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Research Paper

Energy Conversion of Industrial Wastewater on Microbial Fuel Cell (MFC)-Based with Biocatalysts and Pretreatments: A Review

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Abstract
The purpose of this review is to provide current information regarding industrial wastewater treatment with Microbial Fuel Cell (MFC) technology with the addition of biocatalysts and pretreatments. Moreover, this review also updates on industrial waste treatment technology with MFC technology in Indonesia. Industries produce waste with relatively high organic content. However, this organic material is not easily degraded by biological treatment. Instead of reusing, wastewater treatment, presently, aims merely to meet standards quality. In Indonesia, the reuse processes which generate energy are still rare. Industries that can process and convert wastewater to energy can help the government implement sustainable development in the energy sector. One of the technologies is MFC. MFC uses anode in wastewater as a substrate source and generates electrons under anaerobic conditions. Electron formation could be accelerated by adding biocatalysts such as enzymes and specific microorganisms. The process occurred in an anaerobic anode could be enhanced by increasing the substrate's biodegradability in waste. The biodegradability can be improved by pretreatment with ozone or ultrasonic technology. In Indonesia, research on industrial wastewater treatment with MFC as well as biocatalyst and pretreatment is limited.

Keywords
MFC, Waste to Energy, Industrial Wastewater, Electrochemical, Anaerobic, Biocatalyst

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1. INTRODUCTION

Urbanization and industrialization in developing countries like Indonesia create problems in the treatment and disposal of wastewater and energy needs. This situation causes severe problems of public and environmental health, especially in the aspect of sustainable development. The sustainable development goals (SDGs) are access to clean, affordable, and sustainable energy. Stakeholders need to minimize the use of fossil fuel energy and its resulting pollution.

The need for fuel energy and depletion of fossil fuels has resulted in the demand for alternative energy in various research fields to find potential, economical, and the manufacture of renewable energy sources.. Renewable energy development is expected to reduce the dependence on fossil fuels and to increase energy independence in each country (Kaygusuz, 2012). Indonesian Government Regulation No.79/2014 concerning National Energy Policy is a clear form of the government's efforts to achieve sustainable development goals in the energy sector. This policy aims to reduce fossil fuel used by less than 25% and to increase renewable energy use by more than 23% (Ramadan, 2017). Renewable energy has provided great benefits, especially for electricity, including increasing economic, social, and public health value. Some areas in Indonesia are not entirely self-sufficient, therefore they are not covered by electricity in rural areas and, even, in urban areas. This concern could accelerate the development of alternative energy sources, such as fuel cells (Sivagami, 2015; Martinez-Duart et al., 2015; Salvi and Subramanian, 2015; Guo et al., 2014).

In Indonesia, industries is one of the largest energy users and producers of waste that are not environmentally friendly. The reduction of ecosystems and the health impacts of industrial pollutants have necessitated the development of various advanced processing technologies. Processing technology applications are still limited due to high energy requirements and other chemical consumption and complex operations and maintenance. Industrial waste such as agricultural, plantation, palm oil, textiles, pier, and household are ideal substrate for the production of alternative energy because it was rich with organic content. Organic materials in this wastewater were highly considered in waste to energy technology.

The treating process of wastewater with the method of (Feng et al., 2008) Microbial Fuel Cell (MFC) emerged as an alternative in the late 1990s. The history of this technology began in 1912, with Potter as the founder (Potter, 1911) . MFC is a methodology that reuses and reduces energy demand. Recently, the production of valuable energy and other by-products were more critical. MFC is a system in which chemical energy is converted into electrical energy or bio-electrochemical systems (BES) by catalytic reactions of microorganisms (Kondaveeti et al. (2014); Logan et al. (2006)) . Other BES have been developed to produce useful products, such as hydrogen (Santoro et al. (2017);Escapa et al. (2016)), methane (Babanova et al. (2016); Villano et al. (2011);Van Eerten-Jansen et al. (2012)), or desalinated water (Cao et al., 2009).

Many things need to be conducted before reaching the industrialization of MFCs (Trapero et al. (2017); Rahimnejad et al. (2015)). The implementation of industrial waste is more complicated because it has to work in more complex conditions (Pant et al. (2010);Pandey et al. (2016)). Several innovations that can be combined are the addition of biocatalysts and pretreatments. This innovation can be used as a reference of a starting point for MFC industrialization growth, especially in Indonesia. This review aims to identify the type of MFC use in the wastewater industry and the challenge of using biocatalyst waste and pretreatment in MFC applications.

2. EXPERIMENTAL SECTION

2.1 Methods

This study uses a review obtained from the google scholar database. Identification was carried out using the keyword of Microbial Fuel Cell (MFC). The data used were data from journal sources, proceedings, and dissertations. Data were analyzed using descriptive. Previous research results from journals, proceedings, and dissertations were compared.

3. RESULTS AND DISCUSSION

3.1 Previous Research

The MFC research that has been conducted currently focuses more on laboratory scale reactors while the application in the field is required to use a relatively large scale. Several laboratory-scale research results on industrial waste have resulted in developments that have the potential to be applied in the field. The summary of this study are described in Table 1. Researches on the addition of the catalyst shown in Table 2 are quite potential. Pretreatment also has the potential to increase the value of energy conversion and waste treatment as shown in Table 3.

3.2 Develops Scale of MFC reactor

Several groups have examined MFC as a reactor for wastewater treatment from the lab scale to pilot scale. Upscaling to a volume of 1 m^3 aimed at treating the wastewater of a brewery in Yatala, Queensland, Australia has been carried out with satisfactory results (Logan, 2010). A 105 L MFC unit pilot system was also recently implemented (Zhang and He, 2015). In these examples, the primary objective is to detect compounds or degradation of organic and energy potential. The forecast for cheap electricity prices grow as the use of MFC will be a promising alternative. MFC reactor performance from operating variables such as COD, flow rate, or reactor volume might vary depending on the application and wastewater, and making it a useful tool for future assessment by potential investors in this technology (Trapero et al., 2017).

Applications of MFC have been reported to meteorological power buoys (Tender et al., 2008) and wireless temperature sensors (Dewan et al. (2014);Ewing et al. (2014)). Other types of MFC have also demonstrated the capability of turning on environmental sensors (Schievano et al. (2017);Khaled et al. (2016);Pietrelli et al. (2014)). Several other applications have been reported, including charging mobile phones (Ieropoulos et al., 2013) and on smartphones (Walter et al., 2017) as well as LEDs for lightning (Gajda et al., 2015). This particular application has been developed for trials in refugee camps and slums (Ieropoulos et al., 2016).

3.3 Administration of biocatalysts in MFC

Currently, MFC research commonly uses artificial wastewater instead of actual wastewater (Pant et al. (2010);Pandey et al. (2016)). The use of MFC reactors for research was limited to a laboratory scale with a volume of less than 1 L. Large scale MFC reactor has also been conducted, but the reactor with such volume only potentially degrades organic compounds in waste (Zhang and He (2015);Ge et al. (2015)).

In general, waste has low biodegradability but high organic content,particularly for some industries such as textiles and even metals (Apritama et al., 2020). Much industrial wastewater is treated in conventional ways (Suryawan et al., 2019). Some industrial waste, which cannot be treated conventionally, utilizes organic material contained in the waste. The conversion of waste energy could be accelerated by adding a biocatalystsuch as microorganisms (bioaugmentation).

This review focuses on the addition of the enzyme from agricultural waste into the MFC reactor. Agricultural wastes such as straw, rice husk, and corn could potentially produce specific enzymes that were able to accelerate the substrate degradation rate in waste. The high organic content and low BOD content in industrial waste cause a low biodegradability value and leads to biological processing difficulty. Thus, preliminary processing (pretreatment) are needed to increase the biodegradability of the waste. Some of the MFC reactor integrated pretreatments were carried out such as ozone and ultrasonic (Yusoff et al., 2013) . There was still a

Table 1. Laboratory scale MFC research on industrial waste

No	MFC system	Types of Industrial Waste	Ref
1	Dual-chamber with aeration and addition of potassium ferricyanide catholyte	Composite industrial wastewater (18.6 g COD/L; 56.8 g TDS/L).	(Mohan et al., 2009)
2	Dual-chamber MFC with the addition of the Fenton system	H_2O_2 added in colored wastewater and anode chamber in sequential operation.	(Fu et al., 2010)
3	MFC with dual-chamber with ozone membrane (0.08–0.12 g/L)	Polymer wastewater with a 165 ml volume with a cathode of 1 M HCl and 1 M NaOH.	(Li et al., 2017)
4	Dual-chamber MFC with a volume of 500 mL	Substrate and anodes from leather, dairy, and domestic industrial wastewater.	(Aswin et al., 2017)
5	Single chamber with batch and continuous conditions with the volume of 0.25/0.20 L	The substrate from the oil refinery wastewater is processed continuously.	(Srikanth et al., 2016)
6	Single chamber in batch condition with volume 0.5/0.43 L	Pharmaceutical wastewater was obtained from the massive drug manufacturing unit.	(Velvizhi and Mohan, 2012)
7	Single MFC (nonmediator; non-catalytic graphite electrode; open-air cathode).	The anaerobic consortium obtained from a Full-scale anaerobic sludge blanket reactor (UASB) operating with composite chemical wastewater used as a biocatalyst in the MFC anode chamber.	(Goud and Mohan, 2011)
8	Pre-fermentation & UBFC with the addition of a biocatalyst	The waste substrate from biodiesel wastewater, palm oil, and seafood.	(Sukkasem, 2013)
9	Single Chamber MFC reactor with a total and working volume of 350 and 300 mL, respectively.	Petroleum refinery wastewater used as a substrate and alkalinity.	(Mohanakrishna et al., 2018a)
10	The 4L anoxic aerobic MFC reactor was used for this study. The MFC reactor was inoculated with aerobic sludge and operated in continuous HRT and SRT mode for 20 days.	Used caustic wastewater is industrial wastewater with high COD concentration influenced by high sulfur content, salinity,	(Fazli et al., 2018)
11	Plexiglas dual-chamber MFC pressed to both sides of the proton exchange membrane (PEM) without tubes.	Both the anode and cathode electrodes consist of graphite fiber brushes and titanium wires that collects electrons for the external circuit.The anodic compartment of MFC is inoculated with activated sludge.	(Jiang et al., 2011)
12	The design type of dual-chamber MFC has two chambers consisting of anode and cathode compartments. Each volume was 500 ml.	POME (Palm Oil Mill Effluent) organic waste in the anode compartment with variations addition of Escherichia coli and Saccharomyces cerevisiae (10% v/v). The cathode compartment contains 200 ppm KMnO4 solution and aerobically conditioned with the aid of an aerator.	(Yogaswara et al., 2017)

small number of research that focused on MFC substrates pretreatment and needs to be studied further, especially in the field of industrial wastewater.

3.4 MFC integrated waste pre-treatment

Ultrasonic waves are longitudinal mechanical waves with frequencies above 20 kHz. These waves could propagate in solid, liquid, and gas mediums due to interaction with molecules and the inertia properties of the medium passed through (Ramadan, 2017).

Industrial wastewater usually has a very low biodegradability index thereforeprocessing applications using microorganisms is a major challenge. Some pretreatments are important to increase the biodegradability index (BOD_5/COD). The higher biodegradability index is a measure for the biodegradability increase of organic pollutant degradation. This biodegradability increase could be achieved when the COD removal is moderate, and the ozonation time is short. Besides, the pretreatment process was suitable for a biodegradability index of less than 0.3 and increased it to be greater than 0.4. Several studies have also shown the ozonation success in increasing the industrial wastewater biodegradability (Suryawan et al. (2019); Suryawan et al. (2020)).

3.5 Wastewater treatment industry development with MFC

Along with the times, the population in the world, including Indonesia, is increasing. The existence of rapid population growth demands living facilities used to meet various needs. Therefore, more and more industries are being built and operating to meet people's needs in Indonesian and the world. The development of industrial centers could be followed by higher waste generation, one of which is wastewater. This industrial wastewater needs to be treated beforehand to comply with quality standards if discharged into a water body. This domestic liquid waste could be processed using the MFC system to reduce organic contaminants by degrading this organic material into electricity. For high concentration of COD, the longer the degradation process, the greater the anode compartment of the proton ions (H^+) and electrons (e^-) would be (Haslett, 2012). Various utilization of MFC technology in Indonesia still focuses on domestic wastewater and leachate water. Meanwhile, the utilization of industrial wastewater is still low. Table 4 shows various research that utilizes industrial waste for MFC technology.

Dual chamber modifiedMFC technology generally dominates industrial wastewater conversion to energy. There are few reported literature on MFC using catalysts for industrial wastewater media, thus it is necessary to conduct further research using biocatalysts such as bioaugmentation with microorganisms. The findings will undoubtedly offer economic, social and environmental benefits.

4. CONCLUSIONS

MFC technology for wastewater treatment has not been widely developed. Waste could be generated from domestic activities along with non-domestic activities, such as industries. Research in MFC is mostly limited to the laboratory scale. Studies using both biocatalysts and pretreatments can be potentially developed to improve the MFC technology. In Indonesia, MFC work has been carried out in several industries and has produced acceptable results. However, MFC technology development needs to be furtherexplored, using biocatalysts, ozone, and ultrasonic pretreatment to compromise the challenges in current treatment technology using microorganisms. The pretreatments can improve biodegradability index (BOD_5/COD). Microbial Fuel Cell technology utilizes microorganism toreduce the organic contaminants by degrading this organic substances and converting into electricity. MFC treatment uses anode in wastewater as a substrate source and generates electrons under anaerobic conditions. Electron formation could be accelerated by adding biocatalysts such as enzymes and specific microorganisms. The anodic compartment of MFC technology is inoculated with activated sludge from biological treatment.

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Table 2. Previous MFC research with the addition of biocatalysts

No	Biocatalysts used	The effect of adding biocatalyst	Ref
1	The addition of an electrogenic mixed culture of rusted metal dominated by iron bacteria, sulfur oxidizer producer bacteria, and acid bacteria was used as the inoculum.	The electrode surface area was smaller, but the power yield was good enough for process improvement.	(Srikanth et al., 2016)
2	The anaerobic consortium taken from the anaerobic pharmaceutical wastewater scale was used as a biocatalyst in the anodic chamber in MFC.	The electrogenic activity of a fuel cell depends on many factors, especially the microorganisms' catabolic activity used as anodic biocatalysts.	
3	Food waste processing that has been previously fermented in an anaerobic reactor for 24 hours with a consortium of the anaerobic mixture as a biocatalyst, at pH 7 under anaerobic conditions	A significant increase in power output was seen after fermentation	(Goud and Mohan, 2011)
4	Immobilized biocatalytic basic electrode, each material was inoculated in activated sludge obtained from industrial waste water treatment plants	The carbon fiber brush immobilization base was increased UBFC performance by 17.54%.	(Sukkasem, 2013)
5	Wastewater is a good source of several bacterial strains types at the anode and cathode.	This resulted in an increase of 30% in COD removal compared to MFC with biocatalyst at the anode.	(Mohanakrishna et al., 2018b)
6	Shewanella oneidensis strain 700-550.	The contribution of direct electron transfer mechanisms to the electricity production in microbial fuel cells was demonstrated by the physically maintaining of Shewanella oneidensis using a dialysis membrane and immobilizing cells in alginate. 66-74% of the transferred electrons could be attributed to direct electron transfer. The research results that could be increasing direct electron transfer in Shewanella spp are suggested as future MFC processing.	Fapetu et al. (2016)
7	The microorganisms added to the POME waste substrate were Saccharomyces cerevisiaefungi and Escherichia coli bacteria.	Saccharomyces cerevisiae addition to the POME substrate decreased MFC's performance, seen from a decrease in the value of electric current, electric voltage, resulting in adecrease in the resulting power density.	(Yogaswara et al., 2017)

Table 3. Previous MFC research with pretreatment

No	Type of Pretreatment	Result	Ref
1	Ultrasound pretreatment	MFC with an electrical load > 0.6 W / ml increased the total COD removal rate from 11.3% to 19.2%	(Jiang et al., 2011)
2	Ozone pretreatment	Pretreatment was carried out using ozone and microwave. Ozonation was carried out for 2 and 4 hours. When 2- and 4-hour samples of ozonation were introduced in the MFC reactor, the voltages were increased to more than 150 mV and 120 mV respectively.	(Yusoff et al., 2013)

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Table 4. Previous MFC research with pretreatment

No	Wastewater type	Catalyst	Volume	MFC type	COD removal	Electricity Generation	Source
1	Pulp and Paper Industry	-	3.47 L	ML-MFC (Membrane less Microbial Fuel Cell)	38.50%	118.8 mV	(Pramono et al., 2015)
2	Fishery industry	-	1.8 L	Single chamber MFC	59.34%	340 mV	(Ibrahim et al., 2017)
3	Pome	E.coli	500 ml	Dual-chamber	14.23%	103.02 mW/m^2	(Yogaswara et al., 2017)
4	Tempe and Tofu Waste	Lactobacillus bulgaricus	1 L	Dual-chamber	-	282 mV	(Sulistiyawati, 2020)
5	Tempe liquid waste	0.1N electrolyte solution	800 ml	Dual-chamber	-	675 mV	(Syahri et al., 2019)
6	Slaughterhouse	-	1 L	Dual-chamber	71%	4738.55 mW/m^2	(Ali and Widodo, 2019)
7	Preserve fish without drying (pindang) waste	-	-	Dual-chamber	90%	6.84 mW	(Ibrahim et al., 2020)
8	Fish fillet industrial waste	-	2 L	Single chamber MFC	77.92%	550 V	(Safitri et al., 2020)

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