Advances in wastewater treatment by combined microbial fuel cell-membrane bioreactor

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Abstract
A combined approach of treating domestic wastewater using microbial fuel cell (MFC) and membrane bioreactor (MBR) has been developed as a promising and reliable technology of wastewater treatment. Treatment of wastewater in a single stage MFC has limitation to achieve the required treatment efficiency and utilize the effluent for irrigation or any other possible reuse without further treatment. Therefore, a two-stage continuous process was developed for treating medium strength industrial wastewater combining MFC and submerged MBR, resulting recovery of high quality effluent through ultrafiltration membrane.

Synthetic wastewater with sucrose as carbon source, having total chemical oxygen demand (COD) of 3 g/L, was introduced in anodic chamber of MFC in continuous mode at a constant organic loading rate of 1.5 kg COD/m^3.day during the experimental period. MFC was operated with hydraulic retention time (HRT) of 2 days and effluent was continuously collected in aerobic MBR, operated with 10 h of HRT. Submerged hollow-fibre membrane assembly was attached to draw permeate from MBR.

In the first stage, MFC generated effluent with reduced total and soluble COD of 0.76 ± 0.07 g/L and 0.370 ± 0.012 g/L. The electrical behaviour of MFC was studied by polarization curve resulting in maximum volumetric power density of 1.021 W/m^3. The MFC effluent was further treated in MBR which demonstrated 93.70 ± 0.28 % and 76.86 ± 2.78 % of soluble COD and nitrogen removal efficiency, respectively. MBR effluent, after passing through ultrafiltration membrane, produced permeate with total COD and TSS concentration as 0.05 ± 0.01 g/L and less than 0.005 g/L, respectively. Hence, the study revealed a two-stage reliable process of organic wastewater treatment using MFC–MBR technology, overall achieving more than 98% removal of total COD and almost complete removal of suspended solids. The combined process effectively generated high – quality recyclable effluent and bio-electricity for onsite application.

Keywords: Bio-electricity; COD removal; membrane bioreactor; microbial fuel cell; permeate; wastewater treatment

INTRODUCTION

Conventional aerobic wastewater treatment processes are energy intensive and require high capital investment, operation and maintenance cost, costs for excess sludge handling and disposal, and skilled manpower. However, these processes are useful to reduce oxygen consuming organic matter and nutrients, achieving high rate treatment and better quality effluent. Anaerobic processes of wastewater treatment are low-grade energy consuming, rather producing useful form of energy and can offer a sustainable solution, except for requirement of post-treatment for safe effluent disposal (Grady et al., 1999; Oh & Logan 2005). Hence, to achieve high treatment efficiency, it is essential to develop the right combination and sequence of appropriate and advanced biological wastewater treatment processes. The organic matter present in the wastewater could itself be considered as an energy source and by selecting proper technology this energy present in the wastewater can be harvested (Oh et al., 2010). Microbial fuel cell (MFC) is a bioelectrochemical device that allows electrochemical energy production by breaking chemical bonds of organic compounds into electrical energy through catalytic reactions of microorganisms under anaerobic conditions. MFC comprises anode, covered with electrophilic bio-film that can typically oxidize organic matter present in wastewater under anoxic condition; the process extends bio-electricity generation combined with simultaneous treatment of wastewater in anodic chamber. Recent advances in MFC research demonstrated enhanced power output by adopting innovative reactor configuration and modified operation regime, making this technology promising for alternative and clean energy production (Martinez-Huitle & Ferro 2006; Zhou et al., 2013).

To achieve practical application and increase acceptance of MFC for wastewater treatment, there are still many biological and engineering aspects to consider and improve. One approach to overcome barriers and optimize unit processes is to combine MFC with membrane technology (Wang et al., 2012; Ma et al., 2015). Membrane bioreactor (MBR) is a suspended growth system where the process of aerobic biodegradation of organic matter present in wastewater is combined with microfiltration (MF) or ultrafiltration (UF). The latter is typically used in lieu of secondary sedimentation tank used in conventional activated sludge process (ASP) (Côté et al., 1997). MBR is widely used for municipal and industrial wastewater treatment with large plant sizes up to 80,000 population equivalent (i.e. 48 million L/ day) (Van Dijk & Roncken 1997; Rosenberger et al., 2002). While treating domestic wastewater, MBR process evidenced better treatment efficiency and it produces high quality effluent that can be discharged to surface or brackish water-stream or can be recycled for urban irrigation. Other advantages of MBR over conventional processes include small footprint achieving effective treatment at higher mixed-liquor suspended solids (MLSS) concentrations compare to conventional ASP, thus reducing the reactor volume to achieve the same loading rate (Yoon et al., 2004). Recent technical innovation and significant reduction of the cost of UF membranes has enabled MBR technology to become an effective and efficient process option over the existing technologies for wastewater treatment, demonstrating the advantages of low-cost operation compare to high process efficiency and widespread versatile application (Zheng et al., 2013; Hasan et al., 2012).

An integration of MFC with conventional ASP was first reported by Cha et al. (2010), where the aeration tank in ASP was used as the bio-cathode chamber for MFC and wastewater after anodic treatment was applied to cathodic chamber of MFC. The aerobic bio-film developed on cathode served as low-cost and self-sustainable bio-catalyst for further degradation of organic matter present in effluent of MFC. The aeration tank was followed by a clarifier to support continuous flow operation and excess sludge was returned in succession. Nevertheless, this setup demands extra cost for the clarifier construction (Min & Angelidaki 2008). However, in MBR, the membrane module is attached along with the aeration tank, either submerged or side-stream membrane module, to improve biomass retention in order to achieve effective treatment of particulate contaminants passed by MFC. Thus combining the MFC with membrane bioreactor technology can further achieve higher and complete removal of organic matter from wastewater (Yuan & He 2015).

Herein, an effort was made by employing a two-stage continuous process of combining MFC with MBR facilitated with submerged UF membrane for an effective and reliable wastewater treatment. The combined treatment process was optimized to attain higher efficiency of organic matter removal from wastewater, having initial chemical oxygen demand of 3 g/L. The wastewater was treated in two stages by introducing first in MFC, having air-breathing cathode configuration. The MFC effluent was treated further in a separate aerobic MBR. The combined system was aimed to produce the final effluent with considerably reduced chemical oxygen demand (COD) and completely devoid of total suspended solids (TSS), along with simultaneous generation bio-electricity during the process.

MATERIALS AND METHODS

Reactor fabrication and operating principle

Ceramic cylinder (working volume 1.5 L) was used as anodic compartment to configure the air-cathode MFC. Untreated carbon felt with projected surface area of (22 cm x 37 cm) 814 cm^2 and (22 cm x 27 cm) 594 cm^2 was used as cathode and anode, respectively. The outer surface of the cylinder was coated with layers of C/TiO_2 suspension (Lu et al., 2009) with a loading of 0.5 mg Vulcan carbon powder XC 72/cm^2 and 0.75 mg of TiO_2 nanoparticles (mixture of Anatase/Rutile)/cm^2 of cathode surface area. A hydrophobic binder polyvinyl alcohol (PVA) of loading 1.5 mg/cm^2 with acetone as mixing solvent was used to make the coating ink. The MFC was kept in an open environment but not under the direct influence of fluorescent light. Synthetic wastewater with sucrose as carbon source was prepared, as per the composition given by Jadhav & Ghangrekar (2009), for treating it in anodic chamber of MFC. Synthetic wastewater was maintained with organic matter concentration of 3 g COD/L with pH adjusted to 7.4 and supplemented with trace nutrients. The MFC was operated with hydraulic retention time (HRT) of 2 days.

The effluent from MFC was continuously collected in aerobic MBR (working volume of 1 L), operated at HRT of 10 h. In MBR, aeration was provided with air flow pump using stone diffusers, placed at the bottom to provide appropriate mixing and to keep the bacterial biomass under homogenous suspension. Hollow-fibre polysulfone made UF membrane (pore size 80 nm, OD 1 mm and ID 0.8 mm) module was submerged inside the MBR and permeate was recovered applying 0.1 bar vacuum suction pressure in a batch process. Around 300 cm^2 membrane area was required of achieve high permeate flux of 38 l/m^2.h. This process was followed to maintain the biomass content inside MBR in a higher range. The membrane was back flushed or cleaned (with 0.5% sodium hypochlorite for 1 h) at regular intervals to reduce the bacterial fouling on the membrane wall.

Electrochemical monitoring and data acquisition

The potential difference and current generated by MFC was measured using a digital multimeter with data acquisition unit (Agilent Technologies, Malaysia). Power was calculated according to the Eq. 1:

$$P = I*V \qquad \text{(Equation 1)}$$

where P, power, W; I, current, A; and V, acquired voltage, V. Anodic potentials was measured using Ag/AgCl reference electrode (CH Instruments, Inc., RE-5B; + 0.197 V vs. a standard hydrogen electrode, SHE). Polarization curve was obtained to determine the maximum generation of power density, normalized to the volume of anodic chamber of MFC, by monitoring the voltage output at various external resistances, ranging from 30,000 Ω to 5 Ω. This study was also followed to obtain the relationship between voltage and current. The whole cell internal resistance of the MFC was measured from slope of the linear portion of polarization plot (voltage vs. current). Coulombic Efficiency (C_E) was calculated by integrating the measured current over time relative to the maximum possible generation of coulombs during experiment based on observed removal of COD (Logan 2008) as per Eq. 2:

$$C_E = \frac{M_s \int_0^t I\,dt}{F b_{es} V_{An} \Delta COD} \qquad \text{(Equation 2)}$$

where, M_s is the molecular weight of substrate (g/mol), ΔCOD is the change in substrate concentration over a batch cycle (g/L), V_{An} is the anodic volume (L), F is Faraday's constant (96485 C/mole$^-$) and b_{es} is the generated electron during each mol of substrate oxidation (mol e$^-$/mol of substrate).

Analytical methods

Total and soluble COD, MLSS, mixed-liquor volatile suspended solids (MLVSS) total Kjeldahl nitrogen (TKN) and alkalinity were determined for the samples collected from MFC and MBR in regular time interval according to the procedure described in Standard Methods for the Examination of Water and Wastewater (APHA 1998). The characteristic contents of permeate (COD, solid analysis and alkalinity) generated through UF membrane facility was also monitored.

RESULTS AND DISCUSSION

Treatment of medium strength organic wastewater in combined MFC-MBR system

Performances of air-cathode MFC. The performance of MFC with TiO_2 modified cathode was tested during the first stage of wastewater treatment. Wastewater with COD concentration of 3 g/L was treated initially in MFC and electrical potentials were monitored. An open circuit potential of 536 ± 25 mV was achieved under steady state operating condition and over 100 Ω of external resistance the working voltage reached upto 260 ± 12 mV. Polarization curve was generated to evaluate the relationship between resistance and current during MFC operation. During polarization, maximum volumetric power density of 1.021 W/m^3 was obtained with much lower whole cell internal resistance of 10 Ω (Figure 1). The COD removal efficiency of 78.4 ± 2.14 % was observed during MFC treatment.

Similar treatment efficiency was also achieved by Lu et al. (2009); however, it was suggested to expose the reactor to irradiation light source (with UV cut-off filter) in order to achieve higher photo-catalysis on the cathodic side and generate power in the higher range. The coulombic efficiency of MFC was calculated as 4.35 % (Eq. 2), similar with the values obtained by More & Ghangrekar (2010), using synthetic wastewater containing sucrose as carbon source. The TiO_2 modified cathode surface was observed to be more resistant of salt deposition and bio-fouling even after eight months of continuous operation.

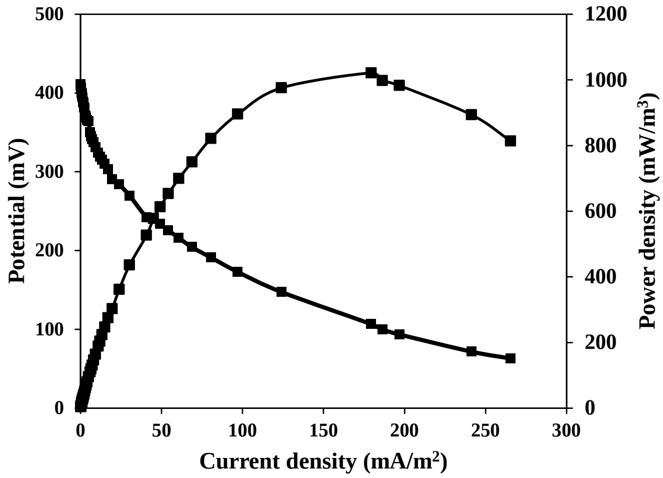

Figure 1. Polarization and power curve of MFC

Treatment of wastewater in MBR: MFC effluent, containing 0.67 ± 0.30 g/L of COD, was continuously fed to MBR, maintained with MLSS concentration within the range of 6 – 8 g/L (MLVSS, 5.37 ± 0.37 g/L). Wastewater in MBR was kept in contact with active biomass in order to achieve further reduction of organic matter by aerobic bacterial metabolism. Calculated amount of sludge has been wasted after accomplishing 10 h treatment cycle in order to maintain constant sludge retention time (SRT) within the reactor (Table 1). The F/M ratio was maintained very low and equal to approximately 0.08 kg COD/kg MLSS.day for MBR operation. Clear permeate was drawn out through UF membrane submerged within the MBR, by applying vacuum suction pressure and maintaining high permeate flux. Compositional characteristics of sample collected from MBR and permeate were evaluated. Soluble COD and TKN removal from MBR was around 93.70 ± 0.28 % and 76.86 ± 2.78 %. Permeate was detected with 0.050 ± 0.010 g/L of total COD and nearly complete removal of TSS (< 0.005 g/L) (Table 2). The physico-chemical characteristics of final effluent generated in this study was similar to a previous study carried out by Su et al. (2013), showing more than 90 % COD and ammonia removal efficiency by combined MFC-MBR process. Hence, the study revealed a two-stage process of MFC–MBR technology for overall 98% removal of organic content in the wastewater. The effluent thus produced can be utilized for agro-irrigation or disposed safely in inland water channels.

Table 1. Characteristics of effluent at different stages of MFC-MBR treatment

Parameters	Response [a]		
	Wastewater (MFC reactor influent)	**MFC reactor effluent**	**MBR effluent**
Total COD	3.02 (0.03)	0.71 (0.04)	0.18 (0.02)
Soluble COD	2.65 (0.02)	0.59 (0.03)	0.16 (0.01)
TKN	0.31 (0.05)	0.147 (0.02)	0.056 (0.02)
TS	3.67 (0.05)	5.09 (0.08)	11.58 (0.56)
TSS	1.99 (0.06)	2.05 (0.03)	7.09 (0.48)

MLVSS	-	0.92 (0.22)	5.89 (0.36)
pH	7.53 (0.14)	7.31 (0.11)	7.3

[a] All units are in g/L, except pH; numbers in the parenthesis are standard deviation

Table 2. Characteristics of permeate generated from MBR

Parameters	Response
DO (mg/L)	0.011
pH	7.3
Cond (µS)	396
TSS (g/L)	4.36
Total COD (g/L)	< 0.005
TDS (ppm)	0.050
TKN (g/L)	221

Analysis of bio-kinetic parameters of MBR

The MBR was maintained with constant volume, MLSS and SRT to minimize sludge production and bio-fouling of ultra-filtration membrane, by wasting calculated amount of biomass-sludge from the reactor. Bio-kinetic coefficients were determined for the wastewater treatment in combined MFC-MBR process (Figure 2). Biomass growth rate was calculated by Monod equation (Eq. 3):

$$\mu = \mu_m \frac{S}{K_s + S} \qquad \text{(Equation 3)}$$

Where, μ_m is the maximum specific growth rate, S is the concentration of growth limiting substrate and K_s is saturation constant. Kinetic parameters were calculated under certain assumptions: the MBR is in completely mixed condition; almost no amount of biomass has been allowed to pass in permeate, although this parameter has been considered during the kinetic analysis; no substrate is rejected other than the calculated amount of wastage; effluent from MFC is assumed to contain constant amount of VSS.

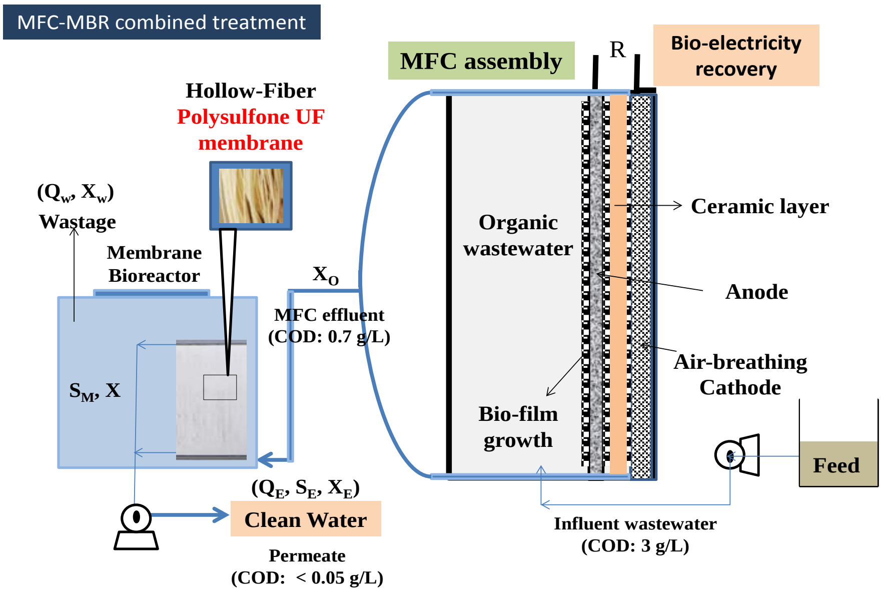

Figure 2. Schematic diagram of MFC-MBR process for evaluation of kinetic parameters

Hence, the rate of change of biomass in MBR can be demonstrated by biomass balance equation (Eq. 4):

$$V.\frac{dX}{dt} = \mu XV - k_d.XV - Q_wX - Q_EX_E \qquad \text{(Equation 4)}$$

where, V, reactor volume; X, biomass concentration within MBR; k_d, endogenous decay coefficient; X_w, biomass concentration in wastage flow (equals to X); Q_w, wastage flow rate; X_E, biomass concentration in permeate and Q_E, permeate flow rate.

At steady state condition, $dX/dt = 0$, Eq. 4 can be deduced as:

$$\mu = k_d + \frac{Q_w}{V} + \frac{Q_E}{V}.\frac{X_E}{X} \qquad \text{(Equation 5)}$$

The SRT can be calculated from the following equation (Eq. 6)

$$SRT\ (\theta_c) = \frac{VX}{Q_wX + Q_EX_E} \qquad \text{(Equation 6)}$$

The SRT was calculated as 15 days, which was much longer than the conventional ASP (Grady et al., 1999). Now, substituting Eq. 6 in Eq. 5,

$$\mu = k_d + \frac{1}{SRT} \qquad \text{(Equation 7)}$$

Thus, the final equation for substrate utilization (Eq. 8) can be demonstrated as following:

$$S = \frac{K_s\left(\frac{1}{SRT} + k_d\right)}{\mu_m - \left(k_d + \frac{1}{SRT}\right)} \qquad \text{(Equation 8)}$$

By using Eq. 8 the endogenous decay constant (k_d) was measured as 0.07 d^{-1}. Similarly, the substrate balance equation can be derived to demonstrate the expression for biomass generation in MBR (Eq. 9):

$$X = \left[\frac{Q(S_0 - S) - S_E.Q_E}{\left(k_d + \frac{1}{SRT}\right)}\right]\frac{Y}{V} \qquad \text{(Equation 9)}$$

The sludge-yield coefficient (Y), calculated as 0.216 kg VSS/kg of COD was in well agreement with the previously reported value by Su et al. (2013).

CONCLUSIONS

The two-stage MFC-MBR system can effectively treat medium strength organic wastewater in terms of COD and TSS removal, producing a high quality effluent. However, the energy demand for this treatment process is considerably high comparing to electrical energy produced MFC. The total COD was reduced from 3 g/L to around 0.05 g/L, resulting around 98% overall COD removal and more than 99% TSS removal. Using air-breathing cathode for MFC reduced additional energy requirement for external aeration to achieve cathodic reduction. The UF membrane fouling was mitigated by intermittent cleaning using chemical and regular back-flushing with air. Additional efforts are required to understand the feasibility of combined MFC-MBR process in terms of electrical energy required/produced and treatment efficiency compare to traditional treatment systems. More optimal treatment would likely to be attained by regulating the HRTs of the two systems and to achieve an economical benefit in terms of power generation the overall HRT should be minimized. Following these sustainability studies, this technology offers immense potential for further full-scale research and development with a scope of its commercial application.

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