PRETREATMENT OF DEWATERED SLUDGE FOR MICROBIAL FUEL CELL APPLICATION

NUR FATIN SYAHIRA BINTI RUSDI

UNIVERSITI SAINS MALAYSIA

2017

PRETREATMENT OF DEWATERED SLUDGE FOR MICROBIAL FUEL CELL APPLICATION

by

NUR FATIN SYAHIRA BINTI RUSDI

Thesis submitted in partial fulfillment of the requirement for the degree of Bachelor of Chemical Engineering

June 2017

ACKNOWLEDGEMENT

First and foremost, I would like to express my deepest and sincere gratitude to my supervisor Prof. Madya Dr. Vel Murugan Vadivelu for his precious encouragement, guidance and generous support throughout this work.

I would also extend my gratitude towards all my colleagues for their kindness cooperation and helping hands in guiding me carrying out the lab experiment. They are willing to sacrifice their time in guiding and helping me throughout the experiment besides sharing their valuable knowledge. I am hugely indebted to Abdul Rasyid bin Ruslan, a postgraduate student who had assisted me throughout my lab works, he deserved my special mention.

Apart from that, I would also like to thank all the lab technicians and staffs for their kindness cooperation and helping hands. Indeed their willingness in sharing ideas, knowledge and skills are deeply appreciated.

Once again, I would like to thank all the people, including those whom I might have missed out and my friends who have helped me directly or indirectly. Their contributions are very much appreciated. Thank you very much.

Nur Fatin Syahira Binti Rusdi

June 2017

TABLE OF CONTENTS

	Page
ACKNOWLEDGEMENT	**ii**
TABLE OF CONTENTS	**iii**
LIST OF TABLES	**v**
LIST OF FIGURES	**vi**
LIST OF SYMBOL	**vii**
LIST OF ABBREVIATIONS	**viii**
ABSTRAK	**ix**
ABSTRACT	**x**
CHAPTER ONE : INTRODUCTION	1
1.1 Research background	1
1.2 Problem Statement	2
1.3 Research objectives	3
1.4 Scope of Study	3
1.5 Report organization	3
CHAPTER TWO : LITERATURE REVIEW	5
2.1 Pretreatment of biomass	5
2.1.1 Pretreatment	6
2.1.2 Biomass	9
2.2 Microbial fuel cell	10
2.2.1 MFC Designs	11
CHAPTER THREE : MATERIALS AND METHODS	13
3.1 Equipment and Chemicals	13
3.2 Research methodology flow chart	15
3.3 Sample collection	16
3.4 Sample pretreatment	16
3.5 MFC configuration	16
3.6 Analytical method	17
3.6.1 Determination of biomass	17
3.6.2 Determination of electricity generation	17
CHAPTER FOUR : RESULTS AND DISCUSSION	18
4.1 pH variations	19

4.2 Alkaline Pretreatment 22
4.2.1 Effect of pH on SCOD release 22
4.2.2 Effect of pH on voltage generation 24
4.3 Acidic Pretreatment 26
4.3.1 Effect of pH on SCOD release 26
4.3.2 Effect of pH on voltage generation 29
CHAPTER FIVE : CONCLUSIONS AND RECOMMENDATIONS 31
5.1 Conclusions 31
5.2 Recommendations 31
REFERENCES 33

LIST OF TABLES

		Page
Table 3.1	List of Equipment	13
Table 3.2	List of Chemicals	14
Table 4.1	NaOH-Deionized Water ratio	20
Table 4.2	HCl-Deionized Water ratio	21
Table 4.3	Maximum Output Voltage at different pH	30

LIST OF FIGURES

		Page
Figure 3.1	Research methodology flow chart	15
Figure 4.1	Variations of pH with time for alkaline pretreatment	20
Figure 4.2	Variations of pH with time for acidic pretreatment	21
Figure 4.3	SCOD for alkaline pretreatment throughout experiment	23
Figure 4.4	SCOD increment in first 24 hours for alkaline pretreatment	24
Figure 4.5	SCOD reduction in 7 days for alkaline pretreatment	24
Figure 4.6	Voltage generation for alkaline pretreatment	25
Figure 4.7	SCOD for acidic pretreatment throughout experiment	27
Figure 4.8	SCOD increment in first 24 hours for acidic pretreatment	27
Figure 4.9	SCOD reduction in 7 days for acidic pretreatment	28
Figure 4.10	Voltage generation for acidic pretreatment	29

LIST OF SYMBOL

	Symbol	Unit
I	Current	mA
P	Power	mW
R	Resistance	Ohm
SCOD	Soluble Chemical Oxygen Demand	mg/L
T	Temperature	℃
V	Voltage	mV

LIST OF ABBREVIATIONS

EPS	Extracellular Polymeric Substances
HPH	High Pressure Homogenization
MEC	Microbial Electrolysis Cell
MFC	Microbial Fuel Cell
SCOD	Soluble Chemical Oxygen Demand
TH	Thermal Hydrolysis
UV-VIS	Ultraviolet-Visible Spectroscopy

RAWATAN AWAL BIOJISIM DALAM APLIKASI SEL BAHAN API MIKROB

ABSTRAK

Dalam kajian ini, kesan daripada kaedah rawatan awal enapcemar yang dikeringkan yang berbeza terhadap sel bahan api mikrob (MFC) diselidik. Kajian ini meyelidik kesan kaedah rawatan awal iaitu rawatan awal secara alkali dan asid dengan nilai pH yang berbeza (9, 8, 7, 6, 5, dan 4) dalam waktu 24 jam rawatan awal. Pertama, kesan terhadap rawatan awal enapcemar dianalisa dengan larutan Permintaan Oksigen Kimia (COD) dan Asid Organik Meruap (VOA). Selepas 24 jam rawatan awal, COD dan VOA untuk alkali adalah lebih tinggi berbanding rawatan awal asid. Kedua, melalui 7 hari operasi mod kelompok, sel bahan api mikrob ruang tunggal (SCMFC) dijalankan degan enapcemar terawat (rintangan luaran - 1000Ω). Rawatan awal alkali menunjukkan penurunan SCOD sehingga 46% manakala rawatan awal asid 23%. Berdasarkan data eksperimen, ia menunjukkan maksima keluaran voltage dengan voltan litar terbuka (OCV) adalah 691mV untuk sample pH 6 yang dijana sepanjang 7 hari operasi. Nilai konduksi enapcemar terawat untuk kedua kaedah rawatan awal menurun sepanjang 7 hari operasi. Maka, data menunjukkan bahawa dengan menggunakan enapcemar terawat sebagai substrat di dalam MFC membolehkan pengurangan enapcemar dan juga penjanaan elektrik dan rawatan awal enapcemar yang berkesan dapat memperbaiki keseluruhan prestasi proses.

PRETREATMENT OF BIOMASS FOR MICROBIAL FUEL CELL APPLICATION

ABSTRACT

In this study, influence of different method of pretreatment of dewatered sludge for microbial fuel cell (MFC) performance was investigated. This study investigated the effects of different methods (alkaline and acidic pretreatment) with varying pH (9, 8, 7, 6, 5, and 4) on 24 hours of pretreatment. First, effect of sludge pretreatment was analysed by Chemical Oxygen Demand (COD) solubilisation and Volatile Organic Acids (VOA). After 24 hours of pretreatment, COD solubilisation and VOA was higher for alkaline pretreatment and lower for acidic pretreatment. Second, with 7 days of operation at batch mode, single chamber microbial fuel cell (SCMFC) was run with pretreated sludge (external resistance - 1000Ω). Alkaline pretreatment showed a decrease of Soluble Chemical Oxygen Demand (SCOD) up to 46% meanwhile the value for acidic pretreatment was 23%. From experimental results, it was indicated that the maximum voltage generation with open circuit voltage (OCV) of 691mV at pH 6 was generated in 7 days. The conductivity of the pretreated sludge for both methods decreased during the 7 days operation. Thus, these results showed that using pretreated sludge as the substrates in MFC could achieve both sludge reduction and electricity generation, and proper pretreatment of sludge could improve the overall process.

CHAPTER ONE

INTRODUCTION

1.1 Research background

Around the world notable steps are being taken to advance from today's fossil-based economy to a more sustainable economy based on biomass. In addition, to cope with challenges such as high demand and escalating fuel prices, researchers have introduce sustainable and cost-effective methods of energy production.

As world is going towards renewable energy sources, microbial fuel cell (MFC) is getting attention nowadays. MFC offers numerous potential to produce energy in the form of electricity. The strength of MFC is the potential of direct converting chemical energy to electrical energy via biological pathway, thereby allowing it the biological adaption to handle various chemical substrates at different concentrations (Lee et all.,2015).

Generally, pretreatment of biomass refers to the disruption of the naturally resistant carbohydrate-lignin shield that limits the accessibility of enzymes to cellulose and hemicellulose. Pretreatment of biomass play a key role in the development of bioprocesses and products from lignocellulosic and algal biomass, working on the principle of biorefinery.

In order to improve the rate of hydrolysis and the anaerobic digestion performance, sludge disintegration was developed as a pretreatment process to accelerate the anaerobic digestion and to increase the degree of stabilization (Jayashree et al., 2014).

Different pretreatment methodologies are to be adopted to derive the useful components from the biomass. A variety of physical (comminution, hydrothermolysis), chemical (acid, alkali, solvents, ozone), physicochemical (steam explosion, ammonia fiber explosion) and biological pretreatment techniques have been developed to improve the accessibility of enzymes to cellulosic fibers.

Various modifications in the design of the MFC and sludge degradation with sludge pretreatment have resulted in increased performance efficiency. Hence, by applying pretreatment methods with MFC application, rate of voltage generated could be observed from process of sludge hydrolysis by comparing with pre-treated and untreated sludge.

1.2 Problem statement

MFC are devices that use bacteria as the catalysts to oxidize organic and inorganic matter and generate current. It has been proven to be capable of using different of sludge as anodic fuels for electricity generation. Advancement in MFC technologies would provide a sustainable wastewater treatment and management system toward efficient and sustainable sources (Yusoff et al., 2013).

Sewage sludge, as an inevitable byproduct of wastewater treatment, needs to be dewatered to reduce its volume and thus dewatered sludge is generated. The disposal processes of dewatered sludge include incineration, sanitary landfill and composting. This process caused an issue of sludge disposal and utilization space to handle it.

Although many researchers have investigated sludge pretreatment for power generation, yet there are still uncertainties about the MFC optimum performance. In addition, in most of the sludge pretreatment only one type of sludge sample is being used. Besides, in the sludge anaerobic digestion, pH is one of the most important controlling parameters which can significantly affect the hydrolysis of sludge. Hence, in this study, alkaline pretreatment method was investigated by varying the pH level of the samples and the effect of pretreatment processes on the sludge was observed by evaluating voltage and power density generated.

1.3 Research objectives

The potential that ensued from those problem lead to this study with the following objectives

a) To study the effect of pretreatment method of dewatered sludge in terms of electricity and power generated in microbial fuel cell.

b) To study the characteristics of dewatered sludge before and after pretreatment.

c) To study the effect of pretreatment method of dewatered sludge towards SCOD produced and consumed in microbial fuel cell.

1.4 Scope of study

In this research, pretreatment methods were proposed to treat biomass to be used as sludge sample in MFC. The performance of MFC due to the effect of pretreatment was analyzed by power generation, voltage, total solid, soluble chemical oxygen demand, volatile fatty acid, volatile solid, conductivity and pH level. The sludge sample was collected from Kerian Indah Water Treatment Plant around Parit Buntar areas.

1.5 Report organization

In this report, there are five chapters were carried out accordingly and each chapter was described by the sequence of the research

Chapter 1 covers the application of the microbial fuel cells in the existing technologies and how it can be used to produce energy as a new main resource to the upcoming days. This chapter also discussed on problem statement, research objectives, scope of the research and thesis organization.

Chapter 2 presents an outline of the related principle of the pretreatment method and MFC configuration. Different types of pretreatment method and its selectivity, biomass characteristics, type of MFC, and the effect of pretreatment on the performance of MFC are reviewed in detail.

Chapter 3 introduce to the materials and procedure explaining the experimental steps in the research for MFC configuration. This chapter also presents the analysis of sample and the power generated.

CHAPTER TWO

LITERATURE REVIEW

2.1 Pretreatment of biomass

Pretreatment is the first and most important step in lignocellulosic biomass processing. It is the main process by which the recalcitrant lignocellulosic biomass could be modified so as to make it amendable to further processes or reactions in order to convert into other products (Logan et al., 2007).

In the view of the beneficial role in sludge disintegration, pretreatment has gained much more concerns within scientific communities in the past decade especially the ever-growing importance of pretreatment played in sewage sludge anaerobic digestion.

The process involves pretreatment is to alter or remove structural and compositional impediments to hydrolysis in order to improve the rate of enzyme hydrolysis and increase yields of fermentable sugars from cellulose or hemicellulose. The effectiveness of enzymatic hydrolysis of pretreated lignocellulosic biomass can be significantly enhanced if lignin an its derivatives are removed or effectively modified before adding enzymes because lignin and its derivatives interfere with the path for cellulases action and they are also toxic to microorganisms, slowing down enzymatic hydrolysis (Qing et al., 2010; Yang and Wyman, 2008).

The ultimate pretreatment process produces a disrupted, hydrated substrate that is easily hydrolyzed but avoids the formation of sugar degradation products and fermentation inhibitors. However, significant considerations need to be taken for selecting a pretreatment technology such as technical, operational and economic-environmental benefit.

2.1.1 Pretreatment

The main purpose of pretreatment is to disrupt extracellular polymeric substances (EPS) matrix and cell wall and to make the available nutrients accessible to microbes thus speeding up the conversion of organic solids and methane productivity. To make it clear, pretreatment methods are proposed to improve anaerobic biodegradability.

The pretreatment methods will result physical and/or chemical changes in the lignocellulosic biomass, hence, pretreatment technologies are normally classified into physical/mechanical, chemical, physiochemical, and biological.

2.1.1(a) Physical/Mechanical pretreatment

Physical methods involve breakdown of biomass size by coarse size reduction, chipping, grinding, shredding, and milling in order to increase the available specific surface area and reduce the degree of polymerization, enhancing the digestibility of lignocellulosic biomass (Agbor et al., 2011; Brodeur et al., 2011). The pretreated biomasses by physical methods are subjected to heating, mixing and shearing resulting in physical and chemical modifications.

Another physical method is extrusion that disrupts the lignocellulose structure and increases the accessibility of carbohydrates to enzyme attack. Another example of physical pretreatment includes microwave and microwave-chemical, ultrasonification, electrokinetic disintegration and high pressure homogenization (HPH).

2.1.1(b) Thermal hydrolysis

Thermal hydrolysis (TH) is a well-known and commercially implemented pretreatment technology that, originally used to enhance sludge dewaterability. The performance of the TH process primarily relies upon treatment temperature and time used.

TH can be conducted over wide ranges of operating conditions, pretreatment time and such is the case with the liquid/solid ratio.

2.1.1(c) Chemical pretreatment

Chemical pretreatment employs strong reagents to deform the cell wall and membrane, favoring the availability of sludge organic matter for enzymatic attacks. The major reagents employed in the literature include acids, alkali and oxidants (ozonation and peroxidation) (Zhen et al., 2016).

Generally, chemical pretreatments show a high degree of selectivity for the biomass component they degrade and also involve relatively harsh reaction condition and result in the possible production of toxic substances and their possible effects on downstream biological processing. In most chemical pretreatments, degradation of lignin has been observed and particularly in dilute-acid and lime pretreatments (Samuel et al., 2011).

Acidic and alkali pretreatment have shown of huge potential in biomass solubilization due to their numerous advantages, e.g. a simple device, high methane conversion efficiency, ease of operation and low cost. Acidic hydrolysis is performed using acids such as HCl, H_2SO_4, H_3PO_4 and HNO_3 while alkali pretreatment usually employs several alkaline solutions, inducing NaOH, KOH, $Ca(OH)_2$, $Mg(OH)_2$, CaO and ammonia.

The addition of acid or base avoids the necessity of high temperature and thus can be operated at ambient or moderate temperatures. The effectiveness of acidic or alkali pretreatment may vary with the types and characteristics of the studied substrates because of their distinct affinity to organic components.

Acidic pretreatment solubilize the hemicellulose, and by this, make the cellulose more accessible. The main reaction that occurs during acid pretreatment is the hydrolysis of hemicellulose, especially xylan as glucomannan is relatively acid stable. Alkali pretreatment is comparatively suitable for lignin breakdown. During alkaline pretreatment, the first reactions taking place are solvation and saponification. This causes a swollen state of biomass and makes it more accessible for enzymes and bacteria.

Alkali method gains higher popularity in sludge disintegration before being sent to the digesters when considering its unique benefits in providing additional alkalinity that increases the buffer capacity of systems, specific methanogenic activity and process stability.

Another method that can be classified in chemical pretreatment are ozonation, Fenton oxidation, and Fe(II)-activated persulfate oxidation.

2.1.1(d) Biological pretreatment

Biological pretreatment employ microorganisms mainly brown, white and soft-rot fungi, which degrade lignin, hemicellulose and cellulose in small proportion (Alvira et al., 2010). Currently, this method gained attention as its benefits over conventional physical/chemical pretreatment methods, such as environmentally friendly, low capital cost, low energy, no chemicals requirement and mild environmental conditions.

Nevertheless, the main disadvantages to develop this approach are the low hydrolysis rate obtained in most biological materials and the relatively long time of the pretreatment compared to conventional methods. In addition, more space and longer processes are required, which affect the operating costs. Microbial electrolysis cell (MEC) and temperature phased anaerobic digestion (TPAD) can be classified into biological pretreatment methods.

2.1.1(e) Physicochemical pretreatment

The purpose of steam pretreatment, steam explosion or liquid hot water, is to solubilize the hemicellulose to make the cellulose better accessible for enzymatic hydrolysis and to avoid the formation of inhibitors. During steam pretreatment parts of the hemicellulose hydrolyze and form acids, which could catalyze the further hydrolysis of the hemicellulose. To avoid the formation of inhibitors, the pH should be kept between 4 and 7 during the pretreatment (Hendriks and Zeeman, 2009).

This approach introduce methods such as wet oxidation which use oxygen as oxidation agent, carbon dioxide pretreatment at high pressure and high temperature, ammonia fiber explosion (AFEX), ammonia recycled percolation (ARP) and soaking aqueous ammonia (SAA).

The pretreatment approach discussed earlier such as ammonia, steam explosion, liquid hot water, dilute acid pretreatment are the most studied methods because they have potential as cost-effective pretreatments. Other options such as biological, microwave and conventional pretreatment methods are either low effective, long-time treatment or too expensive and additional research should be studied before they can be competitive.

2.1.2 Biomass

Lignocellulosic biomass is the most lavish organic compound on Earth and represents the main portion of the world's annual production of renewable biomass. Lignocellulosic materials predominantly contain a mixture of carbohydrate polymers such as cellulose and hemicellulose and lignin.

Cellulose is an unbranched linear polymer of glucose. Hemicelluloses belong to a group of heterogeneous polysaccharides containing both 6-carbon and 5-carbon sugars. Lignin is a very complex molecule with phenylpropane units linked in a three-dimensional structure.

The amount of cellulose, hemicellulose and lignin depends on the type of material. Normally the cellulose content may vary between 30% and 50%, hemicellulose 20-40% and lignin 10-30%. The carbohydrate polymers in the lignocellulosic material are to be converted to simple sugars before fermentation.

Due to the heterogeneous and very complex nature of the lignocellulosic biomas, enzymatic hydrolysis is not an efficient method for native biomass. Thus, the biomass need to be pretreated so as to make it amenable to enzyme action.

2.2 Microbial fuel cell (MFC)

Microbial fuel cell (MFC) technologies represent the latest approach for generating electricity-bioelectricity generation from biomass using bacteria. MFC are devices that use bacteria as the catalysts to oxidize organic and inorganic matter and generate current. In an MFC, microorganisms degrade (oxidize) organic matter, producing electrons that travel through a series of respiratory enzymes in the cell and make energy for the cell in the form of ATP. The electrons are then released to a terminal electron acceptor (TEA) which accepts the electrons and becomes reduced.

In most MFCs, the electrons that reach the cathode combine with protons that diffuse from the anode through a separator and oxygen provided from air, the resulting product is air. Chemical oxidizers, such as ferricyanide or Mn (IV) can also be used although these must be replaced or regenerated (Logan et al., 2006).

Oxygen in the anode chamber will inhibit electricity generation, so the system must be designed to keep the bacteria separated from the oxygen. This separation of the bacteria from oxygen can be achieved by placing a membrane that allows charge transfer between the electrodes, forming two separate chambers: the anode chamber, where the bacteria grow and the cathode chamber, where the electrons react with the catholyte. The cathode is sparged with air to provide dissolved oxygen for the reaction. The two electrodes are connected by a wire containing a load (resistor).

MFC also have been proven to be capable of using various sludges (e.g. manure sludge, surplus sludge, petroleum sludge and fermented primary sludge) as anodic fuels for electricity generation while accelerating anaerobic degradation (Dental et al., 2004). Restated, Jiang et al. (2011) has proven the fuel cell reactions degraded additional 7.9% total COD (TCOD) of raw sludge in MFC and sludge degradation in MFC can be characterized as a combined process of anaerobic digestion and electrochemical oxidation, being complementary in function to each other.

2.2.1 MFC Designs

Many different configurations are possible for MFCs. A commonly used and inexpensive design is a two-chamber MFC built in a traditional "H" shape, consisting usually of two bottles connected by a tube containing a separator which is usually a cation exchange membrane or a plain salt bridge.

In the H-configuration, the membrane is clamped in the middle of the tubes connecting the bottle. An inexpensive way to join the bottles is to use a glass tube that is hated and bent into a U-shape, filled with agar and salt (to serve the same function as a cation exchange membrane). The salt bridge MFC, however produces little power due the high internal resistance observed.

Several variations on these basic designs have emerged in an effort to increase power density or provide for continuous flow through the anode chamber. Systems have been designed with an outer cylindrical reactor with a concentric inner tube that is the cathode and with an inner cylindrical reactor with the cathode on the outside.

MFCs technologies are a promising and yet completely different approach to wastewater treatment as the treatment process can become a method of generating energy in the form of electricity or hydrogen gas, rather than a drain on electrical energy. The growing pressure on our environment, and call for renewable energy sources will further stimulate development of this technology.

CHAPTER THREE

MATERIALS AND METHODS

3.1 Equipment and Chemicals

The equipment and chemicals used throughout the study are listed in Table 3.1 and Table 3.2, respectively.

Table 3.1 : List of Equipment

Equipment	Purpose
Oven	Drying
Centrifuge	Separation
Vortex mixer	Mixing
Weighing balance	Measurement of weight
Multimeter	Measurement of voltage
Resistor	Resistance/load for the circuit
pH meter	Analysis
UV-VIS	Analysis
Spectrophotometer	Analysis
Incubator	Pretreatment

Table 3.2 : List of Chemicals

Chemicals	Purpose
Sodium Hydroxide (NaOH)	Pretreatment
Nitric acid (HNO_3)	Analysis
Hydrogen peroxide (H_2O_2)	Analysis
Sodium Hydroxide (NaOH)	pH buffer
Hydrochloric acid (HCl)	pH buffer

3.2 Research methodology flow chart

Figure 3.1 shown below is the flow chart of the research.

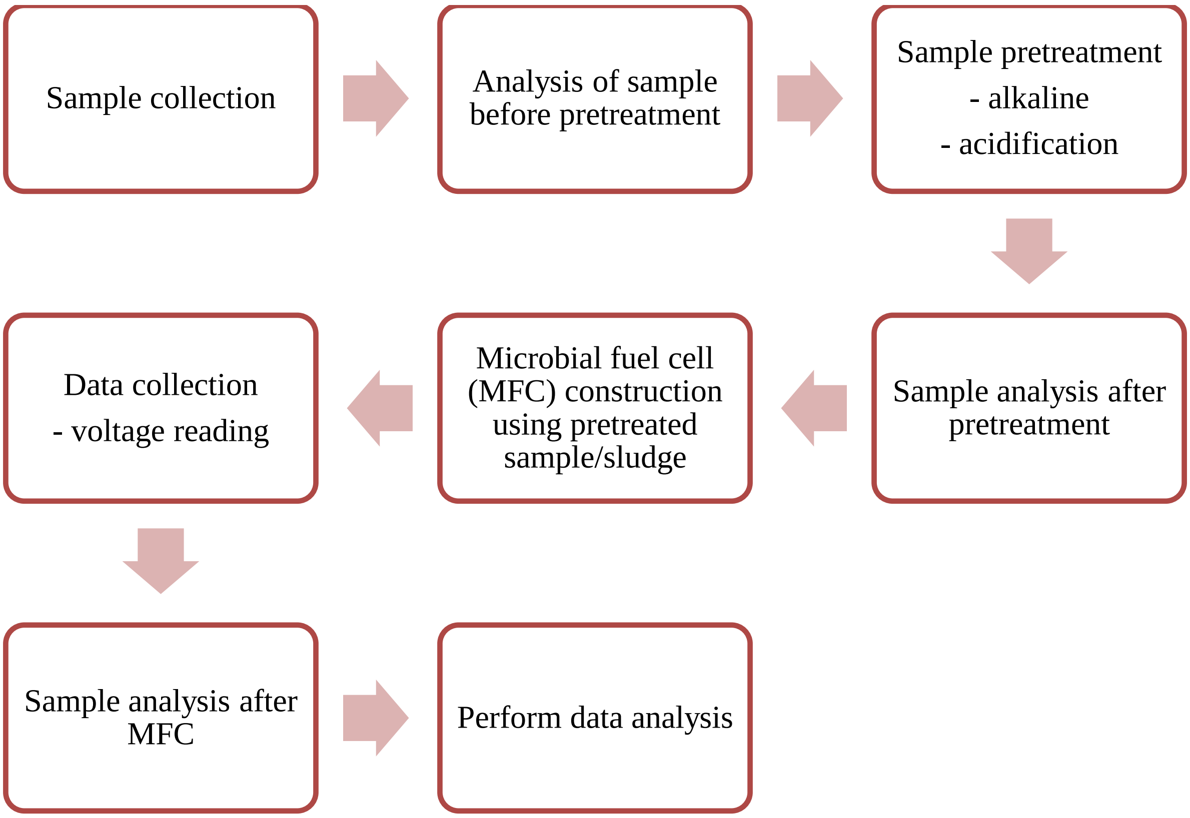

Figure 3.1 : Research methodology flow chart

3.3 Sample Collection

Activated sludge was collected after went through dewatering process in a secondary treatment system from Kerian Indah Water Treatment Plant (IWK), Parit Buntar. The experiment was conducted on the day of sample collection to ensure the optimum performance of MFC.

3.4 Sample Pretreatment

The moisture content and total solid was calculated from the dewatered sludge to perform pretreatment. Six chambers of samples in a glass jar were prepared with 2 chambers for blank sample and 4 chambers with different volume of NaOH was added. For each chamber, pH analysis was done and data was collected. Data collection involves the voltage generated, and SCOD analysis. All six chambers were kept at $35^{o}C$ for 24 hours.

3.5 MFC Configuration

The dewatered sludge was prepared into the bottom layer of MFC chamber with approximately 50g. The anode electrode was placed on top of the sludge. Then, the balance of 150g of the sludge was added. Then, put cathode electrode on the top surface of the sludge. The chamber was closed using a lid and incubated at room temperature for 7 days in an anaerobic condition. By using a digital multimeter, voltage reading was taken for every 6 hours.

3.6 Analytical method

3.6.1 Determination of biomass

The biomass was calculated by determining the dry weight of the biomass collected for every hour until the weight is constant. The biomass sample was left inside an oven at 105^{o}C for 24 hour, and the weight is determined as follows :

Biomass = (weight of dry filter paper + weight of dried sludge) – (weight of dry filter paper)

$$\text{Biomass} = (\text{weight of dry filter paper} + \text{weight of dried sludge}) - (\text{weight of dry filter paper}) \quad (3.1)$$

3.6.2 Determination of electricity generation

The data for electricity produced was evaluated by using a multimeter. The flow of electrons from anode to cathode is called current and was determined by using Ohm's Law :

$$V = I.R \quad (3.2)$$

V is the potential difference between the anode and the cathode (in Volts), I is the current (in Amps), and R is the resistance applied (in Ohms). The power in MFC was calculated using this equation :

$$P = I.V \quad (3.3)$$

CHAPTER FOUR

RESULTS AND DISCUSSION

This chapter presents the experimental results and discussion consisting of three main sections. The first section illustrates the experimental design applied for pH and electricity conductivity (EC) analysis and pH as a parameter in this study. The second and third section respectively discusses the alkaline and acidic pretreatment respectively and their effects on SCOD, and voltage generated.

4.1 pH variations

The pH changing in the substrate was observed. As shown in figure 4.1, the pH of the sludge first had a slight increase after 24 hours of pretreatment and showed the same trend in 7 days. However, the sludge pH was maintained between 6.5 and 9.0 after 7 days of operation including a significant rising in 0-7 days of operation.

The pH was controlled by adding different volume of NaOH. The ratio of NaOH solution and sludge was maintained at 1:5. From table 4.1, 6 samples were labelled as B1,B2,1,2,3, and 4 to differentiate the volume of NaOH added into the dewatered sludge.

The ammonia content increase should be the vital factor for the pH change. Due to the anaerobic storage, sludge with lower pH is not suitable for microbial activity. The ammonia formed from ammonification of organic nitrogen (such as protein, amino acid, nucleic acid and amine) in the anode sludge by ammonification microbes has a significant role in organic nitrogen mineralization and nitrogen cycle.

The loss of ammonia is usually by means if nitrification, microbial assimilation, and ammonia gas escape. The ammonia formation exceeding loss leads to the increase of ammonia, which is usually in the form of NH_4^+ or dissociative ammonia and difficult to escape in the acid environment. In addition, the nitrification is not the dominant action in the anaerobic process during MFC operation.

Therefore, the increase of ammonia nitrogen was another signal of dewatered sludge degradation and mineralization, indicating that the sludge tended to be more mature and stabilized.

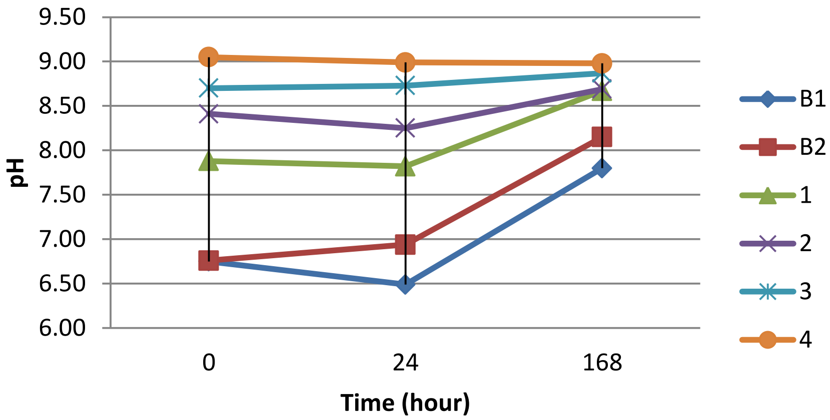

Figure 4.1 Variations of pH with time for alkaline pretreatment

Table 4.1 NaOH-Deionized Water ratio

SAMPLE	NaOH (ml)	DI (ml)	∑ NaOH + DI (ml)
B1	0.00	50.00	50.00
B2	0.00	50.00	50.00
1	12.50	37.50	50.00
2	25.00	25.00	50.00
3	37.50	12.50	50.00
4	50.00	0.00	50.00

From figure 4.2, the same procedure was done with varying the pH value of the sample by adding HCl solution. Table 4.2 showed the amount of HCl needed for acidic pretreatment. At 24 hours, all 6 samples had a slightly increase value of pH and further increased at 168 hours (at day 7).

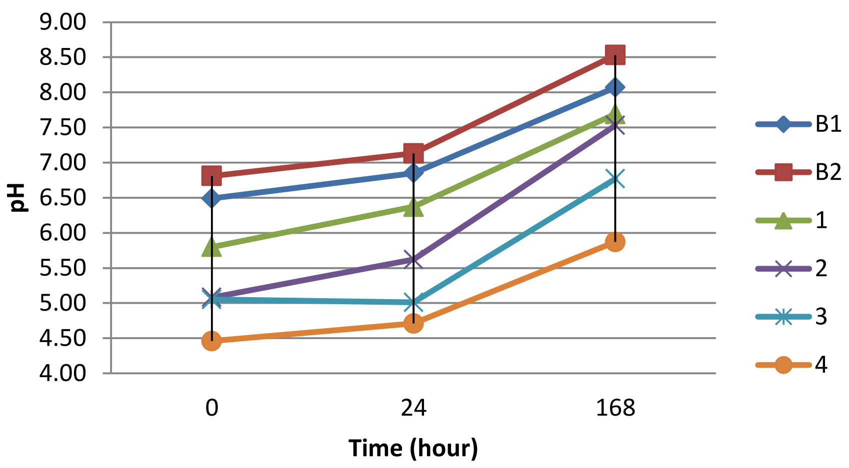

Figure 4.2 Variations of pH with time for acidic pretreatment

Ratio of solution being added into dewatered sludge was calculated previously by using Total Solid and Moisture Content calculation.

Table 4.2 HCl-Deionized Water ratio

SAMPLE	HCl (ml)	DI (ml)	∑ HCl + DI (ml)
B1	0.00	28.78	28.78
B2	0.00	28.78	28.78
1	7.20	21.59	28.78
2	14.39	14.39	28.78
3	21.59	7.20	28.78
4	28.78	0.00	28.78

4.2 Alkaline Pretreatment

4.2.1 Effect of Alkaline Pretreatment on SCOD release

From Figure 4.3, 4.4 and 4.5 it demonstrates the SCOD contents in the sludge, increment and reduction at initial, after 24 hours and after 7 days of MFC operation respectively. In average, after 24 hours pretreatment process, all 6 samples at different pH showed a significant increment of SCOD at almost double the initial value. Sample 3 with pH 8.7$\pm$0.1 showed the most increasing trend from 261 mg/L to 824 mg/L.

This also can be inferred as 215.71% increment from initial value. Sample 4 and sample 2 also showed a remarkable increase with 134.9% and 113.33% respectively. This high SCOD in the sludge supernatant suggests that there was disintegration of the insoluble suspended sludge flocs which later partly transformed into soluble organic components by the treatment.

Then, after 7 days of MFC operation, SCOD value showed a reduction trend. This is due to the SCOD was consumed during the MFC process from all substrates supplied. The highest consumption of SCOD was detected from sample 3 with pH 8.7$\pm$0.1, which showed more than 46% reduction. The lowest reduction can be observed from sample 1 with 5.73%.

An increase in SCOD indicates that more organic substances were released. The organic substances were easily dissolved during the diluting and stirring processes of the raw dewatered sludge. The variation in SCOD verified the solubilisation of organic matter during NaOH treatment.

Acceleration of the sludge hydrolysis would improve the subsequent anaerobic digestion, but the increase in pH would inhibit anaerobic bacteria. The fall in SCOD after 24 hour could be due to the occurrence of refractory compounds catalysed by the thermal energy over prolonged period of treatment. Similar effect was observed in previous studies.

In summary, the pretreatment processes have brought changes on the physical structure and the organic content of the sludge and with alkaline pretreatment method, the optimum pH 8.7±0.1 has delivered more accumulation of SCOD after pretreatment and more reduction in SCOD after MFC operation.

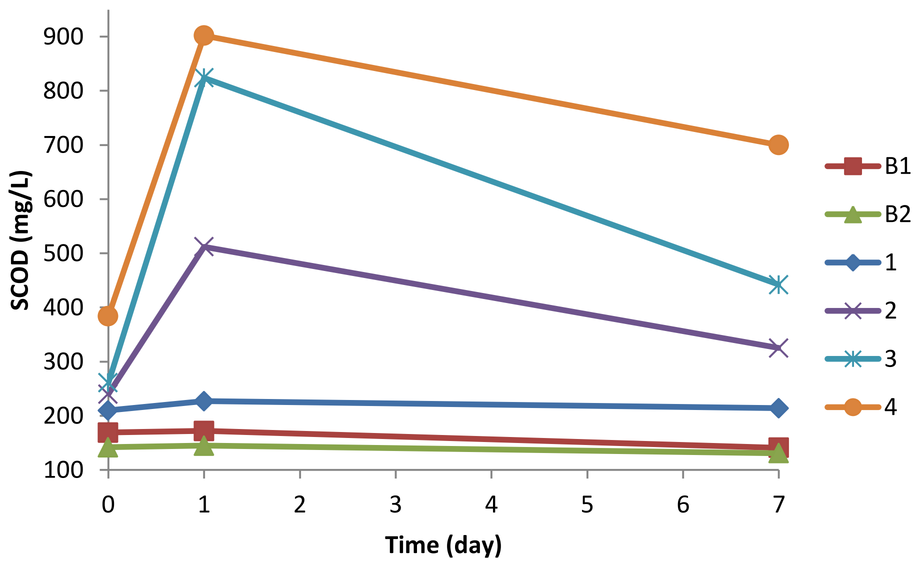

Figure 4.3 SCOD for alkaline pretreatment throughout experiment

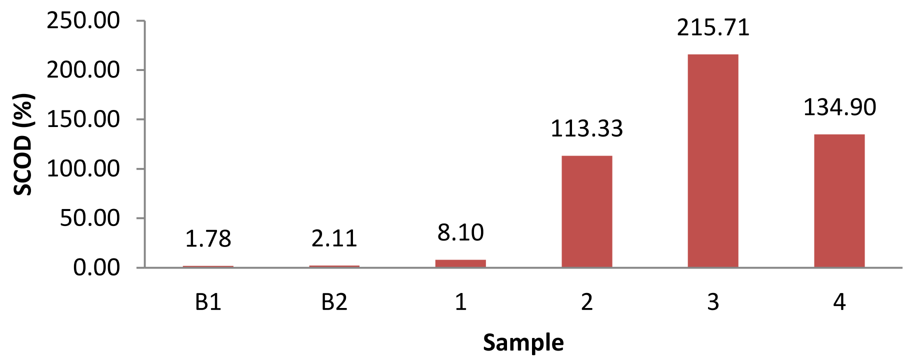

Figure 4.4 SCOD increment in first 24 hours for alkaline pretreatment

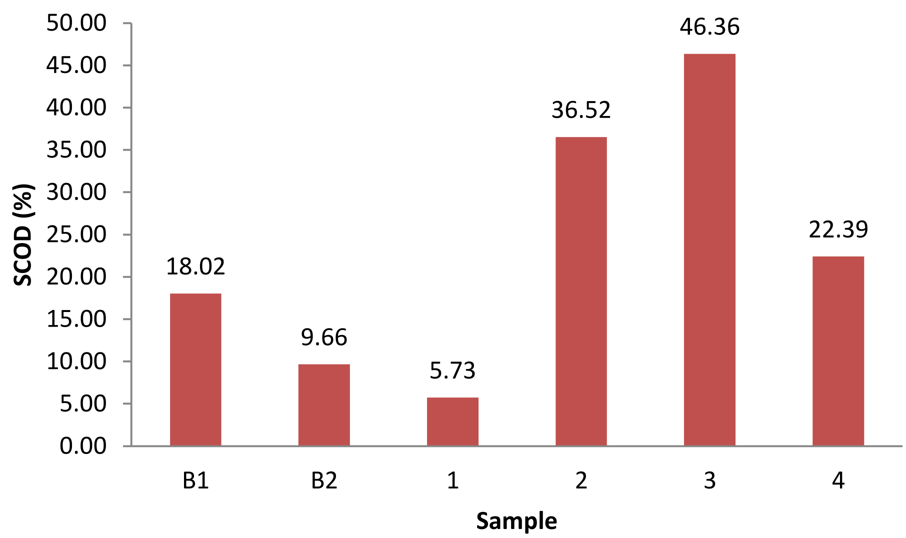

Figure 4.5 SCOD reduction in 7 days for alkaline pretreatment

4.2.2 Effect of Alkaline Pretreatment on Voltage Generation

The microbial fuel cell was acclimatized for 7 days with pretreated sludge then the MFC got stabilized at day 8 with a maximum stable open circuit voltage is 691mV for sample B1 with pH 6.7.