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Real textile and domestic wastewater treatment by novel cross-linked microbial fuel cell (CMFC) reactor

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ABSTRACT

Domestic wastewater has been used as a co-substrate with real textile wastewater (RTW) in a novel cross-linked microbial fuel cell (CMFC) reactor for its treatment and bioelectricity generation. In novel CMFC, two H shaped MFCs were stacked hydrodynamically for providing sequential anaerobic and aerobic treatments in the bio-anode and bio-cathodes, respectively. Both MFCs are electrically connected in parallel mode to enhance power generation. Performance of CMFC was observed in terms of power generation, COD, and color removals at different blending percentage of RTW (20, 30, 40, and 50%) with domestic wastewater. The maximum blending percentage of RTW in domestic wastewater was found 40% optimum at their inherent pH and conductivity with 24 h hydraulic retention time per chamber. Further at this percentage, pH and conductivity of the feed were maintained at 6.4 and 8 mS cm^{-1} by phosphate buffer solution. Under these control parameters and with change in organic loading rate (OLR), CMFC achieved power density, COD, and color removals of 337 Wm^{-3}, 82, and 60% respectively. Membrane-less-CMFC gave enhanced power density (750 Wm^{-3}) but a lower COD (79%) and color (45%) removals in comparison to CMFC. Bio-cathode (aerobic treatment) also shown its potential in CMFC by removing aromatic amines produced at the bio-anode due to anaerobic treatment of azo dyes present in RTW. Adding domestic wastewater as a co-substrate neutralizes RTW and also provides sufficient nutrients for biological treatment, hence increases its treatability and reduces its treatment cost. CMFC also proves its potential to sustain in real-world conditions and can be upgraded and scaled up after further modifications.

Keywords: Microbial fuel cell (MFC); Real textile wastewater; Domestic wastewater; Sequential treatment; Membrane-less microbial fuel cell; Stacking

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1. Introduction

Increasing wastewater and decreasing energy resources are the global problems in today’s world. Therefore, world requires an adequate wastewater treatment along with energy generation. This work deals with the treatment of real textile and domestic wastewaters. Real textile wastewater (RTW) has low biological oxygen demand (BOD) to the chemical oxygen demand (COD) ratio from 0.2 to 0.5, which implies the requirement of chemical treatment. RTW also has a greater color appearance (30–60 g dye), high

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total dissolved solid, suspended solids, high temperature, and variable pH (from 5 to 9) [1,2]. Wastewater generated in the textile industry is recalcitrant, noxious, and hence unmanageable. Textile industry uses around 60–70% azo-dyes by the virtue of ease of application, versatility, and reliable coloring.

In today's world, biological treatment process is promoted to get sustainability in treatment. Biological methods for treatment of textile wastewaters are anaerobic and aerobic degradation. But purely anaerobic degradation of azo-dye produces aromatic amines. Aromatic hydrocarbons containing amine group (–NH2 or –NH–) are called Aromatic amine. They are highly complex in structure containing conjugated aromatic or heterocyclic structure and multiple substitutions. Those are highly toxic, carcinogenic, and mutagenic because they produce some intermediates through biochemical routes and these intermediates get attached with DNA and cause cancer [3]. Some examples of cancer causing amines are 3,3´-Dimethylbenzidine, 3,3´-Dichlorobenzidine, 2,4-Diaminoanisole etc. [4]. Anaerobic decolorization takes place with the help of anaerobic azoreductase and co-substrate such as glucose and acetate, which provide electrons (e^-) for cleavage of the azo links [5,6]. Aerobic deterioration alone is not able to degrade all dyes, and also produces high amount of sludge [7,8]. Sequential application of anaerobic degradation followed by aerobic has provided a solution with the advantage of economical, reliable, and complete degradation along with ecological benefits [9–11]. On the other hand, domestic wastewater treatment is also an issue because it requires higher infrastructural investment to handle its large volume. Domestic wastewater has almost neutral pH, high BOD, adequate nutrients, a neutral temperature, high volume, enriched microbial consortium, and easy availability. Therefore, domestic wastewater can be mixed with RTW for providing sufficient conditions for effective biological treatment of textile wastewater.

A microbial fuel cell (MFC) is an up-surging technology in the field of bioenergy generation along with wastewater treatment. It generates electrical power with the help of microbes that make it a green future source of energy. In MFC, anaerobic microbes degrade organic matter and produce hydrogen ions (H^+) and electrons (e^-) at the anode. H^+ ion diffuses through the proton exchange membrane (PEM) and e^- transfer through an electrode via an external circuit to the cathode. At the cathode, e^- and H^+ ions combine with oxygen to form water (H_2O); this result in power generation [12]. MFC has limited open circuit voltage (OCV) of 1.14 V because of the standard redox potential of NADH/Nicotinamide adenine dinucleotide (NAD^+) and O_2/H_2O of −0.32 and +0.82 V, respectively [13]. NAD^+ is a coenzyme found in all living cells. It carries electrons in redox reactions during metabolism.

Double chamber MFCs are proved to be more efficient over single chamber MFC for the removal of COD, BOD, nitrate, etc. [14,15]. Advantage of aerobic condition at the cathode has taken in either abiotic or biotic form. Recently, the bio-cathode has attracted the attention of many researchers because microbes act as an electron mediator and also provide aerobic treatment. It also provides a variety of terminal electron acceptors for electron transfer, which diminish requirement of expensive metals like platinum and electrolyte [16]. A sequential treatment system for wastewater was suggested by Freguia et al. [17] and Wen et al. [18]. They got maximum power density of 830 mW m^{-3} with 91–96% COD removal. Kalathil et al. [19] worked on real dye wastewater in single chamber bio-cathode MFC and got 8 W m^{-3}. Sun et al. [20] obtained 300% increment in power density by using bio-cathode with respect to abiotic cathode. Hence, sequentially configured bio-anode (anaerobic treatment), and bio-cathode (aerobic treatment) assemblies may enhance performance of the MFC [17].

Recognized challenges in MFCs for real-world conditions are scalable design, stacking, economic efficiency, and enhanced power density [20–25]. But most of the studies in literature are based on synthetic wastewaters like glucose, acetate, sucrose etc. [26–31]. There are very limited studies available on actual wastewaters. Most of the studies are in batch mode and less on continuous double chamber MFCs with real wastewater as substrate.

In this study, three major goals were identified: (i) the efficient treatment of combined real textile and domestic wastewater, (ii) the production of bioelectricity from wastewater by stacking MFCs, and (iii) cost efficient microbial fuel cell. Therefore, we designed a novel cross-linked microbial fuel cell (CMFC) by cross-linking two double chamber MFCs hydrodynamically for sequential treatment of wastewater. Domestic wastewater is used as a co-substrate for decolorization and fulfilling other requirements like nutrients, neutralizing acidity, and temperatures etc. For CMFC reactor, an optimum blending of textile and domestic wastewater was proposed to produce better power production with the efficient removal of COD and color. Further, the effect of pH, conductivity, high organic loading rate (OLR), and surface areas of the cathodes and anodes were monitored on the performance of CMFC. Finally, membrane-less cross-linked microbial fuel cell (ML-CMFC) was also observed under controlled parameters to enhance its cost efficiency.

2. Material and methods

2.1. Configurations of CMFC

A novel CMFC was proposed by stacking two H shaped MFCs with some modified specification from our previous study [32] using cylindrical chambers (Fig. 1). Each cylindrical chamber designed with 2 L capacity (radius = 5.5 cm; height = 22 cm), made from borosilicate glass material having four openings as inlet, outlet, and two sampling ports on top and bottom. The working volume of each of the chambers was 1.5 L. The anode compartments were covered with hemispherical heads for maintaining anaerobic condition. To transform MFC to CMFC these two MFCs were stacked. Therefore, CMFC is a stack of two hydrodynamically cross-linked double chamber MFC, i.e. feed from a reservoir enters into anodic chamber of MFC 1 for anaerobic treatment and effluent of MFC 1 then goes to cathodic chamber of MFC 2 for aerobic treatment and vice versa. Therefore, anode of first MFC and cathode of other MFC share same feed in continuous mode to give maximum treatability by sequential treatment. After cathodic treatment effluent was collected for analysis and discarded. Effluent was not recirculated in the system. Then, both cells were connected in parallel mode via external resistance to avoid cross polarity because of liquid continuity and to reduce internal resistance by increasing surface area of the bioelectrode. Economical carbon electrodes were used in CMFC having diameter of 1.5 and 17.5 cm length. There were totally nine electrodes in each chamber. The surface area of each single carbon electrode was 85.96 cm^2; hence the total surface area of electrodes was 773.62 cm^2, and the effective surface area was 667.64 cm^2. In similar fashion, all chambers were fixed. Electrodes were at 0.5 cm away from each other in every chamber [32]. Each electrode was drilled and soldered with copper wires. MFCs were coupled by membrane coupling assembly and fixed with stainless steel nut bolts. PEM (Ultrex, Membrane International Inc. USA), having effective area of 19.63 cm^2 was placed between the anode and cathode of MFC by nozzle coupling arrangement. Anodic chambers were flushed with nitrogen gas to remove traces of oxygen for attaining an anaerobic condition. In the aerobic chamber, air was sparged from the bottom of the compartment by an air pump. The anode and cathode of MFCs were connected by copper wires with the 150 Ω resistance via an external circuit unless stated otherwise.

2.2. Feed solution

The feed was the blend of RTW and domestic wastewater. RTW was collected from nearby textile industry, and domestic wastewater was from a sewage pumping station of the Surat city, twice in a week to maintain its aliveness. Table 1 gives the general characteristics of RTW, domestic wastewater and their blends.

2.3. Inoculation, start-up, and operational conditions

CMFC was operated in a batch mode during start-up, after that it was continuously operated with four

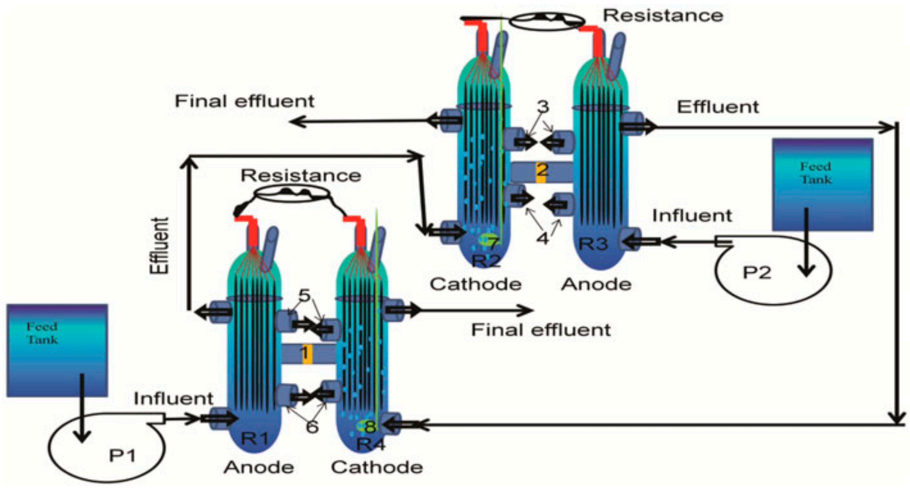

Fig. 1. Schematic sketch of CMFC used in the experimental study; R1 and R3 (anode) R2 and R4 (cathode), R1 and R4 form MFC 1, R2 and R3 form MFC 2; P1 and P2 are peristaltic pumps; 1 and 2 PEM; 3, 4, 5, and 6 sampling port; 7 and 8 are air spargers.

chambers (R1, R2, R3, and R4). In which R1 and R3 were anodic chambers (anaerobic); whereas, R2 and R4 were cathodic chambers (aerobic). R1 and R4 made MFC 1 while R3 and R2 made MFC 2 by electrically connecting anode and cathode. Similarly, R1, R2 made Pair 1 and R3, R4 made Pair 2 by connecting hydrodynamically.

Anaerobic sludge was taken from nearby upflow anaerobic sludge blanket reactor (100 million liters per day (ML d^{-1})) based on full scale sewage treatment plants for anodic and cathodic chambers. In batch mode, primarily system was operated for 15 d to acclimatize microbes and assisting the formation of biofilm on electrodes. Each chamber was fed with 400 mL sludge (8 g L^{-1} of volatile suspended solids (VSS)) and with domestic wastewater having a COD of 350 mg L^{-1}. Accordingly, F/M ratio was taken as 0.16 considering initial effective VSS of 2.13 g L^{-1}.

Continuous operation of CMFC was started with the domestic wastewater having 48 h HRT per chamber. The wastewater was pumped into the CMFC by peristaltic pump with 25 mL h^{-1} flow rate. Finally on 42nd day, the CMFC was conciliated at 24 h HRT per chamber with 50 mL h^{-1} flow rate having overall HRT of 48 h (considering one anaerobic and aerobic unit). HRT was selected based on the literature suggesting RTW a slow degrading and complex waste [18,33–36]. 20, 30, 40, and 50 were the different blending percentage of RTW in domestic wastewater.

Samples were taken after every 24 h per chamber based on their HRT. Sampling starts from 4th day after new composition was fed in CMFC. CMFC performance parameters were studied to attain optimum performance. Reproducibility was checked at maximum blending percentage. At this blending percentage, the effect of pH, conductivity, high OLR, and surface areas of the cathode and anodes were monitored on the performance of CMFC. Finally, at optimum and stable condition, CMFC was operated without PEM and named as ML-CMFC. The rubber sheet was used in place of PEM in CMFC to restrict diffusion of ions. Performance of ML-CMFC was evaluated by the COD, color removals, and power density.

2.4. Methods of analysis and calculations

2.4.1. Wastewater and sludge analysis

COD of influents and effluents of MFCs was determined using the close reflux method [37]. Dissolved oxygen (DO), conductivity, oxidation–reduction potential (ORP) and pH were measured by using different probes (HACH, USA). For RTW UV spectra range from 200–350 nm was used to determine the presence of aromatic amines in sample [38,39]. For RTW, color was also measured by UV–vis spectroscopy absorbance. To measure color in samples; samples were filtered by microfiber filter and centrifuged for 10 min at 7,000 rpm. Then sample absorbance was measured at a wavelength of maximum absorbance that usually ranges between 400 and 750 nm [40]. Percent color removal was determined based on the maximum absorbance of UV–visible spectrum using Eq. (1) [40].

$$\text{Color removal}\,(\%) = \frac{A_i - A_e}{A_i} \times 100 \tag{1}$$

A_i and A_e are the influent and effluent maximum absorbance values of the sample.

Sludge characteristics as VSS and total suspended solids (TSS) were carried out as per procedures given in the standard methods [37].

2.4.2. Calculations for electrical performance of CMFC

Voltage and current were directly measured by digital multimeter (UNI-T brand digital multimeter, 1,000 V). Voltage and current reported in this paper is evaluated after electrically stacking both MFCs in parallel mode. Current density and power density were calculated by Eqs. (2) and (3), respectively. The coulombic efficiency for the system was calculated by using Eq. (4) [41]. The polarization slope method given by Logan [12] was used to calculate internal resistance.

$$\text{Current density} = I/V \tag{2}$$

$$\text{Power density} = \text{Voltage} \times \text{Current density} \tag{3}$$

$$\text{Coulombic efficiency} = 8I/Fq\ \Delta\text{COD} \tag{4}$$

where: F = Faraday's constant, V = Volume of anodic chamber, I = Current, q = Flow rate, and ΔCOD = removal of COD.

3. Results and discussion

3.1. Start-up of CMFC

The system was operated in batch mode initially for 15 d with real domestic wastewater to acclimatize the sludge and for biofilm generation on electrodes. The system was observed in batch mode, but start-up data is not reported here. CMFC operated from 16th to 41st day in continuous mode at 48 h HRT per chamber with almost 140 mg COD L^{-1} d^{-1} OLR. Initially, domestic wastewater was pumped into CMFC by peristaltic pump with a flow rate of 25 mL h^{-1}. Fig. 2 shows the variations in the percentage COD removal of both pairs and OCV of parallel connected MFCs in CMFC. Prior fluctuations in OCV were because of the initiation of continuous feeding and less acclimatized biofilm on electrodes. There was a slight difference in treatability of both pairs, but trends were same as seen in Fig. 2. CMFC fed with mixed microbial cultured sludge which may have produced a difference in treatability. The system was approaching towards stability and gave around 90% COD removal. OCV got stabilized around 0.55–0.6 V in parallel stacking. Performance of CMFC was becoming consistent as the biofilm flourished and sludge acclimatized according to the feed wastewater. These start-up studies reveal beneficial results of the sludge utilization and adaptation of the microbes.

3.2. *Optimization of RTW percentage in domestic wastewater*

One of the prime objectives of this study was to find an optimized percentage of RTW in domestic wastewater based on percent COD and color removal along with power density. Domestic wastewater was used for the following purposes: (i) supply variety of co-substrate for the degradation of variable dyes, (ii) neutralization of pH, (iii) lowering the temperature and toxicity of RTW, and (iv) addition of diversified microbial consortium. Domestic wastewater also influences influent COD by its microbial activity which can change feed COD with time. Domestic wastewater is not only zero cost co-substrate but practically feasible and also dynamic in nature in comparison to glucose, acetate, and other substrates used in MFC for dye degradation in available literature [34,35].

CMFC was operated from 42nd day at 24 h HRT per chamber with the different blending percentage of RTW in domestic wastewater. Performance of CMFC was assessed based on its biological and electrochemical consistency for each combination of feed wastewater. Maximum percent COD, color removal, coulombic efficiency, internal resistance, and power density for different blends were measured and given in Table 2.

The biological efficiency of CMFC was analyzed by the overall COD and color removals for both pairs with varying OLR at different combinations of RTW and reported in Fig. 3. At 20% RTW (Fig. 3), COD and color removals were 69 and 39%, respectively. 30% RTW gave a maximum of 92% COD removal and 61% color removals. On the other hand, 40% RTW gave lower removals of COD (88%) and color (45%) in comparison with 30% RTW. On increasing RTW in feed above 30%, COD and color removals were started declining. At 50% RTW, values of COD, color removals were declined to 76 and 34%, respectively. CMFC showed better functioning at 30% RTW in comparison of other blends of RTW in domestic wastewater. As RTW in feed rises, toxicity (due to accumulation of dyes) increases, which affect the activity of microbes [42] and results in low COD and color removals with 40 and 50% RTW.

In CMFC, two MFCs were stacked in parallel by connecting R1, R3 (anode) and R2, R4 (cathode)

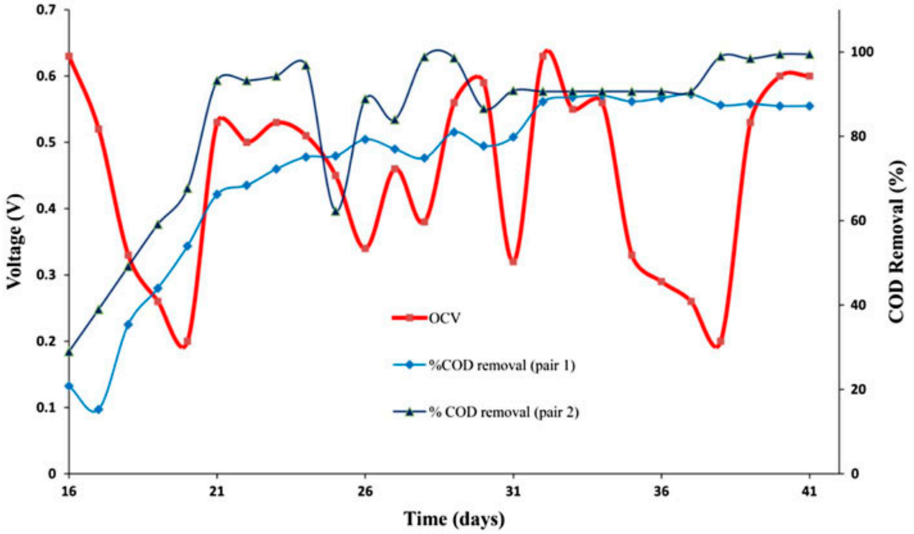

Fig. 2. Start-up values of OCV and percent COD removal of both pairs at 48 h HRT with domestic wastewater.

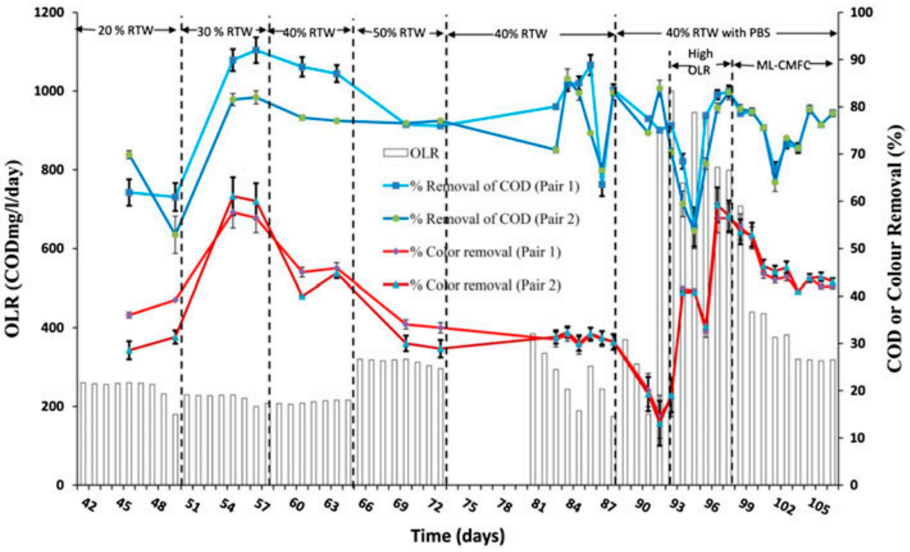

Fig. 3. Variation of COD and color removal at 24 h HRT with different percentage of RTW with, OLR and for ML-CMFC.

through an external load. In parallel, power density rises due to the reduction in internal resistance [22] with an increase in the cross-sectional area for ion flow. Polarization curves (Fig. 4) were generated by varying the resistance from 100 to 10,000 Ω on the 8th day after new blend was fed; assuming CMFC electrochemically stable because it generated stable voltage with variation of ±0.001 V. Power density and OCV (Fig. 4) for 20, 30, 40, and 50% RTW were 100, 138, 135, and 100 W m^{-3} and 0.6, 0.56, 0.53, and 0.45 V, respectively. Internal resistances were calculated at different RTW variations and found 443, 285, 334, and 350 Ω for 20–50% RTW (Table 2). Due to increase in % RTW, OCV decreased while power density increased till 30% RTW (Table 2). This is because of the fact that on increasing RTW, conductivity and COD removal increases till 30% (Tables 1 and 2). On further increment in RTW conductivity and COD removal both decreased, which reflected enhancement in internal resistance, therefore power density and OCV decreases.

By observing Figs. 3 and 4 simultaneously, it is clear that the performance of CMFC at 30% RTW yielded maximum performance. However, in case of 40% RTW; 88% COD removal and 135 W m^{-3} power densities, which were comparable to 92% and 138 W m^{-3} for COD and power density at 30%, respectively. But in the case of the color removal difference was more. Therefore, 30% or 40% RTW could be concluded as an optimum combining percentage. Hence, to achieve optimum performance for maximum volume of RTW, 40% RTW was selected as optimum percent.

3.3. Performance of CMFC

CMFC was fed again with selected 40% RTW at their inherent pH and conductivity from 74 to 88th day for the verification of reproducibility. As shown in Fig. 3 (40% RTW region), percent COD and color removals were 88 and 32%, respectively. The data were found to be reproducible with some fluctuation due to variation in the composition of real wastewaters. Maximum %COD removal for pair 1 remained almost constant at 88%, while, for pair 2, it was increased from 77 to 85% owing to better acclimatization and utilization of microbes. Percentage of color removal for pair 1 decreased from 45 to 31% might be due to the presence and accumulation of degradation resistive dyes. Similar decline was also found in pair 2 from 44 to 32%. Fluctuations in COD removal, color removal, and power generation (as shown in Figs. 3 and 4) might be because of two reasons: (i) protons and electrons needed for both power generation as well as azo-dye degradation simultaneously; therefore, they follow competitive mechanism, and (ii) variations in the constituents of pollutants in real wastewaters.

In this study, we also determined individual effectiveness for anaerobic and aerobic treatment processes at optimized 40% RTW in each reactor. Variations of COD and color removals were analyzed separately for influent and effluent of R1, R2, R3, and R4 as shown in Figs. 5(a) and (b). DO was found in between 7 and 8 mg O_2 L^{-1} in R2, R4 in which air was pumped and, therefore, suited well for aerobic degradation. But DO values found in R1 and R3, were between 0.01 and 0.07 mg O_2 L^{-1}, which facilitated the anaerobic

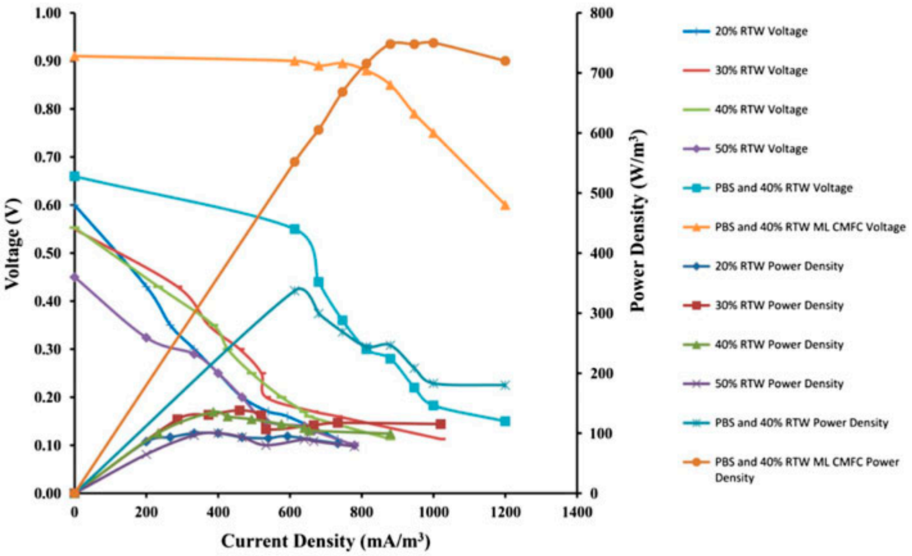

Fig. 4. Polarization curves at different percent of RTW.

Table 1
General characteristics of feed

Parameter	Unit	Domestic wastewater	RTW	20% RTW	30% RTW	40% RTW	50% RTW	40% RTW + PBS at high OLR
pH		6.4–7.5	7.5–8.7	7.20–7.56	7.36–8.00	8.10–8.36	8.35–8.56	6.4
COD	mg L^{-1}	300–550	450–770	225–325	250–287	260–270	370–400	950–1,300
ORP	mV	−200 to −300	20–50	−252 to −260	−260 to −270	−250 to −265	−280 to −310	−280 to −300
DO	mgO_2 L^{-1}	0.01–0.7	0.01–0.03	0.01–0.5	0.01–0.5	0.01–0.07	0.01–0.1	0.01–0.02
Conductivity	μS cm^{-1}	1,800–3,500	1,500–5,000	3,000–3,500	4,000–4,500	3,500–4,200	3,000–4,000	7,000–8,000

Table 2
Performance parameter of CMFC

Parameter	System	RTW (%)				RTW and PBS	
RTW (%)		20	30	40	50	40	40% ML-CMFC
COD removal (%)	pair 1	61	92	88	76	82	80
	pair 2	69	82	78	76	79	77
Color removal (%)	pair 1	39	57	45	34	56	45
	pair 2	31	61	44	30	60	44
Power density (W m^{-3})	CMFC	100	138	135	100	337	750
Coulombic efficiency	CMFC	12	56	33	15	45	36
Open circuit voltage (V)	CMFC	0.6	0.55	0.53	0.45	0.66	0.91
Internal resistance (Ω)	CMFC	443	285	334	350	284	106

process. Some variations in influent COD values were found due to the storage of actual wastewater and availability of active microbes. Both reactors were fed from different reservoirs might be the reason for the variations. Accordingly, COD removal fluctuations were also found in anaerobic and aerobic chambers of both pairs (Fig. 5). Maximum removals of COD were in the range of 70–75% in both R1 and R3 (anaerobic chamber). Meanwhile, in case of R2 and R4 (aerobic chamber) percent COD removals were from 55 to 60%. Similar trends were also found for the color removals. Almost 30% of color removal was given by R1 and R3, while 22% by R2 and R4 (Fig. 5(b)). The aerobic process seems less effective than anaerobic process because of an accumulation of dyes/aromatic amines and less availability of electrons for dye degradation.

Fig. 6 shows the variation of conductivity and pH in R1, R2, R3, and R4. Variation in inlet pH was from 7.0 to 8.1 as a consequence of an inherent property of real wastewater. pH values decreased in R1 and R3 and increased in R2 and R4, which reflect the proper functioning of an anaerobic and aerobic process in CMFC. Conductivity variation shown in Fig. 6 reflects ionic concentrations in anodic (R1, R3) and cathodic (R2, R4) chambers. Ions were produced in anodic chambers as H^+, Cl^-, SO_3^{2-}, etc. by a biological process which increased the conductivity [9]. The ions produced in the anodic chamber got consumed in the cathodic chamber by an electrochemical process, which decreases the conductivity [12]. Fig. 7 shows the variation of current with OLR at 500 Ω with and without phosphate buffer solution (PBS). For 40% RTW (from 81st to 88th day) (Fig. 7), current fluctuated from 1.0 to 1.5 mA and got stabilized at around 1.4 mA.

3.4. Performance parameters

Influence of pH, conductivity, OLR, and surface area of anodes and cathodes were evaluated based on the performance of CMFC.

3.4.1. Effect of pH and conductivity

pH and conductivity of influent were controlled to deduce their effect on the performance of CMFC. To get maximum performance from MFC, optimum pH of the feed should be in between 6.25 and 6.50 [43]. PBS

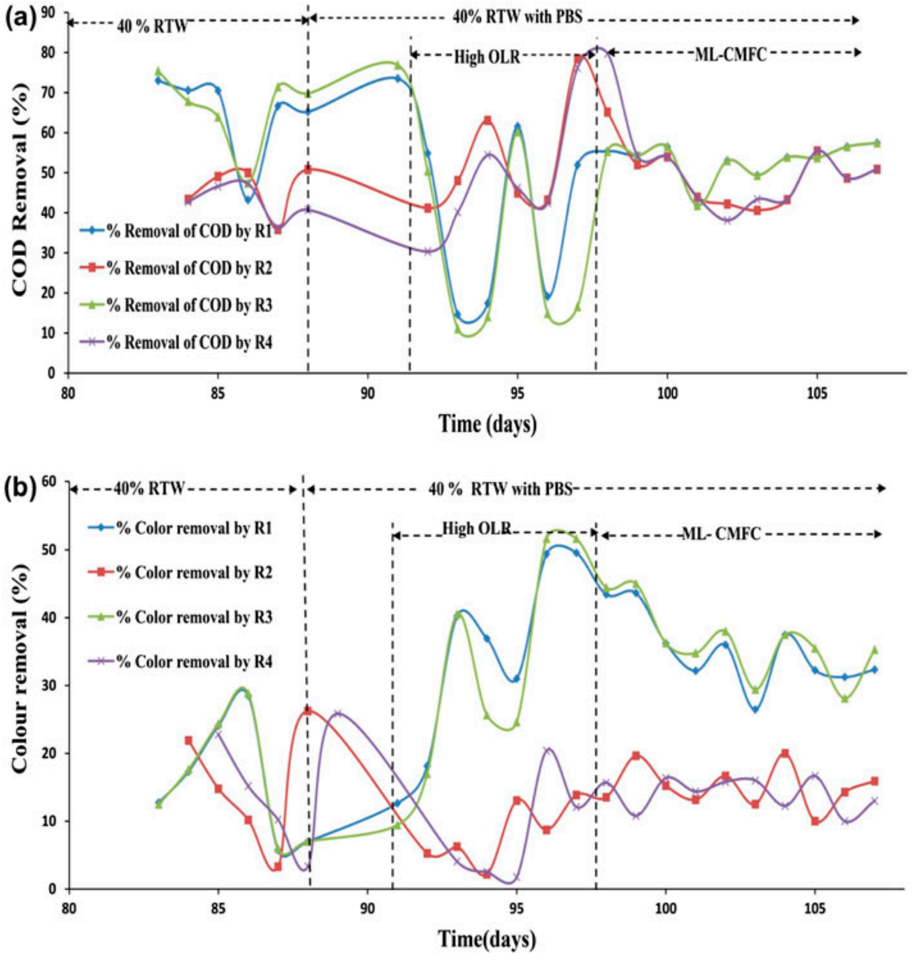

Fig. 5. (a) Percent COD removal (b) Percent color by R1, R2, R3, and R4 at 40% RTW and 40% RTW with PBS.

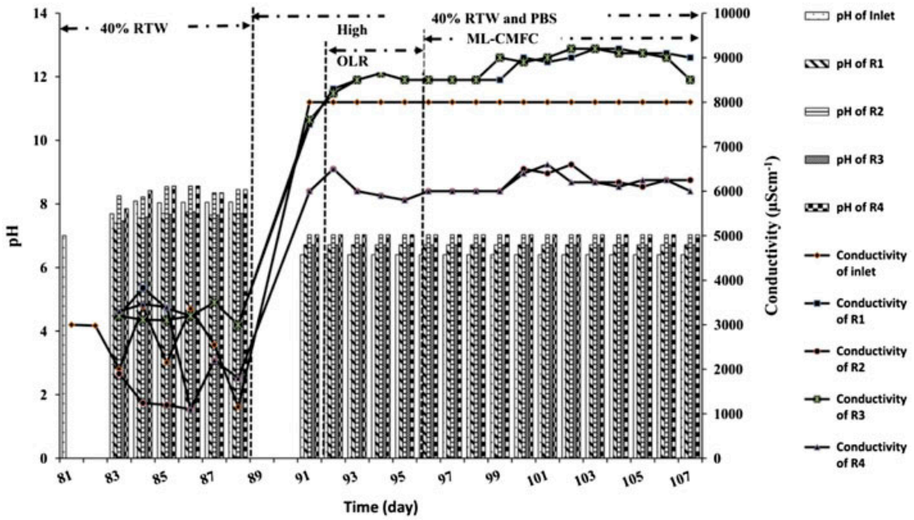

Fig. 6. Variation of pH and conductivity at 40% RTW and 40% RTW with PBS.

was used to control pH and conductivity of influent at 6.4 and 8 mS cm^{-1}, respectively. CMFC charged with feed having controlled pH and conductivity from 88th day. Fig. 6 shows the variation in pH and conductivity of individual chamber with and without PBS. From 88 to 97th day, impact of controlled pH and conductivity can be observed in Fig. 3. Maximum power density (Fig. 4) increased from 135 to 337 W m^{-3} with controlled conductivity and pH (Fig. 6). It might be due to increasing in ionic mobility and number of acetogens. At the same time, percent COD removal decreased from 88 to 82% as seen in Fig. 3.

In anaerobic degradation, methanogenesis occurs from 6.5 to 7.5 pH [44], during which protons and electrons are consumed to produce methane. Therefore, 6.4 pH of the feed was maintained to restrict methanogenesis and to enhance acetogenesis process, thereby increasing production of protons and electrons. PBS also adds conductivity, which resurge in better ionic mobility which increased power density as shown in Table 2. Current also increases as conductivity increases from 1.30 mA to 1.73 mA on 88th day and stabilized afterwards at 1.8 mA. Use of PBS as the buffer exhibited positive impact on color removal that can be observed from Figs. 5(a) and (b) after 88th day. Therefore, PBS enhanced the performance of R1 and R3 in terms of COD and color removal (Fig. 5) with respect to R2 and R4. pH and conductivity was found

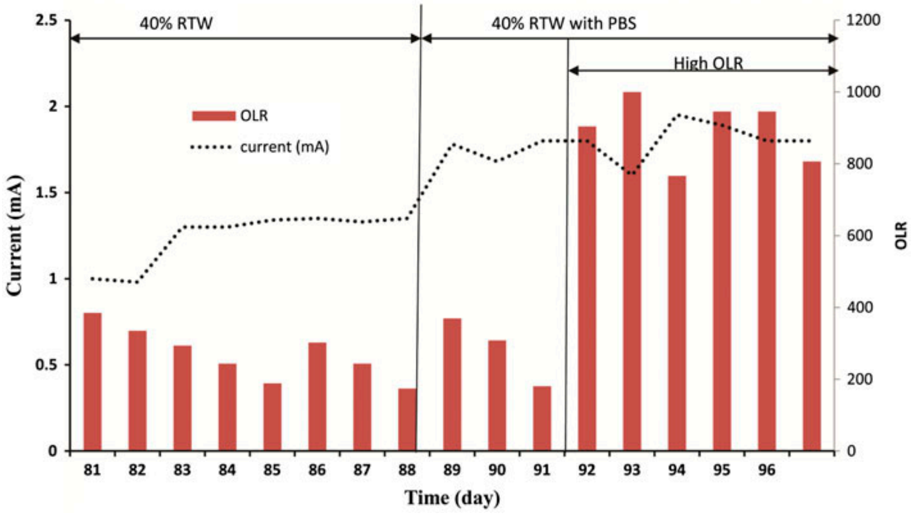

Fig. 7. Variation of current (500 Ω) without PBS and with PBS.

as the influencing parameters for stability and performance of MFC. pH is responsible for the microbiological performance in MFC. Therefore, pH can be directly correlated with biological activity, whereas conductivity influenced the conduction of ion in between the chambers. Diffusional resistances acting in MFC causes internal resistance which makes conductivity as most dominating parameter.

3.4.2. Effect of high OLR

OLR was raised from 450 mg COD L^{-1} d^{-1} to 1,000 mg COD L^{-1} d^{-1} by adding glucose in the feed from 92nd to 97th day. Fig. 7 shows the influence of OLR on the current production. Current production was less affected (insignificant change from 1.5 to 1.8 mA) by OLR (Fig. 7) which contradict with previous study shown by Freguia et al. [17] on sequential system. According to Freguia et al. [17], increase in OLR suppress current due to lower anode pH and high substrate concentration which left from anode and entered into cathode. High substrate induces the heterotrophic bacterial growth in the biotic cathode and elevated the mass transfer limitation of oxygen. But in this study current production was less affected because of controlled pH and increased conductivity.

As seen in Fig. 3, COD removal decreases, but color removal increases when compared with low OLR. Color removal increased from 32% to 60% after adding glucose at 40% RTW. As shown in Fig. 5(b), high OLR enhances performance of aerobic degradation. Percent color removal is rised on the ground as more protons and electrons generated by the higher availability of co-substrate in the feed as discussed earlier. Availability of proton and electron rises in the cathodic chamber due to the cross-flow pattern of water. This high availability of proton and electrons are also utilized by the heterotrophic bacteria present in suspended fluid in cathode. This enhance the declorization but do not influence the electrogenic culture present at electrode due to controlled pH and high conductivity which promote fast neutralization of ions. Hence, it can be suggested that in real system, controlling of pH and conductivity are the basic requirement for stable electrochemical performance of CMFC.

3.4.3. Effect of surface area of anode and cathode on voltage generation

OCV of individual MFC was found around 0.3 V. To deduce a correlation between the surface areas of electrodes on voltage generation, OCV was observed with the varying surface areas of the anode and cathode. OCV was observed across one anode electrode connected via a multimeter with two electrodes of cathode to double the area of the cathode. In similar fashion, different combinations i.e. using two, three, and four cathodic electrode against one anode and vice versa were observed. The result indicates that, on doubling, tripling, and quadrupling the area of the cathode, OCV rises to 330, 500, and 620 mV respectively. Similarly, as anode area was increased to two, three, and four times, the cell gave 30, 46, and 50 mV only. On increasing cathode area, voltage output also increased. Increase in OCV can be correlated with the availability of oxygen and other electron acceptors present at cathode. As an area of cathode increases, it provides more opportunity for oxygen to accept electrons. This phenomenon stimulates electron donor to produce more electrons due to increased potential difference, which accelerates H^+ ions and electron production. Therefore, availability of oxygen as an electron acceptor at the cathode can be considered as a necessary and sufficient condition for maximizing power generation. This interpretation patronizes in scale up of the CMFC and also in the enhancement of its performance sustainability.

3.5. Study of ML-CMFC

As described earlier that in CMFC, two MFCs were connected electrically in parallel mode to increase its current generation. Assumption was that CMFC would operate without membrane. This hypothesis was carried out experimentally and found that CMFC could perform well without membrane. The system was operated in membrane-less mode from 98th to the 107th day of the experiment. As per Fig. 3, ML-CMFC gave around 79% COD and 45% color removals. From Fig. 4, without PEM, CMFC generated power density of 750 W m^{-3} that was just doubled when compare to 337 W m^{-3} with membrane. COD removal was down slope from 82 to 79% as seen in Fig. 3 similarly for color also. Fig. 6 shows the increment in conductivity in anode and cathode chambers with respect to the previous value. Variation in pH (Fig. 6) was as before which shows its biological steadiness due to the addition of buffer. The individual effects of R1, R2, R3, and R4 shown in Fig. 5(a) indicate a decrease in COD removal in R1 and R3. In CMFC, protons are conducted toward the cathode through PEM and with continuously flowing water. While in ML-CMFC, those are through flowing water only from anode to cathode, which decreases the polarization acting across membrane. In CMFC, internal resistance of membrane is also included, while in ML-CMFC it is not. This phenomenon induced

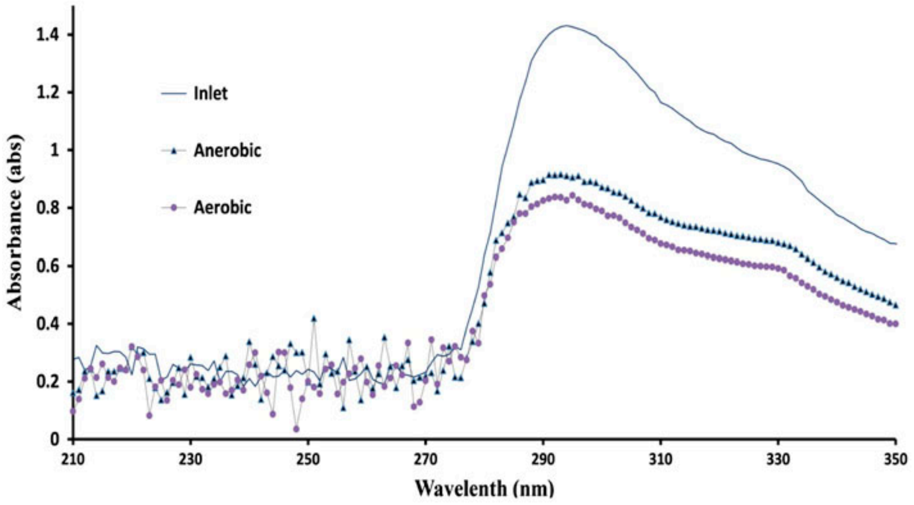

Fig. 8. UV–vis spectra of influent, effluent of anodic chamber and effluent of cathodic chamber.

Table 3
UV spectra of feed, anaerobically treated effluent and aerobic process treated effluent

Feed		Anaerobic		Aerobic	
nm	abs	nm	abs	nm	abs
294	1.43	292	0.91	295	0.84
265	0.26	274	0.32	292	0.83
260	0.25	270	0.21	275	0.32
255	0.23	267	0.27	271	0.34
254	0.24	263	0.35	266	0.22
250	0.24	261	0.17	263	0.18
246	0.24	257	0.34	258	0.24
243	0.23	254	0.28	254	0.25
233	0.23	248	0.3	251	0.18
231	0.25	244	0.28	246	0.3
228	0.24	240	0.33	241	0.3
222	0.31	235	0.24	238	0.2
217	0.30	231	0.21	235	0.19
215	0.29	228	0.24	228	0.18
210	0.27	221	0.29	225	0.2
203	0.43	212	0.23	220	0.32
–	–	207	0.15	215	0.26
–	–	202	0.36	208	0.13
–	–	–	–	202	0.3

increment in potential difference in ML-CMFC. Ion flow got unidirectional that also gain stability to ML-CMFC in terms of color and COD removals with minor fluctuations as seen in Fig. 3. Fangzhou et al. [45] also operated a continuous flow membrane-less MFC in a double chamber, got only 24.33 mW m^{-3} with synthetic wastewater. Liu and Logan [46] had tested power generation in an air-cathode single chamber MFC containing carbon electrode (batch mode) in the presence and absence of a polymeric PEM. They found decrement in power generation without PEM due to reverse diffusion of oxygen which induces the loss of substrate due to aerobic oxidation by bacteria in the anode chamber. Effect of reverse diffusion of oxygen was not dominating in ML-CMFC because of continuous flowing of wastewater from anode to cathode and its hydrodynamic design.

3.6. Degradation of dyes

In MFC toxic dyes (azo dyes) were degraded by anaerobic micro-organisms at bio-anode and produced some more toxic intermediate like aromatic amine [47]. These intermediates can be further converted to non-toxic compound by aerobic treatment passing through aerobic environment in bio-cathode. UV–vis analysis (Fig. 8) was carried out for the influents and effluents of anaerobic and aerobic treatment given in R1 and R2 reactors reflects this phenomenon. It was verified by the new peaks generated in the sample analysis as given in Table 3. Fig. 8 shows blue shift and decrement in intensity of effluent in comparison of influent. Since, azo-dye degradation leads to decolorization and generation of aromatic amines. Table 4 shows spectral region of some aromatic amines produced by textile industry. Peaks in Table 3 were compared and found in agreement with standard peaks ranges of some aromatic amines tabulated in Table 4. These new peaks developed by aromatic amines either get abolish or less intense after aerobic degradation (Fig. 8). Further study is needed for evaluation of system efficiency for the removal of aromatic amine at different HRT.

Table 4
Main spectral region of absorbance in UV range for some aromatic amine consist with observed wavelength in experiment

Aromatic amines	Main absorbance regions (nm)			References
Aniline derivatives				
Anilinium ion	196–206	239–260	–	[48]
m-Phenylenediamine	211	238	289	[48]
o-Phenylenediamine	210	239	295	[48]
p-nitroaniline	229	297–310	373	[48]
Sulfanilic acid	191	215	258–269	[48]
Metanilic acid	235	260–270	290	[49]
2,4-Diaminophenol	207	301	–	[48]
2,4-Diaminophenol anion	213	244	315	[48]
2,6-Diaminophenol	213	280	–	[48]
2,6-Diaminophenol anion anion	220	291	–	[48]
2-Aminoresorcinol	205	234	271	[48]
p-Chloroaniline	242	295		[49]
2,3-Dichloroaniline	236	292		[50]
m-Methylaniline	234	284		[50]
m-Trifluoromethylaniline	235	290		[50]

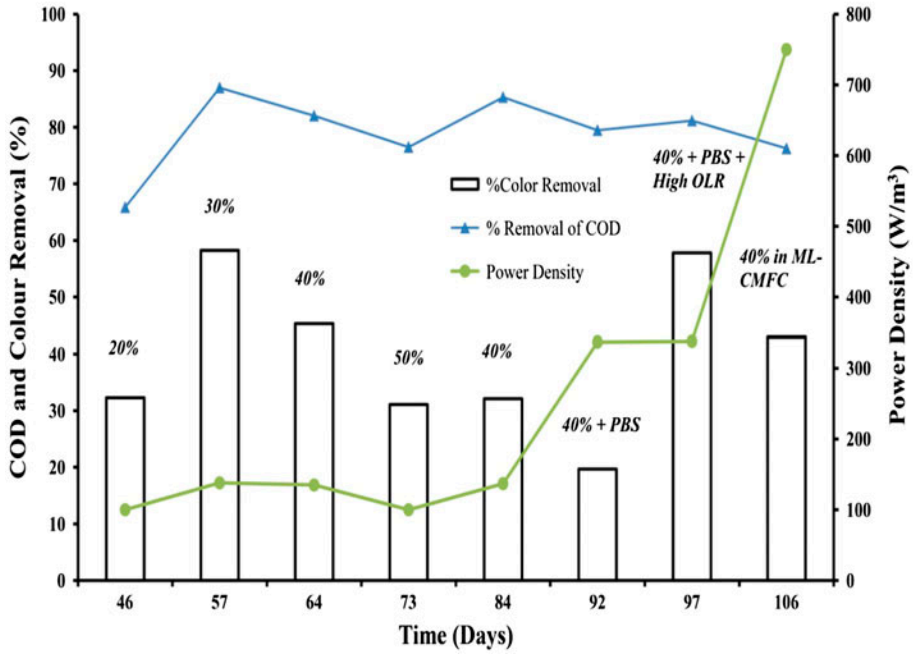

Fig. 9. Performance variation of COD, color, and power density at different cycle.

3.7. Discussion and concluding remarks

A novel CMFC was found effective for the treatment of RTW by utilizing domestic wastewater as a co-substrate. The dynamic nature of domestic wastewater satisfies the key requirements for the biological degradation of textile wastewater with reduction in treatment cost. Performance of CMFC depends on the microbial activity which can be affected due to change in pH, accumulation of toxic substances (dyes/aromatic amines), and conductivity; therefore, their effects were evaluated on CMFC. Totally eight variations were tested in CMFC, in which seven in feed (20 to 50% with OLR) and one on reactor configuration (ML-CMFC). For the appropriate evaluation of the

CMFC every variation was taken as a cycle. Fig. 9 shows the best obtain percentage COD and color removals for every cycle on particular day with maximum power density. Average values of percentage COD and color removals rendered by both pairs were considered. On comparing performance of first four cycles, 30% RTW might be taken as optimum blending percentage. But, 40% RTW (3rd cycle) was chosen for maximizing the treatment volume. Performance of 3rd cycle was also found reproducible on comparing performance with 5th cycle. To minimize the effects of varying conductivity and pH on microbial consortia present in CMFC, PBS was added after 5th cycle. Sixth cycle reveals that controlling pH gave effective enhancement in power density. CMFC provides COD (82%), color (60%) removals, and power density (337 W m^{-3}) with specified range of pH and OLR due to proper microbial activity and increased conductivities. By observing whole scenario, the best performance was given by 8th cycle. ML-CMFC provides COD and color removals of 79 and 45%, respectively, with power density of 750 W m^{-3}. ML-CMFC is cost effective because it performs without PEM which is considered very costly. Internal resistances and reverse diffusion of oxygen were reduced due to the hydrodynamic flow arrangement in the system. It is also clear from Fig. 9 that for the long run, CMFC seems efficient and was able to give better performance with fluctuating loads. For future studies, these fluctuations should be controlled for better performance. Toxicity is an important criterion which affects the performance, therefore, need to be studied in detail. For scale up, increment in cathode area should also be considered.

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