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MICROBIAL FUEL CELL (MFC) IN TREATING SPENT CAUSTIC WASTEWATER

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Abstract

Some of the major problems encountered by the world are water pollution and natural resources depletion. One of the major factors which contribute to water pollution is insufficiently treated wastewater whereas the depletion of natural resources is due to the dependability of the fossil fuel as the main energy source. Both of these issues show the world urgently required an effective technology of wastewater treatment and energy recovery. Microbial Fuel Cell (MFC) is a treatment method that can achieve the needs of effective treatment of wastewater and energy recovery simultaneously. As mentioned, insufficiently treated wastewater is one of the main causes which contributes to water pollution. Spent caustic wastewater is one of the industrial wastewater that is difficult to be treated, handled and disposed due to its noxious properties. Existing treatment method of treating spent caustic wastewater are limited by low efficiency. However, by applying MFCs, organic and inorganic contaminants are oxidized by biomass and produce electron that is transferred to electrode. The movement of the electron from anode to cathode generates electricity and turns MFC into a treatment method that able to provide both wastewater treatment and energy production. This article presents a review of spent caustic wastewater and its existing treatment method as well as the MFC researches in terms of its configuration and factors affecting its performance.

Keywords: Wastewater treatment, energy recovery, spent caustic wastewater, Microbial Fuel Cell

1.0 INTRODUCTION

The increase in both population and urbanization has caused two major problems to the world which are environmental pollution and depletion of energy source. Environmental pollution such as water pollution has caused many main water bodies being severely impacted causing the demand for freshwater to increase. It is reported that the water of the rivers was severely impacted and encountered continuous quality degradation due to direct and indirect discharge from industries, commercial premises, human settlements and agriculture plantations (DOE, 2004). As reported by Arora. (2012), it is a challenge to have a sustainable clean water (Arora, 2012) and according to the United Nations, one of the main contributor to water pollution is the insufficiently treated wastewater (UNDESA, 2014). The annual statistics on main water resources in Romania 2006 reported that total volume of wastewater discharged into natural receivers was 3586.126 Mm3/year in which 62.7% is industrial wastewater and 37.3% is urban wastewater (Chitu, 2009). To ensure the sufficiently treated of the huge volume of wastewater discharged, the world required urgently required a technology that can effectively treat wastewater. Besides that, the increase in population and urbanization had caused natural resources exhaustion. Fossil fuel can be in terms of coal, oil and gases and the world is currently continue to depend on the fossil fuel as major automotive fuel and energy source in which can be observed in Figure 1 (Ritchie and Roser, 2017). Not only the use of fossil fuel might encounters its depletion someday, but the consumption of this natural resource also contribute to environmental problems as its consumption discharges a huge amount of carbon dioxide into the atmosphere which leads to global warming (Varman et al., 2013).

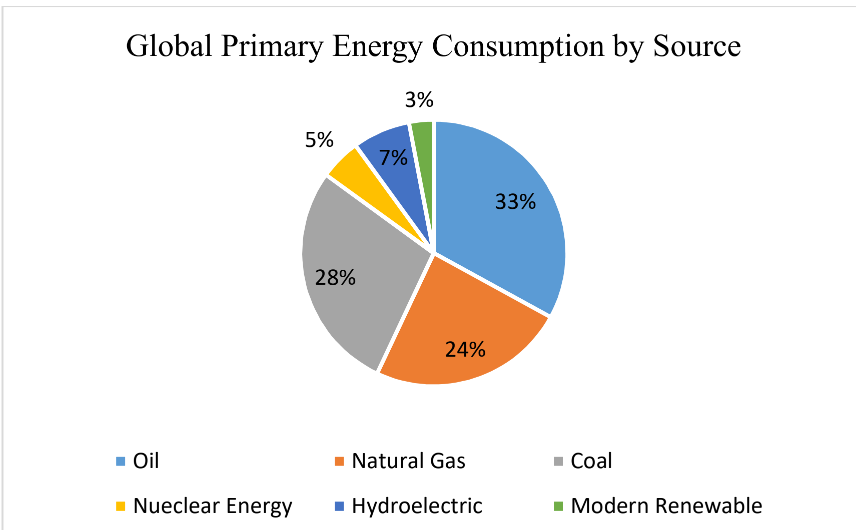

Figure (1) Global primary energy consumption by source (Rapier, 2017)

These show that the the technology of energy recovery to generate thousands of products without depending on the non-renewable and non- environmental friendly fossil fuel is urgently required (Varman et al., 2013). Concerning on overcoming these issues, the Microbial Fuel Cell (MFC) treatment method has gained the interest of many researchers as this method is known for its ability to treat wastewater while generate electricity at the same time. Therefore, both of the wastewater treatment and energy recovery issues could be resolved by using this environmental friendly method. Basically, MFC is a bioreactor that can convert the biomass energy in the wastewater into electrical energy (Logan et al., 2006). The general MFC reactor configuration is consisting of an anode and cathode chamber. This method employs microorganisms which act as the biocatalyst to catalyse the oxidation and reduction reaction that occurs at the anode and cathode compartment (Logan and Rabaey,

2012) and while catalysing the reaction, microorganisms generate protons and electrons. The transfer of these protons and electrons from anode to cathode eventually led to electricity generation. With its advantages such as energy benefits, produces less sludge and insensitive to operation environment (He et al., 2017), this method has high potential to be implemented in the conventional wastewater treatment application. However, despite its significant advantages, MFC is still in developing stage whereby to date the application of MFC is only limited to lab scale operation and low power density produced (He et al., 2017). Therefore, further study on MFC should be conducted for the development of this highly potential of wastewater treatment and energy recovery method.

2. SPENT CAUSTIC WASTEWATER

2.1 Spent Caustic Wastewater and Its Characteristic

Spent caustic wastewater is one of the type of wastewater that is difficult to be treated, handled and disposed due to its hazardous contaminants (Hawari et al., 2015). Spent caustic wastewater is hazardous industrial wastewater that is mainly produced from the refineries and petroleum chemical plants (Hariz et al., 2013). The spent caustic effluent is highly specific which made spent caustic stream as a very important stream from the refineries (Nuñez et al., 2009). Spent caustic wastewater is named after the used or wasted caustic soda. Caustic soda or also known as sodium hydroxide solution is used as the scrubbing agent in the desulphurisation process to remove different gases including hydrogen sulfide and carbon dioxide from different hydrocarbon streams (Nuñez et al., 2009). Caustic soda itself is a hazardous chemical solution as it contains contain harmful substances such as 5-12 wt% sodium hydroxide, NaOH and 0.1- 4wt % sulphide, S^{2-} and can be characterized according to their origin and composition (Veerabhadraiah et al., 2011;Hariz et al., 2013). During the removal process or also known as caustic scrubbing process, hazardous gaseous react such as hydrogen sulfide and thiols contaminants being absorbed producing a waste solution known as the spent caustic (Heidarinasab and Hashemi, 2011;Hariz et al., 2013). Hydrogen sulfide is a toxic and corrosive compound, and is removed from the pipes in the refining process as the presence of this impurities might cause corrosion in the refining pipes. Also, if Liquefied Petroleum Gases is used, it might also cause corrosion in the engines of the car and the machines (Hariz et al., 2013). The spent caustic effluent is dark brown to black colour as it also contains other toxic organosulfur and aromatic compounds such as methaniol, benzene, toluene and phenol (Alnaizy, 2008). According to Conner et al. (2000), hydrosulfide and sulfide are the dominant compounds present in the spent caustic wastewater with concentration that may exceed 2-3 wt% (Conner et al., 2000). Table 1 summarizes the contaminants that are commonly found in the refinery spent caustic.

Table (1) Typical contaminants present in the refinery spent caustic

Contaminant	Content
Sulfide (wt %)	1 – 4
Mercaptans (wt %)	0.1 – 4

Phenols (ppm)	0 – 2000
Total Organic Carbon (TOC) (ppm)	6000 – 20,000
Chemical Oxygen Demand (COD) (ppm)	20,000 – 60, 000
Biochemical Oxygen Demand (BOD) (ppm)	5000 – 15,000

Source: Hariz et al., 2010

Spent caustic is known for its noxious properties such as has high level of COD which might be influenced by the high level of sulphur compounds. Besides that, spent caustic wastewater also possess high alkalinity (pH > 12) and high salinity (sodium 5 -12 wt %) (Kumfer et al., 2010;Olmos et al., 2004). Spent caustic wastewater can be classified into 3 types which are sulfidic, cresylic and napththenic. The classification is depending on their production industry and the type of hydrocarbon stream that has been treated (Hawari et al., 2015;Hariz et al., 2013). However, refineries generally do not separate the spent caustic wastewater according to their type which is referred as mixed refinery spent caustic (Alnaizy, 2008). Table 2 shows the type of spent caustic wastewater with their respective characteristics.

Table (2) Types of spent caustic and their main characteristics

Type of spent caustic	**Sulfidic**	**Cresylic**	**Naphthenic**	**Reference**
Source	Ethylene and Liquefied Petroleum Gas (LPG) and scrubbing operation	Gasoline and heavy gasoline sweetening	Kerosene and Diesel	(Kumfer et al., 2010;Nuñez et al., 2009)
Content	High concentration of sulfide and mercaptans	High concentration of phenols and cresols	High concentration of polycyclic aliphatic organic compound	(Kumfer et al., 2010)
Chemical Oxygen Demand (COD) (ppm)	5000-90,000	50,000-100,000	150,000-240,000	(Ahmad, 2010)
Sulfide (ppm)	2000-52,000	<1	0-63,000	(Ahmad, 2010)
Total phenol (ppm)	2-30	1900-1000	14,000-19,000	(Ahmad, 2010)
Total Organic Carbon (TOC) (ppm)	20-3000	10,000-24,000	24,000-60,000	(Ahmad, 2010)

It is reported that only a small volume (0.1 to 8 m^3/h) of spent caustic wastewater are typically discharged. However, the value also depends on the size of refineries and layout of the plant (Nuñez et al., 2009). Another study reported that typical amount of spent caustic production rate may be up to 15 m^3/day (Olmos et al., 2004). In general, when 1Mt of crude oil being processed, around 500t of spent caustic is produced (Nuñez et al., 2009) .

2.2 The Effects of Spent Caustic Wastewater to Human and Environment

From Table 1 and Table 2, it is observed that spent caustic wastewater is containing high concentration of hazardous contaminants. Due to the presence of these contaminants, the exposure of spent caustic wastewater is harmful to both human and environment. The possible exposure route for spent caustic wastewater could be through eyes, ingestion and inhalation. According to its Material Safety Data Sheet. (2012), exposure via the eyes would cause irritation to the eyes and eye burns. Dermally contacted with spent caustic would cause irritation and burns to the skin which can be characterized by itching, scaling, reddening or blistering. The ingestion of spent caustic would cause burns to oral cavity, lips, upper airway, oesophagus and possibly the digestive tract. Spent caustic solution would cause severe irritation to the respiratory system and may cause burns to the respiratory tract and mucous membranes (MSDS, 2012). Since spent caustic wastewater is highly toxic, the discharge of spent caustic to the environment would impact the biological system. For example, the release of spent caustic into water bodies would cause the pH, TSS and COD concentration to increase and that would create a no longer suitable condition for the survival of the aquatic life. The discharge of raw spent caustic waste will not only affects the water bodies, but it will also likely to be volatile in the air thus affecting the air quality as well. The livings might end up to breath in the harmful air which would cause them to suffocate and could not survive the condition. Also, spent caustic wastewater might as well remains and sediment in the soils. This will impact the living organisms in the soil and plant. Plants might not be able to grow well as it absorbs harmful substances from the soil. Not only that, the consumers of the plant could have consumed poisonous plant and cause their health to be severely impacted. Therefore, to ensure human and environment not to be effected by spent caustic wastewater, safety handling and disposal of spent caustic is very crucial.

To ensure the quality of the effluent discharge of spent caustic, spent caustic need to undergo special management before being treated with the conventional wastewater treatment method (Hawari et al., 2015). Besides that, it is also mandatory for the manufacturing plants that produced spent caustic to abide the laws and regulation aligned by the environmental bodies. In Malaysia, amongst the laws relevant to water quality management includes Water Act 1920, Street, Drainage and Building Act 1974, Town and Country Planning Act 1976. These are the laws that focused on specific areas of activity (Zubaidah and Mustafa, 2008). However, complex environmental issues has bring upon another important legislation known as 1974 Environmental Quality Act (EQA). This act comes into force for the purpose of prevention, abatement and control of pollution and enhancement of the environment. Under this Act, the acceptable conditions of sewage discharge of Standard A and B have been outlined in Environmental Quality (Sewage) Regulations 2009 and Environmental Quality (Industrial Effluent) Regulations 2009 and are listed as in Table 3. Standard A is for the discharge of upstream of raw intake while Standard B is for the discharge of downstream of raw intake. The treated wastewater content must be controlled according to the regulation to ensure the effluent is safe for discharge. Department of Environment (DOE) is a responsible body for wastewater effluent quality regulated by EQA 1974 and its regulations. Water Quality Index is used to determine the quality of surface water. DOE has also established a designated classifications in the National Water Quality Standards for Malaysia to determine the suitability of surface water for irrigation purpose (Mat et al., 2013). EQA 1974 should be strictly implemented and reinforced to gain cooperation from the operating industries. The operating industries should ensure their waste discharge are able to comply with the standards aligned by EQA 1974 in order to preserves the water resources and human health. Table 3 shows the standards aligned by EQA 1974.

Table (3) Environmental Quality Act 1974, Environmental Quality (Sewage and Industrial Effluents) Regulations 1979. Parameter limits of Effluent Standard A and B

Parameter	Unit	Standard A	Standard B
Temperature	˚C	40	40
pH value	-	6.0-9.0	5.5-9.0
BOD5 at 20	mg/l	20	50
COD	mg/l	50	100
Suspended solids	mg/l	50	100
Mercury	mg/l	0.005	0.05
Cadmium	mg/l	0.01	0.02
Chromium, hexavalent	mg/l	0.05	0.05
Arsenic	mg/l	0.05	0.10
Cyanide	mg/l	0.05	0.10
Lead	mg/l	0.01	0.50
Chromium, trivalent	mg/l	0.20	1.0
Copper	mg/l	0.20	1.0
Manganese	mg/l	0.20	1.0
Nickel	mg/l	0.20	1.0
Tin	mg/l	0.20	1.0
Zinc	mg/l	1.0	1.0
Boron	mg/l	1.0	4.0
Iron	mg/l	1.0	5.0
Phenol	mg/l	0.001	1.0
Free chlorine	mg/l	1.0	2.0
Sulfide	mg/l	0.5	0.50
Oil and grease	mg/l	Not detectable	10.0

Source: Environment Quality Act (1974)

2.3 Existing Treatment of Spent Caustic Wastewater

In order to comply with existing law and regulations, it is crucial to treat the spent caustic wastewater before being discharge. Spent caustic wastewater is always reported as difficult to be treated as it can create odours and safety problems from the result of containing high level of sulfide (Maugans et al., 2010). The treatment also involved high cost of transporting and handling. On the other hand, the disposal of this waste for either reuse or recovery purposes are not so economical (Alnaizy, 2008). However, despite any difficulties, spent caustic wastewater still need to be treated to ensure the quality of the ecosystem. There are many existing treatment that can be used to treat spent caustic wastewater. All of these existing treatment can be classified into 3 type which are biological, chemical and thermal process treatment method (Hariz et al., 2013). Each treatment method comes with their respective advantages and disadvantages.

Example of biological treatment method are such as oxidation by using attached or suspended cells and bioelectrochemical treatment. Conventional biological treatment method is a standard practice at many refineries. This could be due to biological method as a safer and cheaper alternative for the wastewater treatment. Besides that, the process of biological method also accour at atmospheric condition. However, there are some significant disadvantages of biological method which might affects its efficiency in treating spent caustic wastewater. It is reported that biological is limited to high pH and sulfide toxicity of spent caustic treatment (Vaiopoulou et al., 2016). Another study reported that it could be easily disturbed by fluctuating pH condition, increasing salt concentration and accumulation of toxic compounds (Metcalf and Eddy, 2003). This has made biological method not applicable for the treatment of large amount of complex spent caustic streams (Metcalf and Eddy, 2003). Sulfide oxidizing bacteria are often used to achieve sulfide removal in a wastewater treatment method. However, previous research that applied sulfide oxidizing bacteria for the biological treatment of spent caustic refinery reported that the process shows limitations related to their kinetics and their effectiveness due to certain type of inhibitors (de Graaff et al., 2011). Generally, biological treatment method employs the use of filamentous bacteria which could lead to formation of bulking sludge which might cause severe operating problems (Nielsen, 1985). Due to significant disadvantages of biological treatment method, this method is applicable as the post treatment for spent caustic wastewater which means spent caustic wastewater required pre-treatment process before being fed to the biological treatment reactor. Examples of pre-treatment process are such as biomass acclimatization and neutralization process. It is reported that, biomass acclimatization and sludge handling could overcome the limitations imposed by the high toxicity, pH and COD load (Hariz et al., 2013). Also, for the sulfide oxidizing bacteria, the waste need to be applied with dilution factors up to three in order to reduce the pH and sodium level down to acceptable concentration for neutrophilic sulfide- oxidizing bacteria (Sipma et al., 2004).

Chemical treatment method is another common method of treating spent caustic wastewater. Example of chemical treatment method are such as chemical oxidation and neutralization. Basically, in the chemical oxidation method, chemical oxidant is directly added to the waste stream in order to oxidize contaminants in the waste. Examples of the commonly used chemical oxidants are such as chlorine, chlorine dioxide, oxygen, persulfate, permanganate, ozone and hydrogen peroxide (H_2O_2) (Hawari et al., 2015). In the chemical oxidation by using H_2O_2, H_2O_2 will act as the oxidant as its radical possess high oxidation potential. Hydrogen peroxide can oxidizes most of organic and inorganic compounds. However, this reaction involves high operating risks as it possess high risks of operation. Also, the operation involve high operating cost (Veerabhadraiah et al., 2011). Besides that, some of other disadvantages of chemical oxidation with H_2O_2 is the reaction often gives incomplete oxidation of dissolved sulfide to thiosulfate. Furthermore, the storage and handling of H_2O_2 is associated with considerable safety measures (de Graaff et al., 2011). Advanced chemical oxidation (AOPs) is another chemical treatment method that is encouraged for the treatment of extreme wastewater such as spent caustics (Munter, 2001;Davarnejad and Bakhshandeh, 2017). In the AOPs reaction, highly reactive hydroxyl radicals will be formed at sufficient quantities to attack the complex chemical contaminants in the waste streams (Munter, 2001). The formation of the hydroxyl radicals were achieved by using one or more strong oxidants (e.g. H_2O_2, O_2 and O_3) and/or catalysts (e.g. titanium dioxide, transition metal ions) and/or energy sources (e.g. ultraviolet radiation). AOPs treatment are often coupled with other treatment system to achieve the required level of treatment (Munter, 2001). Examples of AOPs reaction are such chemical oxidation, Fenton, and photo-Fenton processes, ultraviolet (UV)-based processes, photocatalytic redox processes, supercritical water oxidation, sonolysis and electron beam under the advance oxidation technique (Nidheesh and Gandhimathi, 2012). Among the AOPs method, oxidation using Fenton's reagent is considered as an attractive and effective technology for degradation of large amount of hazardous and organic pollutants due to lack of toxicity of reagents (Nidheesh and Gandhimathi, 2012). Fenton's reagent is a solution of hydrogen peroxide and an iron catalyst that is used to oxidize contaminants or wastewaters (Nuñez et al., 2009). Neutralization is one of the chemical treatment method for wastewater treatment. However, neutralization process only reduces the alkalinity without reducing or eliminating the other constituents. Therefore, the neutralization process is a practical method to be used followed by steam stripping process (Grover and Gomaa, 1993). The disadvantages of neutralization method is that this method is consumed large amount of acid and required other following process such as the stripping process after neutralization in order to remove mercaptans and sulfide in the waste (Berne and Cordonnier, 1995).

Wet-air oxidation (WAO) method and incineration method are the examples of available method under thermal treatment method of spent caustic wastewater. By using WAO method, soluble and suspended compounds are partially or completely oxidized at elevated temperatures and pressures using air-oxygen as the oxidizing agent (Ellis, 1998). This process involved high pressure treatment (25-90 bar) at elevated temperatures (200-300˚C) (Jagushte and Mahajani, 1999). Some of the disadvantages of this method is that this method is not able to give complete reduction of COD to zero because carboxylic acid is formed and that resist further oxidation. Also, this method is expensive, energy consuming and the safety concern is minimal, as the system is operated under high pressure and high temperature (Heidarinasab and Hashemi, 2011;de Graaff et al., 2011).

3. Microbial Fuel Cell (MFC)

All of the existing treatment methods of spent caustic wastewater have their respective advantages and disadvantages. According to Oh et al. (2010), the organic matter present in the wastewater itself could be considered as an energy source and by selecting proper technology this energy present in the wastewater can be harvested (Oh et al., 2010). However, majority of the available treatment methods are focusing on the wastewater treatment without utilizing the capability of producing renewable energy method from the wastewater treatment system. MFC is different than the other method as it is a method that focuses on both wastewater treatment and energy recovery. MFC is basically a bioreactor that utilizes the use of microorganisms which served as the catalyst to catalyze the oxidation and reduction process occur in the reactor. The oxidation and reduction process involved the movement of electron which will generate electricity. According to Du et al. (2007), MFC is a bioreactor that can convert the bioenergy of biomass in wastewater into electrical energy (Du et al., 2007). Therefore, by using MFC treatment method, not only it contribute to a sustainable wastewater treatment but a renewable source of energy could be obtained as well.

3.1 MFC Configuration and Design

A typical configuration of an MFC reactor should consists of two compartments of anode and cathode chamber, a proton exchange membrane (PEM) or salt bridge and electrodes submerged in both anode and cathode chamber. As reported by Tekle and Demeke. (2005), the basic MFC design consists of an anode, a cathode, a PEM and an electrical circuit (Tekle and Demeke, 2015). The anode and cathode chamber is usually connected by the PEM and both of the electrode at the anode and cathode chamber is connected by wires constructing an electrical circuit. An anode and cathode of the MFC are one of the crucial part in an MFC operation. Both of the oxidation and the reduction reaction occur at the anode and cathode compartment (Logan and Rabaey, 2012). In the anode, the bacteria oxidizes the substrates in the wastewater. The bacteria generates electrons and protons while oxidizing the substrates. Generally, hydrogen is ionized at the anode chamber and carbon dioxide is produced as an oxidation product. However, there is no net carbon emission because the carbon dioxide in the renewable biomass originally comes from the atmosphere in the photosynthesis process (Rabaey et al., 2005). The typical reaction occur at anode taking acetate as an example substrate is shown below.

Anodic reaction (Rabaey et al., 2005): $CH3COO^- + 2H_2O \rightarrow 2CO2 + 7H^+ + 8e^-$

The protons and electrons generated move to the cathode compartment through. The protons and electrons that reach the cathode compartment then react with the electron acceptor at the cathode and form water (Logan and Rabaey, 2012;Sawasdee and Pisutpaisal, 2016). The reaction that occur at the cathode chamber is shown below.

Cathodic reaction (Saba et al., 2017): $O_2+4H^++4e^- \rightarrow 2H2O$

At the cathode, oxygen reduction occur. Oxygen is the common electron acceptor used in MFC. This is due to its sustainability especially in air-cathode compared to other substances such as hydrogen peroxide or ferricyanide (He et al., 2017). Oxygen is also reported to have high redox potential and abundant availability therefore it is commonly favorable to be used as electron acceptor (Zhao et al., 2006).

As mentioned earlier, the compartment of anode and cathode chamber is separated. It is reported that the separator plays the major role as it can be the limitation to MFC due to its ability to increase the internal resistance as well as decrease the MFC performance (He et al., 2017). Generally, a PEM is used to partition the anode and cathode compartment (Kim et al., 2003). A PEM is made up of proton conductive materials that able to inhibit the transfer of other material such as fuel (substrate) or electron acceptor (oxygen) while conducting protons to the cathode at high efficiency (Min et al., 2005). In other word, a PEM should only allow the transfer of protons from the anode to cathode compartment as well as block fuels from the anode and oxygen from the cathode (Wu et al., 2017). The absence of the exchange membrane would allow the oxygen to diffuse from the cathode to anode chamber, where it competes with the electrode as an electron acceptor and this could lead to low coulombic efficiency (Commault et al., 2017). The most common material used as the PEM is Nafion (Min et al., 2005;Wu et al., 2017). However, it is often reported that Nafion is an expensive material therefore many researches has been conducted to find the alternative material to replace Nafion as PEM. Among the material tested are such as polyvinylidenefluoride (PVDF) and polytetrafluoroethylene (PTFE)- BASED material (Dong et al., 2012), ceramic based material (Yousefi et al., 2017), polyvinyl alcohol-hydrogel (PVA-H) (Wu et al., 2017), clayware ceramic separator (Behera et al., 2010) and proton permeable porcelain layer (Park and Zeikus, 2003). Besides using a PEM, another method to assist the proton transfer within the anode to cathode compartment is salt bridge. Example of the use of salt bridge in MFC operation are such as salt bridge filled with phosphate buffer solution (Min et al., 2005). Besides that, another alternative is to use the membrane electrode assembly (MEA) which is the combination of PEM with electrode. It is reported that this combination could lead to decrease in the mass transfer limitation of protons and air and the cathode reaction time could be reduced as well (Hernández-Flores et al., 2016;Owejan et al., 2014).

3.1.1 Dual and single chambered MFC reactor

The design of an MFC reactor can be as a single chambered reactor, dual chambered reactor and other types of design such as tubular MFCs, plate MFCs and stacked MFCs (Tommasi and Lombardelli, 2017;Abourached et al., 2016;Tekle and Demeke, 2015). However, MFC is usually designed as dual chambered reactor including the anode and aerated cathode (Saratale et al., 2017). Dual chambered MFC is the simplest type of MFC design as it consists two chambers separated by material such as PEM that conducts the protons between the chambers. Figure 2 shows the general schematic diagram of two chambered MFC. As shown in the figure, a typical two chambered MFC reactor consisting of an anodic and cathodic chamber connected by a PEM or salt bridge. The anodic chamber contains biodegradable substrate and nutrients such as nitrogen, phosphorus, oxygen and trace minerals. It is reported that the oxygen should not be diffuse into the anode chamber and the rate of oxygen diffusion into anode for MFC reactor without a PEM is slightly higher than the MFC reactor with PEM (Logan et al., 2006). However, two chamber MFC reactor is difficult to be scaled up although it can be operated either in batch or continuous mode (Du et al., 2007). On the other hand, for single chambered MFC reactor, both of the anode and cathode compartment are located in the same compartment with cathode chamber being exposed directly to the air (Park and Zeikus, 2003). Since the cathode of the single chamber is not located in an aerated chamber and is directly exposed to the air, thus MFC is left with only a single anode chamber and often being hot pressed with membrane to form membrane electrode assembly (MEA) (Pandey et al., 2011). It is often reported that a single chambered reactor is easier to be scaled up than dual chambered MFC reactor (Tekle and Demeke, 2015;Du et al., 2007). By using single chambered MFC reactor, the aeration in water is not required as the oxygen from air can be directly transferred to the cathode (Pandey et al., 2011).

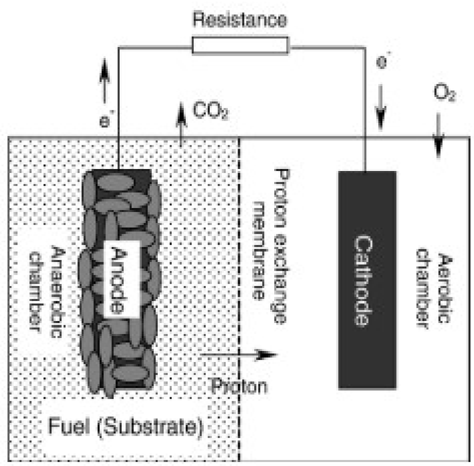

Figure (2) General schematic diagram of two chambered MFC (Du et al., 2007)

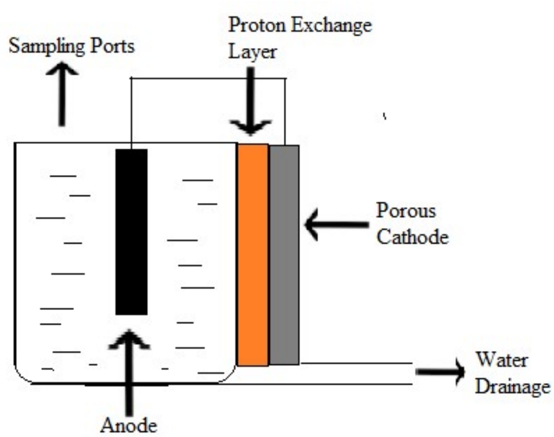

Figure (3) Schematic diagram of single chambered MFC (Park and Zeikus, 2003)

3.1.2 Stacked MFC reactor

Besides the MFC single and dual chambered reactor, there are other types of MFC design. Most of these designs are in accordance with the purpose of scaling up of the MFC with the aim to increase the power density. Stacked MFC reactor is one of the available design of MFC. In the stacked MFC, the multiple small MFC modules is combined to form larger stack therefore could increasing the size of an individual reactor (Ieropoulos et al., 2008). This type of MFC construction end up forming the MFC into battery of fuel cell and is reported to increase the output of the overall battery to be comparable to normal power source and the stacked can be in series or parallel (Aelterman et al., 2006). For the case of MFC units were fluidically connected, the connection either in series or parallel increased the total available electrode surface area but did not change the reactor volume (Zhuang et al., 2012). Previous research on continuous electricity generation at high voltages and currents using stacked MFC conducted by Aelterman et al. (2006) reported that stacked MFC could provide enhanced power density. He also reported that the stacked MFC does not affects the individual columbic efficiency of each cell. Columbic efficiency is described as the amount of substrates used for the electricity generation before the stream flowed out of the MFC (Du et al., 2007). Wu et al. (2016) conducted the 72L pilot scale stacked MFC with granular activated carbon packed bed electrodes reported that the system could achieved high COD removal using synthetic wastewater (Wu et al., 2016). Another research by Chang et al. (2014) who study the baffled stacking MFC in treating high strength molasses wastewater has proved that the stacked baffled MFC can effectively degrades the organic and nitrogen containing pollutants in real molasses wastewater and able to generate bioelectricity (Chang et al., 2014).

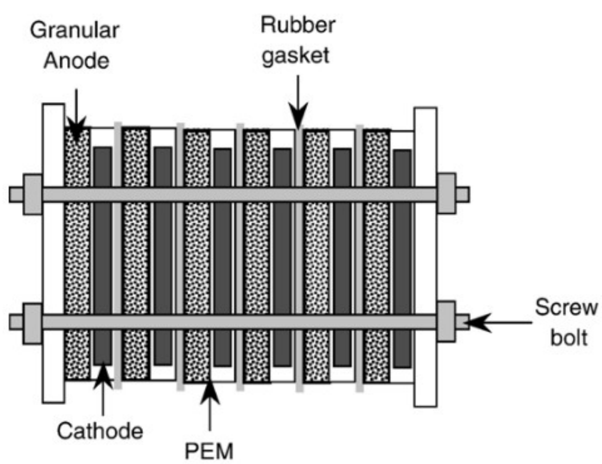

Figure (4) Stacked MFC configuration of 6 individuals units with granular graphite anode (Aelterman et al., 2006).

From all of the efforts attempted by using the stacked MFC reactor, it is shown that stacking multiples MFC modules allowed larger total volume capacity while each reactor can function and maintained independently (Lu et al., 2017).

3.1.3 Up-flow MFC reactor

Generally, the up-flow MFC is in cylindrical shaped MFC consisting of an anode at the bottom and the cathode at the top.

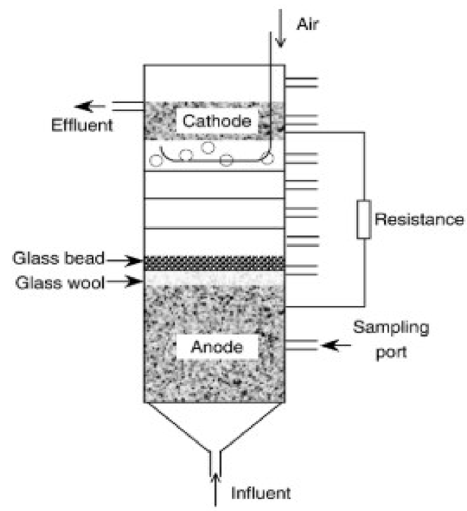

Figure (5) Up-flow MFC reactor configurations (Du et al., 2007).

Both of the anode and cathode is separated by glass wool and glass bead layers (Du et al., 2007). In the up-flow MFC reactor, the fluid flow upwardly whereby fluid entering the bottom of the anode and travel through the cathodic chamber and exits at the top continuously (Moon et al., 2005). He et al. (2005) tested up-flow MFC reactor on artificial wastewater and reported that the up-flow MFC system is limited by its internal resistance affecting its power production (He et al., 2005).

3.1.4 Tubular MFC reactor

A tubular MFC generally has cylindrical or tubular shape rather than a rectangular shape (Kim et al., 2009). A tubular MFC is a system in which the cathode is the outer and anode is the inner part of the MFC reactor. The inner anode were made based on graphite granules (Du et al., 2007). A tubular MFC typically employs membrane electrode assembly (MEA) in which it is wrapped around the central anode chamber and the cathode is exposed to the air (Kim et al., 2009).

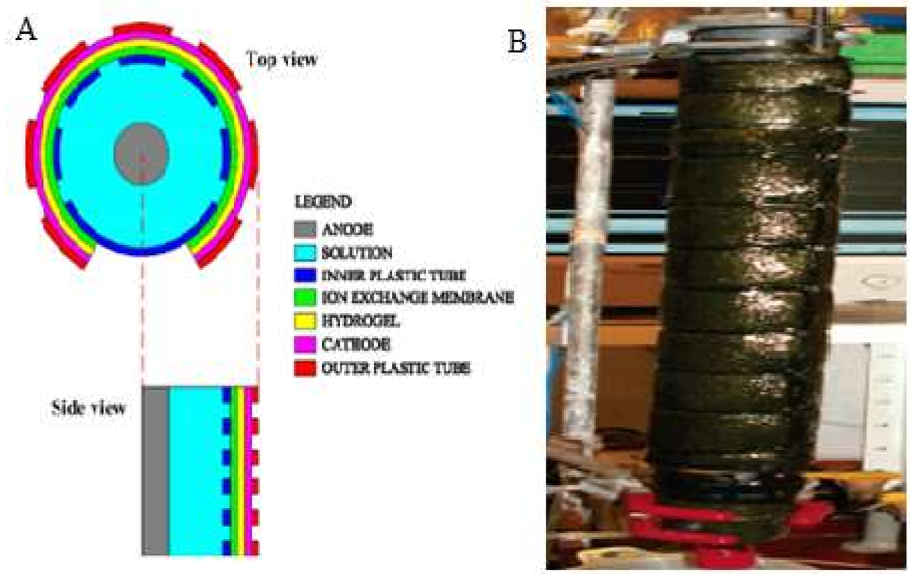

Figure (6) A) Schematic Diagram of tubular MFC (top and side view) (Kim et al., 2009). B) Up-flow tubular MFC with inner graphite bed anode and outer cathode (Logan et al., 2006).

A tubular MFC could increase the sludge retention time and reduce the hydraulic retention time in which it would reduce the long term operation cost. As the anode is made of graphite granules, this system provide easy bacterial attachment (Oh et al., 2010). However, it is reported that although this system encourage higher bacterial attachment in which high density of exoelectrogens on the surface anode was noticed, the system was still resulting in lower energy production.

3.1.5 Operating condition of MFC reactor.

The MFC reactor can be operated as aerobic or anaerobic condition. An aerobic MFC requires constant oxygen supply and can lead to increase in the energy required to conduct the process. Whereas, anaerobic MFC reactor does not required oxygen supply, therefore, anaerobic MFC reactor has lower energy requirement demand which makes it become more environmental friendly (Abbasi et al., 2016). It is reported that anaerobic anode chamber is often used in a typical MFC reactor. According to Huang et al. (2017) whom conducted study on decolorization of azo dye and electricity generation in MFC, he reported that anaerobic bioelectrochemical environment in the anode of MFC creates favorable condition for azo dyes decolorization (Huang et al., 2017). The anode chamber are maintained under anoxic or anaerobic conditions to prevent the capture of microbial electrons by dissolved oxygen (Rodrigo et al., 2007). Besides that, it is also reported that electric current generation is made possible by keeping the microbes separated from oxygen and any other end terminal acceptor other than the anode in which the condition is known as the anaerobic anodic chamber (Du et al., 2007). According to Feng et al. (2017), to achieve the anaerobic condition of the anode, the dissolved oxygen (DO) should be under 0.5 mg/L whereas for the cathode to be in the aerobic condition, the DO of the cathode chamber should be approximately 4–6 mg/L (Feng et al., 2017). For the condition of cathode in MFC, it is reported that biocathodes can be classified into aerobic and anaerobic biocathodes depending on the condition of the cathodic chamber. For the aerobic biocathode, the normally served as the terminal electron acceptor. Whereas for the anaerobic biocathode, the oxygen diffusion into the anode via the proton exchange membrane can be completed eliminated and this is useful in preventing the loss of electrons to oxygen (He et al., 2017).

3.2 MFC in Treating Spent Caustic Wastewater

MFC is one of the highly potential wastewater treatment and energy recovery method. In the MFC application, wastewater is an important factor as it is a substrate that act as nutrient source of the cell (Sun et al., 2010). When it comes to wastewater characterizations, the factors that should be taken into account are such as Chemical Oxygen Demand (COD) and biochemical oxygen demand (BOD). COD is the measure of oxygen equivalent to the material in the wastewater including organic and inorganic material that can be oxidized chemically in 2 hours whereas BOD is the measure of the amount of oxygen that microorganisms need to consume and break down organic matter From these factors, the 'hardness' and biodegradability of wastewater can be determined. High ratio of BOD5/COD i.e. BOD5/COD 0.5 indicates the wastewater as readily biodegradable, whereas low ratio of BOD5/COD i.e. below 0.5 indicates slowly biodegraded or contains a part of non-biodegradable or toxic element. There is no specific range to differentiate between low, medium and high strength wastewater as it is also depends on the type of industries e.g. in area of biodegradable wastewater, when COD is less than 1000mg/L, it is considered as low strength level. However, for petrochemical industries, 1000mg/L COD is considered as high strength level. For the food industries, 1000 mg/L of COD is considered as medium strength level wastewater (Mutamim, 2012).

Previous researches reported that some of the simple liquid substrates tested for MFCs application were such as solution with glucose (Chaudhuri and Lovley, 2003), volatile fatty acid (Daghio et al., 2015) and alcohol (Kim et al., 2007) and the common type of the complex mixture used as the feed sample for the MFC system were such as domestic wastewater (Chen et al., 2008;Dong et al., 2012;Liu et al., 2010), swine wastewater (Ding et al., 2017), agro food wastewater (Cecconet et al., 2017), artificial wastewater (He et al., 2005), synthetic wastewater (Mateo et al., 2017;Nam et al., 2010;Nandy et al., 2015), fruit processing wastewater (Abourached et al., 2016), tannery wastewater (Sawasdee and Pisutpaisal, 2016), brewery wastewater (Lu et al., 2017) and etc. MFCs application has also been tested to landfill leachate (Hassan et al., 2018). Table 4 shows the COD removal efficiency of various type of wastewater treated by using MFC application. All of the types of the wastewater mentioned contains various types of pollutants. However, it is reported that by using MFCs application, the contaminants such as sulphide, ammonia, nitrite, perchlorate, chlorinated compounds, copper, mercury and iron could be effectively removed (Clauwaert et al., 2007;Aelterman et al., 2006). As mentioned earlier, spent caustic wastewater is the high strength industrial wastewater and is commonly produced by the petrochemical refineries. However, only a few of MFC researches employed spent caustic wastewater in MFC study whereas most of them adopted domestic wastewater in the MFC study. Hence, MFC application in treating domestic wastewater is reported to be successful (Cheng and Logan, 2011) whereas the MFC capacity in treating spent caustic wastewater is not really known. However, study conducted by Srikanth et al. (2016) on electro-biocatalytic treatment of petroleum refinery wastewater using MFC reported that the system could achieved 84.4% substrate degradation when being operated in continuous mode and 81% when being operated in batch mode. The system was also able to produce power density of 225 mW/m^2. This shows that MFC has potential in efficiently treat high strength industrial wastewater such as spent caustic. In fact, Kim et al. (2016) reported that power densities could be improved by using higher strength of wastewater such as brewery and animal wastewater (Kim et al., 2016). However, high strength wastewater required longer treatment duration than domestic wastewater to ensure good quality of effluent (Kim et al., 2016) . Velasquez-Orta et al. (2011) also reported that different type of organic matter in different type of wastewater can have dissimilarities in their biodegradability which can affect the COD removal rate (Velasquez-Orta et al., 2011).

Table (4) COD removal efficiency of various type of wastewater treated by using MFC application.

Type of MFC	**Source of wastewater**	**COD influent (mg/L)**	**COD removal (%)**
Single chamber air-cathode (Ding et al., 2017)	High strength swine wastewater	2735 ± 15	82.5 ± 0.5
Two air-cathode MFC reactor continuous flow operation (Kim et al., 2016)	Swine wastewater	7600± 700	84
Continuous fed upflow anaerobic MFC (Tamilarasan et al., 2017)	Surgical cotton industry wastewater	600 ± 50	78.8
H- type dual chamber MFC (Hassan et al., 2017)	Landfill leachate	7000	90.0±1.2
Dual chamber MFC (Chang et al., 2014)	High strength Molasses wastewater	1000	53.2
Tubular air-cathode MFC (Zhuang et al., 2012)	High strength Swine wastewater	5845	83.8
Flat panel air-cathode MFC (FA-MFC) (Park et., 2017)	Domestic wastewater	500	85
Membrane electrode assembly with MFC (HEM-MFC)	Molasses wastewater	1500	95.6

(Wu et al., 2017)

3.3 Factors Influencing the MFC Performance

MFC application is often reported as still in the lab scale and efforts are constantly being made by the researches to bring MFC technology to the real world application (Jiang and Li, 2009;Zhou et al., 2011;He et al., 2017). Besides that, MFC performance is also unable to achieve its ideal performance (Tekle and Demeke, 2015) whereby He et al. (2017) reported that the energy production of MFC is too low to meet energy-neutral operation at practical scale. The efficiency of MFC performance might be due to the certain factors that could be the limitation to MFC performance. Previous researches has reported several factors that could influence the MFC performance. Electrode materials (Sangeetha and Muthukumar, 2013), distance between electrode (Hussein et al., 2012), electrode surface area (Ghangrekar and Shinde, 2007), proton exchange membrane (Hernández-Flores et al., 2016), temperature (Tee et al., 2016), pH and etc. The operating conditions of MFC such as its organic loading rate (Tamilarasan et al., 2017), solid retention time (D'Angelo et al., 2017), hydraulic retention time (Arya et al., 2016) are also some of the parameters that affects the performance of MFC. It is crucial to identify the optimum parameter of the MFC operation to ensure the MFCs system could achieve an ideal performance.

3.3.1 Electrode materials

Performance of MFC depends on the electrode materials. In the design of MFC, the important aspects when dealing with electrode material is the performance and cost of the electrode itself (Hussein et al., 2012). Better performance of electrode is expected to improve the MFC performance. An electrode material influence the power loss of the fuel cell in terms of internal resistance (Oh and Logan, 2005). A good electrode material should be conductive, biocompatible and chemically stable in the reactor solution (Sangeetha and Muthukumar, 2013). Various types of electrode have been employed in the MFC operation. The commonly tested electrode materials are such as graphite, aluminium, titanium, copper, iron, stainless steel and etc. Table 5 shows the MFC performance with their respective electrode material.

Table (5) MFC performance of various types of electrode materials.

Type of wastewater treatment system	**Type of wastewater**	**Electrode material**	**COD removal**	**Voltage produced**	**Reference**

Electrolytic reactor	Secondary treated sewage	Aluminium	82.25%	Current density, 7.52mA/cm^2	(Chopra and Sharma, 2013)
Electrocoagulation batch reactor	Textile industry wastewater	Iron	90.12%	14V	(Akanksha et al., 2013)
Doubled MFC chambered reactor	Domestic wastewater	Aluminium - Carbon	Not stated	2.6V	(Hussein et al., 2012)
Dual chambered MFC reactor	Sago processing wastewater	Graphite	94%	Current density, 333.34 mA/m^2	(Sangeetha and Muthukumar, 2013)
Dual chambered air-cathode MFCs reactor	High strength swine wastewater	Graphite fibre brushes	59%	Power density,750 ± 70 mW/m^2	(Kim et al., 2016)
Tubular air-cathode MFCs reactor	Swine wastewater	Carbon fibre cloth	77.1%	0.38V	(Zhuang et al., 2012)
Single chambered MFCs reactor	Swine wastewater	Carbon cloth with carbon coating	84 ± 1%	Power density, 225 ± 1.4 mW/m^2	(Srikanth et al., 2016)

Among all of the type of electrode material used, graphite electrode is often reported as the best electrode material. Comparing to the other electrode material, graphite electrode is lacked with conductivity property however graphite electrode has surface morphology that encouraged higher bacterial adhesion than the other electrode material. Graphite electrode apparently has higher surface roughness which lead to a more bacterial adhesion and attachment (Yang et al., 2000;Tang et al., 2007). Many of the previous researches has test graphite as electrode material and reported that graphite electrode is highly effective highly effective for COD, SS and nutrients removal for dischargeable wastewater with enough reaction time (Akarsu et al., 2017). The other cathode material such as aluminium and copper possessed high conductivity however these types of electrode material are not applicable in MFCs as it has toxicity property of trace material ions to the bacteria. metal anode consisting of non-corrosive stainless steel mesh can be utilized, however copper is not suggested due to its toxicity to bacteria (Tekle and Demeke, 2015). In terms of electricity generation, the electrocatalytic properties of the electrode materials influenced the transfer of electrons required in harvesting electricity from organic matter and their resistance on the voltage versus intensity performance (Rodrigo et al., 2007). Higher conductivity of the electrodes are favorable as it improves the electron transport from the anode to cathode. As for carbon electrode, besides having good conductivity, it could as well allow bacteria to attach firmly on the carbon surface and can simultaneously provide electron transfer paths to anode

(Asensio et al., 2017). Also, the rough surface of electrode can stimulates bacteria to produce their nanowires which help them to form bond between each other and provide an electron transfer bridges (Cui et al., 2014).

3.3.2 Hydraulic retention time (HRT) and solid retention time (SRT)

The operating conditions such as hydraulic retention time (HRT) and solid retention time (SRT) are factors that affects the performance of MFC. HRT is defined as the amount of time in hours for wastewater to pass through a tank e.g. aeration tank (Gerardi, 2002). It is reported that MFCs application on the treatment of low strength wastewater is effective at HRTs similar to aerobic process. However, longer HRT is required for high strength wastewater (Kim et al., 2016). On the other hand, SRT is the the amount of time in days, that solids or bacteria are maintained in the activated sludge system. In many cases, the SRT affects the sludge activity and sludge production. Higher SRT resulted in higher COD removal (D'Angelo et al., 2017), which could be due to a higher SRT provides longer period of time for the establishment of the slow growing bacteria and lead to higher concentration of biomass within the system(Belli et al., 2017). In MFCs application, the microorganisms within the system might consists of electrogenic, non-electrogenic and other competing microorganisms. Higher SRT could lead to high population of other competing microorganisms thus could cause the inefficiency of the MFC system. Electricity generation of MFC system is improved at low SRT in which low SRT led to increase in electrogenic bacteria population that has higher growing rate of the other competing microorganisms whereas higher SRT tends to cause the increase in competitions among microorganisms (D'Angelo et al., 2017). Low SRT allows the microorganisms with lower growth rate to be washed out from the system. Operating MFC at low SRT allows the elimination of other microorganisms thus reducing the competition for substrate (Penteado et al., 2016).

3.3.3 Mixed liquor suspended solid (MLSS)

MLSS is the concentration of suspended solids in mixed liquor. Mixed liquor is the mixture of raw or settled wastewater and activated sludge contained in an aeration basin in the activated sludge process. In the MFCs application, low MLSS would contribute to higher current production of the system as lower MLSS concentration allow higher rate of oxygen consumption at the anode and contributes towards the MFC energy production (Wang et al., 2014). Table 6 shows different MLSS range of various type of wastewater treatment system.

Table (6) Wastewater treatment of various range of MLSS concentration.

Type of treatment	Type of wastewater	MLSS range (mg/L)	Optimum MLSS (mg/L)	COD removal	Reference
Integrated MFC-membrane	Synthetic dairy wastewater	2000, 4000, 6000	2000	67% with 138 mW/m^3	(Zinadini et al., 2017)

separation process					
Integrated MFC-tubular membrane reactor	Food wastewater	3400, 4340, 5870, 6780, 8580,10090, 12240	4340	0.76mA	(Wang et al., 2014)
Aerobic/ Anoxic sequencing batch reactor	Synthetic wastewater	3000, 4000, 5000, 6000	3000-4000	93%	(Alattabi et al., 2017)
Sequencing batch reactor	Pharmaceutical wastewater	4000, 6000	4000	83.9%	(Elmolla et al., 2012)

3.3.4 Organic loading rate (OLR)

Organic loading rate (OLR) is defined as the rate of introduction of organic compound (Bitton, 1998). OLR indicates the amount of volatile solids that to be fed to the digester each day. Volatile solids represent that portion of the organic-material solids that can be digested, while the remainder of the solids is fixed. The 'fixed' solids and a portion of the volatile solids are non-biodegradable (Mattocks, 1984). In the MFCs application, a higher OLR could lead to lower COD removal. This could be due the activity of the bacteria to increase their quantity in order to balance with the food in the chamber at higher OLR. However, in terms of electricity generation, higher OLR is favorable as at high OLR, the organic matter is accumulated at higher rate than at low OLR. This relates with the high microbial activity at higher OLR, thus improving its energy recovery (Prasertsung and Ratanatamskul, 2013). Different OLR would produce different bacterial activity, internal resistance and cathode reaction limitation (Nam et al., 2010). Table 7 shows MFC performance at different OLR of various type of wastewater treatment.

Table (7) MFC performance at different OLR of various type of wastewater treatment.

Type of treatment	**Type of wastewater**	**Organic Loading Rate (g/Ld)**	**Optimum Organic Loading rate (g/Ld)**	**COD removal and energy production**	**Reference**
Single chamber MFC	Fermented wastewater	1.92, 2.88, 3.84, 4.80	3.84	2.981 mW/m^3	(Nam et al., 2010)

Anaerobic MFC	Surgical cotton industry wastewater	0.7, 0.9, 1.2, 1.9, 2.7, 3.8	1.9	78.8% with 2.2 mW/m^3	(Tamilarasan et al., 2017)
Single chamber MFC	Cassava wastewater	0.56, 1.44, 2.79, 4.14, 6.25	0.56	91.44% (COD removal)	(Prasertsung and Ratanatamskul, 2013)
			6.25	28680 mW/m^3	
Membrane-less MFC	Synthetic sewage	0.68, 0.72, 0.75, 0.78, 0.87, 1.32, 2.0, 2.65		91.4% at OLR 2.65 13.65 mW/m^3 at OLR 0.87	(Ghangrekar and Shinde, 2008)

4.0 CONCLUSION

MFC is a wastewater treatment and renewable energy technology serves as an interesting alternative method to overcome the water pollution and energy recovery issues encountered by the world. MFC technology involved a bioreactor that involve microorganisms as the biocatalysts to catalyse the oxidation and reduction reaction within the system. General MFC configuration consists of anode and cathode chamber, electrodes, electrical circuit and electron exchange membrane. There are different types of MFC design available each developed with efforts to improve the MFC efficiency. The efficiency of the MFC depends on various factors such as type of wastewater as the source of substrate, electrode material, solid and hydraulic retention time, mixed liquor suspended solid concentration, organic loading rate and other operating conditions. MFC is in developing stage, thus wide research in MFCs field should be conducted in order for MFC to be implemented as the conventional industrial wastewater treatment and energy recovery method. MFC as an environmental friendly energy benefits and wastewater treatment application should be further explored to overcome its disadvantage such as low power production. Integration of MFC with other wastewater treatment system could be an excellent alternative to overcome its advantage and improve its efficiency.

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