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Performance Evaluation of Microbial Fuel Cells for the Treatment of Industrial Wastewater

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Abstract
Wastewater treatment has traditionally been an energy intensive process, consuming between 950 and 2850 kJ/m3 of wastewater treated. By one account, wastewater contains 9.3 times more energy than is used to treat an equivalent volume, thus creating the desire to harness this energy through the use of a Microbial Fuel Cell (MFC). MFCs oxidize organic substrates, allowing simultaneous wastewater treatment and electricity generation. Previous research has primarily focused on the development of MFCs for electricity generation, mainly at the small, laboratory scale. Herein, an industrial-scale MFC process is proposed for the treatment of wastewater from a microbrewery based on a previously published model describing MFC operation. Through optimization and scale-out, a two chamber MFC process is developed for the treatment of wastewater with an inlet Chemical Oxygen Demand (COD).

Keywords: Microbial fuel cell, Series-stacked, Substrate concentration, Voltage reversal.

Introduction

Recently, most of the developing countries are deeply helpless to change in water supply. India is one of such countries facing such problem. The heavy increase in water demand and complex consumption patterns are the reasons for such problem. The water demand is met by transporting water for longer distance. The sustainable management of water is very much required by recycling or reusing the wastewater after proper treatment. The wastewater without treatment is sent back to the eco system which is almost 70 to 80% according to the report from Central Pollution Control Board. The report says that only around 37% of wastewater only is being treated; out of around 60,000 MLD around 22,000 MLD only is treated. Apart from this most of the treatment plants are not meeting the standards specified and they are not running with full capacity of design value. 1.1.2 Comprehensive Environment Pollution Index The concept of Comprehensive Environmental Pollution Index (CEPI) was explored by CPCB during 2009 to 2010. If the score of CEPI exceeds 70, then that particular region is declared as critically polluted area and in the same way, if score is in between 60 to 70, then that area is marked as severely polluted area. One of the main criteria in calculating CEPI score is the water environment. The proper wastewater treatment will lead to make the above index value less and subsequently CEPI demarcation will be lifted by CPCB. Thus the proper wastewater treatment and recycling is much needed in India for industrial and infrastructure development.

On the other side, India's energy sector which directly affects the infrastructure and subsequently the growth of economy. The industrialization, growing population and living standards are proportional to the energy consumption for all developing countries. The report from Central Electricity Authority (CEA)

says that more than 60 percent of energy demand of India is met by coal thermal power plants (Fig 1.1). The depletion of natural resources, pollutants emission and green house emission are the main problems associated with thermal power plants. Thus we are in need of the technology by which the problems of both wastewater treatment and energy demand to be solved.

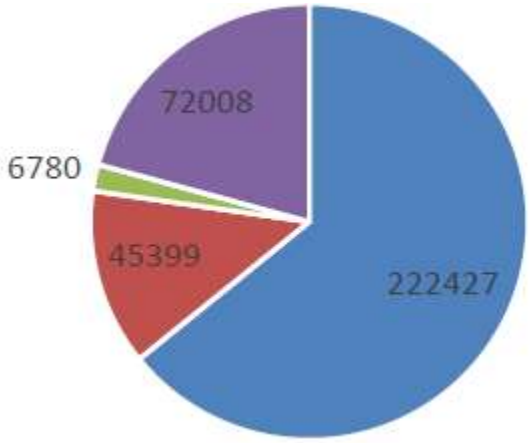

Figure 1: Fuel wise installed capacity (MW)

This section covers the energy scenario and the types of energy production and the challenges involved in the production.

Related Work:

Leather Industry, occupies a distinct place in the world economy, in terms of potential foremployment, growth and exports. Leather processingrequires various chemicals to treat and soften hides.The wastewater is generated from the almost all process of tanning (Ozgunay, 2007). This wastewater contains several contaminants likesulphides, chromium, polyphenolic compounds, dyeand solvent chemicals (Tunay et al., 1995). Even after the metal treatment, the treated water is not meeting the norms with respect to organic parameters (Bartlett and James, 1988). The presence of extremophilic microbial flora in wastewater can survive in the worst level environment of tannery (Aono and Inoue,1998; Horikoshi, 1998). These microorganisms haveability to protect themselves from the toxicity of heavy metals (Megharaj et al., 2003).Despite the high concentrations of Chromium(Cr) in contaminated soils and sediments, the presence of microbial population has been explored (Aono and Inoue, 1998). Microbialfuel cell (MFC) is an emerging technology, whichenjoys the benefit of electricity generation during wastewater treatment by utilizing bacterialmetabolism (Jang et al., 2004; Liu et al., 2004;Logan, 2004; Min et al., 2005; MathuriyaandSharma, 2009; Mathuriya 2014).

A typical MFC has anodic and cathodic section. In the anode compartment, substrate oxidation takes place and it resulted in the release of e- and H+. E-s are transported viaanexternal circuit while the protons pass through via cationexchangemembrane, in whichwater is formed by the combination of electrons with protons(Delaney et al., 1984, ParkandZeikus., 2000). Generally Oxygen is used as an electron acceptors considering its several advantages (Zhao et al., 2006).

Methodology:

Experiments suggest that acetate is oxidized in the anode by the reaction of an eight-electron transfer as described in Eq. (R1). Since the anode chamber operates under anaerobic or anoxic conditions, the acetate

degradation/oxidation can be modelled in a similar manner toADM1, where aMonod-type equation is adopted. In addition, the operating conditions remain nearly unchanged except for variations in the external resistances. Various microbial consortia are thus lumped to a single quantity (biomass). Since (R1) is a bioelectrochemical reaction controlled by the electrical potential in an electrochemical cell, the Butler–Volmer expression is incorporated. Furthermore, since the reverse reaction is insignificant, only the forward reaction is used to formulate the reaction rate (Eq. (1)). It is noted that Eq. (1) is similar to the expression in the literature [14].

$$(CH_2O)_2 + 2H_2O \rightarrow 2CO_2 + 8H^+ + 8e^- \qquad (R1)$$

$$r_1 = k_1^0 \exp\left(\frac{\alpha F}{RT}\eta_a\right)\frac{C_{Ac}}{K_{Ac}+C_{Ac}}X \qquad (1)$$

where: CAc and X are the concentrations of acetate and biomass in the anode compartment, respectively; a is the anodic overpotential; k01 is the rate constant of the anode reaction at standard conditions (maximum specific growth rate); KAc is the half velocity rate constant for acetate; ¸ is the charge transfer coefficient of the anodic reaction, F is the Faraday constant, R is the gas constant, T is the cell operating temperature.

Since MFCs employ a variety of inorganic chemicals to support the microbial metabolism, cations such as K+, Na+, NH4 +, Mg2+, and Ca2+ are dissociated and their concentrations are typically 105 times higher than that of protons at neutral pH. Thus the number of cations transported from the anode to the cathode compartments other than protons are the same as the number of electrons transferred through the circuit [5,17,18]. This indicates that virtually no protons are transported in the MFC, and electro-neutrality is sustained mainly by the transport of cations instead of protons. An analysis [17] of a Nafion 117membrane in a two-compartment MFC shows that K+ andNa+ occupied about 74% of the sulfonate residues. In order to maintain Nafion conductivity in the long run, the Nafion membranewas boiled in 0.1MHCl before use to replace any cations attached to the sulfonate residues with protons. It is believed that the cation occupation is not permanent, but transient. Under these conditions, it is still possible for the cathode reaction to consume protons available from the dissociation of water.

For the sake of simplicity, it is assumed that only univalent cations M+ transport through the membrane and the M+ ions do not involve in the reaction at cathode. Consequently, the reduction of dissolved oxygen in the cathode is suggested as:

$$O_2 + 4e^- + 2H_2O \rightarrow 4OH^- \qquad (R2)$$

It was found that dissolved oxygen exhibits Monod-type behaviour [5] and our preliminary study shows that the reverse reaction of oxygen reduction is negligible. Therefore, the rate of reaction in the cathodic chamber is formulated as Eq. (2). Again, the Butler–Volmer expression is incorporated to describe the electrochemical reaction.

$$r_2 = -k_2^0\frac{C_{O_2}}{K_{O_2}+C_{O_2}}\exp\left[(\beta-1)\frac{F}{RT}\eta_c\right] \qquad (2)$$

where: CO2 is the concentration of dissolved oxygen in the cathode compartment; c is the over potential at the cathode; KO2 is the half velocity rate constant for dissolved oxygen; k0 2 is the rate constant of the

cathode reaction under standard conditions; ˇ is the charge transfer coefficient of the cathodic reaction. Water concentration is assumed constant (excess component in liquid mixture).

Similar to DAAFC modelling [16], it is assumed that both the anode and cathode compartments can be treated as a continuously stirred tank reactor (CSTR). Phase mixture, i.e., all mass-transport processes, is assumed to be so fast compared with the biochemical and redox reactions, such that the concentrations of all reactants in the bulk solution can be regarded to be equal to those on the surface of electrodes. In addition, carbon dioxide and acetate are assumed not to diffuse into the membrane, and the gas-phase formation by release of carbon dioxide bubbles is not taken into account. Consequently, the mass balances of the four components in the anode compartment, namely, acetate, dissolved CO2, hydrogen ion and biomass, are expressed by Eqs. (3)–(6), respectively:

$$V_a \frac{dC_{Ac}}{dt} = Q_a(C_{Ac}^{in} - C_{Ac}) - A_m r_1$$

$$V_a \frac{dC_{CO_2}}{dt} = Q_a(C_{CO_2}^{in} - C_{CO_2}) + 2A_m r_1$$

$$V_a \frac{dC_H}{dt} = Q_a(C_H^{in} - C_H) + 8A_m r_1$$

$$V_a \frac{dX}{dt} = Q_a \frac{(X^{in} - X)}{f_x} + A_m Y_{ac} r_1 - V_a K_{dec} X$$

In the above equations, the subscripts ‘a’ and ‘in’ denote the anode and the feed flow, respectively. V, Q and Am are the volume of the compartment, the feed flow rate, and the cross-section area of membrane, respectively. In Eq. (6), fx represents the reciprocal of the wash-out fraction, Yac the bacterial yield, and Kdec the decay constant for acetate utilisers.

In the cathode compartment, the mass balances of dissolved O2, hydroxyl, and cationM+ are expressed by Eqs. (7)–(9), respectively:

$$V_c \frac{dC_{O_2}}{dt} = Q_c(C_{O_2}^{in} - C_{O_2}) + r_2 A_m$$

$$V_c \frac{dC_{OH}}{dt} = Q_c(C_{OH}^{in} - C_{OH}) - 4r_2 A_m$$

$$V_c \frac{dC_M}{dt} = Q_c(C_M^{in} - C_M) + N_M A_m$$

The subscript ‘c’ denotes the cathode. In Eq. (9), NM is the flux of M+ ions transported from the anode to cathode compartment via the membrane. It is noted that the following relationship is held for the cell current density and the flux of ions via the membrane [24]:

$$i_{cell} = F \sum_i z_i N_i$$

where: zi is the charge number of the ith species; Ni is the superficial flux of the ith species, icell denotes the cell current density. As mentioned previously, onlyM+ ions are assumed to be transported through the membrane, thus the flux of M+ ion (molm−2 h−1) can be calculated as follows, where the coefficient 3600 is the factor of unit conversion.

$$N_M = \frac{3600 i_{cell}}{F}$$

The charge balances at the anode and cathode are given by Eqs. (12) and (13), respectively, where Ca and Cc are the capacitances of the anode and cathode, respectively.

$$C_a \frac{d\eta_a}{dt} = 3600 i_{cell} - 8Fr_1$$

$$C_c \frac{d\eta_c}{dt} = -3600 i_{cell} - 4Fr_2$$

It is assumed that the ohmic drops in the current-collectors and electric connections are negligible, and the cell resistance is solely due to the resistances of the membrane and the solution. Consequently, the cell voltage Ucell is calculated as:

$$U_{cell} = U^0 - \eta_a + \eta_c - \left(\frac{d^m}{k^m} + \frac{d_{cell}}{k^{aq}}\right) i_{cell}$$

where: U0 is the open-circuit voltage; dm and dcell are the thickness of the membrane and the distance of the electrodes, respectively; km and kaq are the conductivities of the membrane and the solution, respectively.

Result and Discussion:

With the parameters listed, the component concentrations and reaction rates are evaluated with respect to the changes in cell current density. As shown in Fig. 4a, the reaction rate of acetate oxidation in the anode chamber ($r1$) and the rate of oxygen reduction ($-r2$) in the cathode chamber are proportional to the cell current density.

The sensitivity of the 6 model parameters is further studied by the local relative sensitivity analysis method [26], to evaluate the ratio of changes in the computed power density to the changes in the parameters. The following equation is used for the 6 model parameters. A dynamic simulation of step change in acetate feed flowrate from 2.2 × 10-5 to 1 × 10-5 (m3 h-1) was conducted to examine the sensitivities of the 6 parameters. The results are shown in Fig. 1, and the order of parameter sensitivity (from the highest to the lowest) is beta > k^1_0 > alpha > K_{Ac} > k^2_0 > K_{O2}. Apparently, the electron transfer coefficient beta is the most sensitive parameter, whereas K_{O2} is the least significant and remains almost unchanged. The parameter sensitivity analysis has shown that the cathodic reaction may be the most significant factor limiting the performance of MFCs. This result agrees with the findings of Zhao et al. [18], who reported that the cathodic reaction often limits the performance of chemical fuel cells, such as polymer electrolyte membrane fuel cells and solid oxide fuels, and MFCs also share this problem. To improve the cathodic reaction, one of the most important issues is to develop efficient cathode materials which is, however, beyond the scope of this study and should be the focus of further investigation.

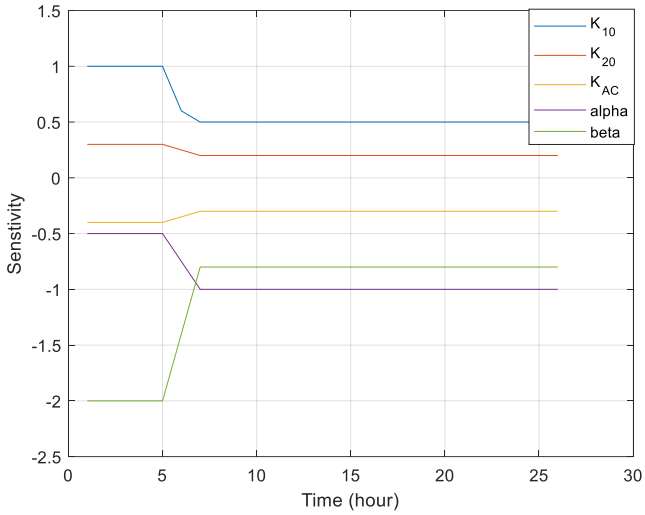

Figure 1: Resultant sensitivities of 6 model parameters of acetate MFC model.

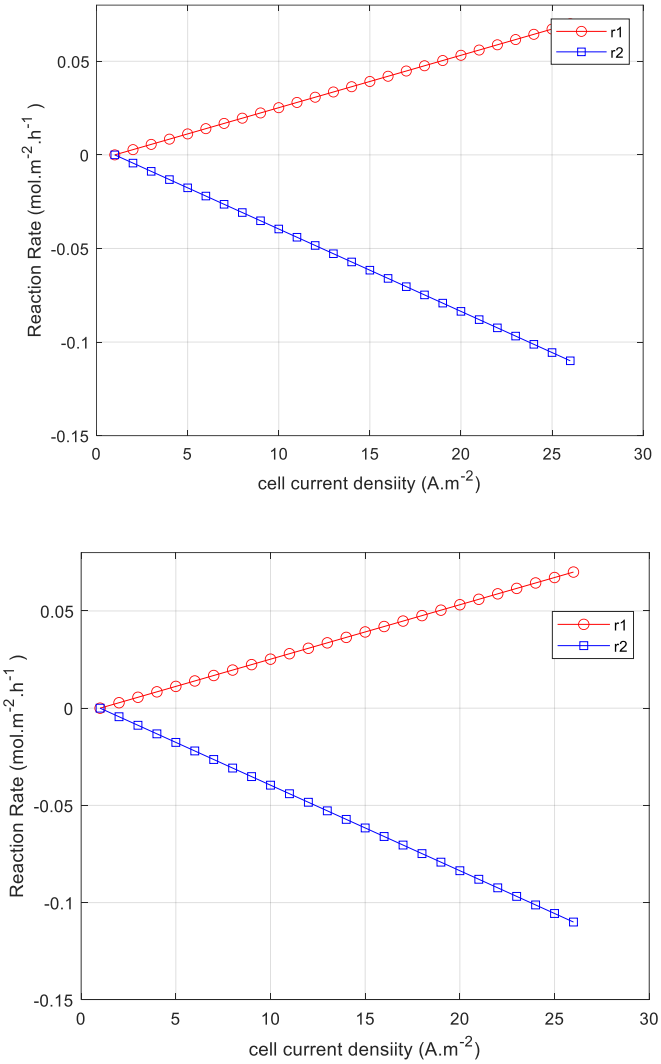

Fig. 2. Results of steady-state simulation of acetate MFC. (a) Reaction rates of acetate oxidation *r*1 and oxygen reduction *r*2.

Steady-state simulation:

With the parameters listed, the component concentrations and reaction rates are evaluated with respect to the changes in cell current density. As shown in Fig. 2, the reaction rate of acetate oxidation in the anode chamber ($r1$) and the rate of oxygen reduction ($-r2$) in the cathode chamber are proportional to the cell current density.

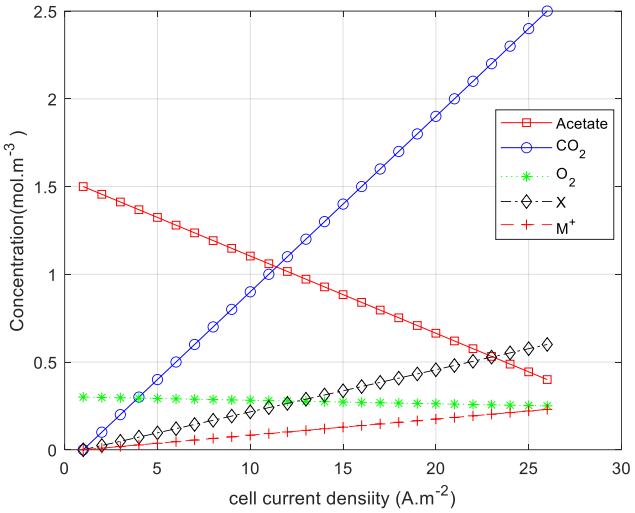

Fig.3.Concentrations of acetate, dissolved CO2,biomass (*X*), dissolved oxygen (O2) and M+.

The resultant concentration of 5 components, i.e., acetate, CO2, biomass (X) in the anodic chamber, and dissolved oxygen and M+ in the cathodic chamber, are plotted in Fig. 3. Obviously, CO2 and biomass linearly increase while acetate decreases with respect to *icell*. Indeed, a higher current density leads to a faster reaction which consumes more fuel (acetate) and generates more CO2. Similarly, a higher current density results in faster decrease in the dissolved oxygen in the cathode chamber although it is not pronounced. It follows from Eq. (9) that M+ concentration is proportional to the M+ flux, which is a linear function of cell current density (Eq. (11)). Therefore, M+ concentration linearly increases with current density.

Conclusion:

The present work describes a method for modelling the microbial fuel cell (MFC). The basis of the method is mass and charge balances with the integration of bio-electrochemical reactions. It is worthwhile to note that the model describes the experimental findings, i.e., virtually no protons are transported in the MFC and electro-neutrality is mainly sustained by the transport of cations instead of protons. The results of this modelling explain the trends in the experimental data under a steady or quasi-steady state, and give insights into how various parameters affect the power output.

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