EFFECT ON VARIOUS ELECTRODE MATERIALS IN TREATING SPENT CAUSTIC WASTEWATER USING BIOELECTROCHEMICAL CELL (BeCC)

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Thesis submitted in partial fulfilment of the requirements
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Dedicated to my family, supervisor, and my friends.

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ABSTRACT

Spent caustic is an industrial wastewater that is generated from petroleum refineries and it is the most difficult of all industrial wastes to dispose or treat properly. In this study, treatment of wastewater using bioelectrochemical cell (BeCC) seems to be promising technology to treat spent caustic because it shows efficient treatment besides recovery energy. Principally, the voltage generated will depend on various factors including the electrode material performance. Therefore, the great significance is to select and develop suitable electrode materials to promote the efficiency of BeCC. The objectives of this study are to investigate the performance of BeCC towards removal efficiency; namely chemical oxygen demand (COD) and sulphide. Next is to access the performance of BeCC on electricity generation by using different type of electrode materials and to study the effect on surface of various electrode materials by analyse using scanning electron microscopy to get SEM image. A reactor of BeCC was operated under ambient conditions. Spent caustic wastewater samples from industry is collected and entered with the flowrate of 0.2 L/d into BeCC for treatment and treated for 3 weeks. The great treatment efficiency for COD in BeCC is achieved 94% removal using carbon-carbon electrode at constant hydraulic retention time (HRT) of 20 days. The various combinations of anode and cathode material is studied and the maximum voltage of 189.1mV is generated when spent caustic samples is treated using carbon-carbon electrode, while 153.7mV generated using copper-carbon electrode and minimum voltage of 125.1mV is generated using aluminium-carbon electrode. After that, surface of each electrode is analyzed using SEM-EDX to investigate the morphological properties of the anode and cathode surface before and after operation and show that there are microorganism attachment on the surface of electrode. Thus, the suitable combination of electrodes can be determined. Finding shows that electrode combination of carbon-carbon is the best since it gives high COD and sulphide removal, instead of high voltage generated.

ABSTRAK

Spent caustic merupakan sisa air buangan industri yang dihasilkan dari kilang penapis petroleum dan ia merupakan bahan buangan industri yang paling sukar untuk dilupus dan dirawat dengan betul. Dalam kajian ini, rawatan sisa air buangan mengunakan *Bioelectrochemical cell (BeCC)* menjanjikan teknologi yang berkesan dan dalam masa yang sama menghasilkan tenaga. Secara prinsipnya, penghasilan voltan bergantung kepada beberapa faktor termasuk bahan elektod yang digunakan. Oleh itu, pemilihan bahan elekrod yang sesuai memberi impak yang besar untuk menggalakkan kecekapan *BeCC*. Objektif kajian ini adalah untuk menyiasat prestasi *BeCC* terhadap kecekapan penyingkiran; iaitu *Chemical Oxygen Demand (COD)* dan *Sulphide*. Seterusnya ialah untuk mengakses prestasi BeCC pada penjanaan elektrik dengan menggunakan pelbagai jenis kombinasi bahan elektrod dan mengkaji kesan terhadap permukaan morfologi setiap elektrod dengan menganalisa menggunakan *Scanning Electron Microscopy (SEM)*. *BeCC* reaktor telah beroperasi di bawah keadaan ambien. Sisa air buangan *spent caustic* di ambil dari sebuah industri dan dimasukkan dengan kadar aliran 0.2L/hari ke dalam reaktor dan dirawat selama 3 minggu. Kecekapan terbesar dalam penyikitan COD dicapai pada 94% manakala 99.95% penyikiran *sulphide* dengan mengunakan karbon-karbon elektrod pada *hydraulic retention time (HRT)* yang ditetapkan iaitu 20 hari. Pelbagai kombinasi bahan anod dan katod dikaji dan kajian menunjukkan voltan maksima 189.1mV dijana apabila sampel s*pent caustic* dirawat menggunakan karbon-karbon elektrod, manakala 153.7mV dijana menggunakan kuprum-karbon elektrod dan voltan minima dijana pada 125.1mV menggunakan aluminium-karbon elektrod. Selepas itu, permukaan setiap elektrod dianalisa menggunakan *SEM-EDX* untuk mendapatkan imbasan morfologi dan elemen yang terdapat di anod dan cathode. Dengan itu, kombinasi elektrod yang sesuai dapat ditentukan. Kajian membuktikan pengunaan kombinasi karbon-karbon elektrod merupakan yang terbaik kerana mencapai penyingkiran *COD* dan *sulphide* yang terbesar, disamping menghasilkan penjanaan voltan yang tertinggi.

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V	volume
Q	flow rate
C	carbon
Cu	copper
Al	aluminium

LIST OF ABBREVIATIONS

BeCC	Bioelectrochemical Cell
MFC	Microbial Fuel Cell
COD	Chemical Oxygen Demand
TSS	Total Suspended Solid
HRT	Hydraulic Retention Time
SRT	Solid Retention Time
SEM	Scanning Electron Microscopy
MLSS	Mixed Liquor Suspended Solid
MLVSS	Mixed Liquor Volatile Suspended Solid
SVI	Sludge Volume Index

CHAPTER 1

INTRODUCTION

1.1 Background of the Study

Biological treatment of spent caustics, at ambient condition of atmospheric pressures and temperatures would be a cheaper and safer alternative to the currently employed physico-chemical treatment processes. On-site treatment of spent caustics in conventional biological wastewater treatment plants is standard practice at many refineries. Meanwhile, many research and technological advancements have been made in the wastewater treatment area as renewable energy sources and technology especially in treating spent caustic. This is because existing spent caustic wastewater treatment, such as WAO, these treatment is considered to be a reliable technique for disposal of spent caustic but high investment makes a disadvantage to use this method (Heidarinasab et al., 2011).

Microbial fuel cell (MFC) is one of the bioelectrochemical cell (BeCC) system which uses microorganisms to catalyse an oxidation and reduction reaction on anodic and cathodic electrode. Over a past few year, BeCC study has received wide attention among researchers as clean environment plays vital role in human life. It is undeniable that BeCC has become a promising technology to generate electricity and simultaneously the wastewater is being treated, which means the energy is converted from chemical energy to electrical energy (Logan et al., 2006). Nevertheless, current wastewater treatment technologies are not sustainable to meet the ever-growing water sanitation needs due to rapid industrialization and population growth, simply because they are energy- and cost-intensive (Gude, 2016).

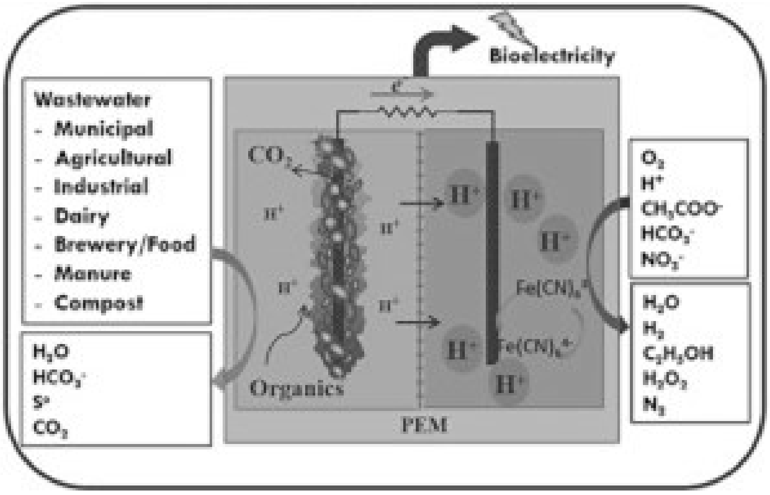

Figure 1-1: Basic principle of bioelectrochemical system

[Source: Gude, 2016]

1.2 Motivation

Spent caustic streams from the oil and gas industries consist of very high COD levels and several other hazardous contaminants. Due to these contaminants in refinery spent caustic, these existing treatments of wastewater are difficult to treat because of uncomplete reaction and very harmful to the environment. Consequently, spent caustic wastewater treatments can be both challenging and expensive. As example, commonly industrial process for spent caustic treatment is the use of wet air oxidation (WAO) reactor (Maugans & Howdeshell, 2010). During this process, sulphides were oxidized at 200°C into oxidation product such as sulphate ions. However, this process is very expensive and due to severe reaction condition, safety is a major concern. Nevertheless, another existing treatment of spent caustic processes also present limitations bound to the effectiveness due to certain types of inhibitors, cost or to the need for generating a more harmful pollution. (Hariz et al., 2013). BeCC is considered to be a promising sustainable technology to meet increasing energy needs, especially using wastewaters as substrates, which can generate electricity and at the same time treating wastewater, thus may offset the operational costs of wastewater treatment plant. Bacteria can be used in BeCC to generate electricity while accomplishing the biodegradation of organic matters or wastes.

1.3 Problem Statement

Electrode material performance has become one of the factor involve in the power output generation of BeCC (Liu et al., 2005). Moreover, as a main component, the electrode materials determine the cost of BeCC and thus influence the cost of overall treatment process. In this study, different electrode materials have used to investigate the performance of BeCC on electricity generation. Since spent caustic containing high levels of sulphide compounds together with phenolic, cresylic and naphthenic acids which expose to toxicity and odorous properties (Hariz et al., 2013), it also can cause considerable environmental problems if discharged without effective treatment. Nevertheless, energy consumption is one of the largest expenses in operating a wastewater treatment plant. Changes in biological treatment processes such as by using BeCC could be alternative in treating the wastewater and have the potential to significantly reduce the energy demand at the industry and effluent clean environment at the same time. This energy recovery become alternative energy for future consumption. Thus, BeCC can give high performance of energy recovery and accomplish wastewater treatment.

1.4 Objectives

Based on the problem statement described in the previous section, therefore the objectives of this research are:

a) To investigate the performance of BeCC in treating spent caustic wastewater towards removal efficiency; namely COD and sulphide
b) To access the performance of BeCC on electricity generation by using different type of electrode materials.
c) To study the effect on surface of various electrode materials by analyse using scanning electron microscopy (SEM)

1.5 Scopes of Study

In order to achieve as mentioned in the objective above, the following scope has been drawn:

a) Construction of novel experimental rig for BeCC
b) Analysis of COD removal and sulphide removal
c) Analysis of voltage generated
d) Experimental analysis of sludge settleability
e) SEM-EDX analysis on various electrode materials

CHAPTER 2

LITERATURE REVIEW

2.1 Spent Caustic Wastewater

Spent caustic often generate from the industries that manufacturing liquefied petroleum gas (LPG) and natural gas (NG) that containing high levels of sulphide compounds together with phenolic, cresylic and naphthenic acids which expose to toxicity and odorous properties (Hariz et al., 2013). Spent caustic characteristics can greatly vary from refinery to refinery. It is possible to find trace of special catalysts as well. Spent caustics typically have a pH greater than 12. Hydrosulphide (HS-) and sulphide (S2-) typically are the most dominant sulphur compounds found in spent caustics with concentrations that may exceed 2–3 wt%. Depending on the source, spent caustic may also contain phenols, mercaptans, amines, and other organic compounds that are soluble or emulsified in the caustic (Heidarinasab et al., 2011). Table 2-1, summarize the characteristic of typical spent caustic.

Table 2-1: Characteristic of typical spent caustic composition

Component	**Sulfidic**	**Phenolic**	**Naphthenic**
Sodium hydroxide, wt%	2-10	10-15	1-4
Inorganic sulphides, wt%	0.5-4	0-1	0-0.1
Mercaptide, wt%	0.1-4	0-4	0-0.5
Cresylic acid, wt%	-	10-25	0-3
Nanpthelic acids, wt%	-	-	2-15
Carbonate, wt%	0-4	0-0.5	-
pH	13-14	12-14	12-14

[Source: Veerabhadraiah et al., 2011]

Meanwhile, Table 2-2 summarizes the three main types of spent caustic and their main characteristics more details compared in Table 2-1. According to Alnaizy (2008), usually refineries do not separate each type of spent caustic and they mix the three types, this is referred to as the mixed refinery spent caustic. Numerous efforts have been made to develop and to enhance the treatment process of spent caustic. Treatment methods for spent caustic can be classified into three main categories: biological, chemical and thermal processes (Ahmad, 2010).

Table 2-2: Different spent caustic types and their characteristics.

Type of spent caustic	**Sulfidic**	**Cresylic**	**Naphthenic**	**Ref.**
Source	Ethylene and Liquefied Petroleum Gas (LPG)	Gasoline	Kerosene and Diesel	(Kumfer *et al.*, 2010)
Content	High concentration of sulfides and mercaptans	High concentration of phenols & cresols	High concentration of polycyclic aliphatic organic compounds	(Kumfer *et al.*, 2010)
Chemical Oxygen Demand (COD) (ppm)	5000–90,000	50,000–100,000	150,000–240,000	(Ahmad, 2010)
Total Organic Carbon (TOC) (ppm)	20–3000	10,000–24,000	24,000–60,000	(Ahmad, 2010)
Sulfides (ppm)	2000–52,000	<1	0–63,000	(Ahmad, 2010)
Total phenol (ppm)	2–30	1900–1000	14,000–19,000	(Ahmad, 2010)

2.2 Existing Treatment of Spent Caustic Wastewater

Table 2-3, mainly summarize on the existing treatment of spent caustic wastewater which are from thermal processes and chemical processes. These processes have its own advantages and disadvantages and most commonly used in industry is chemical process (Hawari et al., 2015).

Table 2-3: Existing treatment of spent caustic wastewater

Type	Approach	Technology	Advantages	Disadvantages
Thermal	Incineration	Special lined down-fired combustor	Low COD brine, high destruction efficiency	High capital and operating cost.
	Wet Air Oxidation (WAO)	High temperature WAO for refining caustic Medium-high temperature WAO for ethylene caustic	Heat of oxidation of organics provides most of thermal energy, high COD reduction	High capital cost, nickel lined high pressure vessel. Vent gas stream needs further treating. COD reduction “floor” due to refractory organics
Chemical	Direct chemical oxidation	Hydrogen Peroxide or other chemical oxidant, with or without catalyst	Low temperature, liquid phase reaction	Cost of chemical reagents
	Deep neutralization and separation	MERICON	Low capital cost, low pressure and temperature, reliable operation	COD reduction limited by solubility of organics in the brine.

[Source: McGehee, 2015]

2.3 Law and Regulation

According to Ho et al., (2012), the industrial discharge carries various types of contaminants to the river, lake and groundwater. The quality of fresh water is very important to human life, aquatic living organism, plant and etc. In order to promote healthy environment to avoid any pollution from the industrial effluent which can caused a harm or hazard to the surrounding, mainly; society and environment, the Malaysian government is intent on making environmental laws and regulations more effective. Hence, Environmental Quality (Industrial Effluents) Regulations 2009 should be strictly implemented in all industries where it is high strength industrial or low strength industrial. Under these regulation, acceptable conditions for discharge of industrial effluent or mixed effluent of standards A and B are as follows:

Table 2-4: Acceptable conditions for discharge of industrial effluent or mixed effluent of standards A and B

Parameter	**Unit**	**Standard A**	**Standard B**
Temperature	°C	40	40
pH value	-	6.0-9.0	5.5-9.0
BOD_5 at 20°C	mg/L	20	40
Mercury	mg/L	0.005	0.05
COD	mg/L	50	100
Suspended Solids	mg/L	50	100
Sulphide	mg/L	0.50	0.50

2.4 Bioelectrochemical Cell (BeCC)

Microbial fuel cells (MFCs) is one of the example of a rapidly developing biotechnology, generally known as bioelectrochemical cell (BeCC) systems, that combine biological and electrochemical processes to generate electricity, hydrogen or other useful chemicals. BeCC represent the new method of renewable energy recovery and provide safe environment. The cell that has been developed not only to generate electricity, but treats wastewater as well (Abbasi et al., 2016). Compared to other biological treatment processes of wastewater, BeCC have many advantages, such as high theoretical energy conversion rate, less sludge, and no gas processing (M. Zhou et al., 2011). According to Tchobanoglous et al., (2003), attached growth treatment may also be known as fixed-film processes which the microorganisms responsible for the conversion of the organic matter or other constituents in the wastewater to basically transform the organic material to electricity.

BeCC produce clean electricity directly from organic matter in wastewater without any need for separation, purification and conversion of the energy products. BeCC generally made up of four important components, which are the anode and cathode(electrode), the proton exchange membrane, substrate and bacteria (Jin, 2014). In wastewater, there are billions of bacteria or microbes to break down organic matter at the anode under anaerobic (without oxygen) conditions. When breaking down the organic material, the bacteria release electrons (negatively charged particles), protons (positively charged hydrogen ions) and carbon dioxide into solution and also released energy. This energy is used and stores by microbes for growth purpose. The anode collects the electrons, which then travel to the cathode via an external circuit during the oxidation process and generating current. The protons travel through the solution in the cell to the cathode. The carbon dioxide can be captured and reused. In BeCC, electricity is produced by extracting it from the electron-carrying external circuit. The electrons arriving at the cathode under aerobic conditions, i.e. in the presence of oxygen, combine with the protons and oxygen, typically from the air, to form water (Gude, 2016). Cell voltage and electrode potentials in MFCs are usually measured using voltage meters and multimeters (Logan et al., 2006).

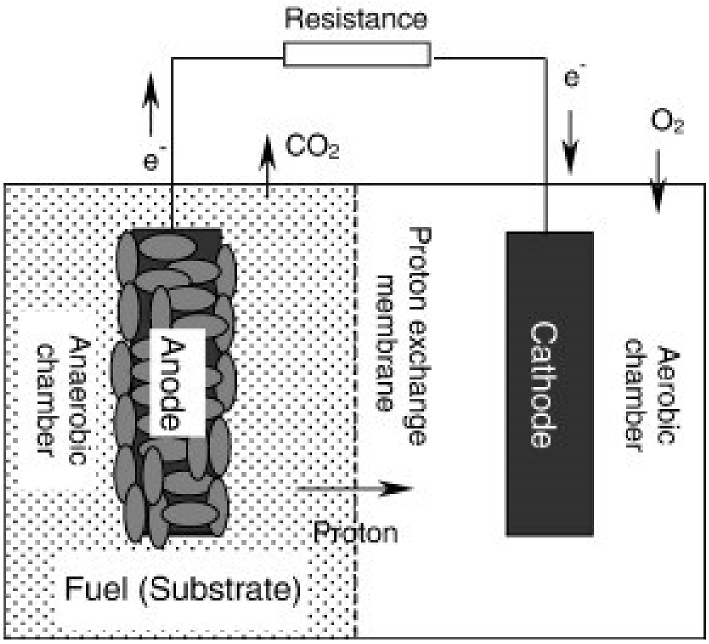

Figure 2-1: Schematic diagram of a BeCC
[Source: Du et al., 2007]

2.5 Factor Affecting the Performance of BeCC

There are a lot of factors affecting the performance of BeCC; including the different type of wastewater uses. This is because the wastewater use will consume different types of organic matter in spent caustic that can have dissimilar biodegradability which can affect rate of COD removal (Velasquez-Orta et al., 2011). Besides, there also several factors that need to be taken into consideration such as flowrate and concentration at the inlet, hydraulic retention time (HRT), solid retention time (SRT), mixed liquor suspended solid (MLSS), mixed liquor volatile suspended solid (MLVSS) (Mutamim et al., 2013) and type of electrodes (Pant et al., 2010) to obtain good quality effluent and promote the performance of BeCC.

2.5.1 Total Suspended Solid (TSS)

TSS is a known volume of well-mixed water to be filtered by precombusted, pre-weighed, glass fiber filter. The residue and filter are then dried at 105°C in a drying oven, and the mass is recorded. The difference in mass between the post weight and pre-weight is the total suspended solids for the volume of water (Tchobanoglous et al., 2003).

$$TSS = \frac{W_a - W_0}{sample\ size, L} \qquad \text{(Equation 2-1)}$$

Where,

TSS is in unit g/L

W_0 is tare mass of filter after drying in unit g

W_a is residue on filter after drying in unit g

2.5.2 MLSS

MLSS is the biomass solids in a bioreactor is commonly measured as TSS. While the mixture of solids resulting from combining recycled sludge with influent wastewater in the reactor is termed MLSS and MLVSS. TSS and MLSS is used a same method of analysis, generally MLSS concentrations are greater than 1,000 mg/L, but lower than 4,000 mg/L. The concentration of suspended solids found in the mixed liquor is typically much greater than that found in the raw or treated water (Tchobanoglous et al., 2003).

2.5.3 MLVSS

Meanwhile, MLVSS, is a test for the amount of volatile suspended solids found in a sample of mixed liquor. Volatile solids are those solids which are burnt up when a sample is heated to 550°C. Most of the volatile solids in a sample of mixed liquor will consist of microorganisms and organic matter. As a result, the volatile solids concentration of mixed liquor is approximately equal to the amount of microorganisms in the water and can be used to determine whether there are enough microorganisms present to digest the sludge (Kumar et al., 2014).

2.5.4 HRT & SRT

HRT and SRT are gradually two major factors that affect the wastewater treatment (Ersahin et al., 2016). HRT is a measure of the average length of time that a soluable compound remains in a reactor, while SRT is the average time the activated-sludge solids remains in the system. Kim et al., (2015) stated in the journal, HRT by using efficient treatment that are continuous flow conditions of BeCC requires to have similar or less than those of conventional methods such as activated sludge.

The theoretical HRT is calculated from effluent flow rate (Q, ml/h) and reactor volume (V, ml) as;

$$HRT = {}^{V}/_{Q_{effluent}}$$ (Kim et al., 2015) (Equation 2-2)

Meanwhile, SRT is calculated from the influent flow rate of wastewater by following equation;

$$SRT = {}^{V}/_{Q_{influent}}$$ (Mutamim, 2012) (Equation 2-3)

2.6 Electrode Materials

A large number of recent studies on BeCC have focused on electrode materials and surface area impacts. The effects of electrode materials have been tested by a few research groups, focusing on the use or addition of metals such as manganese, copper and gold (Park & Zeikus, 2002; Crittenden, Sund, & Sumner, 2006; Kargi & Eker, 2007).

According to Zhou et al., (2011), electrode is the key component in deciding the performance and cost of BeCC. Each electrode material has its own physical and chemical properties such as surface area, electric conductivity and chemical stability. Thus, it's also vary in making impact on microbial attachment at the anode, electron transfer, electron resistance, and the rate of electrode surface reaction. Therefore, it is great significance to select and develop the most suitable electrode materials to optimize and enhance the performance of BeCC. A good anode material should have good electrical conductivity and low resistance, strong bio-compatibility, chemical stability and anti-corrosion, large surface area and also high mechanical strength and toughness. Meanwhile, the electrode at the cathode should have a high redox potential and capture protons easily.

Table 2-5: Examples of real wastewater that has been treated by BeCC using different electrodes

Type of wastewater	Type of electrode		Surface area (cm^2)	COD removal (%)	Pmax (mW/m^2)
	Anode	Cathode			
Distillery (Zhou *et al*., 2011)	Graphite plate	Graphite plate	25	72.84	124.35
Brewery (Liu *et al*., 2006)	Carbon fiber	Stainless steel net	7	40	264
Electroplating (Li *et al*., 2008)	Carbon felt	Graphite paper	10	99.5	1600

CHAPTER 3

METHODOLOGY

3.1 Introduction

This chapter describe the experimental studies used to develop and construct a novel experimental rig of Bioelectrochemical Cell (BeCC) to study the effect on various electrode materials in spent caustic wastewater treatment.

3.2 Material Description

Spent caustic wastewater, COD reagent, sulphide 1 reagent, sulphide 2 reagent, graphite rod, copper electrode, aluminium electrode, sodium sulphide, sodium bicarbonate and sugar.

3.2.1 COD Reagent

COD is used as a measure of oxygen requirement of a sample that is susceptible to oxidation by strong chemical oxidant. COD reagent used consists of sulphuric acid and potassium dichromate act as oxidants because of its superior oxidizing ability, applicability to a wide variety of samples and ease of manipulation. Oxidation of most organic compounds is 95-100% of the theoretical value. The COD reagent also contains silver and mercury ions. Silver is a catalyst, and mercury is used to complex chloride interferences. The COD reagent may cause harmful by inhalation, causes severe burns and may causes cancer. Therefore, it is necessary to wear a proper protective equipment when conducting the test.

3.3 Wastewater Preparation

Spent caustic wastewater is collected from industry in Gebeng, Kuantan. The sample is analysed using DR-2800 Spectrophotometer. The wastewater was injected with sodium sulphide and sodium bicarbonate before feed to the treatment process. The wastewater must undergo a pretreatment by acclimatization (Hussain et al., 2015) which is an adaptation of bacteria exist to a new climate. Previous research has shown that reactors acclimated to wastewater can be greatly effective to be used for treating (Ren et al., 2013).

3.4 Electrode Preparation

3 set of materials are prepared in this studies. Each material is chosen based on their strength and capability for microbial to attached at the anode while the cathode should capture protons easily (Zhou et al., 2011).

Table 3-1: Set of electrodes

Set	Anode	Cathode	Size (cm^2)	Ref.
1	Carbon	Carbon	900	(Ashoka *et al*., 2012) (Jadhav *et al*., 2009)
2	Carbon	Copper	900	
3	Carbon	Aluminium	900	

3.5 BeCC Construction and Operation

Figure 3-1 illustrated the construction of BeCC operation for spent caustic wastewater treatment. A reactor of BeCC is operated under ambient condition (pressure of 1atm and temperature at 25°C-28°C). The BeCC was made of glass material and it consists of two components; anode and cathode, with reactor volume of 4L. Two pump are used in this study; first at the inlet of reactor to pump from the wastewater, and the other at the anode to transfer the treated water for settlement before the analysis is conducted. The magnetic stirrer is used in the anoxic chamber, to make sure there are no sludge sediment at the bottom of the reactor. The theoretical HRT is calculated from flow rate (Q, ml/h) and reactor volume (V, ml) as HRT = V/Q. Spent caustic wastewater is entered the reactor with flow rate of 0.2L/d, thus HRT set is 20 days (Kim et al., 2015). The anode and cathode electrodes are connected using a copper wires to form a circuit. The inner part of the cell is separated using baffle into half to reduce the oxygen enter to the anode, while the cathode side is filled with aerator to provide oxygen.

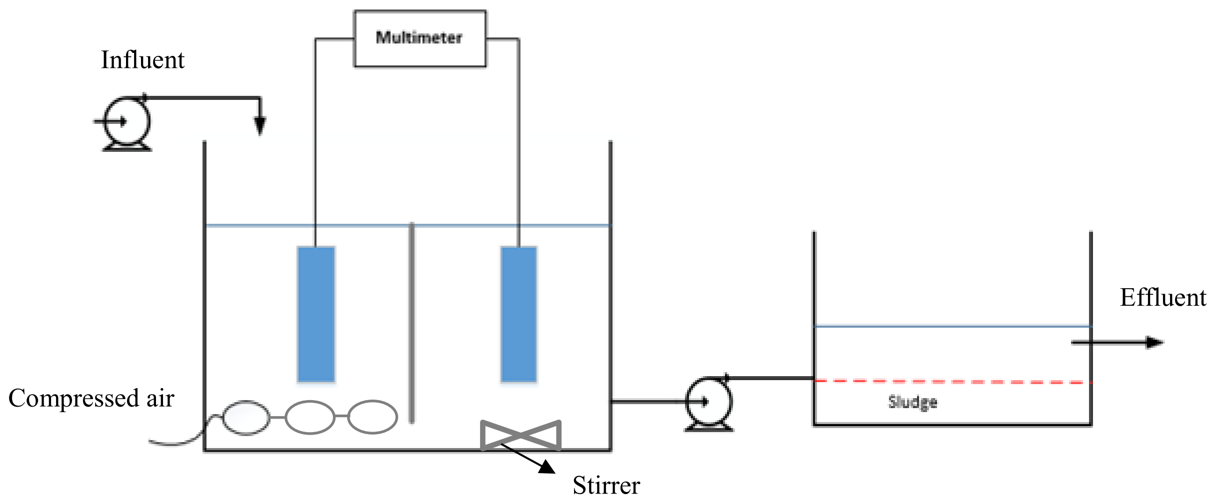

Figure 3-1: BeCC Construction

3.6 Analysis and Measurement

3.6.1 Analytical Method

Wastewater quality analysis of influent and effluent samples including the COD and sulphide removal are analyzed using the Standard Methods by APHA (2005). The pH of sample is determined using a pH meter and the initial pH are adjusted to a desired value using sulfuric acid (Gameel et al., 2015), meanwhile dissolve oxygen is measured at the beginning and end of the experiment using DO meter.

3.6.1.1 MLSS

A known volume of well-mixed water to be filtered by precombusted, pre-weighed, glass fiber filter. The residue and filter are then dried at 105°C in a drying oven, and the mass is recorded. The difference in mass between the post weight and pre-weight is the total suspended solids for the volume of water (Tchobanoglous et al., 2003).

$$MLSS = \frac{W_a - W_0}{sample\ size, L} \qquad \text{(Equation 3-1)}$$

Where,

MLSS is in unit g/L

W_0 is tare mass of filter after drying in unit g

W_a is residue on filter after drying in unit g

3.6.1.2 MLVSS

Volatile solids are those solids which are burnt up when a sample is heated to 550°C. Most of the volatile solids in a sample of mixed liquor will consist of microorganisms and organic matter. As a result, the volatile solids concentration of mixed liquor is approximately equal to the amount of microorganisms in the water and can be used to determine whether there are enough microorganisms present to digest the sludge (Kumar et al., 2014).

$$MLVSS = \frac{W_a - W_b}{sample\ size, L} \qquad \text{(Equation 3-2)}$$

Where,

MLVSS is in unit g/L

W_a is residue on filter after drying in unit g

W_b is residue on filter after burnt up to 550°C in unit g

3.6.1.3 COD Removal

COD is consistently checked by taking a small amount of sample from the effluent for every 24hr by reactor digestion method according to DR-2800 Spectrophotometer. The samples are tested using COD digestion vials(Hach), where the sample is placed within digestion vials, heated at 150oC for 2 hours. Digestion vials are then allowed to cool naturally to ambient temperature before measuring COD, The COD removal percentage are defined as:

$$\% \, COD \; Removal = \frac{C_i - C_f}{C_i} \times 100\% \qquad \text{(Equation 3-3)}$$

Where;

Ci is the initial COD concentration (mg/L)

Cf is the final COD concentration (mg /L) (Gameel et al., 2015)

According to the DR-2800 manual procedure, test result for the 2000 to 15,000 mg/L COD range are measured at 620 nm which consider high range COD.

3.6.1.4 Sulphide Removal

Sulphide is analysed by spectrophotometric method. (APHA, 2005). According to the DR-2800 manual procedure, the intensity of the blue color is proportional to the sulphide concentration and the wavelength of the sulphide used in the spectrophotometer is 665nm. The method for sulphide test are by preparing a blank and sample. To prepare the blank, the sample cell is filled with 10mL of deionized water. While for sample, carefully pipet 10mL of sample to a second sample cell. Then 0.5mL of Sulphide 1 Reagent is added to each sample cell. Next, immediately swirled the sample cell to make sure they are well mixed. Next, 0.5mL of Sulphide 2 Reagent is added to each sample cell. Immediately closed the sample cell and inverted the sample cell to mix. A pink color will develop initially. If sulfide is present, the solution becomes blue. Then 5 minute of reaction time is started at the instrument timer. After it done, the sample cells are cleaned to remove fingerprints and other marks in order to let the light penetrate. The sample cells are then put into the cell holder, the instrument reads the barcode, then selects and performs the correct test. Result are in mg/L S2-.

3.6.2 Settleability Test

A settling test commonly using a settleometer, often used to control the rate of return sludge pumping based on the sludge volume index(SVI). The SVI is determined by placing a mixed-liquor sample from the clarifier into a 100mL cylinder and then the settled volume is measured after 30 min and corresponding sample MLSS concentration (Tchobanoglous et al., 2003).

$$SVI\ (mL/g) = \frac{(settled\ volume\ of\ sludge, mL/L\ ) \times 10^3 mg/g}{(suspended\ solid, mg/L)} \qquad \text{(Equation 3-4)}$$

The graph of SVI and MLVSS/MLSS ratio versus days were plotted to get the relationship between these variables.

3.6.3 Analysis of BeCC on Voltage Generated

The data of voltage was recorded by using digital multimeter. The graph of voltage versus days are plotted to compare the result gain from 3 set of different electrodes.

3.6.4 SEM-EDX Analysis

The surface of the anode and cathode electrode are visualized by scanning electron microscopy to determine the corrosion of the electrode. The surface of each electrode is captured using SEM before and after the experiment. After the operation of BeCC is done, each of the electrode are kept in the oven at 30°C to remove moisture content for 24hour before doing the analysis. The SEM analysis was conducted to confirm the existence of microbial attachment at the surface of the electrode.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Introduction

This chapter provides the results obtained for all the experimental runs and the explanation on the trend shown for the variations in the effect on different combination of electrode materials in spent caustic wastewater treatment using BeCC.

4.2 Acclimatization Period

Acclimatization period was defined as the operational time before conducting the experiment which take 8 days to ensure the microorganism are fully adapt to a new climate. The figures below show the graph of SVI and MLVSS/MLSS over days:

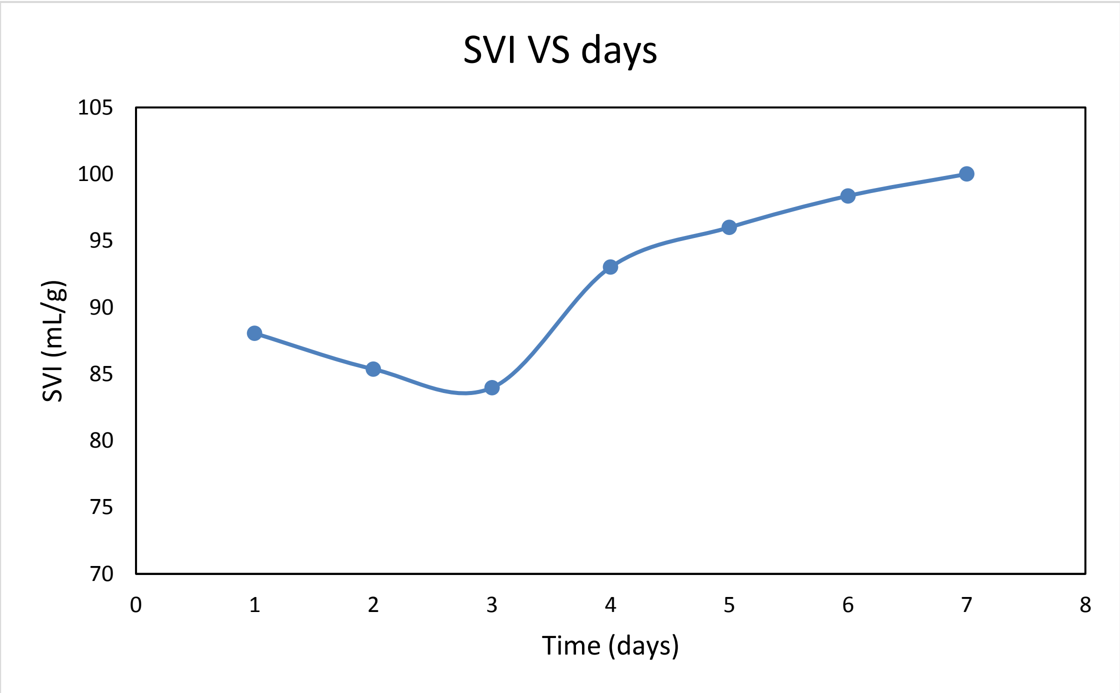

Figure 4-1: Graph of SVI VS Days during acclimatization period of BeCC

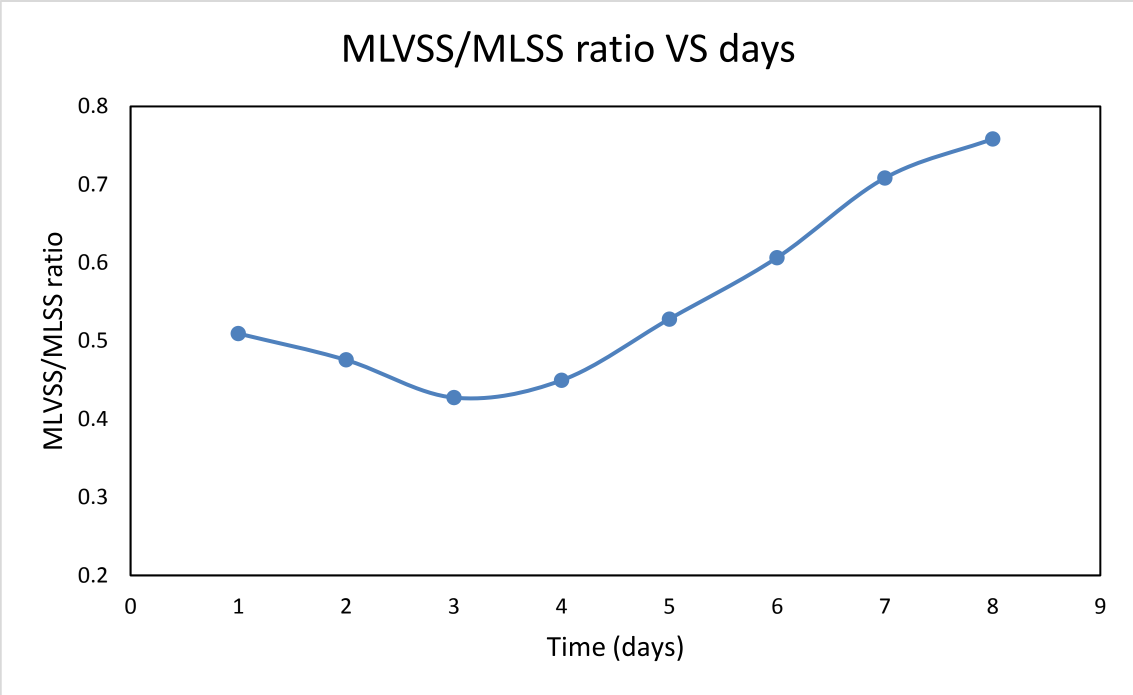

Figure 4-2: Graph of MLVSS/MLSS ratio VS Days during acclimatization period

Figure 4-1 and Figure 4-2 shows the graph of SVI and MLVSS/MLSS ratio over days respectively. From the both graph, it shows the correlation between these variables i.e. as the SVI decreases the MLVSS/MLSS ratio will decreases as well. The trends showed the declined for the first three days of BeCC operation, due to the adaptation to a new climate and condition. After several days, the microorganism shows a positive value by steadily rise of the SVI and MLVSS/MLSS ratio.

4.3 Effect on Various Electrode Materials on COD and Sulphide Removal

The COD result from the experiment and the efficiency of BeCC treating the wastewater using different combination of electrode materials are plotted in Figure 4-3. The results showed that there was significant reduction in COD of wastewaters after they have been treated by BeCC.

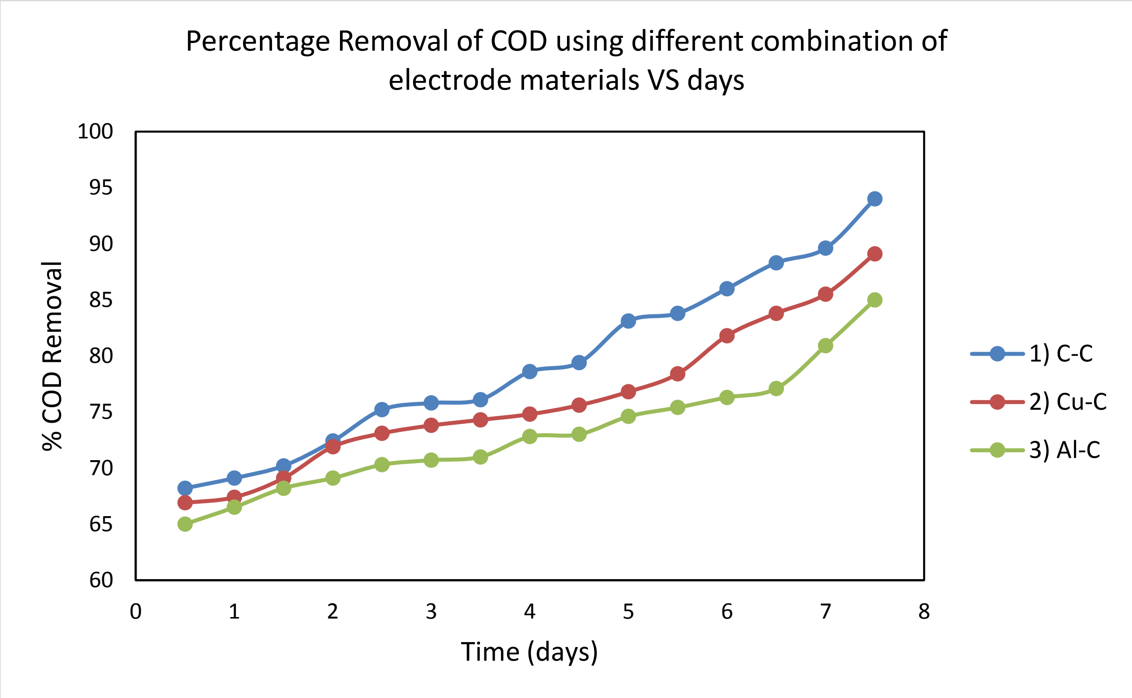

Figure 4-3: Percentage Removal of COD using different combination of electrode materials VS Days

From figure 4-3, it showed that 68% to 94% removed of COD is achieved after the wastewater treated using carbon-carbon electrode, and resulting the highest COD removal among the other combinations of electrodes. Followed by the treatment using copper-carbon electrode, it achieved 66% to 89% removed of COD and the lowest COD removal is achieved after treated using aluminium-carbon as electrode which is 67% to 85% removal.

The sulphide result from the experiment and the efficiency of BeCC using different combination of electrode materials in treating the wastewater to remove sulphide are plotted in Figure 4-4. The results showed that there was a significant change in water quality parameters mainly in sulphide after treatment in BeCC.

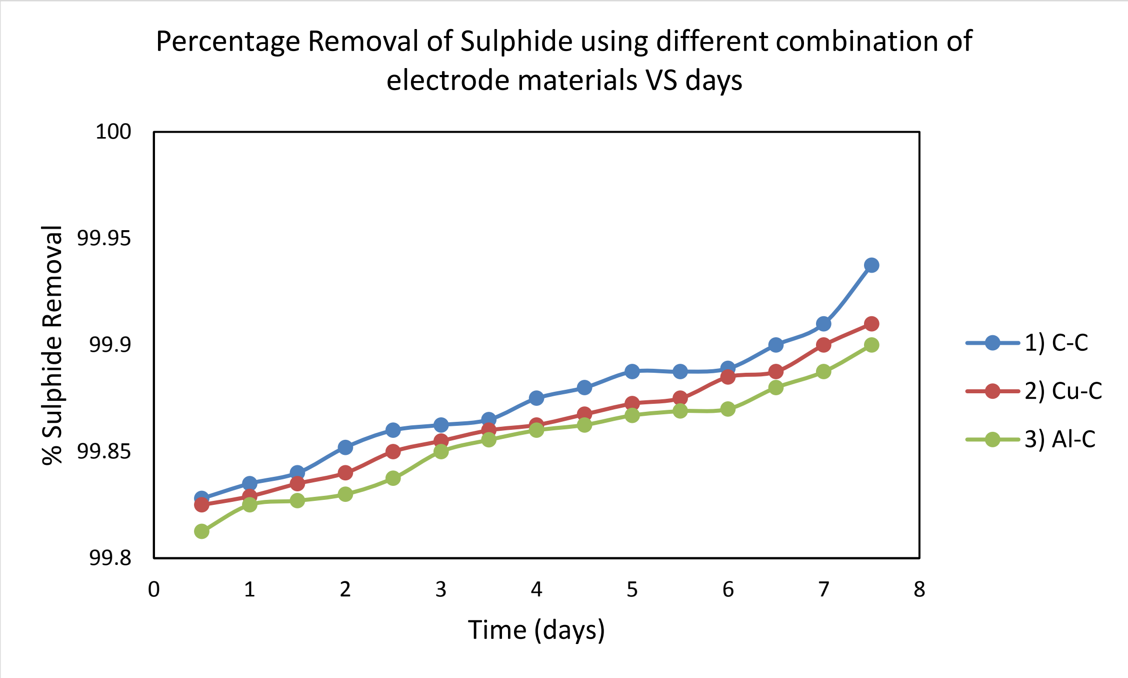

Figure 4-4: Percentage Removal of Sulphide using different combination of electrode materials VS Days

From figure 4-4, the maximum achievable reduction in sulphide is at 99.95% using carbon-carbon electrode. However, the other combinations of electrodes are shown a very significant removal of sulphide, with successfully removed 99.8% to 99.94% removal of sulphide in the wastewater after treated using BeCC.

A positive correlation was found to exist between percentage amount of COD removal and the percentage amount of sulphide removal i.e. the greater amount of COD removed in the BeCC, the greater the amount of sulphide removed (Abbasi et al., 2016 & Izadi et al., 2016). Hence, the best efficiency treatment of the spent caustic is by using carbon electrode as anode and cathode to promote the high performance of BeCC.

The SVI and MLSS/MLVSS ratio are plotted in Figure 4-5 and Figure 4-6 respectively.

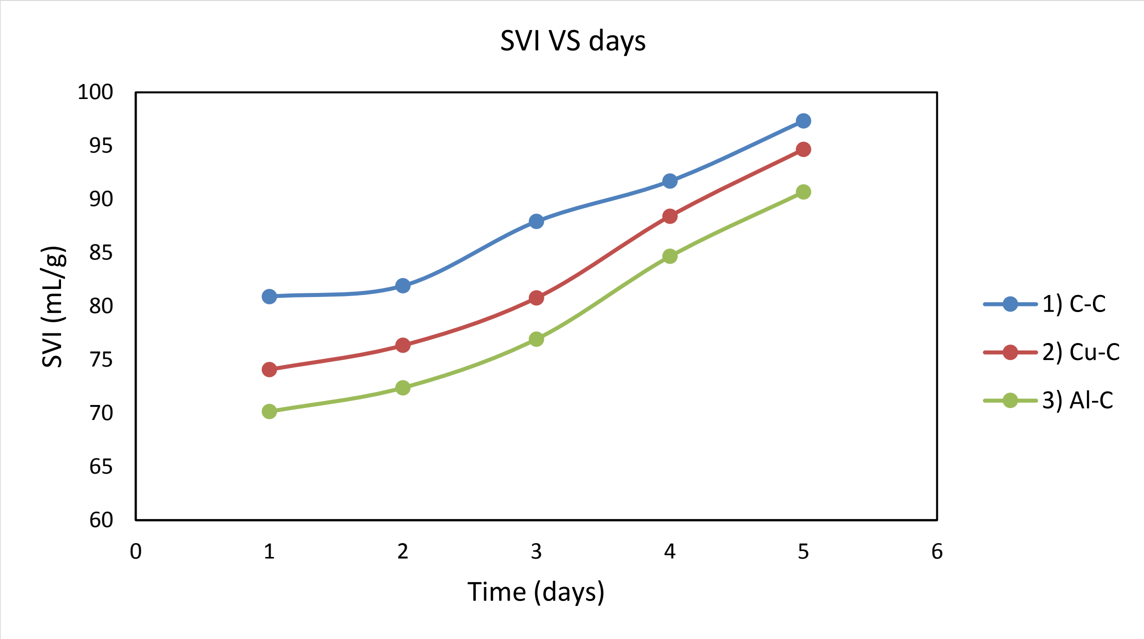

Figure 4-5: SVI VS Days

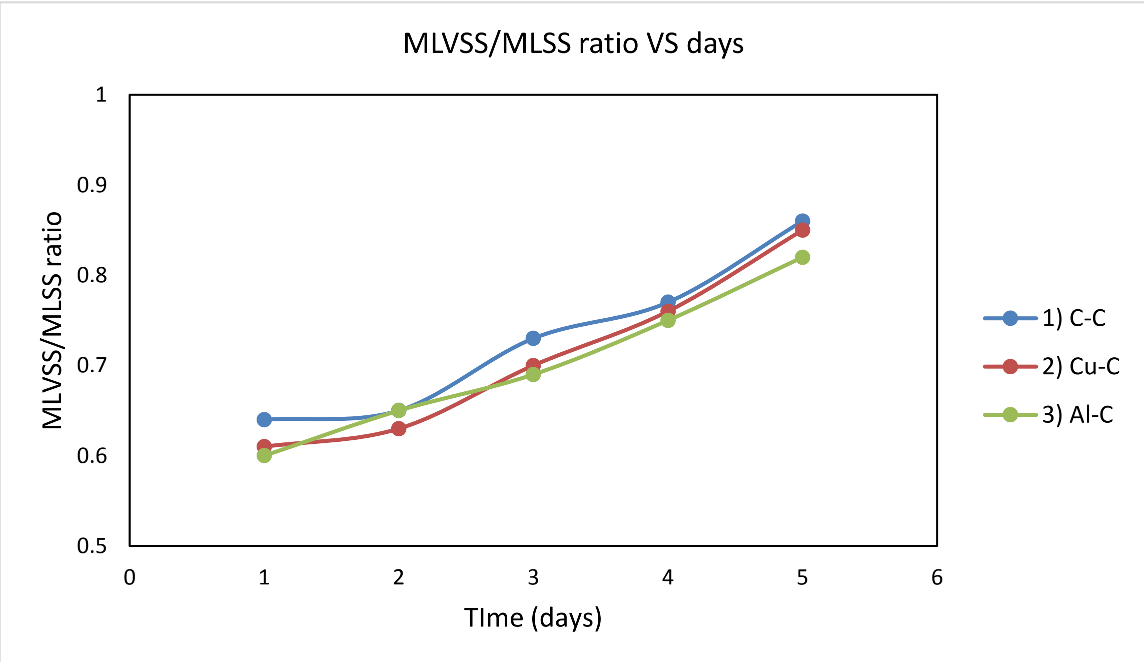

Figure 4-6: MLVSS/MLSS ratio VS Days

From figure 4-5 and figure 4-6, it shows that the trend of the SVI and MLVSS/MLSS ratio are rise moderately over the period of time throughout the BeCC operation. The range of the MLVSS/MLSS ratio are considered acceptable since it is still between the typical range of 0.6 to 8.5 in the conventional activated sludge system (Tchobanoglous et al., 2003).

4.4 Voltage Generated and Efficiency Treatment of BeCC

The voltage result from the experiment are recorded and plotted in Figure 4-7 after the treatment process using BeCC with different combination of electrode materials.

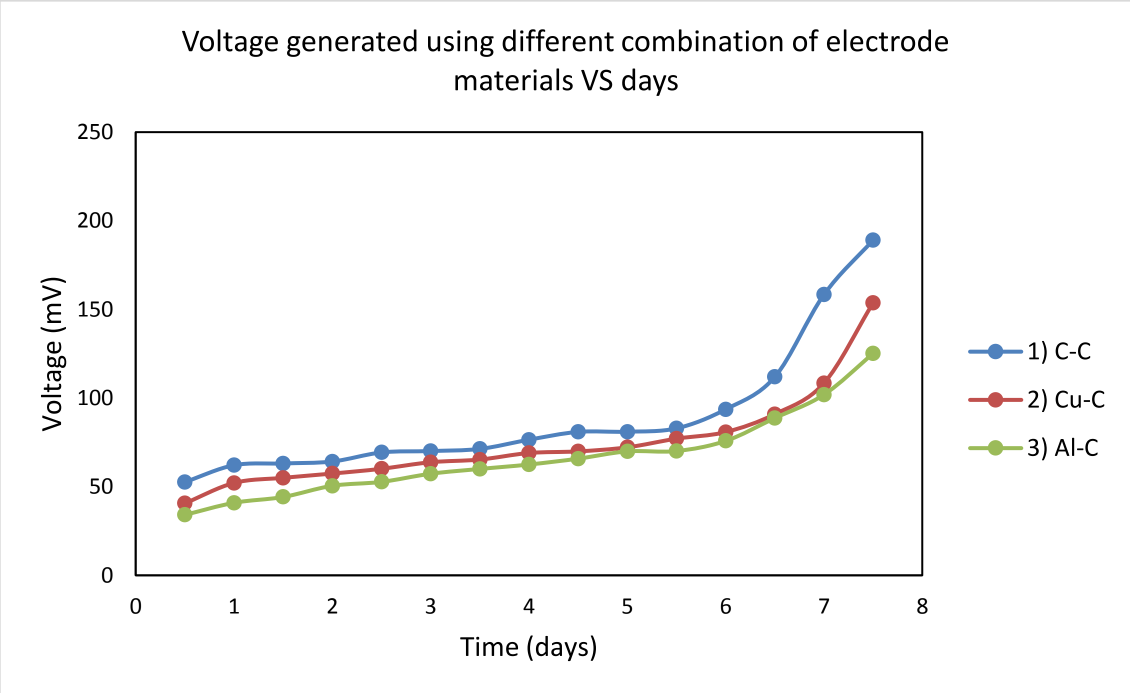

Figure 4-7: Voltage generated using different combination of electrode materials VS Days

From figure 4-7, it showed that carbon-carbon electrode gives the highest value of voltage which is 189.1 mV. While, 153.7 mV voltage generated using copper-carbon electrode and minimum voltage of 125.1 mV is generated using aluminium-carbon electrode. It demonstrated that different electrodes exhibited different behaviours.

Despite the relationship of percentage removal between COD and sulphide, other different aspect need to be considered such as the voltage generated since it generation is one of crucial part in the setup of BeCC system. Based on the studies that has been made by Baudler et al. 2015, carbon is the most common electrode material for BeCC. However, in bioelectrochemical system it is considered as the material of choice and can be changed to enhance the performance of microbial attachment on the electrode, since it is biocompatible, chemically and microbially stable and it can be produced at comparatively low costs from biological treatment. Despite of the used carbon mainly graphite as electrode, other metals like copper, silver, stainless steel and aluminium which are actually antimicrobial metals, on whose surface bacteria do not grow would give a greater effect to the performance of the processes itself. Based on this study, it can be concluded that carbon electrode gives the highest voltage generated due to the system design and sludge used is suitable for carbon-carbon electrode.

4.5 SEM-EDX Analysis of Electrode Before and After Treated using BeCC

According to Najafpour et al., 2016, any biochemical reaction can begin at the anode and end at the cathode. The SEM-EDX analysis was conducted to confirm the existence of microorganism that attached at the surface of the electrode. The SEM was used to investigate the morphological properties of the anode and cathode surface before and after operation.

4.5.1 Carbon-carbon electrode (BeCC-1)

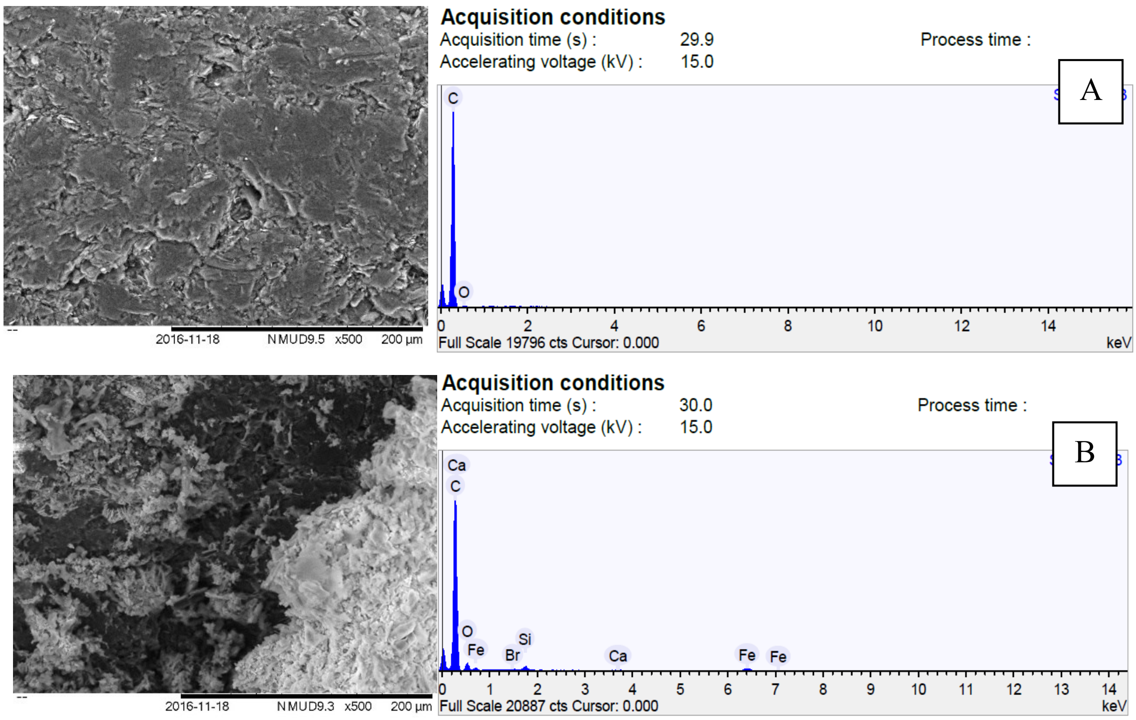

Figure 4-8: [A] SEM and EDX analysis of carbon electrode before treated, [B] SEM and EDX analysis of carbon electrode after treated (Anode)

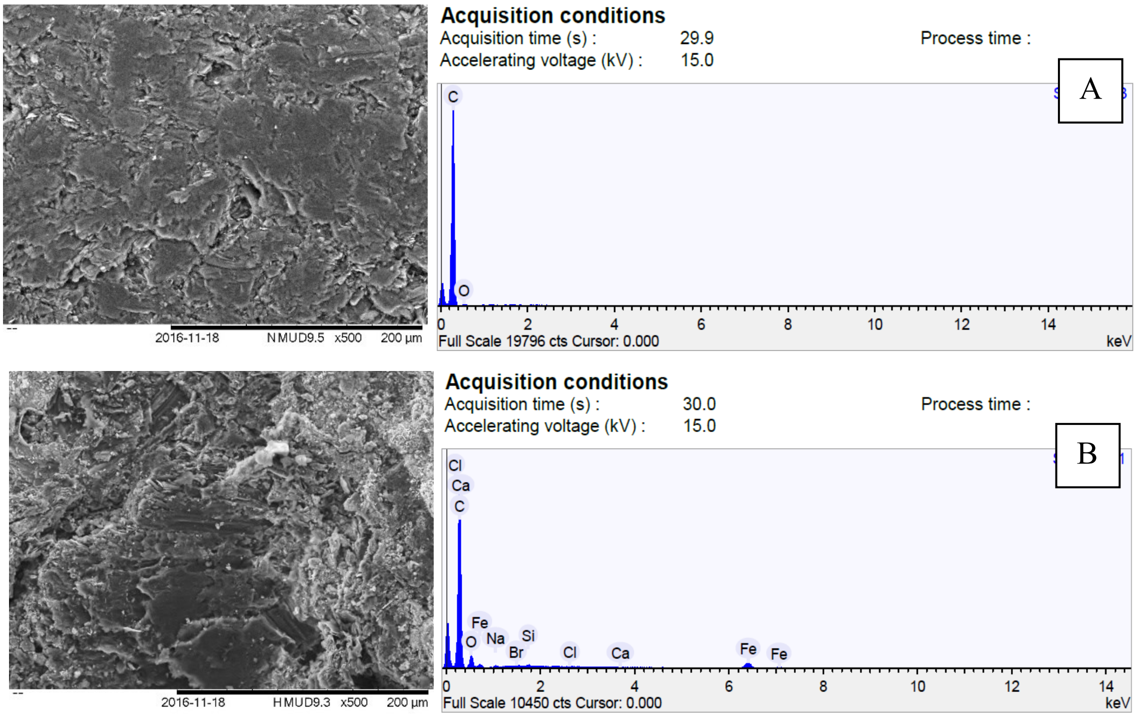

Figure 4-9: [A] SEM and EDX analysis of carbon electrode before treated, [B] SEM and EDX analysis of carbon electrode after treated (Cathode)

In BeCC-1, for the anode, comparing with the clean carbon electrode (Figure 4-8A), microorganism attachment and some substrate deposition on the carbon electrode could be observed from Figure 4-8B. From the EDX result, carbon peaks were predominant in the graphs, however there were still a very small amount of other element peaks. The Fe peaks were slightly low compared to the cathode EDX (Figure 4-9B), indicating that the most of the metals were deposited on the cathode rather than anode. (Yan Li, 2014)

4.5.2 Copper -carbon electrode (BeCC-2)

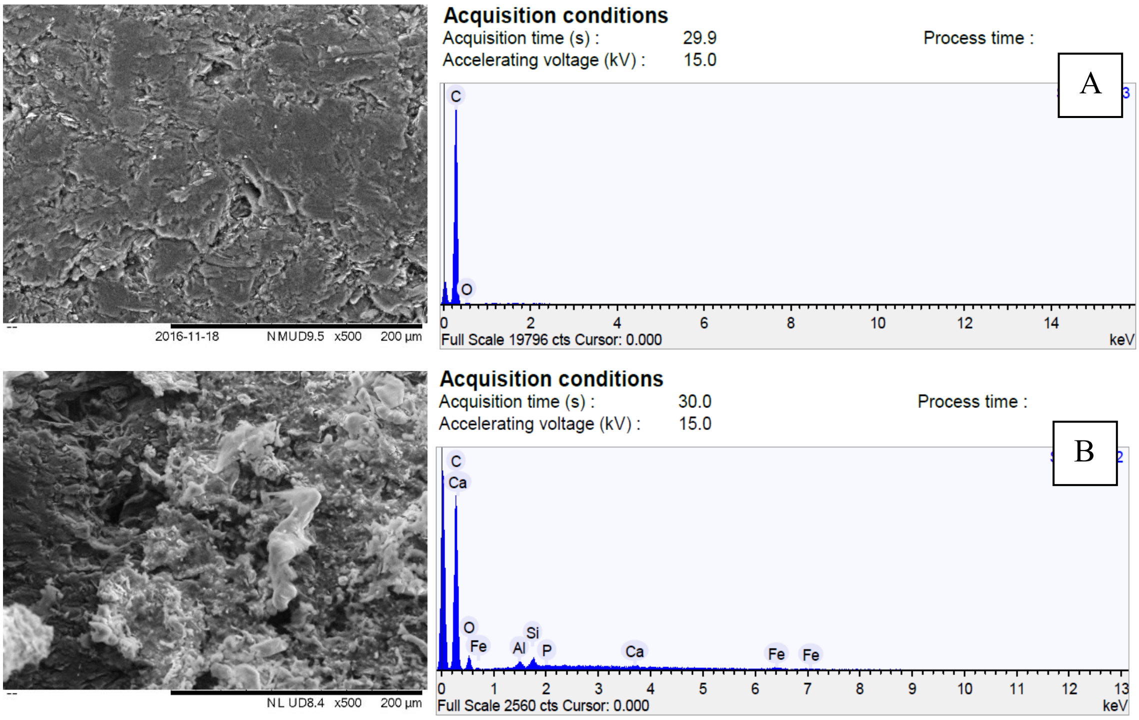

Figure 4-10: [A] SEM and EDX analysis of carbon electrode before treated, [B] SEM and EDX analysis of carbon electrode after treated (Anode)

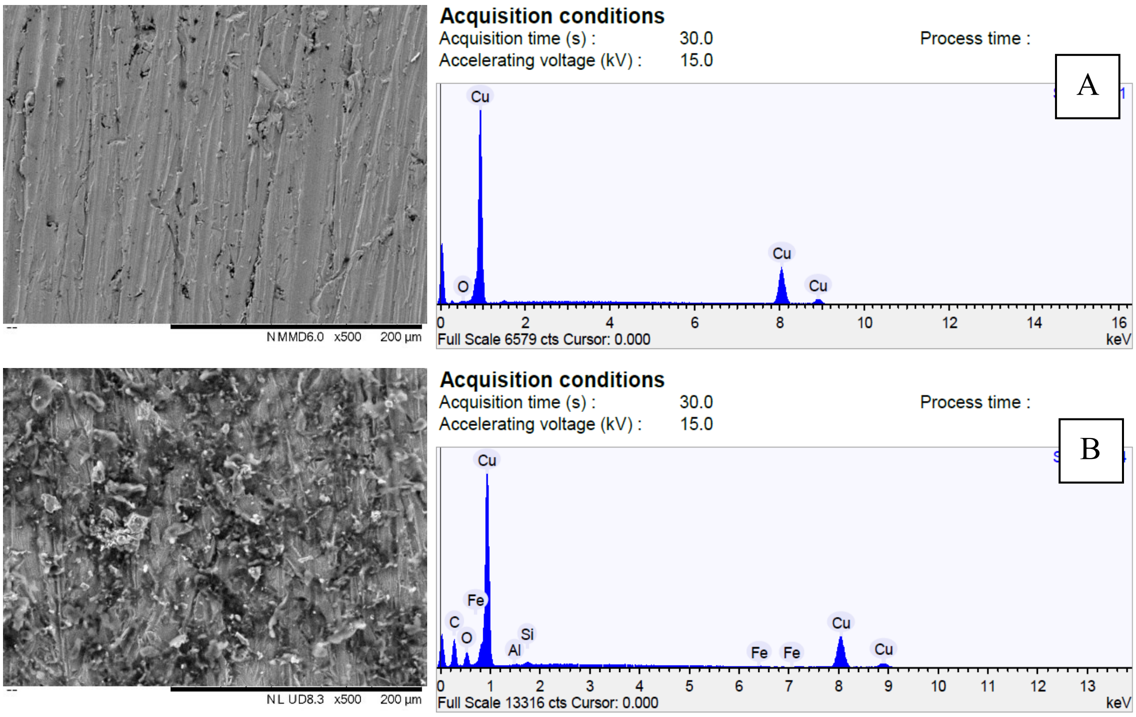

Figure 4-11: [A] SEM and EDX analysis of copper electrode before treated, [B] SEM and EDX analysis of copper electrode after treated (Cathode)

In BeCC-2, for the anode, comparing with the clean carbon electrode (Figure 4-10A), microorganism attachment and some substrate deposition on the carbon electrode could be observed from Figure 4-10B. From the EDX results, carbon peaks were predominant in the graphs but there were still other element peaks when treating with metals, indicating that Fe, Al and the components (P, Si, Ca) were absorbed on the carbon electrode. The Fe and Al peaks in cathode (Figure 4-11B) were obvious or slightly high comparing with those from anode. (Yan Li, 2014)

4.5.3 Aluminium-carbon electrode (BeCC-3)

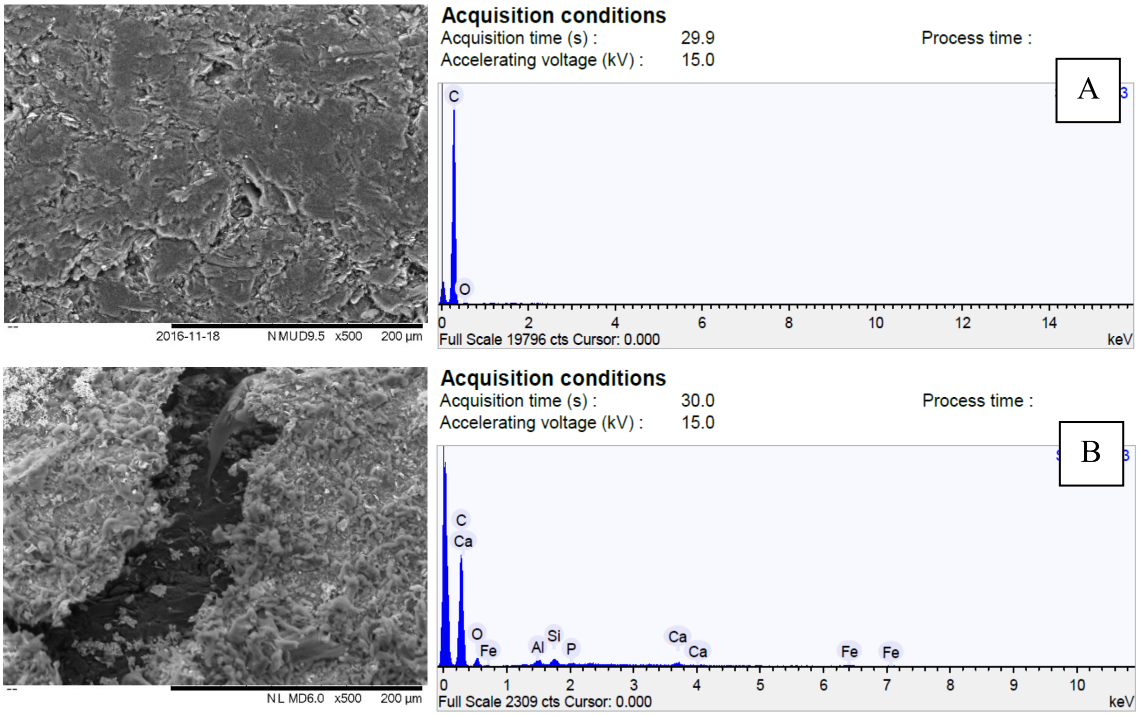

Figure 4-12: [A] SEM and EDX analysis of carbon electrode before treated, [B] SEM and EDX analysis of carbon electrode after treated (Anode)

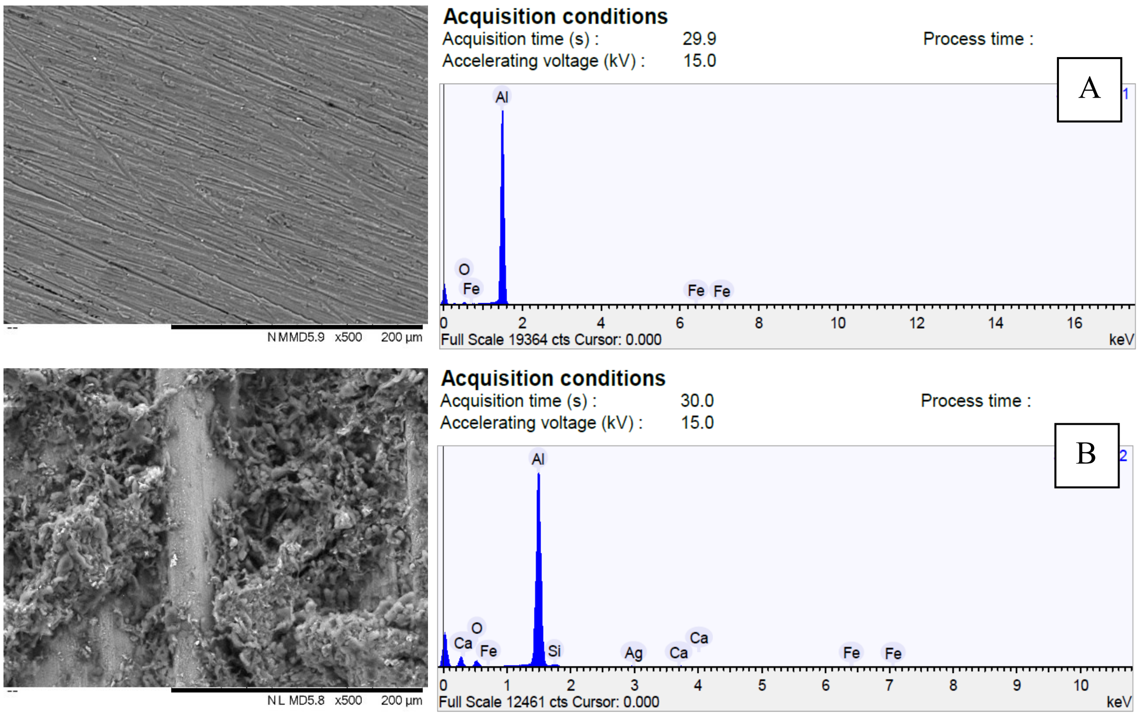

Figure 4-13: [A] SEM and EDX analysis of aluminium electrode before treated, [B] SEM and EDX analysis of aluminium electrode after treated (Cathode)

In BeCC-3, for the anode, comparing with the clean carbon electrode (Figure 4-12A), microorganism attachment and some substrate deposition on the carbon electrode could be observed from Figure 4-12B. From the EDX results, carbon peaks were predominant in the graphs but there were still other element peaks when treating with metals, indicating that Fe, Al and the components (P, Si, Ca) were absorbed on the carbon electrode. The Fe peaks in cathode (Figure 4-13B) were obvious comparing with those from anode while Al peaks were predominant in the graph since the metal used was aluminium electrode. (Yan Li, 2014)

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

BeCC was successfully operated by using different combination of electrode materials in terms of COD removal, sulphide removal, and voltage generated. From the findings, it shows that electrode combination of carbon-carbon is chosen as the best materials since it gives greatest COD and sulphide removal, instead of highest voltage generated. The great treatment efficiency for COD and sulphide are achieved 94% and 99.95% removal respectively using carbon-carbon electrode in BeCC operation, while maximum voltage of 189.1 mV is generated.

5.2 Recommendation

In this study, effective surface area of anode and cathode are very important in order to promote the performance of BeCC. According to Victor 2007, in his research it stated that it is possible to redesign the reactor to ensure that the surface areas of electrode are fully effective with the BeCC design because it will give an impact on the voltage generated. The cathode fouling due to the metal deposition also will resulting in the decreasing of voltage generated. Therefore, cathode surfaces needed to be cleaned periodically to remove metal deposition (Yan Li, 2014). In addition, it also recommended to design the reactor in close system, hence will promote the voltage generated and efficiency treatment for the wastewater.

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APPENDIX

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