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Microbial Fuel Cells: A promising bio-electrochemical system for wastewater treatment and energy generation

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ABSTRACT: Wastewater treatment refers to the removal or degradation of toxic pollutants, microorganisms, and harmful contaminants from the water through conventional physical, biological, and chemical treatments. A large volume of wastewater is treated at the waste-water treatment plants (WWTPs) with the expense of energy and the conventional WWTPs are no longer sustainable in this energy crisis scenario. Microbial fuel cells (MFCs), a bio electrochemical system is now gaining a lot of attention in recent times as a potential wastewater treatment technology which can remove and degrade the organic pollutants at the same time, simultaneously generating the useful electricity. This review articles overviews the basic concepts of MFCs, types, components, electron transfer mechanisms, energy generation with various wastewater treatment substrates and its applications.

Keywords: Wastewater treatment, Microbial Fuel Cells, Bio electrochemical System

1. Introduction

Water is vital for the life to sustain on earth. The global rise in the population, industrialization and therefor the demands for energy and clean water is constantly raising. In-order to meet the demand on rapid socio-economic growth of developed and developing countries, a large volume of the natural resources have been utilizing [1]. This resulting in depletion of available natural resources and parallelly generation of tones of wastes that can causes adverse effects on environment and biotic system [2]. Increased use of fossil fuels generates the harmful green-house gases, whereas excess use of water, generates the wastewater contaminated with various pollutants. The polluted water can originate from domestic and industrial sources such as food processing industries, oil and paper mill industries, textile industries, slaughterhouses, pharmaceutical industries, industrial acid mine drainages etc. The wastewater is the water contaminated with harmful chemicals (organic and inorganic pollutants) and biological agents such as microorganisms (bacteria, protozoa, viruses etc) and making it unfit for consumption and other domestic purposes. In order to maintain a constant supply of water, the wastewater needs to be treated to remove the harmful pollutants and requires the recycle process, thus making wastewater treatment process is an absolute necessary to keep the environment safe [3].

Wastewater is generally processed in a large treatment plant (WWTP) with input of huge energy and expenses [4,5]. The multi-stage processes involve rigorous treatment using biological and chemical agents. Wastewater is a key element in the nexus of water-energy-food triangle. Wastewater treatment offers various possibilities other than treatment such as energy production, value added products recovery. Recently, great advancements had been made in the wastewater treatment process to make it reliable. However, the WWTP still contribute substantially to the greenhouse gas emissions [6]. Hence there is still a need of alternative, more advanced technologies for treatment of wastewater in comparison to the traditional treatment processes in terms of efficiency, reliability at the same time providing opportunities towards the sustainability and resource-recovery. Traditional wastewater treatment process can be of two types i.e aerobic and anaerobic. Trickling filter, activated sludge process are the mostly adopted aerobic processes, which are the part of secondary treatment of the wastewater treatment processes. Anaerobic sludge digestion, waste stabilization ponds are the mostly adopted anaerobic processes [7]. The other processes which are used for WWTP include, adsorption, chemical and electrochemical coagulation, chemical precipitation. Among all these technologies, the aerobic digestion process is most adopted processes in which microbial degradation of organic waste occur with the release of CO_2 or converting complex organic pollutants into simpler organic pollutants suitable for subsequent treatment steps. Though the organic pollutants degradation does occur, large amount of chemical energy that is trapped in the form of organic waste and value-added products or nutrients such as nitrogen, phosphorus in the polluted are simply wasted. If one extracted the energy can used for various useful purposes. For instance, a theoretical calculated amount of 1.93 kWh^{-3} energy can be extracted from the organic oxidation of municipal wastewater and together with the nutrient recovery which can save up to 0.79 kWh^{-3} [8]. The concept of energy generation, value added product recovery, nutrient recovery motivated the scientist to develop newer and advanced technologies for advanced wastewater treatment processes. Bioelectrochemical systems (BES), in which a hybrid of biological and electrochemical reactions occur, has gained a tremendous attention in recent days for their potential applications of wastewater treatment together with the energy generation, value added product and nutrient recovery. Use of first BES for wastewater treatment was initially reported by Monica at al [9] and Habermann and Pommer [10]. Since then, great progress has been made on wastewater treatment using Bioelectrochemical system (BES). The BES based wastewater treatment process is an emerging technique for treating all kinds of wastewater and resource recovery simultaneous generating bio-electricity [11]. This is considered to be an alternate and energy-efficient method for treating wastewater compared to anaerobic digestion and other conventional methods employed in treatment plants. In BES, the contaminants, organic matter, and chemical pollutants present in wastewater are metabolized directly by electroactive microorganisms. The chemical energy released from this process is recovered as electricity through an external electric circuit. Unlike other conventional methods, various types of pollutants such as toxic compounds, heavy metals, chemical dyes, antibiotics, and other complex compounds are metabolized [12-14]. BES employed wastewater treatment has gained much attention in recent times due to its unique mechanism and modest method of operation. Table 1 briefly describes the various BES known so far. In this article we focus on microbial fuel cell (MFC) type of BES that is gaining popularity in recent times for treating wastewater treatment

2. Principle of Microbial Fuel Cells (MFCs)

BES works based on electrochemical conversion proves, in which stored chemical energy in the organic matter is converted to electrical energy with the help of microorganisms (usually bacteria) or enzymes. The electrochemical reactions happen on two half-cell electrodes, namely anode and cathode, separated by a polymeric membrane, called proton exchange membrane (PEM) which only allows the ions to move from anode to cathode. The electrochemical active bacteria catalyze the oxidation of the organic substances on the anode electrode chamber anaerobically. The products of oxidation of organics are ions (eg H^+) and electrons. The generated electrons are transferred from the bacterial surface to the anode electrode and the H^+ ions travel through the PEM to the cathode. The electrons travel from anode to cathode via external electrical circuit, generating the electricity. In the cathode the electrons and protons are combined to form water and other by products based on the type of terminal electron acceptors. Even though the BES were initially proposed for wastewater treatment process, there have been many modifications and advancements had happened in recent times, which lead to the evolution of different types of BES. The BECs are broadly classified into six types (Table. 1) depending up on the mechanism, input and outputs of the system and the ultimate function [15].

Table 1: Various types of bio-electrochemical systems (BES)

Type of BES	Substrate for Oxidation	Terminal electron acceptors	Function
Microbial fuel cells (MFCs)	Organic wastewater from domestic and industrial source	$K_3Fe(CN)_6$, O_2 Other oxidizing chemicals	Generation of electricity and wastewater treatment
Microbial desalination cell (MDC)	Organic wastewater from domestic and industrial source	$K_3Fe(CN)_6$, O_2 Other oxidizing chemicals	Generation of electricity and desalination
Microbial electrolysis cell (MEC)	Organic wastewater from domestic and industrial source	H^+, CO_2, other organic compounds	Bio-hydrogen production, synthesis of H_2O_2, NaOH, CH_4
Microbial solar cells (MSC)	Sunlight induced organic matter produced by photosynthetic microorganisms	$K_3Fe(CN)_6$, O_2 Other oxidizing chemicals	Electricity generation
Microbial chemical cell (MCC)	Organic wastewater from domestic and industrial source	Organics and CO_2	Synthesis of organic compounds
Microbial remediation cell (MRC)	Sediments contaminated with pollutants such as sulfate and nitrate for passive oxidation	O_2	Bioremediation of hydrocarbons

The MFC consists of an oxygen free chamber (anaerobic) in which the bacteria breakdowns the organic substrates (ex. acetate, glucose etc) and oxygen rich chamber /open air system (aerobic chamber). These both chambers may or may not are separated by a solid proton exchange membrane (PEM), which leads to two different design configurations of MFCs called dual chamber (separated by a PEM), single chamber (no PEM) MFCs. In the anode chamber the bacterial breaks down the organic substrate into protons and electrons and CO_2. The generated protons travel from anode to cathode chamber via PEM (dual chamber MFCs) or solution medium (single chamber MFCs), the generated electrons are transferred from the bacterial surface to the anode electrode material either directly or through the mediators and travel through the external circuit performing the electrical work, giving rice to the bioelectricity (Figure. 1). The protons collected at the other chamber combines with the electron acceptors such as O_2 or other oxidizing chemicals and thus completing the reactions.

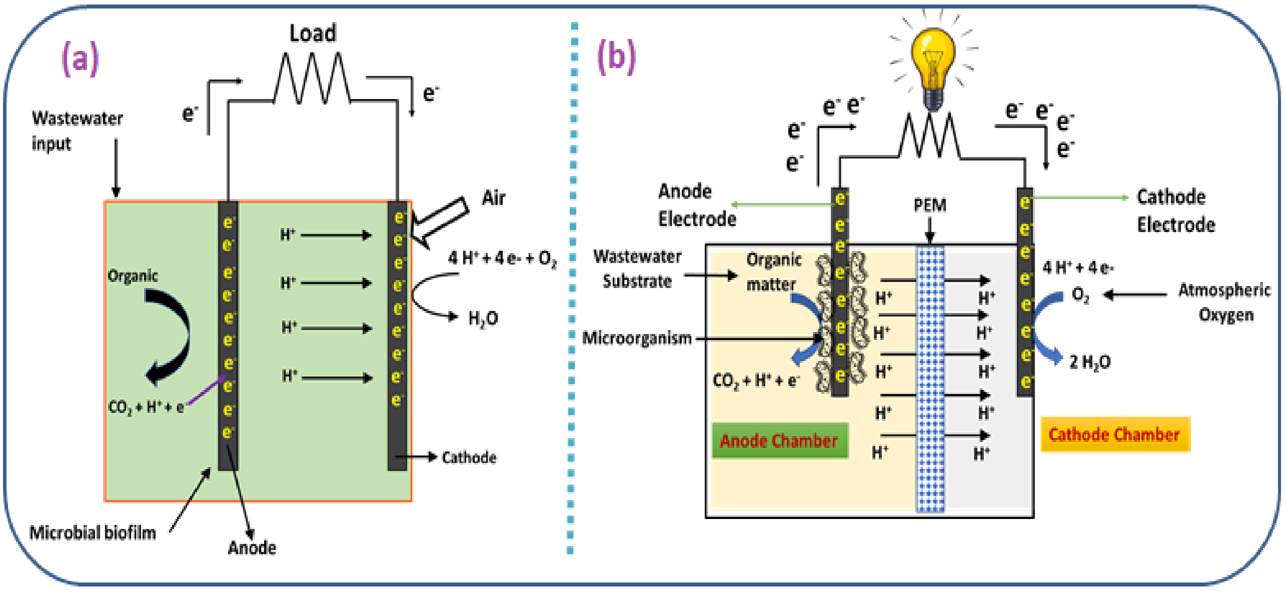

Figure. 1. Pictorial representation of MFCs (a) SCMFCs (b) DCMFCs

3. Components of Microbial Fuel Cells:

3. 1. Electrode materials: An electrode is a substance and a part of an electrical circuit which accept electrons from the bacterial surface or donate the electrons to the terminal electron acceptor. The electrode materials are classified as anodes and cathodes. The electrode materials should possess good electrical conductivity, porosity, sufficient surface area, low cost, good mechanical strength and chemical stability. Materials such as carbon felt, graphite brush, carbon paper, graphite felt, carbon cloth are generally used as anode electrode. The anode material acts as a support on to which bacteria grows and also acts as electron acceptor. The electrons generated after the bacterial metabolism are taken up by the anode electrode.

The cathode electrode is generally the carbon electrodes similar to the anodes. However, the sluggish oxygen reduction reaction occur at the cathode electrode needs high catalytically active catalysts Generally Pt based catalysts or non-Pt based catalysts are used for this purpose. The typical anode and cathode reactions are given below in Table 2.

Table 2: Typical anode or cathode reaction occur in MFCs with direct types of substrates and terminal electron acceptors

Typical Substrate in the wastewater	Respective anode and cathode reactions
Glucose	**Anode:** $C_6H_{12}O_6 + H_2O \rightarrow C_6H_{12}O_7 + 2H+ + 2e^-$ **Overall reaction:** $C_6H_{12}O_6 + 6\ H_2O \rightarrow 6\ CO_2 + 24H^+ + 24e^-$ **Cathode:** $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$ (4 electron pathway) $O_2+2H^++2e- \rightarrow H_2O_2$ $2H_2O_2 + 2H^+ +2e^- \rightarrow 2H_2O$ (2 electron pathway)
Acetate	**Anode:** $CH_3COOH + 2H_2O \rightarrow 2CO_2 + 8e^- + 8H^+$ **Cathode:** $4O_2 + 8H^+ + 8e^- \rightarrow 4H_2O$ (4 electron pathway) $O_2+2H^++2e- \rightarrow H_2O_2$ $2H_2O_2 + 2H^+ +2e^- \rightarrow 2H_2O$ (2 electron pathway
Sucrose	**Anode:** $C_6H_{12}O_{11} + 13H_2O \rightarrow 12CO_2 + 48H^+ + 48e^-$ **Cathode:** $12O_2 + 48H^+\ 48e^- \rightarrow 24H_2O$ (4 electron pathway) $O_2+2H^++2e- \rightarrow H_2O_2$ $2H_2O_2 + 2H^+ +2e^- \rightarrow 2H_2O$ (2 electron pathway)
Glucose,Acetate, Sucrose or any organic substrate in the wastewater	Anode reactions are same as above **Cathode:** $Fe\ (CN)_6^{3-} + e^- \rightarrow Fe\ (CN)_6^{4-}$ **(Mediated electron acceptors or Indirect electron transfer reactions)**

3. 2. Substrate (fuels): The substrate acts as food for the microorganisms and are consumed by the bacteria during its metabolism and growth. The substrates are usually organic pollutants ranging from simple (ex. acetate, glucose) to complex organic matters (ex. cellulose) that are present in the wastewater. The simple and most common substrate is acetate. Acetate is found to be the best substrate with higher energy output, coulombic efficiency and is resistant to the other microbial metabolic processes such as methanogenesis and fermentation. Glucose is the second common substrate used in MFCs. Other examples of the fuel substrates are cellulose from agricultural runoff water, dairy wastewater, slaughterhouse wastewater etc.

3. 3. Microorganism: The type and density of microorganism is playing a key role in degrading the organic contaminants and the efficient transfer of the generated microorganism to the solid anode electrode. The efficient electron transfer improves the MFC performance, and the electron transfer mechanisms differ with different microorganisms. Examples of microorganism include bacteria, arecha, algae, protozoa. Furthermore, the mixed culture bacteria produce less power compared to pure culture of the bacteria, due to the different preferences of substate and their growth rates. However, symbiotic relationship between different microorganism is also proved to be the MFC performance enhancing factor. Also, in most of the practical MFCs indigenous bacteria present in the wastewater are used.

3. 4. Electrolytes: The primary role of the electrolyte is to assist in transferring the protons generated at the anode to the cathode. The electrolyte also acts as a separator which separates the cathode and anode compartment physically and electronically. The most popular electrolyte used in MFCs is Nafion membranes. In addition, various other non-nafion based membranes have also been used [Ref]

Generally, the efficiency of wastewater treatment by MFC is assessed by measuring the extent of organic matter degradation by calculating the change in the chemical oxygen demand (COD). Change in organic content present in wastewater is measured as difference in chemical oxygen demand (COD) before and after treatment as follows.

$$ercentage\ of COD\ reduction\ = \frac{Initial\ COD -\ Final\ COD}{Initial\ COD} \times 100$$

The extent of organics degradation in generating electricity is measured as coulombic efficiency (CE), calculated using the equation,

$$C_E = \frac{M_S \int_0^{tb} I\, dt}{F b_{es}\, v_{an}\, \Delta c}$$

Where, C_E is columbic efficiency, M_s is the molecular mass of the substrate, Δc is the change in substrate concentration of the time tb, F is the faraday's constant (96,485 C/mol), V_{an}, is the volume of anode, b_{es} is the number of electrons exchanged per mole of oxygen, I is the current density produced over time dt.

In wastewater the organic matter is present in undefined form, the equation for calculating the unspecified compound is,

$$C_E = \frac{8\int_0^{tb} I\,dt}{F\,v_{an}\,\Delta COD}$$

Where, 8 is a constant used for COD, based on molecular weight of O_2, $b_{es} = 4$ for the number of electrons exchanged per mole of oxygen and ΔCOD is the change in chemical oxygen demand over time tb.

4. Application of MFCs

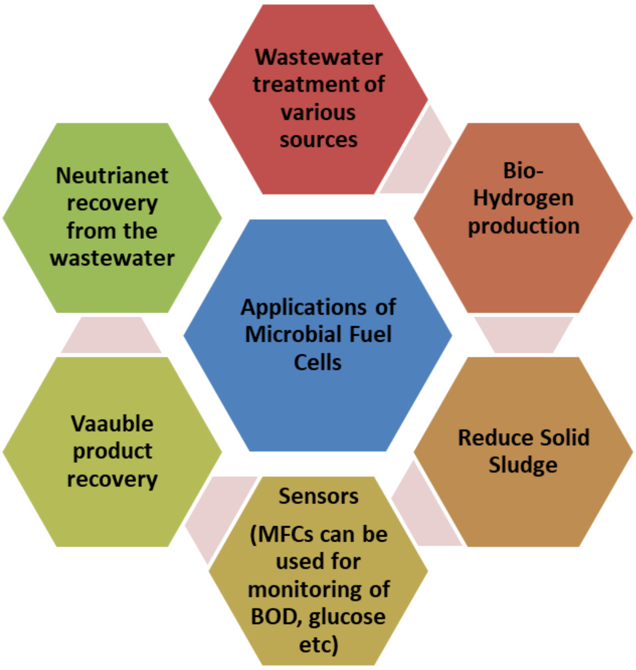

Figure. 2. Pictorial representation of MFCs applications

MFCs have been used for a variety of applications such as simultaneous generation of electricity together with wastewater treatment, for recovering valuable products by electrosynthesis, desalination of salt waster by microbial desalination, as sensors for continuous monitoring of BOD in the WWTPs, production of bio-hydrogen by microbial electrolysis, various nutrients recovery from wastewater etc (Figure. 2). Table. 3 gives the overall performance of MFCs particularly for wastewater treatment process with various types of organic substrates and their performances.

Table 3. Power output of MFCs with various wastewater substrates

Source of Wastewater	**Obtained power density**	**Ref**
Glove industrial wastewater	6.12 mW cm^{-2}	[16]
Septic tank	142 mW cm^{-2}	[17]
Brewery wastewater	124 mW m^{-2}	[18]
Vegetable oil industrial wastewater	6119 mW m^{-2}	[19]
Domestic wastewater	72 mW m^{-2}	[20]
Food waste leachate	657 m^{-3}	[21]
Animal carcass wastewater	2.19 W/m^{-3}	[22]
Piggery wastewater	297 mW m^{-2}	[23]
Coal tar wastewater	4.5 mW m^{-2}	[24]

5. Conclusions

MFCs have been widely used for the purpose of wastewater treat and simultaneous generation of electricity. A lot of efforts have been undertaken to develop MFCs such as developing various cathode catalysts, PEM membranes, exogen’s, developing various integrated technologies which can be directly installed in a real WWTPs. However, so far the performance of MFCs have not been so high enough to realized their commercial use. Efforts needs to be taken to reduce the capital cost of the MFCs, effecting design of MFCs which can deliver high power out put and lost longer.

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