

## MICROBIAL FUEL CELL (MFC) WITH ALGAL BIOCATHODE: BIOENERGY PRODUCTION AND WASTEWATER TREATMENT USING SAGO MILL EFFLUENT

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This declaration is made on the <u>26</u> day of <u>May 2017</u>.

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## MICROBIAL FUEL CELL (MFC) WITH ALGAL BIOCATHODE: BIOENERGY PRODUCTION AND WASTEWATER TREATMENT USING SAGO MILL EFFLUENT

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A dissertation submitted in partial fulfillment

of the requirement for the degree of

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Dedicated to my beloved parents and my family who always bestow me sustainable motivations and encouragements

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# ABSTRACT

Sago industry has become an increasing interest of small sector in developing countries like Malaysia. Producing the product, sago starch is at cost of dealing with high strength sago mill effluent (SME), containing high amount of organic. Improper disposal of the effluent can cause high level water pollution in the surrounding environment. Hence, the effluent must be treated before disposal. With the aim of treating SME in order to comply with Act of Environment Quality (Industrial Effluents) Regulation 2009, this study shows a treatment method by using microbial fuel cell (MFC) with Chlorella vulgaris as electron acceptor. Besides, the current energy production is polluting the environment with its harmful gas emission. With bioenergy production, this study provides one of many progressive steps toward cleaner energy production. The relationship of doubling the volume of MFC and using Chlorella vulgaris as source of electron acceptor are investigated in this study. This study demonstrates the capability of MFC to not only able to improve the water quality but to produce a considerable amount of energy. The highest power generated in this study is  $0.38 \text{ W/m}^2$  which is an increase of 15.1% from MFC with half its volume. Meanwhile, highest power generated for algal assist biocathode is 0.36 W/m<sup>2</sup> which is an increase of 9% compared to air-pump cathode chamber of same volume. The highest treatment efficiency achieved from doubling the chamber volume which are reduction of 96.8% chemical oxygen demand (COD) and 84.9% biological oxygen demand (BOD) respectively. Meanwhile the algal assist biocathode shows COD and BOD reduction of 93.0% and 78.2%, respectively. As compared to algal assist biocathode, the air-pump cathode shows the slight difference in treatment efficiency reduction with COD and BOD reduction of 92.4 and 78.6%.

# ABSTRAK

Industri sago telah menjadi perhatian yang semakin meningkat dalam sektor kecil di negara-negara membangun seperti Malaysia. Dalam menghasilkan produk iaitu kanji sagu adalah pada kos berurusan dengan efluen kilang sagu (SME) yang kuat, iaitu mengandungi jumlah bahan organik yang tinggi. Pelupusan efluen yang tidak sempurna boleh menyebabkan pencemaran air yang teruk dalam alam sekitar. Oleh itu, efluen perlu dirawat sebelum dibuang. Dengan matlamat untuk merawat SME sekaligus mematuhi Peraturan Kualiti Alam Sekeliling (Efluen Perindustrian) 2009, kajian ini menunjukkan satu kaedah rawatan dengan menggunakan Microbial Fuel Cell (MFC) dengan Chlorella vulgaris sebagai penerima elektron. Selain itu, proses penghasilan tenaga kini mencemar alam sekitar dengan pelepasan gas merbahaya. Penghasilan biotenaga dalam kajian ini mencadangkan salah satu daripada banyak langkah progresif ke arah pengeluaran tenaga yang lebih bersih. Hubungkait antara menggandakan isi padu MFC dan menggunakan Chlorella vulgaris sebagai sumber penemrima elektron telah dikaji dalam kajian ini. Kajian ini menunjukkan keupayaan MFC bukan sahaja dapat meningkatkan kualiti air tetapi untuk menghasilkan sejumlah besar tenaga. Ketumpatan tenaga yang berjaya dihasilkan dalam kajian ini adalah 0.38 W/m<sup>2</sup> iaitu peningkatan sebanyak 15.1% dari MFC yang mempunyai setengah daripada isi padu nya. Tenaga tertinggi yang dijanakan oleh algal-katod adalah 0.36 W/m<sup>2</sup> iaitu peningkatan sebanyak 9% jika dibandingkan dengan pam udara-katod yang mempunyai isi padu ruang yang sama. Kecekapan rawatan tertinggi dicapai daripada menggandakan jumlah isipadu yang mengurangkan permintaan oksigen kimia (COD) sebanyak 96.8% dan permintaan oksigen biologi (BOD) sebanyak 84.9%. Manakala biokatod alga menunjukkan pengurangan COD dan BOD sebanyak 93.0% dan 78.2%. Berbanding dengan biokatod alga, katod pam udara menunjukkan sedikit perbezaan dalam pengurangan kecekapan rawatan dengan pengurangan COD dan BOD sebanyak 92.4 dan 78.6%.

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## **CHAPTER 1:**

# **INTRODUCTION**

#### 1.1. Energy Usage

Energy is the ability to do work which can be found in several different forms. Basically, energy can be classified into two main types; kinetic and potential energy. Potential energy which also can be said as stored energy consists of chemical, nuclear, gravitational, or mechanical energy. Meanwhile kinetic energy which found in movement are consists of thermal, sound, motion, electromagnetic radiation and electrical energy (Deb, 2012).

According to Taylor, Francoeur, D'Ortigue, Tam, & Trudeau (2008), the global energy usage is increasing by year; with increased by 23% between 1990 and 2005, compensating with the world's increasing energy demand which grew mostly in transport and service sector. Oil products remained the main energy source with a global share of 37% in 2005. On the other hand, electricity consumption global use increased by 54% between 1990 and 2005. All sectors achieved efficiency improvements, which averaged 0.9% per year between 1990 and 2005 which led to energy saving. However, the efficiency gain is declining from the previous decades. If the energy efficiency improvement has maintained, the energy savings would have been more significant.

Malaysia as developing country is becoming energy dependent as it is needed for development, economic growth, automation and modernization. Currently, the domestic sector, transportation sector and industrial sector such as commercial, residential and agriculture are the major energy consumers in Malaysia (Chong et al, 2015). These different sectors consume energy created from various energy sources. **Figure 1.1** shows the energy production by fuel type in Malaysia between 1993 and 2013.

1



Figure 1.1: Energy production by fuel type in Malaysia (Suruhanjaya Tenaga, 2015)

#### 1.2. Fuel Cell

A fuel cell is a device capable of producing electricity through a chemical reaction. Every fuel cell has two electrodes, cathode and anode which are negative and positive terminal, respectively. At the electrode, fuel cell converts hydrogen and oxygen into water, upon completing the process it produces electric current. It's an electro-chemical energy conversion device that produces electricity, water, and heat ("Fuel Cell Basics," 2008).

#### 1.2.1. Basic Principle of Fuel Cell

A simple comparison can be made between a fuel cells and battery as the operations are quite similar. Both act as electrical energy supplier through chemical reaction, however fuel cell does not require electrical recharging. A battery stores all its chemicals inside and converts chemical energy through its reaction generating electricity. Once those chemicals run out, the battery dies. There are several kinds of fuel cells, and each operates a bit differently. As oppose to battery, a fuel cell receives the chemicals it uses from the outside; therefore, it won't run out. Fuel cells can generate power almost indefinitely, as long as they have fuel to use ("WHAT IS A FUEL CELL?," 2016).

The reactions that produce electricity happen at the electrodes. Every fuel cell has two electrodes, one positive, called the anode, and one negative, called the cathode. An electrolyte barrier separates the electrodes. Fuel goes to the anode side, while oxygen or just air goes to the cathode side. When both of these chemicals hit the electrolyte barrier, they

react, split off their electrons, and create an electric current. A chemical catalyst speeds up the reactions here ("Fuel Cell Basics," 2008).

#### **1.2.2.** Microbial Fuel Cell and Its Application

According to Bruce (2016), microbial fuel cell is a new method of renewable energy recovery which uses bacteria to convert organic matter into electricity. Like a typical fuel cell, microbial fuel cell consists of two compartments; anodic and cathodic which are separated by a cation specific membrane. Microbes are inserted in the anode chamber which are oxygen free. Due to absence of oxygen, the microbes attached itself to the electrode to transfer electron produced.

The conversion involves oxidation of organic and inorganic matter. The electron produced from the oxidation are transferred into the anode and flow to the cathode. Typical constraint in fabricating a microbial fuel cell is the expensive and toxic chemical needed to transmit electrons from the bacteria to the electrode. Plus, most bacteria require purified chemicals such as glucose to grow on as bacteria can be killed by many conditions in its environment.

#### **1.3. Sago Industry Effluent**

Sago palms (*Metroxylon sagu*) is a staple food crop for the people of New Guinea, Moluccas, east Malaysia and Indonesia. In the plant, starch accumulate in the trunk with can reach up to 250 kg dry weight per plant which is the maximum starch content just before the onset of the palm flowers. Recent interests are growing into industrial application of sago palm to produce edible starch and durable leaf thatch (Singhal et al., 2008). As a normal procedure, sago factory produces sago starch through debarking and processing of sago trunk, which generate high organic content effluent (sago starch factory wastewater). In this process, a medium sago processing unit release about 5000-6000 litres of sago effluent per day as outlet (Anbukumar, Prasad, & Kumar, 2014).

Traditional method of starch extraction involves separating the starch in the pith from the cellulosic cell walls of the trunk. The starchy pith is grated into a material resembling sawdust, kneaded with water and filtered through sieves to extract the relatively large (20–60 lm) starch granules. The pith is then washed and the starch milk allow to settle in a troughs which is then sun- or kiln-dried (Shipman, 1967). The commercial process differs with the traditional in term of technology involve in separation of starch from the fibrous log which is summarise as in **Figure 1.2**. The process begins with the bark-like layer to be stripped

from log then rasped by a rasping wheel. The pith drops into one end of a cylindrical washing reel that rotates on a central shaft. Water pipe sprays the washing reel and flushes the rasped pith along the inside the reel in spiral pattern. Loosen starch is washed out in suspension meanwhile waste fibre fall from the lower end of washing cylinder. The fibre is then filtered b coarse wire screen. The starch then can be separated by using cyclone separator and dried on a rotary vacuum drum drier (Singhal et al., 2008).



Figure 1.2: Production of sago starch (Singhal et al., 2008).

Both conventional and current method require huge amount of water, making the industry to be considered as water-intensive industry. The huge water requirement is mainly for washing roots and separation of free starch from fibrous pulp. The effluent contains a very high amount of organic solid in dissolved and suspended state. The high content of organic solid could result in obnoxious odours, irritating colour, lower pH and higher BOD and COD when stored for few days. The effluent resulting from sago debarking and processing are often used for irrigating the nearby farm fields or discharged to nearby water bodies. This inevitably contributes to infertility of the farm land, in case of irrigating it with the untreated effluent, and to water pollution, when discharged into water bodies. This high

concentration effluent requires systematic treatment to reduce the pollutants content before disposal (Anbukumar et al., 2014).

#### **1.4. Problem Statement**

Sarawak as world's largest exporter of sago, exporting up to 40,000-ton sago a year. According to Bujang (2008), a sago mill typically generates about 25t of dried sago starch per day. At minimum 20L of wastewater per kg of starch produced, this generates 500t effluent. The effluent is classified as high organic material mainly due to its high chemical oxygen demand (COD) and biological oxygen demand (BOD) of about 400mg/L and 5500 mg/L respectively. Sago effluent also measured to have high total solids and acidic properties (Anbukumar et al., 2014). The measurements of the properties does not comply with the standard limit discharge enacted in the Environmental Quality Act, 1974; sewage and industrial effluents regulation, 1979 (Awg-Adeni, Abd-Aziz, Bujang, & Hassan, 2010).

When the effluent is released into the environment without proper treatment, it alters the characteristics of ecosystem. Effluent discharged into stream or river causes bacterial growth and lower the amount of dissolved oxygen (DO) in the river. Farmers are using these effluents for irrigation and found that the growth, yield and soil health are reduced. The ignorance of many development sector organizations on wastewater treatment system has caused environmental problem. As claimed by World Wide Fund (WWF) (2016), water management in Malaysia highly depends on the water supply management and leads to unsustainable environment management due to the continuous water uptake.

Due to their expensive operation and chemical sludge disposal the utility of physical and chemical treatment processes of sago effluent has been limited. Owing to these limitations, the recent focus is toward the most versatile and widely used technology; biological treatment process (Sangeetha & Muthukumar, 2012). Plus, as mentioned earlier, energy consumptions are increasing globally and the main source of energy are oil and gases. This type of fuel contributes climate change where atmosphere is being compromised by product of combustion of carbon based fuel. Thus, accelerating energy efficiency improvements is a crucial challenge for energy and climate policies thus saving the environment.

MFC is an excellent choice in wastewater treatment as it able to treat wastewater without emitting harmful secondary product. Application of MFC in wastewater treatment plant believed to able to contribute in solving the increasing energy consumption. Besides, capability of MFC not only treat wastewater but at the same time generate electricity. With enough power generation, MFC can be utilised in wastewater treatment plant thus making it self-sustaining.

### 1.5. Objectives

The aim of this research is to reduce BOD and COD of sago wastewater in order to meet Environmental Quality (Industrial Effluent) Regulation 2009 set by Department of Environment (DOE) Malaysia and at the same time to generate energy. Three objectives have been set in order to achieve the aim of project;

- i. To determine the power output and efficiency of Sago wastewater treatment using MFC
- ii. To investigate the performance of *Chlorella vulgaris* as electron acceptor in MFC.
- iii. To study the effect of scaling up MFC towards its treatment efficiency and power generation.

#### 1.6. Scope of Study

The followings are the scopes of study for this research;

- i. Wastewater used in this research is obtained from Herdsen Sago Mill located in Pusa, Sarawak.
- ii. Microalgae used as electron acceptor in the MFC is Chlorella vulgaris.
- iii. The parameters investigated in this research are pH, MFC power output and the BOD and COD of wastewater after treatment.

## **CHAPTER 2:**

# LITERATURE REVIEW

#### 2.1. Introduction

Microbial fuel cell is a new method of renewable energy recovery which utilise metabolic reaction of bacteria in conversion of organic matter into electricity. Studies have shown the potential of utilising energy generated in microbial fuel cell into wastewater treatment plant. MFC can give enormous environmental benefit as it produces no harmful product and also give benefit towards economic by reducing existing wastewater treatment systems power consumption (Pennsylvania State College of Engineering, 2010) This section elaborates sago mill effluent (SME), microbial fuel cell (MFC) and *Chlorella vulgaris* as electron acceptor.

#### 2.2. Sago Mill Effluent

Sago industry is one of the major water consuming and at the same time release large amount of wastewater which contain organic and inorganic solid wastes. Sarawak exports up to 40,000 tons sago a-year and the effluent are often discharged to nearby rivers. A typical sago mill consumes about 1,000 logs per day and it generate a minimum of 400 tons of slurry effluent which contains about 20 tons of solids (Lo, 2008).

#### 2.2.1. Characteristic of Sago Mill Effluent

The effluent has obnoxious odour, irritating colour, lower pH, higher BOD and COD thus it would be devastating if released into the environment (Monisha, Sundaram, & Ayyasamy, 2013). To summarise its characteristics, **Table 2.1** shows the general characteristics of sago effluent.

Characteristics	Value
Colour	Pale white to black
рН	5.0 to 5.7
BOD	400 mg/l
COD	5500 mg/l
Total solids	3100 mg/l
Total dissolved solids	2950 mg/l
Calcium	42 mg/l
Magnesium	105 mg/l
Potassium	90.5 mg/l
Chloride	487 mg/l

**Table 2.1**: Characteristic of Sago Effluent (Anbukumar et al., 2014).

Biological oxygen demand, BOD can be defined as the amount of oxygen needed by bacteria to decompose organic compound in wastewater. Natural phenomenon of organic matter decay and decompose may accelerate when sunlight and nutrients from wastewater are abundant (APEC, 2000). Meanwhile aerobic bacteria which can be found abundantly in sago mill effluent uses oxygen for cellular respiration and it cannot survive without adequate amount of oxygen (Jilani, 2010). Thus, with increase amount of oxygen consumer, it affects the environment by lowering the amount of dissolved oxygen in rivers and lake. Fish and other aquatic organism which require oxygen to for respiration will unable to live long due to shortage of oxygen supply. Fishes like trout or salmon will die if the level of dissolved oxygen drops below 5 parts per million (APEC, 2000).

Chemical oxygen demand, COD is a measure of total amount of oxygen required to oxidize all organic matter into carbon dioxide and water. Most of organic matters are rather hard or not possible to decompose biologically, thus the decomposition takes place chemically via oxidation (Arts, 2015). Since both biologically oxidizable and biologically inert matter can be oxidized, COD values are always greater than BOD values. Similar with discharge of effluent with high BOD, high COD also capable of depleting the amount of dissolved oxygen in water sources which is lethal for most fish and other aquatic organisms (Krupadanam, Prasad, Rao, Reddy, & Sudhakar, 2004).

Total solids which comprises of 3100 mg/l of sago effluent is made up of a very high organic solid in dissolved and suspended state. These solids contain bacteria and nutrients

mentioned earlier which when left for some days give obnoxious odours, lower pH and higher BOD and COD (Anbukumar et al., 2014). **Figure 2.1** shows the microbial population in sago mill effluent where **Figure 2.1** (a) is for bacterial population **Figure 2.1** (b) is for fungal population. *Enterobacteriaceae* has the highest percentage among the bacterial population; 21.87%. Meanwhile the dominant genus was *Aspergillus spp* accounted for 33.33% of the fungal population.



Figure 2.1 Microbial population in sago mill effluent (a) bacterial population. (b) fungal population (Monisha et al., 2013)

#### 2.2.2. Sago Mill Effluent as Substrate

Sago mill effluent or also known as sago processing wastewater has COD range of 6000 to 10,000 mg/ml; contains a relatively high percent- age of carbohydrates, cellulose, protein and nutrients. These are substrates which can be utilized in energy production via bioconversion (Lu, Zhou, Zhuang, Zhang, & Ni, 2009).

The biodiversity of microbial communities mentioned in previous section provide opportunities for electricity production via oxidation of different substrates. Microbial fuel cell utilise the oxidation of organic matter catalysed by bacteria. Study done by Sangeetha & Muthukumar (2012), shows bacteria identification by using spread-plate technique. The results from the test show the presence of E. Coli bacterial cell which contributed to the power production.

Another study done by Zhang, Xu, Diao, & Shuang (2006), organic matter added to fresh water sediments was used in anaerobic anode compartment of MFC. The result shows decrease in concentration of substrate; acetate and glucose was observed during electricity production. The sample was taken from the anode chamber periodically for substrate concentration monitoring.

#### 2.3. Microbial Fuel Cell

As mentioned in earlier, microbial fuel cell (MFC) is a device which uses bacteria to convert organic matter into electricity. MFC design, working principle and its working principle are discussed in the following sections.

#### 2.3.1. MFC Type and Design

MFC can be classified by the number of chambers or compartments. Basically, there are double chambered, single chambered, up flow mode and stacked microbial fuel cells. In a double chambered fuel cells, both the cathode and anode are contained in two different compartments and connected via a proton exchange membrane or salt bridge (Ringeisen et al., 2006). Function of proton exchange membrane or salt bridge is to act as medium for proton transfer thus completing the circuit. It also prevents direct contact between anode with oxygen or any other oxidizer (Karmakar, Kundu, & Kundu, 2010). **Figure 2.2 (a)** illustrate the schematic design of a double chamber MFC.

Meanwhile a single chambered MFC consist of simple anode compartment with no absolute cathode compartment and may not contain proton exchange membrane. Graphite rods were placed inside the anode chamber and these rods extended outside of the anode chamber and were connected to the cathode via an external circuit as illustrated in **Figure 2.2** (b). With porous cathode electrode, single-chambered MFC can run without artificial aeration in an open-air cathode system as oxygen is obtained from atmosphere and protons diffuse through them on the other side. A direct contact can reduce the internal ohmic resistance by avoiding the use of a catholyte because of combining two chambers("Microbial fuel cell – for conversion of chemical energy to electrical energy," 2016). Thus, single chambered MFC offer simple and cost saving design.