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Effect of organic loading rate on electricity generating potential of upflow anaerobic microbial fuel cell treating surgical cotton industry wastewater

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ABSTRACT

In this study, the performance of continuous fed upflow anaerobic microbial fuel cell operated with surgical cotton industry wastewater was investigated at different Organic Loading Rate (OLR). The potency of power generation, COD and TSS removal efficiency was determined. The highest TCOD and SCOD removal of 78.8% and 69%, respectively was accomplished at an optimum OLR of 1.9 gCOD/L d. A 62% TSS removal efficiency was obtained, with an initial TSS concentration of wastewater as 970 ± 70 mg/L. The maximum power density 116.03 mW/m^2 (2.2 W/m^3) and corresponding coulombic efficiency of 17.8% was achieved at the OLR of 1.9 gCOD/L/d while treating surgical cotton industry waste water.

1. Introduction

Industrial wastewater treatment has attained a lot of worldwide importance due to various environmental issues associated with wastewater discharge. Ecosystem degradation and pollutant induced health effects have necessitated the development of numerous advanced treatment technologies. However, irrespective of the performance of the process, their wide spread application is limited due to high energy demands, and other factors like chemical consumption and post treatment complications. Henceforth, the development of a self-sustaining wastewater treatment process is the need of the hour [1]. Microbial Fuel Cell (MFC) is one of the reviving methodology for reducing this energy demand and is gaining more importance in recent times for the production of valuable energy and other byproducts such as Hydrogen from various wastewaters. Microbial fuel cell or biological fuel cell is a bio-electrochemical system in which chemical energy is converted into electrical energy by the catalytic reaction of micro-organism [2]. Different reactor configuration of MFC like single chambered air cathode, dual chambered, upflow MFC and stacked MFC (series or parallel) are used in the treatment of wastewater. In dual chamber MFC configuration, the anode and cathode chambers are separated by proton exchange membrane (PEM). Anode chamber constitutes the inoculum (microorganism) and the wastewater (substrate). Microbial degradation of substrates liberates electrons and protons, of which electrons are transferred from the anode chamber to the cathode chamber through external circuit for the electricity production [3,4]. At the cathode, the electrons combine with protons diffusing from the anode compartment through the PEM and with oxygen from air otons to form water. MFC performance is influenced by four processes namely microbial catabolism, electron transfer from the microbes to the anode, reduction of the electron acceptors at the cathode and proton transfer from the anode to the cathode [5].

Surgical cotton is also known as the absorbent cotton which is used mainly for medical purposes in the form of bandage. Demand of surgical cotton increases due to increase in number of hospitals, dispensaries, health centers and clinics.

Around 1.3 MLD of wastewater are generated from various surgical cotton manufacturing industries. Manufacturing of surgical cotton involves various processes such as cleaning of raw cotton, bleaching, removal of chemicals, drying, lapping and carding. A large fraction of process water is released during cleaning and bleaching process while cleaning and bleaching of surgical cotton. The surgical cotton industry effluent is highly alkaline due to the presence of detergents and soda. The microbial biomass would be limited in the wastewater due to its high

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alkalinity. However, in the present study the pH of the effluent was neutralized before being introduced into the anode chamber. Moreover, the inoculum in the anode chamber will utilise the neutralized surgical effluent as substrate for power production. No study has been reported so far on the use of surgical industry effluent as substrate in MFC. Moreover, the surgical industry effluent is organically rich (COD 4500 mg/L) to be utilized as a substrate for energy generation in MFC. Though the surgical cotton wastewater was alkaline in nature, its pH was adjusted to neutral (pH – 7) before introducing into the anode chamber of the upflow MFC. Henceforth the pH of the surgical cotton wastewater might not have affected the bacterial species in the inoculum, biofilm formation ability and subsequent power production. The surgical cotton industry is one among the major polluting industry in India and has been categorized under red category [6]. The surgical cotton industry (Ramaraju surgical cotton) from where the waste water was collected has a well established treatment plant comprising of extended aeration process and flocculation unit to meet out wastewater discharge limit of COD less than 250 mg/L [6]. However the treatment process sufferes from sludge disposal problems. Henceforth an alternative technology with potential to treat wastewater with minimum sludge production is required. [7]. MFC can be used as an alternative to above mentioned treatments process as it is known for less sludge production, electricity generation and wastewater treatment [8] .To the best of our knowledge, treatment of surgical cotton wastewater using MFC have not been documented in the literature. The study aims to analyze the effect of organic loading rate (OLR) on power generation and COD removal efficiency of the microbial fuel cell in the treatment of surgical cotton industry wastewater.

2. Materials and methods

2.1. Wastewater sampling and characterization

The surgical cotton wastewater was collected from the Ramaraju Surgical Cotton Pvt Ltd. located in Rajapalayam, Virudhunagar district, Tamilnadu, India. The collected sample was stored at 4 °C till further analysis. The initial characteristics of surgical cotton wastewater such as Total Solid (TS), Total Suspended Solid (TSS), Total Dissolved Solids (TDS), Total Chemical Oxygen Demand (TCOD), Soluble Chemical Oxygen Demand (SCOD) were analyzed as detailed in APHA [9]. Table 1 summarizes the physico – chemical chareacterization of surgical cotton wastewater.

2.2. Microbial fuel cell

The upflow anaerobic MFC has following advantages a) Pt catalyst employed in conventional MFC is replaced with proton exchange membrane (Nafion) in upflow MFC. Hence the cost factor is minimized. b) Since the anode chamber is placed below the cathode chamber, the oxygen diffusion into the chamber is minimized. c) It do not require external mixing as a hydraulic mixing pattern is followed with the influent entry at the bottom of the anode chamber and outlet discharge at the top of the anode chamber. This facilitates continuous mixing throughout the chamber.

The upflow anaerobic microbial fuel cell consists of an anode and cathode chamber separated by a proton exchange membrane (Nafion 117 – per fluorinated membrane: 10*10 cm, Sigma Aldrich). The reactor was made of Plexiglas material having dimensions of 11.5 cm (H), 7 cm (dia). The working volume of each chamber was 500 mL. The anode chamber comprises of ports: inlet port, outlet port for samples and a port for insulated copper wire point input. Cathode chamber consists of ports for aeration and wire point. Activated carbon fibre felt each of dimensions 16 cm × 6.5 cm (Fig. 1) were used as the electrodes in the anode and cathode chamber. The interconnecting flange sealed with a gasket holds the proton exchange membrane of thickness, density and conductivity of 0.1833 mm, 2.0 g/cm^3 and 0.083 S/cm, respectively.

Table 1
Initial characteristics of surgical cotton industry wastewater (triplicate measurements).

S. No	PARAMETER	VALUES
1.	pH	13.56
2.	Total Solids (mg/L)	5990 ± 170
3.	Total Dissolved Solids (mg/L)	5020 ± 120
4.	Total Suspended Solids (mg/L)	970 ± 70
5.	Chemical Oxygen Demand (mg/L)	4500 ± 200
6.	Biochemical Oxygen Demand (mg/L)	1020 ± 150
7.	Chloride (mg/L)	450 ± 50
8.	Total Alkalinity (mg/L)	3390 ± 100

2.3. MFC operation

Waste activated sludge (WAS) from municipal wastewater treatment plant was used as inoculum in anode compartment chamber fed with surgical cotton wastewater. The surgical cotton wastewater was continuously fed to the anode chamber using peristaltic pump and maintained under anaerobic condition. Phosphate buffer was used as substrate in cathode chamber. The MFC was run continuously at an open circuit condition for a period of 1 month to acclimatization the inoculum. Concerned with the acclimatization of the inoculum to the wastewater, normally they are able to utilise substrate for current generation within 24–72 h. Though the inoculum was acclimatised with the surgical cotton wastewater (pH adjusted to 7) for more than 1 week, it resulted in only 46 mV and in spite of employing activated carbon fibre felt (ACFF) as electrode. ACFF is well known for its highly porous nature which favours biofilm formation. Therefore the caustic soda, soda ash and detergents in the surgical cotton wastewater must have contributed for longer duration of acclimatization of the microbial consortium to the wastewater. The reactor was operated at different Organic Loading Rate (OLR) 0.7, 0.9, 1.2, 1.9, 2.7 and 3.8 gCOD/L d by adjusting the flow rate from 0.33 to 1.66 mL/min. For every OLR maintained in MFC, the performance was assessed through power generation, COD removal efficiency (SCOD, TCOD) and solids removal efficiency. The pH of the wastewater in MFC were periodically assessed and maintained at pH 7.

2.4. Electrochemical measurement

At each OLR, voltage produced by MFC is measured using digital multimeter and current generation was calculated as per Eq. (1):

$$3\ I = V/R, \quad (1)$$

where i = Current (A), V = Voltage (V) and R = Resistance (Ω). Resistance was calculated using Ohms Law. Power density (mW/m^2) and current density (mA/m^2) were calculated based on the anode surface area.

$$CE = 8\ I/(F\ q\ \Delta\ COD) \quad (2)$$

Where 8 is a constant, I = Current (A), F = Faraday number (C/mol), q = Influent wastewater (m^3/s), Δ COD = COD removal (g/L). By using the formula stated by [10], the coulombic efficiency (CE) of the continuous mode MFC was calculated. The polarization curve was obtained by varying the circuit external resistance for every OLR, when the performance of MFC came to a steady stage.

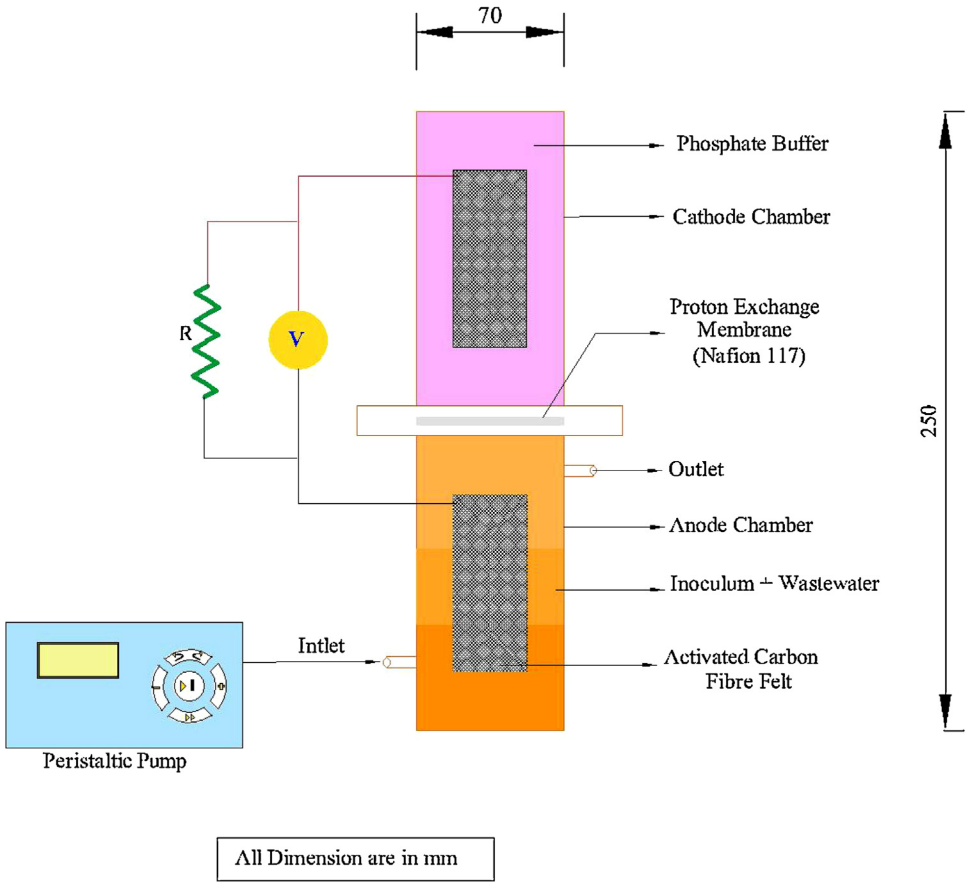

Fig. 1. Schematic diagram of Up-flow Dual Chamber MFC.

4. Results and discussion

4.1. COD removal efficiency at different OLR

The influent TCOD and SCOD in the Surgical cotton industry wastewater was found to be in the range of 800 ± 50 mg/L and 600 ± 50 mg/L, respectively. The TCOD and SCOD removal efficiency of continuous upflow MFC was evaluated by varying the OLR in the range of 0.7 gCOD/L d to 3.8 gCOD/L d. Fig. 2a depicts the TCOD removal efficiency at different OLR. From the figure, it was clearly evident that the TCOD removal increased with increasing OLR showing a maximum removal efficiency of 78.8% at 1.9 gCOD/L d. This clearly demonstrates the role of two factors during the TCOD removal from the surgical cotton industry wastewater, optimum time and OLR required by the microorganism for the effective utilization of the substrate. Increase of OLR beyond 1.9 gCOD/L d, the TCOD removal efficiency gradually declined. At OLR 2.7 gCOD/L d and 3.8 gCOD/L d the removal efficiency dropped to 63% and 50.9%, respectively. At higher OLR, the reduction in COD removal efficiency can be attributed to the methanogenic organism. He et al. [11] has reported that excess of substrate provides a niche for methanogens and methanogenesis must be anticipated whenever substrate loading rate is higher than the maximum electron transfer rate of the MFC.

The SCOD removal showed similar trend at varying OLR. A maximum SCOD removal efficiency of 69% was recorded at the OLR of 1.9 gCOD/L d. SCOD removal efficiency varied in the range of 53–65% at OLR of 0.7–1.2 gCOD/L d. A further increase in OLR above 1.9 gCOD/L d, resulted in decline of COD removal. The SCOD removal dropped to 42% at the highest OLR of 3.8 gCOD/L d. The maximum TCOD and SCOD removal was contributed by the electrogenic bacteria and non electrogenic microorganisms including the methanogens in the anode chamber [10]. Since BES was added to the anode chamber along with the substrate there might be predominant role of electrogenic microorganism in the COD removal [11], who in his study reported that excess of substrate provides a niche for methanogens and methanogenesis must be anticipated whenever substrate loading rate is higher than the maximum electron transfer rate of the MFC. The high COD removal might also be attributed to the adsorption of organics and extensive biofilm development on the surface of the activated carbon fibre felt (ACFF) electrode. High specific surface area and large number of micropores in ACFF contributes to the higher adsorption of organic compounds and are widely employed in wastewater treatment [12]. MFC studies differs in the aspect of nature of the wastewater, source of the inoculums, MFC configurations, flowrate of the wastewater in the MFC, electrode characteristics and surface area and presence of membrane which makes them difficult for comparision. Table 2 enlists the COD removal efficiency of MFC treating various wastewater. In terms of COD removal, the maximum efficiency was observed for surgical cotton industry wastewater (78.8%) when compared with retting wastewater using upflow MFC [13].

4.2. Effect of OLR on the power production

In acclimatization phase, the upflow anaerobic microbial fuel cell reactor treating surgical cotton industry wastewater was kept in open circuit mode and the open circuit voltage (OCV) of 100 mV was recorded after 15 days. The open circuit operation mode was

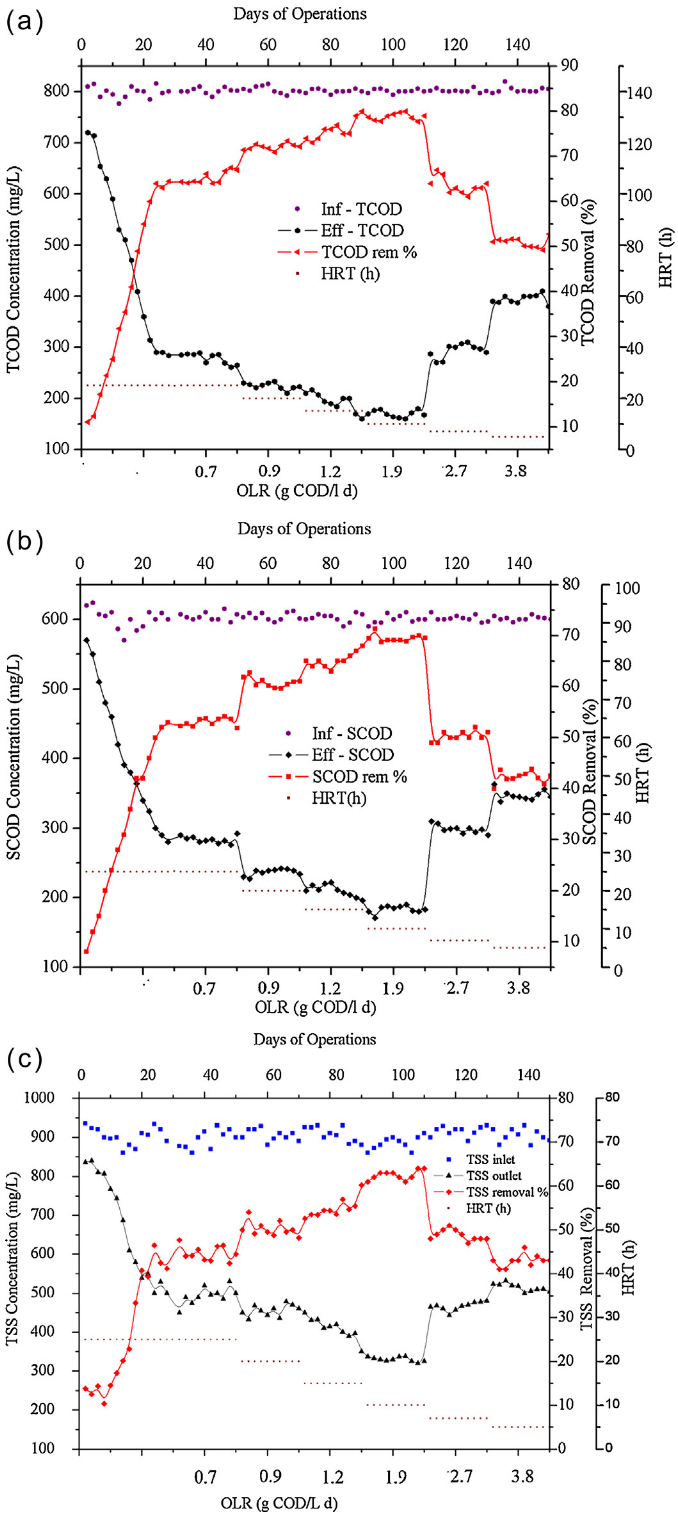

Fig. 2. a) Caoncentration of TCOD and its Removal rate in Wastewater by the MFC as a function of OLR. b) Cboncentration of SCOD and its Removal rate in Wastewater by the MFC as a function of OLR. c) Cconcentration of TSS and its Removal rate in Wastewater by the MFC as a function of OLR.

maintained for 30 days since the micro organism in the inoculums required more duration to stabilize, due to the high alkaline nature of the surgical cotton industry wastewater. Subsequently the circuit was closed and the wastewater was supplied at different OLR in the upflow MFC. Fig. 3a and b depicts the polarization curve obtained during the treatment of the surgical cotton industry wastewater employing upflow MFC. The polarization curve was derived by Based on studies of [4], the range of external resistance 16,000 Ω–100 Ω was chosen and established in polarization curves. After removing the external load, rapid stabilization was observed at higher resistances, unlike lower resistance where stabilization was slow, typical behavior of fuel cell. A maximum power density of 49 and 55 mWm^{-2} was observed for lower and higher resistances. At lower resistances, irrespective of the OLR, the voltage sharply declined initially due to the slow redox reactions at the anode surface. The gradual decrease associated with increasing current densities is due to the ohmic losses caused by ionic resistances of all electric circuit elements [14].

The loading rate of the wastewater plays a crucial role in power production of the MFC [9]. The voltage production of MFC at OLR of 0.7 gCOD/L d was recorded as 457 mV, with power density of 42 mW/m^2 (1.0 W/m^3). A subsequence increase in OLR to 0.9 gCOD/L d and 1.2 gCOD/L d increased the power density and was observed to be 60 and 80 mW/m^2 (1.1 and 1.4 W/m^3), respectively. The voltage and power density continued to increase until the OLR of 1.9 gCOD/L d. Effective utilization of the wastewater by the inoculm could be the possible reason for increased power density with varying OLR. The maximum power density of 116.03 mW/m^2 (2.2 W/m^3) and the corresponding voltage of 590 mV was procured at the OLR of 1.9 gCOD/L d and (external resistance of 300 Ω). The OLR of 1.9 gCOD/L d also recorded the maximum current density of 196.67 mA/m^2. In coherence, highest COD removal obtained at this particular OLR clearly states the rationale for the higher voltage and power generation. At higher OLR of 2.7 gCOD/L d and 3.8 gCOD/L d, the power density of the MFC dropped to 92 mW/m^2 and 60 mW/m^2 (1.7 and 1.1 W/m^3).

The decrease in power density can be associated to the availability of minimum contact time for the degradation of organic substance at higher OLR rate and for saturation microbial activity, which in turn reduces the voltage and power production of the MFC. Pertaining to MFC applications in wastewater treatment, it is mandatory to reduce this internal resistance to derive maximum power production from the system. The internal resistance of MFC is determined by various factors like the reactor configuration, type of electrode material, distance between anode and cathode electrode, and loading rate of wastewater applied to the MFC [15]. Nafion also contributes significantly for the electrolyte resistance [16]. In the present study, the internal resistance was 350 Ω at the OLR of 1.9 gCOD/L d, which recorded the maximum power density of 116.03 mW/m^2 (2.2 W/m^3). To achieve higher power density, the reactor configuration should be minimized, to have lesser ohmic losses [17].

4.3. Coulombic efficiency

The coulombic efficiency was found to be higher at lower OLR and it decreased gradually with subsequent increase in OLR. The maximum coulombic efficiency of 32% was obtained at the OLR of 0.7 gCOD/L d (Fig. 4). At low OLR, utilization of substrate for methane production was reduced, hence couloumbic efficiency increased [18]. The coulombic efficiency dropped to 17.8% at OLR 1.9 gCOD/L d, which achieved highest power density. There was decrease in coulombic efficiency of the upflow MFC due to the competition that takes place between electrogenic bacteria and other bacteria which was induced by high saturation condition in anode surface [19–21]. Minimum coulombic efficiency was achieved at the OLR of 2.7 gCOD/L d and 3.6 gCOD/L d, with the value recorded as 13.13% and 8.7%, respectively. When wastewater strength increased from 84 to 1600 mg/L, CE decreased from 27% to 10% [1].

Table 2
Comparison of COD removal with various wastewater.

S. No	Type of Reactor	Type of Wastewater	Maximum COD removal efficiency	Reference
1	Dual chamber MFC	Dye industry wastewater	84%	[22]
2	Upflow continuous MFC	Retting wastewater	70%	[13]
3	Dual chamber with Flat plate MFC	Domestic wastewater	79%	[4]
4	Upflow continuous MFC	Dairy waste activated sludge	54%	[23]
5	Upflow continuous MFC	Seafood processing wastewater	83%	[24]
6	Upflow Anaerobic Microbial Fuel Cell	Surgical cotton industry wastewater	78.8%	This study

4.4. Effect of total suspended solids (TSS) at various OLR

Initially, TSS in the surgical cotton wastewater varied in the range of 970 ± 70 mg/L. The variation of TSS concentration and its removal efficiency with respect to different OLR was shown in Fig. 2c. It was observed that there was a gradual increase in the TSS removal efficiency and the maximum removal efficiency was obtained at the OLR of 1.9 gCOD/L d, achieving about 62% reduction. When the loading rate was further increased beyond the OLR of 1.9 gCOD/L d, TSS removal efficiency decreased to 49% and 43% at the OLR of 2.7 gCOD/L d and 3.6 gCOD/L d, resectively, due to longitudinal section of the upflow MFC. At higher OLR and HRT, accumulation of intermediate product formed from the fermentable organic matters present in the wastewater decreased the removal efficiency by inducing toxic effect in micro-organism [12]. This led to reduction in biomass which leads to increase in the effluent TSS concentration. At the optimum OLR of 1.9 gCOD/L d, the effluent TSS concentration was minimum. From this it can concluded there was no loss of biomass resulting in maximum removal efficiency.

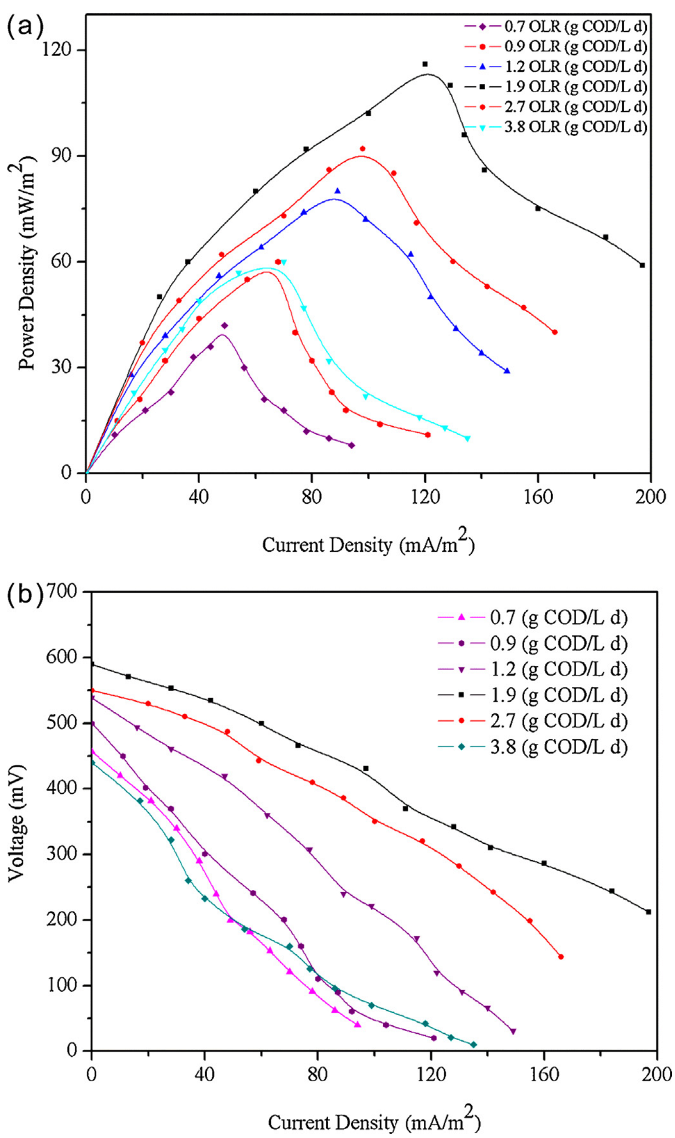

Fig. 3. a) Paolarization curve (power density vs current density). b) Pbolarization curve (Voltage vs Current Density).

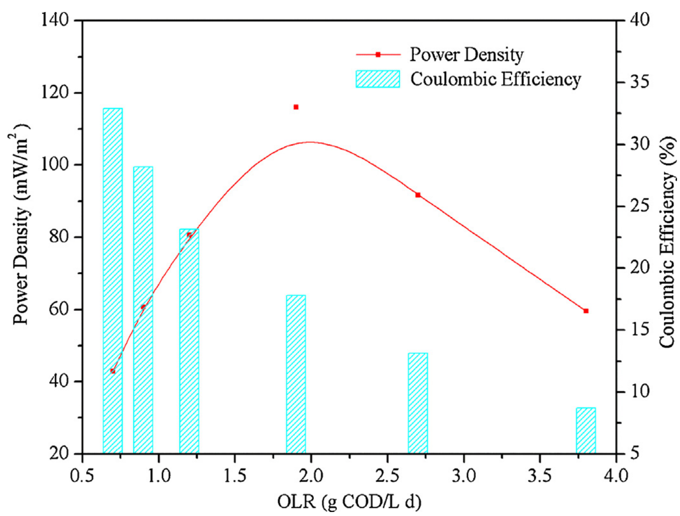

Fig. 4. The Effect of Power density and Coulombic Efficiency in Various OLR.

5. Conclusion

The present study explains that upflow MFC operated in continuous mode with the surgical cotton industry waste water proved to be efficient for generating electricity. The continuous upflow anaerobic MFC achieved maximum efficiency at OLR 1.9 gCOD/L d where the highest power density of 116.03 mW/m^2 (2.2 W/m^3) and maximum TCOD, SCOD and TSS removal of 78.8%, 69% and 62% was observed. Hence, it is concluded that MFC could be feasible option as a primary treatment method to treat and generate electricity from surgical cotton industry wastewater.

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