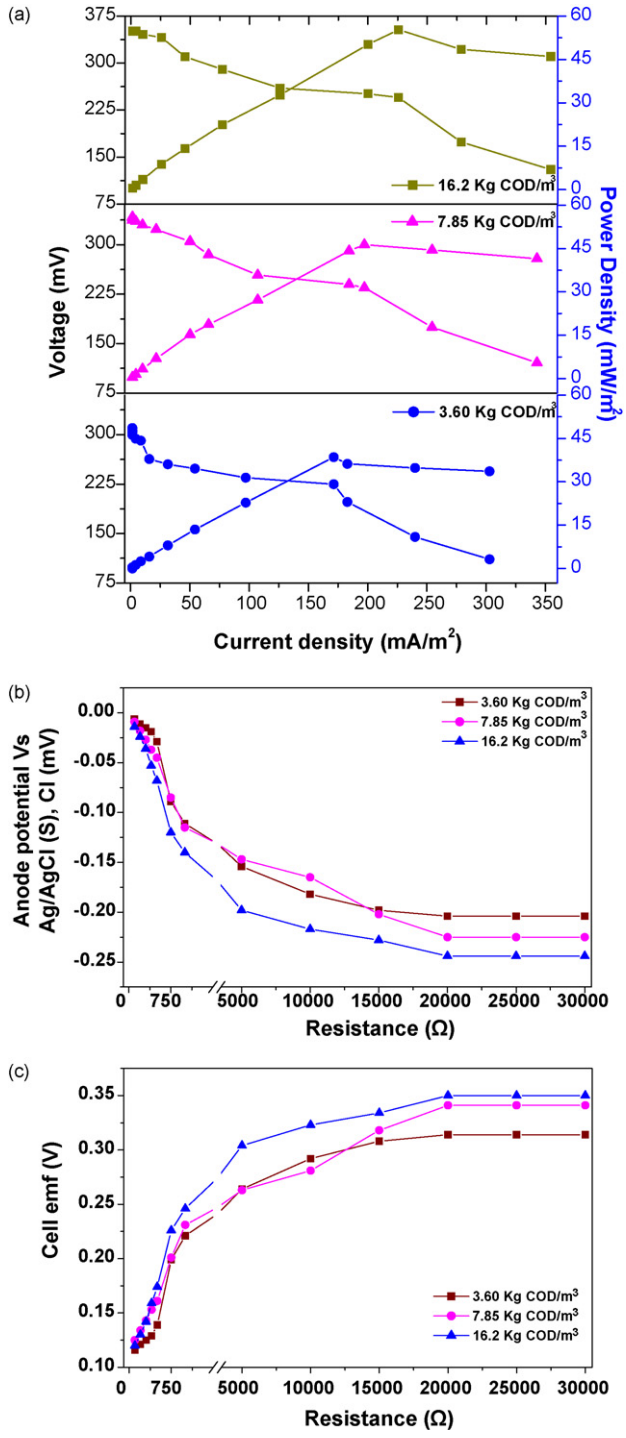

Fig. 4. (a) Polarization curves measured at various applied resistances during stabilized performance at three organic loading rates. (b) Effect of external resistance on the anodic potential with respect to applied external resistance. (c) Effect of external resistance on total cell potential with respect to applied external resistance.

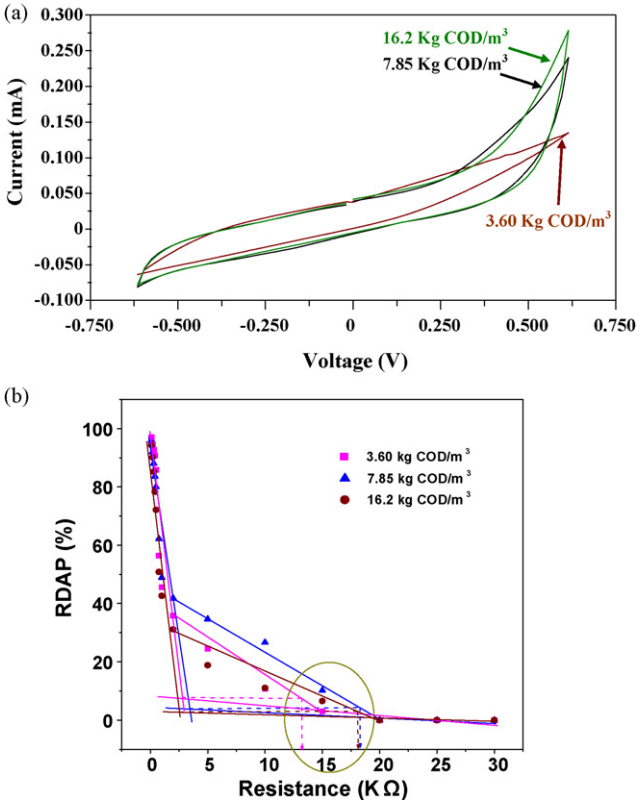

Fig. 5. (a) Cyclic voltammetry profiles generated during stabilized phase of operation at three organic loadings. (b) Effect of external resistance on the variation of percent deviation of anodic potential (RDAP) with respect to applied external resistance during stabilized phase of operation at three organic loadings.

cell design point was observed at 300 Ω resistance with respect to P_D (46.32 mW/m^2) and at this loading MFC can be operated effectively below 300 Ω resistances with stable performance. Corresponding power densities observed at 200 Ω, and 100 Ω were 44.5 mW/m^2, and 41.49 mW/m^2, respectively. On contrary, in the case of 3.60 kg COD/m^3 cell design point was observed at 400 Ω resistance with respect to P_D (38.53 mW/m^2) and at this loading MFC can be operated effectively below 400 Ω resistances with stable performance. Corresponding power densities observed at 300 Ω, 200 Ω, and 100 Ω were 36.20 mW/m^2, 34.8 mW/m^2, and 41.49 mW/m^2, respectively.

3.3.2. Cell potentials

Variation in potentials of the cathode, anode and cell against the external resistance were evaluated during MFC operation at three loading conditions. Cathode potential varied between a narrow range [110 mV (3.6 kg COD/m^3); 106 mV (7.85 kg COD/m^3); 116 mV (16.2 kg COD/m^3)] indicating that the current generated during MFC operation was limited by the anode reaction only. Significant drop in anode potential was noticed during operation with three loadings (Fig. 4b). Anode potential controls the kinetics of electron transfer from the microorganism to the anode. Drop in potential was observed from 2 kΩ at three loading conditions suggests the possibility of effective electron discharge below 2 kΩ external resistances. Cell emf decreased significantly when resistance applied was less than 10 kΩ (3.6 kg COD/m^3) and 2 kΩ (7.8 and 16.2 kg COD/m^3) (Fig. 4c).

3.3.3. Cyclic voltammetry

Electrochemical behavior of MFC under different organic load conditions was evaluated by using cyclic voltammetry (CV). Voltammogram [vs. Ag/AgCl (S)] profiles evidenced visible and significant variations in e^- discharge and energy generation pattern with the function of substrate load (Fig. 5a). Among the three load conditions, 16.2 kg COD/m^3 visualized maximum current of 0.28 A (forward scan; 0.6 V) and −0.07 A (reverse scan; −0.6 V) followed by 7.8 kg COD/m^3 [0.24 A (forward scan; 0.6 V) and −0.07 A (reverse scan; −0.6 V)] and 3.6 kg COD/m^3 [0.11 A (forward; 0.6 V) and −0.06 A (reverse; −0.6 V)] during stable phase of operation. Relatively higher current output was recorded in forward scan of the

voltammogram in three loading conditions suggesting high electrochemical activity. Visible improvement in electrochemical activity was observed with increase in load conditions. Maximum power was recorded at highest load condition suggesting effective electrochemical activity. Charge (derived from CV) also showed increasing trend with increase in substrate load. At 3.6 kg COD/m^3 load, charge of 2.39 C was observed corresponding to SD of 2.04 kg COD_R/m^3. With increase in substrate load to 7.85 kg COD/m^3, a marginal improvement in charge (2.58 C) was noticed corresponding to SD of 5.45 kg COD_R/m^3. While at higher substrate load (16.2 kg COD/m^3) a significant increase in charge (8.53 C) was observed corresponding to the SD of 11.80 kg COD_R/m^3. This enumerates the direct correlation between substrate degradation and e^- discharge pattern observed during MFC operation.

3.3.4. Sustainable power

MFC system (along with external circuit) is considered to be in steady state, when the power production is sustainable there power generated equals to the power consumption for an extended period of time. During operation many steady states are possible and it is important to define conditions where sustainable current reaches a maximum and compute the maximum sustainable power that can be generated. Relative decrease in anode potential (RDAP) with the function of applied external resistance is used to evaluate maximum sustainable power which was calculated using the initial anodic potential ($E_{o,anodic}$) and anodic potentials at each applied external resistance [40,41] as shown in Eq. (1):

$$\text{RDAP}(\%) = \left[\frac{E_{o,anodic} - E_{anodic}}{E_{o,anodic}}\right] \times 100 \quad (1)$$

RDAP with the function of applied external resistance was used to evaluate maximum sustainable power. The linear fit at high external resistance represents a region in which the external resistance controls the power. When external resistance was high, the RDAP increased linearly with decreasing external resistance because the electron delivery to the cathode was limited by external resistance. At applied low external resistance, the electron delivery to the cathode was limited by kinetic and/or mass transfer (or internal resistance), and the RDAP increased linearly with decreasing external resistance. The conditions where external and internal resistance were equal between these two lines, a horizontal line from the intersection was drawn to estimate the external resistor that allowed to measure sustainable power (Fig. 5b). At 3.6 kg COD/m^3 operation, the MFC demonstrated to possess sustainable resistance of 13.5 kΩ in concurrence with sustainable P_D of 0.707 mW/m^2. A marked improvement in both sustainable resistance of 18 kΩ was recorded at higher loading conditions [7.8 and 16.2 kg COD/m^3] indicating stability of system even at higher resistance. However, a marginal improvement in sustainable P_D was recorded with increase in substrate loading from 7.8 kg COD/m^3 (0.484 mW/m^2; 18 kΩ) to 16.2 kg COD/m^3 (0.501 mW/m^2; 18 kΩ). Function of MFC at higher resistance indicated stability of the system in discharging the electrons effectively.

4. Conclusions

Experimental data depicted the multiple functions of MFC as a fuel generator and as an integrated wastewater treatment unit. Apart from power generation, MFC also evidenced good wastewater treatment. Enhanced substrate degradation and TDS and color removal was visualized during MFC operation. System inhibition was not observed even at higher loading conditions. Simultaneous removal of multiple pollutants observed during MFC operation might be attributed to one or all of the unit operations of wastewater treatment viz., biological treatment (anaerobic), electrolytic dissociation and electrochemical oxidation. Key advantages of this integrated treatment approach are the non-requirement of external electrical potential and feasibility of process integrations in a single system (unlike different systems for each of the unit operations). Moreover, integration of different process mechanisms in a single system might have positive influence on the overall process efficiency. This also triggers some of the unknown unit operations and permits their function positively for the required output.

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