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MICROBIAL FUEL CELL AND ITS APPLICATION IN MARINE BIOREMEDIATION: A REVIEW

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ABSTRACT

Pollution in the ocean is a frequent and deteriorate event and sometimes are inevitable. Tonnes of oil had reported to polluted the ocean worldwide and the impacts of the event are projecting to continue for a long term of time. One of the methods to clean up oil pollution is using bioremediation, which performed mainly by microorganism. However, the problem with bioremediation is that it usually took longer time than other method. The use of microbial fuel cell is an alternative to accelerate the bioremediation process of bacteria by adding an external accepting electron in a solid state such as carbon. Here we try to review the main fundamental of microbial fuel cell and its recent application in bioremediation, especially in oil pollution. The microbial fuel cell discuss here will be based on two different systems, which were single chamber microbial fuel cell and dual chamber microbial fuel cell. Overall, microbial fuel cell is a promising tools for generating a sustainable bioremediation process since its also producing electricity as its secondary waste. By optimizing the use of this tools, a better performance of oil removal both from sediment and seawater will be potentially obtained. Future research on its application analysis is urgently needed to provide a better understanding of its operation.

INTRODUCTION

The problem of coastal and marine pollution is never separated from the activities of local communities that produce household domestic waste as well as from the exploration activities of marine biological or non-living resources. One of them is oil and gas exploration activities which are usually carried out offshore or around coastal areas. Until now, petroleum as the main energy source in the world cannot be replaced even though there have been many other alternative energy sources such as biodiesel and bioethanol. Petroleum exploration activities up to the processing stage often produce a large amount of waste and this waste is classified as B3 waste so that it has a negative impact on the environment, especially on aquatic ecosystems.

Petroleum waste has a negative impact on the lives of various marine ecosystems such as mangroves, seagrasses, and coral reefs. Efforts to restore the condition of sediments that have been polluted by petroleum waste can be done by means of bioremediation using bacteria that live in the polluted sediments. Bacteria that live in sediments are generally anaerobic bacteria because there is no oxygen in the sediment (anoxic). A number of microorganisms live in the sediment and consume the organic materials contained in it. Bacteria that live in these sediments along with other large animals play a role in various types of respiration of organic matter [1].

Groups of bacteria that live in sediments, both aerobic and anaerobic bacteria, can utilize organic materials including hydrocarbons (oil) in their metabolism and reproduction processes. But in fact in nature, the degradation process of pollutants by the bacterial community runs very slowly due to the unavailability of suitable electron acceptors [2]. The addition of a Terminal Electron Acceptor (TEA) such as nitrate and sulfur is actually not effective because these compounds in anoxic state can be reduced. Therefore, an alternative electron acceptor that is stable and suitable for microorganisms is needed. One alternative electron acceptor that can be used is the electrodes connected through thecircuit Microbial Fuel Cell (MFC).

Microbial Fuel Cell (MFC) is a fuel cell that can convert chemical reactions into electrical energy through the catalytic activity of microorganisms. The electrodes used in the MFC circuit can be used as electron acceptors for microorganisms so that they can stimulate the anaerobic degradation of pollutants in the sediment. In addition, from this degradation, electrical energy is also obtained which can be used as an alternative source of renewable energy.

The application of MFC technology is considered prospective in overcoming the problem of waste in nature because in addition to being able to degrade pollutants, MFC can also produce electrical energy in a sustainable manner. There are two types of MFC, namely by using a one-vessel or single-chamber and two-vessel or dual-chamber system. Each system has advantages and disadvantages, therefore this study was conducted to determine the effect of the application of single-chamber MFC and dual-chamber MFC on the degradation process of petroleum in sediments and to determine its potential in generating electrical energy. Here we try to review the main fundamental of microbial fuel cell and its recent application in bioremediation, especially in oil pollution.

MICROBIAL FUEL CELL

Microbial fuel cell (MFC) is a derivative of the electrochemical component of a fuel cell whose operation process is similar to that of a hydrogen fuel cell. MFC is a device that can directly convert chemical energy in organic matter into electrical energy through the catalytic activity of microorganisms [3]. Microorganisms catalyze the oxidation of organic matter which produces electrons, protons and CO_2. Protons will go to the electrolyte solution through direct diffusion or through proton carrier ions, such as phosphates and carbonates while electrons will go through the external circuit to the cathode where protons, oxygen and electrons will combine to form water and also an electric current. This flow of electrons occurs because there is a potential difference between the anode and cathode. A simple working scheme of the microbial fuel cell can be seen in Figure 1.

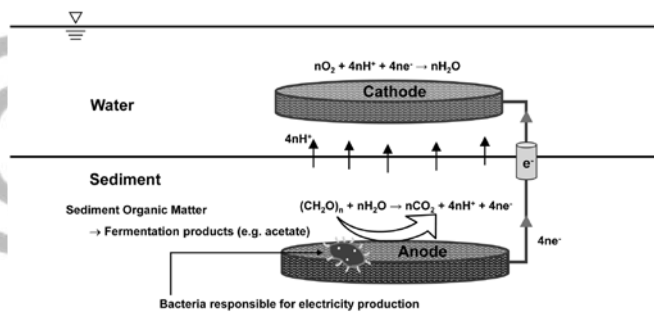

Fig 1. Schematic of Sediment Microbial Fuel Cell [4]

The use of sediment as a substrate at the anode is commonly referred to as Sediment microbial fuel cell (SMFC). The working principle of the SMFC is very simple, where two connected electrodes are placed, namely the anode in the anaerobic chamber in the depths of the sediment and the cathode in the sea water body containing dissolved oxygen [5].

Naturally, microorganisms oxidize organic matter sedimented from the water column and reduce Fe(III) or Mn(IV). Some types of microorganisms also degrade complex organic matter to produce fermentation products, such as acetate, and electron acceptors, such as aromatic compounds and long-chain fatty acids. In MFC, Fe(III) and Mn(IV) are replaced by solid-state electron acceptors, namely the anode.

There are three mechanisms of electron transfer by microorganisms to the anode surface according to [6], namely:

1. Direct transfer of electrons through the outermost membrane proteins of the cell.
2. Transfer via mediators such as neutral red and methylene blue
3. Transfer electrons via bacterial nanowire

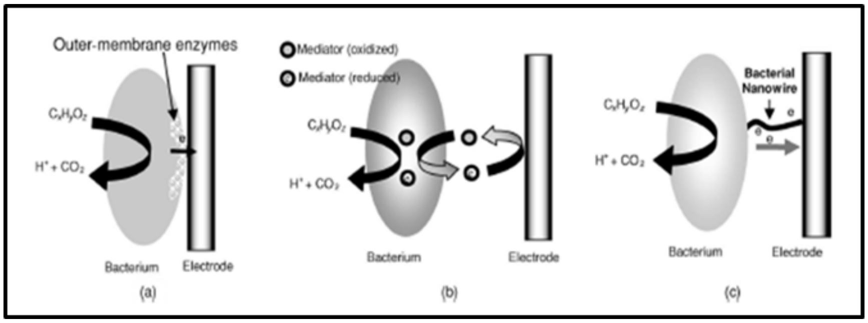

Fig 2. Bacterial Electron Transfer Mechanism [7]

a) Direct electron transfer, b) Transfer via mediator, c) Transfer via bacterial nanowire

MFC Components

Anode

The anode is stored in an anaerobic chamber where the oxidation reaction occurs. The anode must be conductive, biocompatible (according to living things), and chemically stable in the bioreactor solution. Metal can be non- stainless steel corrosive, but the use of copper is not suitable for use because copper has a toxicity value to bacteria. The most commonly used anode material is carbon, in the form of graphite plates (solid, rods, or granules), in the form ofmaterials fiber or fibrousand in the form of glass carbon. This material is used because of its high conductivity, stability, strong structure, suitable surface fordevelopment biofilm and large surface area. The ideal characteristics of carbon are in the pH range between 5-6 (50g/LH_2O, $20^{o}C$), a melting point of 3800oC, and a particle size of 50 m [8].

Cathode

The cathode is stored in an aerobic chamber where the reduction reaction occurs. The development of cathodes with inexpensive and high-performance materials is very important in the application of waste remediation using MFC. Carbon materials such asgraphite plate andgraphite felt can be used directly as cathodes. The power generated is usually lower than that of a cathode that has been coated with a catalyst. As a catalyst, a metal such as platinum can be used as a catalyst for the reduction of oxygen at the cathode. The use of platinum as a catalyst is not suitable because of the high cost. A new, high-performance catalyst at a low cost has been discovered by Cheng et al. [9] and Zhao et al. [10] namely pyrolyzed iron (II) phthalocyanine orcobalt tetramethoxyphenylporphyrin.

Cation Exchange Membrane

A cation exchange membrane or Proton Exchange Membrane (PEM) is a membrane that separates the anode and cathode spaces in the MFC system. The protons contained at the anode will flow through the PEM to the cathode, while the electrons cannot pass through the PEM so that all electrons will accumulate at the anode and all protons will accumulate at the cathode. The presence of electric current-conducting bacteria at the anode causes electrons to flow from the anode to the cathode so that the meeting of the two positive and negative ions can produce an electric current whose current will be measured as the output of the MFC system [11].

Single-Chamber Microbial Fuel Cell

Single-chamber MFC is a system where the anode and cathode are in one vessel. This system has the potential to generate great power. In the single-chamber MFC system with the cathode exposed to air, the power generated is greater because of the higher availability of oxygen than the oxygen available in the water [12].

Higher power is obtained from systems without membranes due to reduced internal resistance. One of the challenges in a system without a membrane is the rapid diffusion of air through the cathode resulting in a decrease in the Columbic Efficiency (CE) because the substrate is used by aerobic bacteria [13]. Oxygen diffusion also limits the distance between the anode and cathode in the vessel to about 1-2 cm [14].

Dual-Chamber Microbial Fuel Cell

Microbial fuel cells are run in asystem dual-chamber or two vessels are arranged with an anode chamber containing bacteria which is then separated by a membrane or a salt bridge with a cathode chamber. The cathode chamber is usually filled with a solution which is then aerated to provide oxygen. The catholyte commonly used is ferricyanide because it can improve MFC performance, but the power produced by using catholyte is unstable and sustainable due to an incomplete reoxidation process by oxygen so the solution must be replaced regularly [15].

ANAEROBIC BIODEGRADATION

Anaerobic biodegradation occurs through the process of anaerobic respiration of an organism's cells. Respiration is considered as a process of reshuffling or breaking down substrates to get food for cells. During respiration, large, high-energy components are broken down into smaller, lower-energy components. There are two types of food obtained from the biodegradation of the substrate, namely carbon and energy. Carbon is used for the synthesis of cell material for growth and reproduction. Energy is used for cell activities including reproduction [16].

When the substrate is degraded in the bacterial cell, energy is obtained from the electrons resulting from the breakdown of the chemical bonds of the substrate (Figure 3). The electrons released from the substrate are transferred through a series of electron transport molecules forming an electron transport system (Figure 3).

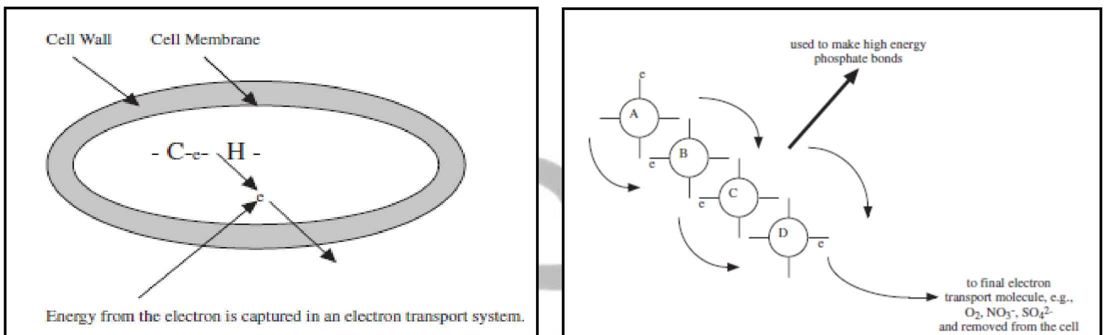

Fig 3. Energy from substrate breakdown (Left) Electron transport system (Right) [17]

When electrons are transferred from one carrier molecule to another, some of the energy from the electrons is taken up by the carrier molecule and stored in high-energy phosphate bonds, namely ATP (Adenosine triphosphate). If the cell needs energy, ATP will be broken down into ADP (adenosine diphosphate). The storage and release of this energy is based on the cleavage and binding of a phosphate group (PO_3^{2-}).

Electrons will eventually be ejected from the cell through the final electron transporting molecule. These molecules take electrons from the electron transport system and release them into the surrounding environment (Figure 4). The final electron acceptor used by bacteria depends on several factors including the availability of molecules, the availability of enzymes needed by bacteria to use the molecules and the redox potential of living bacteria and waste media (Gerardi 2003).

Microorganisms that utilize hydrocarbons in the availability of oxygen have long been known since the early 20th century. The fact that oxygen is not always available in environments where hydrocarbons are present, raises the question for researchers whether hydrocarbon biodegradation can occur under anaerobic conditions. Until the late 1980s, a new type of microorganism was discovered that could degrade hydrocarbons under anaerobic conditions (Widdel and Rabus 2001).

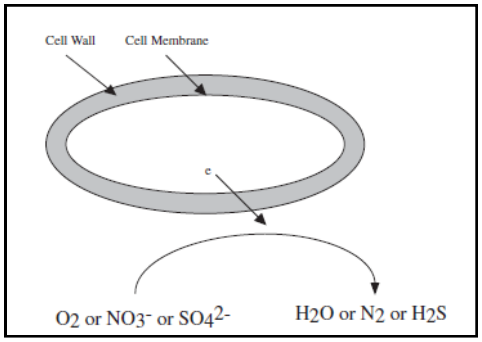

Fig 4. Final Electron Acceptor in Anaerobic Respiration [17]

Under aerobic conditions, oxygen not only acts as an electron acceptor for respiration but also acts as an indispensable reactant in the activation mechanism. By the action of monooxygenases or dioxygenases, one or two oxygen atoms are directly used to form the hydroxylated product. When oxygen is not available, microorganisms use nitrate, ferric iron or sulfate as electron acceptors for anaerobic respiration. These microorganisms grow in syntrophic cocultures or grow by anoxic photosynthesis [18].

Conclusion

It can be concluded that microbial fuel cell is a emerging technology to be applied in the field of bioremediation. It unique system approach that enable us to harvesy energy generated from the bioremediation process is particularly appealing for better green chemistry application. By optimizing the use of this tools, a better performance of oil removal both from sediment and seawater will be potentially obtained. Future research on its application analysis is urgently needed to provide a better understanding of its operation.

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