TREATMENT OF HIGHLY COLORED WASTEWATER
FROM COMMERCIAL BIOGAS REACTOR DISCHARGE

BY

MS. HATAIRUT SAMAKKARN

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE
REQUIREMENTS FOR THE DEGREE OF MASTER OF
ENGINEERING (ENGINEERING TECHNOLOGY)
SIRINDHORN INTERNATIONAL INSTITUTE OF TECHNOLOGY
THAMMASAT UNIVERSITY
ACADEMIC YEAR 2019
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THESIS

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ENTITLED

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was approved as partial fulfillment of the requirements for

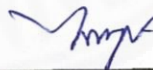the degree of Master of Engineering (Engineering Technology)

on February 27, 2020

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Member and Advisor _____
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Author	Ms. Hatairut Samakkarn
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ABSTRACT

Wastewater effluent from commercial biogas generation is highly colored and poses a serious problem. There is a new standard for control of color from industrial effluent. The new legislation specifies the color value of the discharge from the factory not to exceed 300 ADMI (American Dye Manufacturers Institute method) (Industry, 2017). An effective treatment that can support color removal from wastewater is needed. This work employs a Fenton oxidation process to treat color wastewater from commercial biogas that uses vinasse as its ingredients. The effects of $FeSO_4$ concentrations, H_2O_2 concentrations and pH on the color removal of biogas wastewater were investigated and optimized using a Box-Behnken design (BBD) under a Response Surface Methodology (RSM). Application of a strongly basic anion exchange resins is conducted to increase the color removal efficiency of the Fenton treated effluent.

The optimized condition for color removal using Fenton process is pH 5.5, H_2O_2 9.8 M, $FeSO_4$ 22.3 mM and a reaction time of 24 h. This can achieve a color removal efficiency of up to 98.3±0.1% from the average initial color wastewater of 203,600±3,920 ADMI to 3,540±95 ADMI. This condition achieves a COD removal

efficiency of 71.8±0.1% from the average initial COD of 68,000±148 mg/L to the final value of 17,500±68 mg/L.

Finally, the accomplishment of color removal to be within the new standard for the color of industrial effluent was achieved using 8% (w/v) anion exchange on the wastewater after the Fenton process. The color removal efficiency of this anion exchange process at 1 hour is 92.4±0.3% with a final COD removal efficiency of 31.3±0.3%. The combined color and COD removal efficiencies of the two process then become 99.9% and 82.3% respectively. The final color value of the treated effluent is 272±11 ADMI whereas the final COD value of the treated effluent is 12,000±44 mg/L.

Preliminary microbial fuel cell (MFC) was also applied to reduce COD. The average COD removal efficiency for 270 days is 15.4±2.2% from the average initial COD concentration of 5,640±308 mg/L. It indicates that MFC is not appropriate to treat this type of wastewater neither COD nor color was sufficiently removed.

Fenton process followed by anion exchange is recommended as a means for color removal from biogas wastewater treatment. Further treatment is needed to treat COD to meet the industrial effluent standard. This study can lead to new guidance to effectively remove color industrial wastewater for environmental conservation.

ACKNOWLEDGEMENTS

Ms. Hatairut Samakkarn

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LIST OF SYMBOLS/ABBREVIATIONS

Symbols/Abbreviations	Terms
SIIT	Sirindhorn International Institute of Technology
TU	Thammasat University
TAIST-Tokyo	Thailand Advanced Institute of Science and Technology-Tokyo Institute of Technology
BOD	Biochemical oxygen demand
COD	Chemical oxygen demand
ADMI	American Dye Manufacturers Institute
AOPs	Advanced oxidation processes
MFC	Microbial fuel cell
RSM	Response surface methodology
BBD	Box-Behnken design
HMW	High molecular weight
kDa	kilo-Dalton
ARP	Amadori rearrangement product
HMF	Hydromethylfurfural
DVB	Divinyl benzene
H_2O_2	Hydrogen peroxide
•OH	Hydroxyl radical
BTEX	Benzene, Toluene, Ethylbenzene, Xylenes
UBFC	Up-flow bio-filter circuits
GAC	Granular activated carbon
UFAF	Up-flow anaerobic filter
APHA	American Public Health Association
PBS	Phosphate buffer saline
rpm	Revolutions per minute

EDXRF	Energy Dispersive X-ray Fluorescence
ICP-OES	Inductively coupled plasma-optical emission spectrometry
DF	Degrees of freedom
Adj SS	Adjusted sums of squares
Adj MS	Adjusted mean squares
p-value	Probability value
EAMs	Electrochemically active Microorganisms
SEM	Scanning electron microscopy
EDS	Energy dispersive X-ray spectroscopy
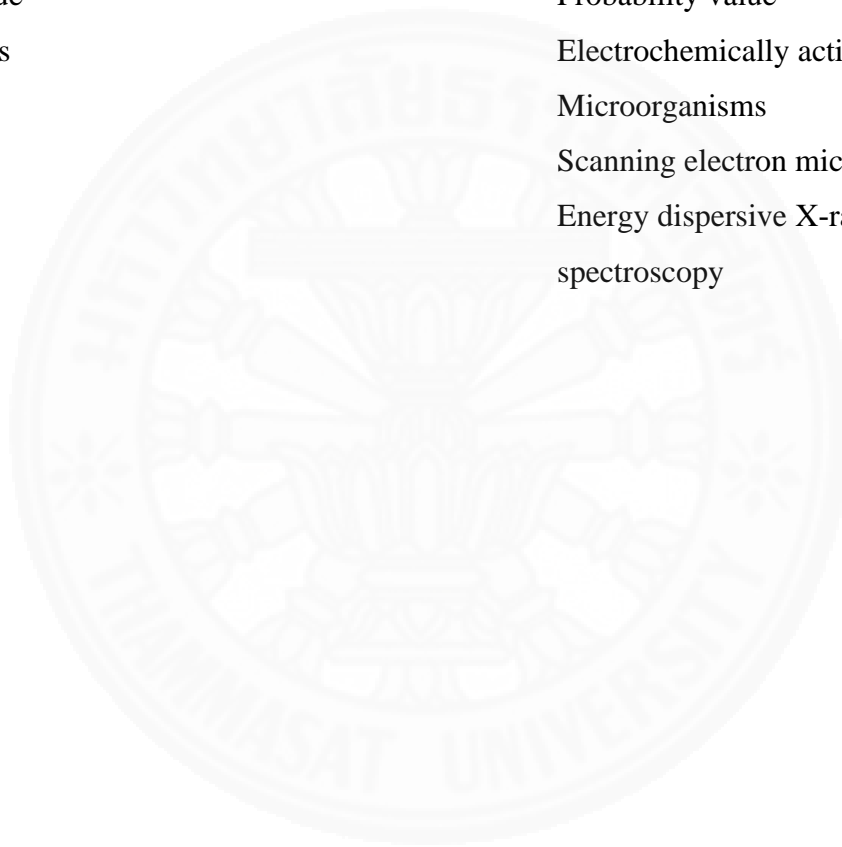
CHAPTER 1
INTRODUCTION

The biogas production is a renewable source of fuel from sugarcane vinasse waste residues from distillation (Bianca Ferrazzo Naspolini, 2017; Cristiano E. R. Reis, 2019) (using molasses as the raw material) to large potential for energy generation. It is produced from anaerobic treatment (Leandro Janke*, 2015) which is bio digestion without combustion resulting in a reduction of greenhouse gases. The raw materials of biogas production are waste residues that availability in usage and makes it a sustainable process. It is important to minimize the dangerous effect on humans and the environment. Although it is the most primary treatment owing to over 80% BOD removal efficiency and source of energy recovery as biogas (Y. Satyawali, 2008), the indirect consequence of biogas byproduct is dark color wastewater. Typically, industrial wastewater has a variety of contaminants. The biogas wastewater has a high concentration of organic pollutants, odor and dark brown color (Zahrim, 2014) which result from recalcitrant compounds (the recalcitrant compound is slowly or non-biodegradable (Bromley-Challoner, December 2003; D.Faber, October 1979)) called melanoidins found in industrial wastewater to involve with using molasses-based raw material (Arimi MM, March 2015).

Melanoidins are condensation products through the Maillard reaction of sugars and amino groups (Sara I.F.S. Martins*, 2001). The huge quantities of wastewater and the presence of organic melanoidins causing quite challenging conventional biological wastewater treatment (Singh, June 2013) because melanoidins are non-biodegradable organics and toxic to microorganisms including in wastewater treatment (M.N. Chavan, July 2006; Rzeski, 22 October 2013) as well. The wastewater can cause environmental problems if it is discharged directly into the water bodies without previous treatment. It threatens terrestrial and aquatic environment for examples visibility of aquatic animals, obstruction of sunlight lead to the reducing of photosynthesis and dissolved oxygen concentration in water nature like lagoons, lake or rivers and eutrophication (Ram Chandra, July 2008; Soni Tiwari, June 2012). More importantly, Thailand has a new standard regulation to control color discharge value not more than 300 ADMI

(Industry, 2017). Thus, color removal of wastewater is the priority parameter even though toxic color wastewater is a serious task. Whereas, from the current situation of central wastewater treatment plants in Thailand that mostly are stabilization pond and activated sludge (Dumrongthai, 2019; Ratanatamskul) as biological wastewater treatment (Al-Hashimi, 2013; B.M. D'Antoni, May 2017) is not consistent with this standard that makes industries have to adjust their wastewater process to handle this change.

But color wastewater removal is difficult to use only a single wastewater treatment method instead of various techniques because each method has advantages or/and disadvantages and one process may not pass the standard. For all these characteristics, three different techniques; Fenton process under advanced oxidation processes (AOPs)and ion exchange for color removal and the bio-electrochemical system as MFC (Włodarczyk, 2019) for COD removal were applied to treat biogas wastewater to achieve the most effective in color and COD removal. Accordingly, AOP is used widely to treat wastewater containing recalcitrant organics compounds as color pigments (Adina Elena Segneanu, 2013; Stasinakis, 2008), so it is an appropriate color wastewater treatment choice. Another application for color removal enhancement is ion exchange. Ion exchange is a chemical process of reversible interchange between free mobile ions of a solid phase (the ion exchanger) and liquid phase by mobile ions of exchanger exchange different ions of a similar charge in solution without permanent structural changes in the ion exchanger (Jain, October 2013). The application of ion exchange is used for removal of heavy metals, dyes, acids, insecticides, phenols (Javier M. Ochando-Pulido, 29 April 2018; Michelle Caetano, 2009), inorganic ions and persistent organic pollutant (Ganna Darmograi, 5 November 2016), which are toxic organic compounds, persist in the environment and resistant to most of the degradation processes (Ashraf, February 2017; Darbre, 2015; Ram Charitra Sah, 2011; Zacharia, April 10th 2019). Anion exchanger comprises a secondary amine, quaternary amine, or quaternary ammonium active group and it will separate negatively charged solutes (Peter F. Stanbury, 2017) Hence, it can remove colorants as melanoidins (Purolite, 2013) because melanoidins are negative charge (He-Ya Wang, October 2011).

In this research, the core color removal treatment of biogas wastewater is Fenton process with applying a standard statistical experiment design of BBD to achieve the optimization and continue the second treatment for increase efficiency by anion exchanger to obtain the lowest color value as much as it can treat to meet the color standard. Besides, another interesting wastewater technique is MFC for COD removal since it is an alternative renewable technology and clean energy source with low energy requirement even though the biological process remain yellow or brown color after treatment (Ahmad SHAHATA, January 2013). Thus, the objectives are optimization of color removal efficiency of actual biogas wastewater by Fenton process, enhancement efficiency of Fenton treated wastewater by anion exchanger to accomplish the color standard and study MFC in COD removal efficiency of diluted biogas wastewater.
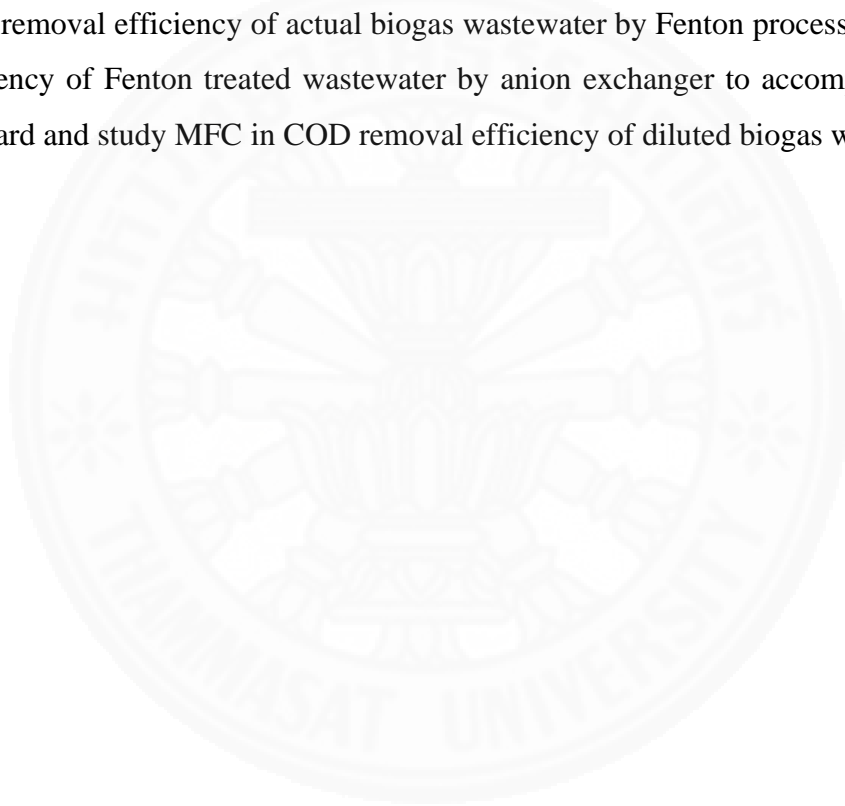
CHAPTER 2
REVIEW OF LITERATURE

2.1 Nature of melanoidins

Since biogas generation is process for producing energy in addition to control environmental pollution by using anaerobic treatment of vinasse. Nevertheless, this treatment cannot eliminate dark brown color as recalcitrant melanoidins of vinasse (Charles Cardona, 2013; Elda España-Gamboa, 2017; Mostafa Parsaee, March 2019; Singh, June 2013) because it takes place repolymerization of compounds resulting in increased color (Elda España-Gamboa, 2017; Ranjan Singh*, 2019; Sushil Kumar Shukla, 2019). Vinasse is named as mosto, stillage, distillery wastewater, distillery spentwash, or distillery slope. It is recalcitrant wastewater from ethanolic distillation and the chemicals composition are some mineral compounds such as phosphorus, potassium, nitrogen, calcium, sulfur and magnesium, alcohols, sugars, aldehydes, ketones, esters, glycerol, lactic acids, acetic acids, phenols (volatile organic compounds), propionic acid (volatile fatty acids)and melanoidins (Mostafa Parsaee, March 2019). Melanoidins are colored polymeric from the Maillard reaction final products, which are amino and carbonyl groups combination (Amundson, 2003). They are generally dark brown colored compounds, high molecular weight (HMW), nitrogen-containing biopolymers, which are not easy to decompose and absorb light at 405 nm (Rzeski, 22 October 2013). They are end-products of Maillard reaction during thermal process of food, bakery, preservation, distillery industry and sugar industry (Singh, June 2013). Furthermore, unpleasant end-products of the Maillard reaction effect on food products, the melanoidins play an essential role in advantage effects. They compose of acidic, polymeric and negatively charged colloids which is presence of the carboxylic acids and phenolic groups (K. Sridevi, 2014). They are antimicrobial (MORALES, April 2007)and antioxidant properties (A.P Echavarría, March 2013), therefore they are toxic to microorganisms that involved in process of wastewater treatment. Moreover, they are difficultly treated by conventional wastewater methods (Sekiguchi M, Mar 01, 1995). Their beneficial effects due to their behavior as anionic hydrophilic polymers so they can incorporate metal cations in the chelation such as

Cu^{2+}, Cr^{3+}, Fe^{3+}, Zn^{2+}, Pb^{2+}, etc. to form complex molecules then can precipitated (Singh, June 2013). Moreover, they are antihypertensive (Jose ´A. Rufia ´n-Henares*, 2007), antiallergenic (Jose Manuel Silvan, 2006)and tumor growth-inhibiting compounds (Hideo Kamei, 1997). Lately, the experiment has been presented melanoidins formula as C$_{17-18}$H$_{26-27}$O$_{10}$Nand molecular weight between 5-40 kDa (Rzeski, 22 October 2013; Singh, June 2013) with very complex structure.

2.1.1 Structure of melanoidins

The structure of melanoidins are not definitively known (Anna Smaniotto, 2009). In the other study about melanoidins that were prepared by monosaccharide using the carbonyl compounds glucose (D-GLC) together with the amino compounds (glycine). A glucose/amino acid Maillard reaction, the carbonyl compound forms through the Amadori product to produce deoxyosones which form each other in an aldol-type reaction and become degradation products of amino-branched sugar. For instance, a nucleophilic attack of carbanion in the C3 of a 3-deoxyhexosulose happens on the C1 of another deoxyhexosulose. Figure 2.1 showing the possible formation of amino acids with unsaturated carbonyl oligodeoxyhexosuloses structure will generate oligodeoxyhexosuloses amine as branched melanoidins with amino compounds. In addition, Figure 2.2 shows the conceivable melanoidins structure from 3-deoxyhexosuloses. This attack pathway on C2 of a 3-deoxyhexosulose is probable, causing to minor changing in the structure. 1-Deoxyhexosuloses, 1-amino-1,4-didesoxyhexosuloses and the ARPs can react with a molecule of deoxyhexosulose to produce the melanoidins skeleton. Even though the melanoidins are diverse chemical, a lot of studies present the melanoidins are negative charge in foods and model systems (BETTINA CAMMERER, April 2002; He-Ya Wang, October 2011).
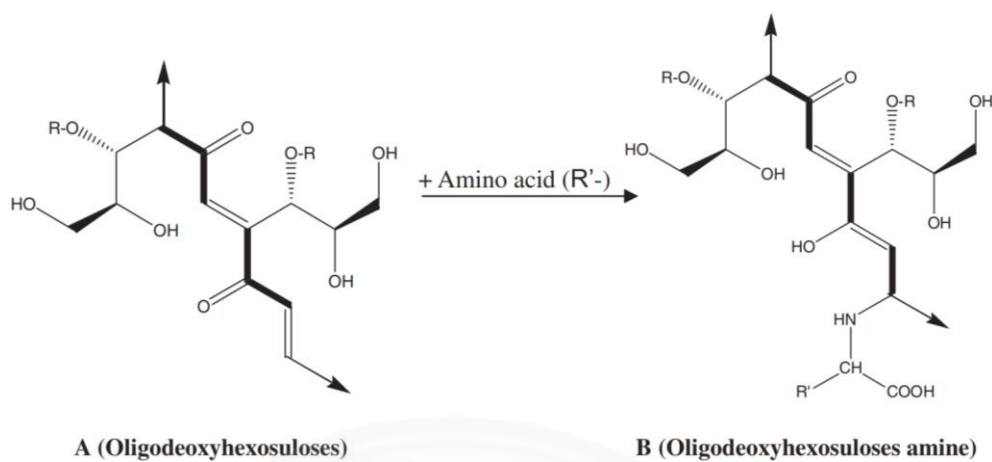
Figure 2.1 The carbohydrate-based of branched melanoidin with amino compounds
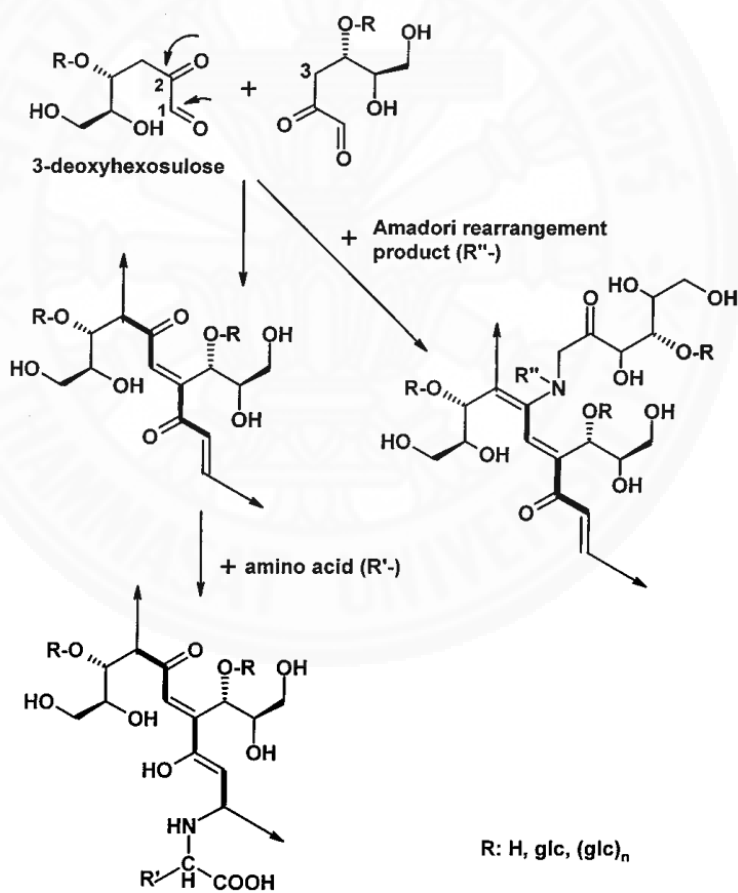
Figure 2.2 Part of possible pathway of melanoidin structure from 3-deoxyhexosulose

2.1.2   Mechanism of the Maillard reaction

The Maillard reaction was named after the French chemist, Louis Camille Maillard who original discovered in 1912. The Maillard reaction is a non-enzymatic browning reaction which complex reaction between amino group and carbonyl group of organics, reducing sugars, as well as close to humic substances in environment. The reaction generates colorants, aroma and flavor precursors for food process. There are divided to two pathways in the Maillard reaction products: the volatile Maillard reaction products and the non-volatile Maillard reaction products. It occurs effectively at temperature more than 50 °C and pH 4-7.

2.1.2.1 Maillard flavors

There are mostly researches in topic the Maillard flavors as volatile Maillard reaction products. The objectives study volatiles structure characterization and quantification involve with aroma formation. Moreover, the series of overview articles on coffee flavors formed by volatile Maillard reaction in coffee beans processing.

2.1.2.2 Melanoidins

There are a few works on melanoidins known as end products of the non-volatile Maillard reaction that compare to Maillard flavors. Melanoidins are commonly defined as macromolecular, nitrogenous, brown colored components Maillard reaction which are formed during household and industrial thermal process of foods and diet like in honey, cocoa, malt, coffee and bread (Bekedam, January 2008). The melanoidins is depend on many factors such as types of reactants, concentration of reactants, types of catalysts, pH, reaction temperature and time, presence of oxygen, water activity and different of metal ions. The Maillard reaction can generate various products from simple gases like CO_2 to complex polymeric chemicals are referred to melanoidins. The mechanisms are generally divided into three stages (Rizzi, 1997) as shown in Figure 2.3.

First, initial reaction of sugar amine condensation between a free amino group such as lysine and α-hydroxyl carbonyl of a reducing sugar. An aldose, reducing sugar, give product an N-substituted aldosylamine which results in a nucleophilic attack by NH_2 amino group on electron preferring carbonyl sugar. It is an amine assisted

dehydration of sugar. The condensation product loses water and is formed to a Schiff base that cyclizes in pentoses and hexoses to the analogical glycosylamine. The N-substituted glycosilamine rearranges to generate the Amadori rearrangement product (ARP). If it is the aldose and amino acid glycine, so the ARP is 1-amino-1-deoxy-2-ketose (monofructoseglycine), whereas the fructose/amino acid glycine is the Heyns rearrangement and give substituted 2-amino-2-deoxyldoses but aminoaldoses are not sable so they readily reactive forming the Amadori compounds. So, the Amadori compounds are the first stable intermediate in the Maillard reaction. It does not happen browning reactions in this initial stage.

Second, the consequent decomposition of Amadori compounds involve pH conditions. In condition pH 7 or below, they undergo 1,2-enolisation to hydromethylfurfural (HMF) (in case of hexoses) or furfural (in case of pentoses). In condition pH above 7, the decomposition undergoes 2,3 enolisation to reductones (4-hydroxy-5-methyl-2,3-dihydrofuran-3-one; HMF^{one}) and a variety of fission products such as acetol, diacetyl and pyruvaldehyde. In addition, all of HMF, furfural, reductone and fission products can react further. The functional group of carbonyl compounds are capable to condense with free amino acids. For instance, nitrogen incorporation of Strecker degradation between dicarbonyl compounds and amino acids will produce aldehydes and α-aminoketones releases CO_2.

Third, some products condense to form brown colorants and polymers. The amino components react the unsaturated carbonyl structures and form branched melanoidins. And polymerization of reactive intermediates form melanoidins. Finally occurring this stage caused by reactions of cyclisation, dehydration, retroaldolisation, rearrangement, isomerisation and condensation bring about the brown nitrogenous polymers as melanoidins (Ibarz, December 2012; Monica Coca, July 2004; Sara I.F.S. Martins*, 2001).
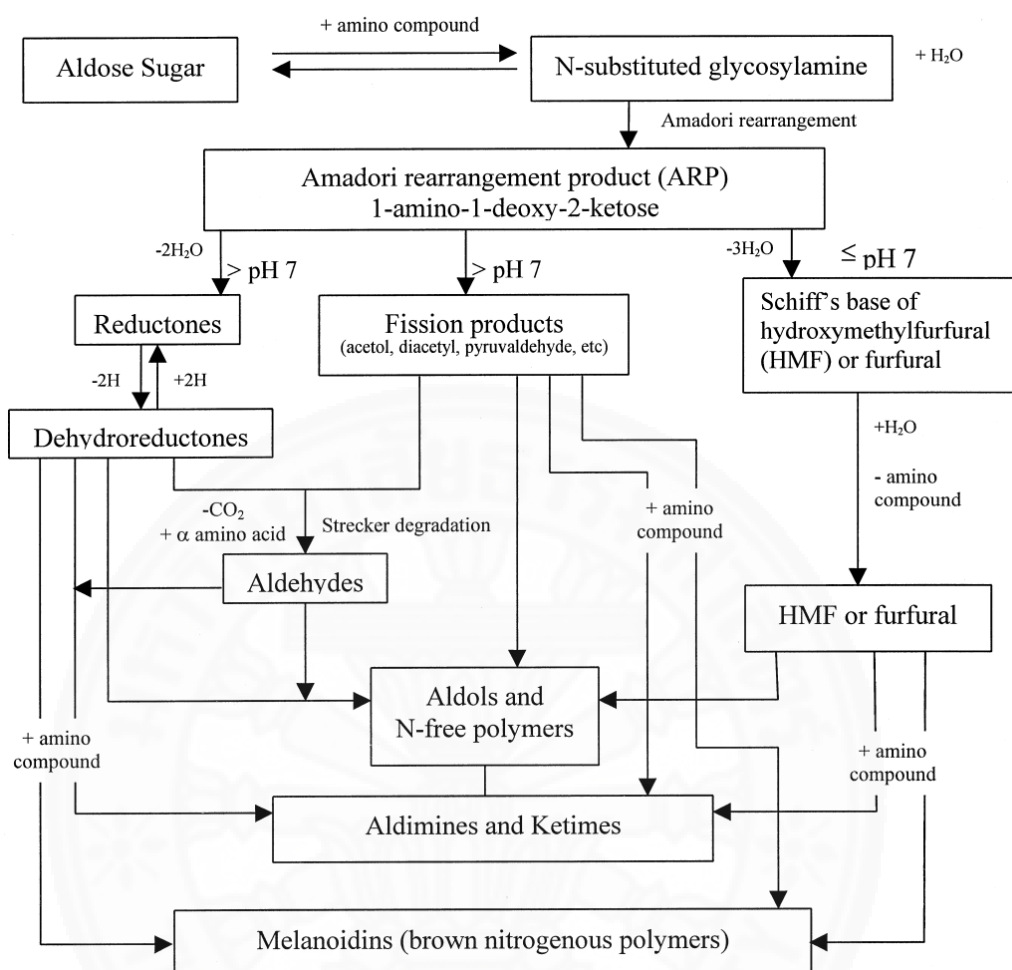
Figure 2.3 Maillard reaction scheme

2.2 Wastewater treatment

Wastewater treatment is the process of elimination unwanted pollutants such as inorganics/organics from wastewater. The aim of treatment is to reduce the contaminants to reach the acceptable levels and make water safe before discharge into the environment. There are divided to 3 methods such as physical, biological and chemical wastewater treatment methods (Kant, 14 January 2012).

2.2.1 Physical wastewater treatment

Physical wastewater treatment is employed to separate suspended solid contaminants in wastewater by naturally forces, such as gravity, van der Waal forces and physical barriers without any changes in chemical structure of target

contaminants including a screening, media filtration, membrane filtration, flotation, adsorption, sedimentation and equalization tank.

2.2.1.1 Coarse-fine screening

The mechanical screening will separate larger non-biodegradable and floating solid materials for instance garbage, plastic residuals or hair from wastewater stream.

2.2.1.2 Media filtration

Media filtrations involve multimedia filtration that uses at least three different layers of media such as anthracite, sand and gravel. The filter allows larger suspended solids to be trapped at the top while smaller suspended solids are able pass through then trapped in deeper. The filtration removes suspended solids including clay, algae, some organic matter or particles from 10-25 microns but does not remove viruses, bacteria or smaller protozoans.

2.2.1.3 Membrane filtration

Membrane filtration removes fine particles and dissolved solids from wastewater under pressure and the membranes which are specific pore size. This method utilizes microfiltration, ultrafiltration nanofiltration and reverse osmosis. Microfiltration membranes remove 0.1-10 microns size which are suspended solids, algae and protozoans. Ultrafiltration membranes remove 0.005-0.01 microns size which are suspended solids, bacteria and certain viruses. Nanofiltration membranes remove 0.005-0.001-micron size which are bacteria, viruses and divalent and multivalent ions (calcium, magnesium). Reverse osmosis used pressure to force water through a semipermeable membrane remove dissolved ions (sodium), bacteria, viruses and other contaminants ranging 0.005-0.0001 microns size.

2.2.1.4 Flotation

Flotation removes suspended particles by producing bubbles from any gas which generally used air because of not highly soluble in liquid, easily accessible, safety and less expensive then bringing them to the surface. This process is typically

used to separate oils, fats and finely suspended particles (Puganeshwary Palaniandy, August 2017).

2.2.1.5 Sedimentation

Sedimentation is a process to remove suspended solid particles which are heavier than water by gravity. In this process normally builds in various shapes tanks that remove accumulated solids from the bottom of tank (Carlsson, Nov 96).

2.2.1.6 Adsorption

Adsorption is a surface process that atoms or ions called adsorbate are transferred onto the surface of a solid adsorbent by physical van der Waals forces (physisorption) or chemical bonding (chemisorption). The adsorbate does not diffuse into the structure of the adsorbent for instance activated carbons (PETRI SJOHOLM, 2001; Rizwan Tareq, 2019; Y.Artioli, 2008).

2.2.1.7 Equalization tank

The main objective of equalization tank is control unstable flow rate, pollutant concentrations and temperature of influent wastewater to reduce interfere factors and increase efficiency of next process.

2.2.2   Biological wastewater treatment

Biological wastewater treatment removes the biodegradable organic matters including both particulate and soluble usually accomplished by natural operation of microorganisms utilize organic contaminants in wastewater as food source for their growth and reproduction. The methods are classified two types as biological aerobic treatment and biological anaerobic treatment and these two process have their advantages-disadvantages as shown in Table 2.1 (Anijiofor Sandra C., July 2017; Chunli Zheng, 2013; E. Gašpariková, January 2005; Iyyanki V. Muralikrishna, 2017; Mittal, August 2011; Samer, October 2015; Shaikh Ziauddin Ahammad, January 2013; Yi Jing Chan, 1 December 2009).

2.2.2.1 Biological aerobic treatment

Biological aerobic treatment is operated in the presence of oxygen and aerobic bacteria degrade organic pollutants to produce simpler organics, CO_2, H_2O, ammonia (NH_3)and cellular energy resulting in purify effluent and biomass sludge. It is used to treat wastewater of low COD (less than 1,000 mg/L). Furthermore, the effluent from aerobic process is higher quality than anaerobic process. Due to the fact that aerobic process produces higher removal of soluble biodegradable organics and lower effluent suspended solids concentration. There are various types of aerobic treatments such as activated sludge process (which is the most widely used in biological treatment (G.Sin, 2013; Scholz, 2006), sequencing batch reactor, trickling filter, rotating biological contactor, aerated lagoon and oxidation pond.

2.2.2.2 Biological anaerobic treatment

Biological anaerobic treatment takes place in absence of oxygen and degrade organics into simple end products, CO_2, hydrogen sulfide (H_2S) causing odor and methane (CH_4) result in sulfate reduction, biogas production from methanogenesis. It has less excess sludge than the aerobic process. It is used to treat wastewater of high COD (over 4,000 mg/L) with low energy, nutrients and chemicals requirement. Moreover, it can treat some persistent organic pollutants while no reaction to aerobic process. However, the effluent from anaerobic process has low quality than aerobic process because of slow growth rate of anaerobes, incomplete degradation and having toxic chemicals effluent as ammonium ion (NH^{4+}) and H_2S. Hence, it needs post treatment followed by aerobic process. The technologies of anaerobic process are anaerobic filter, anaerobic contact process, anaerobic fluidized bed, up-flow anaerobic sludge blanket process, etc.

Table 2.1 Comparison of aerobic and anaerobic biological wastewater treatment

Parameters	Aerobic	Anaerobic
Organic removal efficiency	High	High
Organic loading rate	Moderate	High
Effluent quality	Excellent	Moderate to poor
Sludge production	High	Low
Energy and chemicals need	High	Low to moderate
Startup time	Fast (2-4 weeks)	Slow (2-4 months)
Construction and reactor size	Complex and larger size	Simple and small size
Odor	Less odor problem	High odor problem
Bioenergy recovery	No	Yes
Post treatment	Discharge/filtration/disinfection	Need

2.2.2.3 Bio-electrochemical systems (BESs)

Nowadays, the points of energy and environmental concerns are rising. Energy is necessary for human living especially fossil energy which is nonrenewable resources. This is main source energy to produce electricity in current time that will run out and consequence of climate change and others environmental impacts. Alternate energy that replaces oil and carbon resources are wind power, waterpower, biogas, biomass, hydrogen energy and microbial fuel cell. Thus, the development of environmentally friendly energy sources is increasingly becoming a top priority. Biological fuel cells as MFC can convert chemical energy from substrate in wastewater into electrical energy, since wastewater exist billions of microbes generally known as bacteria (Gude, December 2016; K. Scott, 2012). MFC is a bio-electrochemical system and use bacteria as catalysts to oxidize organic and inorganic constituents in order to produce current (Włodarczyk, 2019). It is wastewater treatment technology, effective for COD removal (Keith Scott, 2016; M. P. D. Prasad, June 2015)and one of alternative energy sources that has potential to generate electricity. It used in application of organic contaminants removal without chemical treatment or nutrient supplement and combustion. It can treat wastewaters by superior efficiency organic matters mineralization that is a transformation of organic contaminants and nutrients to inorganic constituents or small

and simpler organic compounds (in case the organics mineralization is not complete) by single species or consortium microorganisms in addition power generation. It consists of two electrode components, an anode chamber which is anaerobic condition so microbes cannot use the O_2 and the another one is a cathode chamber which is connected with air flow to supply dissolved oxygen. It allows bacteria to grow on the anode chamber by oxidizing and biodegradation the organic contaminants like wastewater to protons and electrons. The bacteria transfer the electrons through an external circuit to oxygen molecules as terminal acceptor in cathode chamber result in completing the electrical circuit to generate electricity and the protons are diffused to cathode chamber. The combination of electrons, protons and oxygen will produce water. The efficiency of MFCs depends on various factors for example substrate, exoelectrogenic microorganisms or electrode materials. The Up-flow bio-filter circuits (UBFC) is a kind of develop biocatalyst microbial fuel cell without membrane. As a result, the development UBFC system will get rid of clogging problem by using granular activated carbon (GAC) as immobilized base material instead of carbon fiber brush. Furthermore, it comprises pretreatment column up-flow anaerobic filter (UFAF). It is an area-less, maintenance-less, cost reduction, renewable energy source, solving clogging problem and high stability. In the future thinking beyond these wastewater treatments are transformed into our demand. MFC is an attractive technology to generate bioelectricity from wastewater (Chontisa Sukkasem, September 2011).
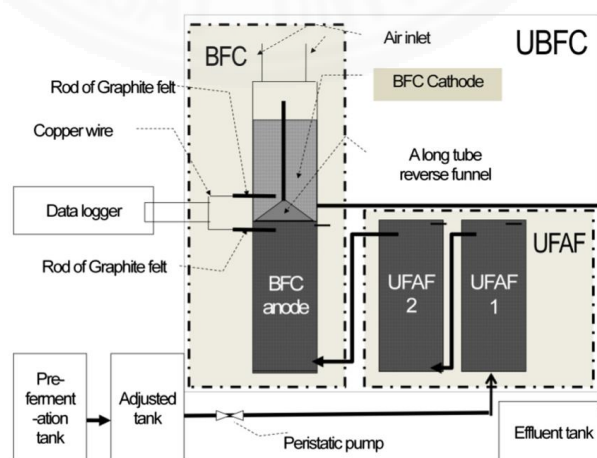
Figure 2.4 Up-flow bio-filter circuits (UBFC) system

2.2.3 Chemical wastewater treatment

Chemical wastewater treatment is wastewater treatment involving chemical reaction. It is used to remove suspended solids or heavy metals such as neutralization, coagulation, precipitation, oxidation, ion exchange and disinfection.

2.2.3.1 Neutralization

Neutralization used to adjust the pH value that adding acids like sulfuric acid, hydrochloric acid or alkali like sodium hydroxide, calcium oxide (lime), or sodium carbonate for precipitation and flocculation. It is used to treat wastewater containing metals.

2.2.3.2 Coagulation

Coagulation is a process that aggregate fine colloid particles size 0.1-1 nm which cannot be naturally removed, with adding positively charged coagulants to destabilize and reduce the negative charge of particles then they form larger as flocs and easily settle.

2.2.3.3 Precipitation

Precipitation is a method to convert soluble matters into solid particles. It is used to remove ionic matters such as heavy metals (zinc, copper, lead, cadmiumand etc.) metallic cations, fluoride, cyanideand phosphateand organic constituents by adding counter-ions to reduce their solubility (Zueva, 2018).

2.2.3.4 Ion exchange

Ion exchange can remove cations or anions from wastewater. There are many types such as zeolite and ion exchange resin. Ion exchange resin is mostly used due to higher efficiency than zeolite. Ion exchange resin is small insoluble plastic beads, 0.5-1.0 mm, made from network of cross-linked hydrocarbons polystyrene and divinyl benzene (DVB) and containing immobile ions. These ions are fixed on the structure. In order to be an electrical neutrality, the resins must be attached with loose counter ions which are mobile ions causing exchange with other ions in aqueous. If the functional groups of fixed ions resin are negatively charged called cation

exchanger while functional groups of fixed ions resin are positively charged known as an anion exchanger. Moreover, the functional group can divide resin into several types (ErikJørgensen, 1989; James R. Couper, 2010; Javier M. Ochando-Pulido, 29 April 2018; JUDITH KAMMERER, January 2011; Vassilis Inglezakis, December 2006).
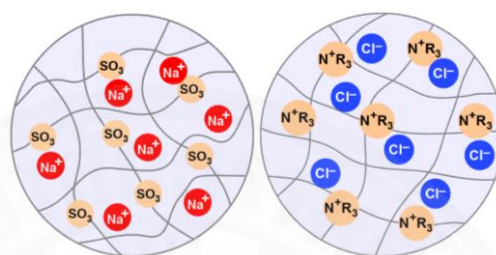
Figure 2.5 The cation and anion exchanger bead

2.2.3.4.1 Cation exchanger

Cation exchanger is divided two types as a strongly acidic sulfonic cation exchanger (SO_3H)and a weakly acid cation exchanger containing carboxylic groups (COOH). The counterions of cation exchanger are sodium cations (Na^+) or hydrogen ions (H^+).
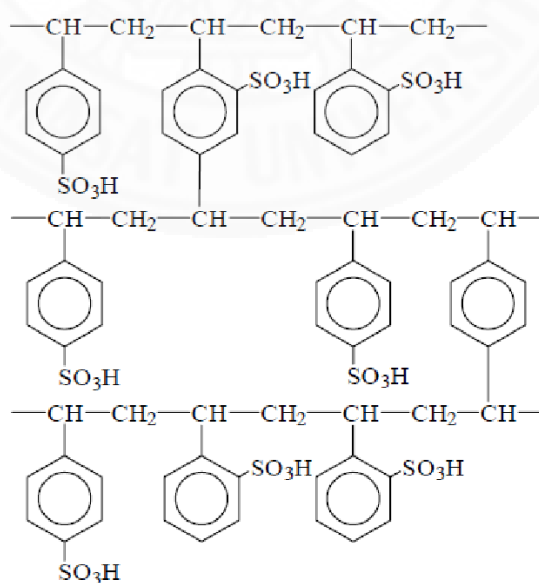
Figure 2.6 A strongly acidic sulfonic cation exchanger

2.2.3.4.2 Anion exchanger

Anion exchanger can classify into a strong base quaternary ammonium anion exchanger (R_3N^+), weak basic anion exchanger containing tertiary amine (RNH), secondary amine (RN) and amine (RNH_2) groups. The counterions of anion exchanger are chloride anions (Cl^-) or hydroxide ion (OH^-).
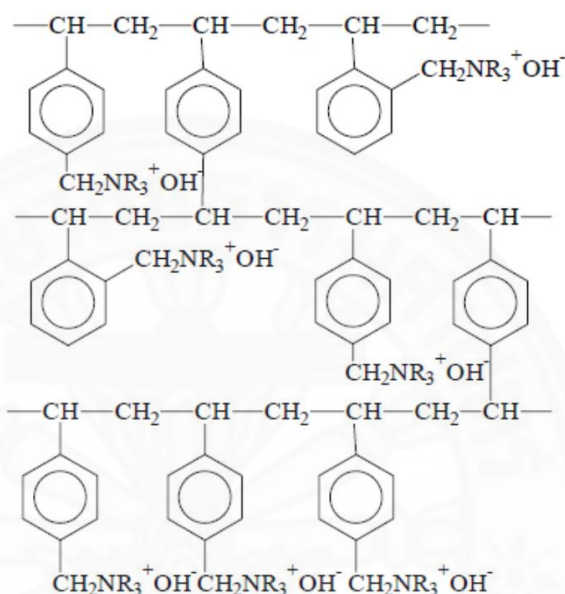
Figure 2.7 A strongly basic quaternary ammonium anion exchanger

Ion exchange removes ionized contaminants in liquid by replace ions from exchanger instead of the ions in liquid. It takes place without any physical changing to the exchanger material only same electrical charged ions are exchanged. It is used to exchange non-desirable ions. For instance, cation exchanger attracts positively charged ions while anion exchanger attracts negatively charged ions for example removal of Ca^{2+}, Mg^{2+}, SO_4^{2-}, Cl^-, heavy metals (arsenic, barium, cadmium, cobalt and zinc) , dyes, acids, insecticides, phenols (Javier M. Ochando-Pulido, 29 April 2018), inorganic ions and persistent organic pollutant (Ganna Darmograi, 5 November 2016). This method resembles adsorption in mass transfer. So, both ion exchange and adsorption are considered sorption process, but ion exchange removes ions while adsorption removes electrically neutral substances. Ion exchange has more advantages than conventional separation and purification methods because of less operation cost and consumption of reagents, easy management and scale-up and

recovering added-value components. Otherwise, when it was exhausted, it can either be regenerated by using chemicals. In part of regeneration, chemicals used are such as NaOH (in case of the anion exchanger containing OH^-), HCl (in case of the anion exchanger containing Cl^-), HCl or H_2SO_4 (if cation exchanger containing H^+) and NaCl (if cation exchanger containing Na^+). From the advantages of anion exchanger properties, industries realize these abilities and apply for color removal in fruit juices, white and rose wine, olive oil mill wastewater and sugar production process. Of all reasons, anion exchanger can enhance color removal efficiency of biogas wastewater since it is able to remove melanoidins. Anionic hydrophilic polymers can exchange negatively charged ions of melanoidins and release OH^- into wastewater instead. Therefore, this research aims to use anion exchanger for color removal.

2.2.3.5 Oxidation-reduction

Oxidation-reduction is a process to remove toxic soluble pollutants that cannot treat by precipitation. This method uses oxidation-reduction to transform the pollutants to become less dangerous compounds by adding either oxidants for example ozone (O_3), chlorine gas (Cl_2), oxygen (O_2), etc. or reductant such as sulfur dioxide (SO_2), sodium borohydride ($NaBH_4$) ,etc. (Works, 2011).

2.2.3.6 Disinfection

Disinfection is an elimination or inactivate of pathogens in wastewater process to protect health from microbes, viruses and protozoan and improve water quality to meet the industrial effluent standard. The chemical disinfection agents are chlorine, O_3, ultraviolet radiation, chlorine dioxide (ClO_2)and bromine (Br) (Samer, October 2015).

2.3 Advanced oxidation processes (AOPs)

The limitations of conventional wastewater treatment methods are ineffective to treat non-biodegradable pollutants of industrial wastewater, especially organic constituents (S Krishnan, June 2017b) so it contribute to a development of highly efficient process as advanced oxidation processes in order to detoxify or remove recalcitrant organic compounds (S Krishnan, June 2017b) that are resistant to conventional methods (Collin G. Joseph*, 2009; Laura G. Covinich, May 2014). AOPs

are a chemical process (Ravindra Kumar Gautam, 2016) that generate reactive hydroxyl radical ($^{\bullet}$OH) in room temperature and atmospheric pressure at low pH value. This process has been removed recalcitrant unwanted pollutants in surface, groundwaters or industrial wastewater. Since the powerful of $^{\bullet}$OH aggressively degrade organic pollutants until these pollutants are completely converted to CO_2, H_2O, inorganic compounds and mineral acids (if the pollutants contain halogens) (Collin G. Joseph*, 2009) and $^{\bullet}$OH is electrophiles (electron preferring) which are nonselective react with nearly electron-rich organic compounds. AOPs are generally used to treat pesticides, color pigments, surfactants, pharmaceuticals and endocrine disrupting chemicals and has been successfully used for reduction the concentrations of recalcitrant organic compounds in pretreatment methods (Stasinakis, 2008).

2.3.1 Hydroxyl radical (•OH)

The $^{\bullet}$OH is one of powerful oxidizing agent and has more effective reduction potential than ozone whereas lower than only fluorine molecule as shown in Table 2.2 and result in reduction treatment costs and system size. Since it is a strong oxidant, it has a high capacity to destroy organic constituents which especially could not be easily oxidized by other conventional chemicals (e.g. O_2 and Cl_2)and it can react with some inorganic species as iron (a. K. M. Arjunan Babuponnusami, March 2014; Jordi Bacardit*, July 2007 ; Pivetz). It is generated from chemical method of hydrogen peroxide (H_2O_2) which comprise two hydrogen and two oxygen atoms. The H_2O_2 is also a strong oxidizing agent and used in versatile application of removal inorganic and organic pollutants from wastewater such as nitrites (NO_2^-), Cl_2, sulphites (SO_3^{2-}), hypochlorites (ClO^-) and cyanides (CN^-) or useful in treatment of gaseous sulphur oxides (SO_x) and nitrogen oxides (NO_x) that converted to acids. Other benefits are bleaching of pulp and paper, organic synthesis, cleaning, decorating, etching of metals and disinfecting agent. The dissociation of the oxygen and water from H_2O_2 by enzymatic and nonenzymatic process can supply oxygen for microorganisms in biological and bioremediation treatment. However, only H_2O_2 alone is not greatly enough for high concentrations contaminants because of low reaction rate. It is activated by metal salts (iron salts), ozone or ultraviolet light can form $^{\bullet}$OH which are more reactive (E. Neyens∗, 17 March 2003; a. S. G. Vrushali Pawar, 2015). Typically, it can

be generated from three methods (Leon M. Dorfman, June 1973). Firstly, radiation chemical method is production of ${}^{\bullet}$OH from absorption energy of ionizing radiation. Second, photochemical method produces ${}^{\bullet}$OH from water by absorption of vacuum ultraviolet light, or absorption of H_2O_2 by absorption of ultraviolet light. And lastly, chemical method is ${}^{\bullet}$OH formation in a chemical reaction such as in Fenton process with H_2O_2. Apart from, it can be categorized into four chemical reactions in water or aqueous solutions (Leon M. Dorfman, June 1973).

2.3.1.1 Addition

The ${}^{\bullet}$OH react with an unsaturated compound, aliphatic or aromatic to produce a free radical product. In equation (2.1) show ${}^{\bullet}$OH addition mechanism.

$$ {}^{\bullet}OH + R \text{ (pollutant)} \rightarrow {}^{\bullet}ROH \tag{2.1} $$
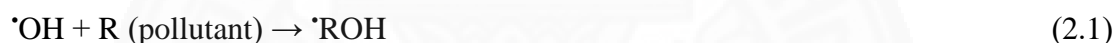
2.3.1.2 Hydrogen abstraction

The hydrogen atom abstraction from the hydroxyl group (R-OH) or the methyl group (R$-$CH$_3$) react with ${}^{\bullet}$OH to produce a free radical and water.

$$ {}^{\bullet}OH + R \text{ (pollutant)} \rightarrow {}^{\bullet}R + H_2O \tag{2.2} $$
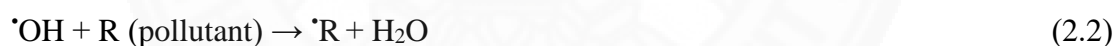
2.3.1.3 Electron transfer

The electron is transferred to ${}^{\bullet}$OH and generate the OH$^-$.

$$ {}^{\bullet}OH + R \text{ (pollutant)} \rightarrow {}^{\bullet}R^+ + OH^- \tag{2.3} $$

2.3.1.4 Radical interaction

The combination of ${}^{\bullet}$OH, or with a different radical or the disproportionate to form a stable chemical product. However, this mechanism scavenges useful hydroxyl radicals for interaction with organic compounds.

$$ {}^{\bullet}OH + {}^{\bullet}OH \rightarrow H_2O_2 \tag{2.4} $$

Table 2.2 Standard reduction potentials for some common oxidants

Oxidants and Reactions		E^0 (V, 25°C)
Fluorine (F_2)	$F_2(g) + 2H^+ + 2e^- \rightarrow 2HF$	3.03
Hydroxyl radical (˙OH)	*˙OH + H$^+$ + e$^-$ → H$_2$O*	*2.80*
Atomic oxygen (O)		2.42
Ozone (O_3)	$O_3 + 2H^+ + 2e^- \rightarrow O_2 + H_2O$	2.07
Hydrogen peroxide (H_2O_2)	$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$	1.78
Hydroperoxyl radical/ Perhydroxyl radical (˙O_2H)	˙$O_2H + 2H^+ + 2e^- \rightarrow 2H_2O$	1.70
Permanganate ion (MnO_4^-)	$MnO_4^- + 4H^+ + 3e^- \rightarrow MnO_2 + 2H_2O$	1.67
Chlorine (Cl_2)	$Cl_2 + 2e^- \rightarrow 2Cl^-$	1.36
Oxygen (O_2)	$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$	1.23

2.3.2 Fenton oxidation process (Fe^{2+}/H_2O_2)

The AOPs have several methods including Fenton process, ozonation, sonolysis, photocatalysis, UV photolysis, wet air oxidation, etc. Among all methods, Fenton process is the one outstanding method of AOPs, simple, economical and has high effective method for degradation of contaminants (Nirmalendu Sekhar Mishra, December 2017; a. P. S. G. Vrushali Pawar, June 2016). Fenton process has been studied for a long century by H.J.H Fenton who original discovered the process in 1894. He provided information that H_2O_2 was activated by ferrous salts to oxidize tartaric acid. Currently, the Fenton process is applicable to treat chemicals in water pollution for instance, phenols, formaldehyde, BTEX referred to chemical of benzene, toluene, ethylbenzene and xylene, pesticide chemicals, rubber chemicals, variety of dyes, surfactants explosives, color and various hazardous organics from wastewater (Anita Maslahati Roudi, January 2015; Stasinakis, 2008; a. S. G. Vrushali Pawar, 2015). The advantages are no need any external energy input to activate H_2O_2 owing to degradation in atmospheric pressure at room temperature. It requires short reaction time and easy to handle, in addition, degrades contaminants to harmless form like CO_2, $H_2O$and inorganic salts. It can destruct recalcitrant compounds better than other treatment techniques. It can also combine with other process as a pretreatment or post treatment.

On the other hand, the high cost of H_2O_2 and the added ferrous iron (Fe^{2+}) might require separation before discharge to nature (a. K. M. Arjunan Babuponnusami, March 2014; P Bautista, October 2008). The efficiency depends on catalyst concentrations, pH, temperature. As a result at pH more than 3.5, the ferric iron (Fe^{3+}) precipitate to ferric hydroxide; $Fe(OH)_3$ (s) (Magdalena Balintova*, 20 April 2011; Meng-hui Zhang, 20 June 2019; Nirmalendu Sekhar Mishra, December 2017) (or more correctly, $Fe_2O_3.3H_2O$) which large orange-yellow solid (yellow boy). At pH more than 8.5, the formation of Fe^{2+} to ferrous hydroxide; $Fe(OH)_2$(s) will increase and cause low Fe^{2+} concentration (Magdalena Balintova*, 20 April 2011). At pH less than 3, Fe^{2+} regeneration by Fe^{3+} and H_2O_2 is prohibited leads to drop Fe^{2+} concentration. High temperature enhances the decomposition of H_2O_2 to O_2 and H_2O in 2.2 times each 10 °C (P Bautista, October 2008). Fenton process commonly is considered as the reaction between H_2O_2 and ferrous salt in acidic aqueous solution at approximate pH 3-4 (Amilcar Machulek Jr., February 2012).

2.3.2.1 Fenton mechanism

In the early stage, Fe^{2+} is oxidized to be Fe^{3+} meanwhile H_2O_2 is reduced to OH^- and $^•OH$ as a strong oxidant (Amilcar Machulek Jr., February 2012; Wang, 2008) shown in equation (2.5).

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + {^•OH} \qquad (2.5)$$

The Fenton kinetic (Fe^{2+}/H_2O_2) is to oxidize Fe^{2+} and generates Fe^{3+} as given in equation (2.6). Even though the reaction of equation (2.6) occurs slower than reaction of equation (2.5) so Fenton process slightly degrade contaminants slowly after the reaction of equation (2.6).

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + {^•O_2H} + H^+ \qquad (2.6)$$
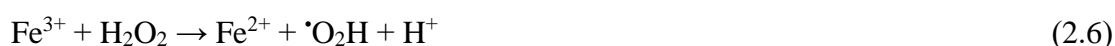
Electron transmission in the Fenton free radical reaction that occurs among the high concentration of Fe^{2+} or nonexistence of organic contaminants involves the sequence mechanisms of $^•OH$ with Fe^{2+} below.

$$Fe^{2+} + {}^{\bullet}OH \rightarrow Fe^{3+} + OH^{-} \tag{2.7}$$

$$Fe^{2+} + {}^{\bullet}O_2H \rightarrow Fe^{3+} + HO_2^{-} \tag{2.8}$$

$$Fe^{3+} + {}^{\bullet}O_2H \rightarrow Fe^{2+} + O_2 + H^{+} \tag{2.9}$$

The mechanisms of free radicals during Fenton process consists of the following equations (2.10) - (2.13)

$${}^{\bullet}OH + {}^{\bullet}OH \rightarrow H_2O_2 \tag{2.10}$$

$${}^{\bullet}OH + H_2O_2 \rightarrow {}^{\bullet}O_2H + H_2O \tag{2.11}$$

$${}^{\bullet}O_2H + {}^{\bullet}O_2H \rightarrow H_2O_2 + O_2 \tag{2.12}$$

$${}^{\bullet}OH + {}^{\bullet}O_2H \rightarrow H_2O + O_2 \tag{2.13}$$

Fenton process requires the existence of H^{+} to break the H_2O_2. In acidity, it can easily decompose and give the high ${}^{\bullet}OH$ concentration. The suitable pH for the process is around the pH 3-4. Owing to the fact that the ${}^{\bullet}OH$ attack all organic compounds depending on the species of organic substances, there have numerous applications of H_2O_2 for treatment. The pathways of ${}^{\bullet}OH$ to attack organic contaminants in wastewater are classified into three different reactions as the addition, the hydrogen abstraction and the electron transfer that were mentioned in equation (2.1)-(2.3) (Al-Asadi, July-September 2018; PABLO SALGADO, 2013; S.H. Bossmann, February 2004). Besides, the organic pollutants can be completely converted to CO_2 and H_2O (E. Neyens∗, 17 March 2003; Sina Matavos-Aramyan*, June 2017; a. S. G. Vrushali Pawar, 2015). Furthermore, a lot of related studies for color removal of wastewater by Fenton process are summarized in Table 2.3 (A. Pala ∗, 2005; M. Nurbas*, August 2014 ; Marco S. Lucas, 2006; Nese Ertugay *, February 2017; Pegah Bahmani, 2013; Semanur Giray Cetinkaya, July 2018; Sheng-Peng Sun, 30 January 2009; Suttipada Amat, 2014; T.R. Sundararaman, August 2009; Xuanmo Liu, 2011) to indicate that this method is highly effective for color removal (almost 90%). Fenton process has some disadvantages. For instance, it generates high anions concentration in treated wastewater, leaves large ferrous iron sludge (Henrik Hansson, 2012; S Krishnan, June 2017a), require low pH and consume reagent chemicals. However, the main advantages are effective to remove

recalcitrant color involving melanoidins and do not produce undesirable by-products (Jason Dwyer, April 2008). Therefore, this research aims to use Fenton process for color removal of biogas wastewater.

Table 2.3 Comparison of related studies for color removal by Fenton process

Topics of related studies	Initial color and COD	pH	Fe (mM)	H_2O_2 (M)	Reaction time	% Color removal	% COD removal
1. Comparison of classic Fenton with ultrasound Fenton processes on industrial textile wastewater	N/A	3.0	0.36	7.18×10^{-2}	90 min.	95 (for Pt-Co)	> 70% (60 min.)
2. Removal of COD and color from Direct Blue 71azo dye wastewater by Fenton's oxidation: Kinetic study	[DB71 dye] = 100 mg/L (λ max 587 nm) COD = 139.9 mg/L	3.0	1.08×10^{-2}	4.08×10^{-3}	20 min.	94	50.7
3. Decolorization of an azo dye Orange G in aqueous solution by Fenton oxidation process	[Azo dye OG] = 1.11×10^{-4} M (λ max 478 nm)	4.0	3.50×10^{-2}	1.0×10^{-2}	60 min.	94.6	-

Topics of related studies	Initial color and COD	pH	Fe (mM)	H_2O_2 (M)	Reaction time	% Color removal	% COD removal
4. Investigation of water decolorization by Fenton oxidation process in batch and continuous systems	[Azo dyes acid Red 88] = 1.2×10^{-4} M	2	0.1	1.0×10^{-3}	60 min	99.4	-
5. Decolorization and COD Removal of Reactive Yellow 16 by Fenton Oxidation and Comparison of Dye Removal with Photo Fenton and Sono Fenton Process	[Reactive yellow 16 dye] = 50 mg/L (Maximum absorbance)	3	3.6	2.94×10^{-2}	-	90	80
6. Evaluation of Fenton oxidation process coupled with biological treatment for the removal of reactive black 5 from aqueous solution	[RB5] = 250 mg/L (λ max 600 nm)	3	0.5	2.90×10^{-3}	15 min	91.5	-
7. Degradation of the Reactive Black 5 by Fenton and Fenton-like system	[Reactive Black 5] = 40 mg/L (λ max 553nm	3.5	0.05	2×10^{-3}	45 min.	97	-

Topics of related studies	Initial color and COD	pH	Fe (mM)	H_2O_2 (M)	Reaction time	% Color removal	% COD removal
8. Decolorization of the azo dye Reactive Black 5 by Fenton and photo-Fenton oxidation	[RB5] $=1.0\times10^{-4}$ M (λ max 595 nm)	3.0	0.15	7.3×10^{-4}	30 min.	97.5	-
9. Decolorization of a baker's yeast industry effluent by Fenton oxidation	Color = 1,790 Pt-Co COD = 640 mg/L	4.0	4.32	2.82×10^{-2}	20 min	99 (for Pt-Co)	88
10. Decolorization and COD reduction of wastewater from ethanol production by Fenton oxidation	Color = 77,500 ADMI COD = 56,000 mg/L	3.5	10	0.1 (H_2O_2 50%)	30 min.	93.5	59.28

2.4 Color removal of wastewater methods

Even though Fenton process is able to effectively remove color wastewater, there have been studied various methods for color removal of wastewater as well. In this research will review other physical and chemical wastewater treatment methods without biological wastewater treatment methods due to the fact that the properties of color pigments of commercial biogas wastewater have antioxidant and antimicrobial resulting in toxic to biological process. The compilation of physical and chemical methods has summarized that the studies investigate color removal efficiency of distillery and molasses wastewater because there is no research about color removal of biogas wastewater and the characteristics of these two wastewater is quite similar to biogas wastewater. Some studies measure both color and COD removal efficiency but some not as present in Table 2.4 below (Ajay Mandal*, October 2003; "Flocculation of

melanoidins induced by inorganic ions ", 1997; Hemangi Kolte, December 2014; Jamaluddin, 2018; Jemal F Nure*, July 2017; M. Pena~ *, July 2003; Mr. Manoj. P. Wagh, May 2015; P. Asaithambi, 3 July 2012; P.D.Nemade, July 2015; Sanna Kotrappanavar Nataraj, August 2006; Siwareeprongtong, 2000).

Table 2.4 Comparison for different color removal methods of distillery and molasses wastewater

Color removal of wastewater methods	% Color removal	% COD removal
1. Coagulation-flocculation by different chemicals for distillery wastewater		
1.1 Polyferric hydroxysulphate (PFS)	95	-
1.2 Ferric chloride ($FeCl_3$)	96	-
1.3 Ferric sulphate ($Fe_2(SO_4)_3$)	95	-
1.4 Aluminium sulphate ($Al_2(SO_4)_3$)	83	-
1.5 Calcium oxide (CaO)	77	-
1.6 Calcium chloride ($CaCl_2$)	46	-
2. Coagulation by lime and alum for distillery wastewater	98	80-82
3. Aeration with sludge-added and coagulation for stillage and molasses wastewater		
3.1 Coagulant of CaO for stillage	95.25	-
3.2 Coagulant of $FeCl_3$ for molasse wastewater	99.65	-
4. Electro coagulation with aeration using 2 types electrodes for distillery wastewater		
4.1 Using Iron electrodes (Fe-Fe)	99.78	85.71
4.2 Using aluminum electrodes (Al-Al)	98.81	85.71
5. Activated carbon produced from bagasse fly ash (BFA) for molasses wastewater	64	61.6
6. Ozonation for molasses wastewater	80	15-25
7. Comparison of ozonation, ozonation-UV and H_2O_2-UV for distillery wastewater		
7.1 Ozonation	62	47

Color removal of wastewater methods	% Color removal	% COD removal
7.2 Ozone with H_2O_2	85	61
7.2 Ozonation with H_2O_2 and UV	88	68
8. Ozonation and electrocoagulation for distillery wastewater	100	83
9. Hybrid nanofiltration for distillery wastewater	100	97.1

From the comparison table shows the color removal efficiency of wastewater treatment techniques but each method also has some drawbacks. The coagulation produces large amount of sludge resulting in handling and disposal problems which increases management cost and consumes chemicals (Grégorio Crini, July 2018). The aeration process requires high initial investment about equipment, consume high energy, need skilled person to operate and maintain (Xin Sun *, December 2014). Electro coagulation has a lot of disadvantages. First, sacrificial anode is needed to routinely replace and maintenance. This method requires high conductivity of sample. Short distance between electrodes can reduce voltages. And anode may produce unwanted leakage of current (Chaturvedi, Jan-Feb. 2013 ; Mickova, 2015). Activated carbon and ozonation have low efficiency. Activated carbon is selective to material types and requires expensive for regeneration and loss of materials. Ozonation has short half-life, high energy consumption, investment and maintenance cost and form unknown intermediates. Nanofiltration requires high energy, maintenance and operation cost. It is rapidly clogging resulting in low throughput and limited flow rates (Grégorio Crini, July 2018).

CHAPTER 3

METHODOLOGY

3.1 Fenton process

3.1.1 Chemicals and materials

Commercial biogas wastewater was received from the ARW Co., Ltd. (Suphan Buri, Thailand) and was kept in dark gallons at temperature of 4°C, without adding any chemical. Hydrogen peroxide 30% w/w, iron (II) sulfate heptahydrate ($FeSO_4.7H_2O$) and sulfuric acid were received in analytical grade from Chemsupply, Dajung Co., Ltd. and Merck respectively. Resin anion AMBERLITE IRA-402 (OH-) was obtained from Dow Chemical Company (Dow) or an affiliated company of Dow. Distilled water was used in experiments.

3.1.2 Method

Response surface methodology (RSM) is a statistical technique. It was fundamentally used to design experiments, build models, analyze effects, optimize conditions, predict target values (Korbahti, 25 June 2007) and identify relationship between the variables and responses (Bong-yul Tak, 25 August 2015). It is an important approach to develop new processes and improve new products in general research, especially useful in the case of high number of variables (Korbahti, 25 June 2007). It reduces research time to obtain a more proper model than conventional one (Yiran Sun, 15 June 2019). Box-Behnken Design (BBD) under the RSM is a type of rotatable or nearly rotatable second-order design based on three levels (-1, 0, +1), incomplete factorial designs (S.L.C. Ferreira, 10 August 2007). The experimental data were analyzed by the response surface method with Minitab 18 software. In this research, BBD is firstly used for experimental design and optimization of color removal efficiency yield of commercial biogas wastewater using Fenton process. BBD was employed to optimize three variables (X_1: pH, X_2: $FeSO_4$ concentration (mM), X_3: H_2O_2 concentration (M)) to achieve yield of the three variables (Dalel Daâssi, 15 October 2012). The number of experiments (N) of BBD required are 2k (k - 1) + C_0

(where k is number of factors and C_0 is the number of central points) (S.L.C. Ferreira, 10 August 2007). In the optimization, the yield was fitted with a quadratic model including the linear term as in the equation (2.14) (Dalel Daâssi, 15 October 2012; Korbahti, 25 June 2007; X. Vecino, May 2012).

$$Y = \beta_0 + \Sigma\beta_i X_i + \Sigma\beta_{ii}X^2_i + \Sigma\beta_{ii}X_iX_j + \varepsilon_i \qquad (2.14)$$

(Where Y is the predicted response, X_i and X_j are variables, β_0 is the constant coefficient, β_i is the linear coefficient, β_{ii} is the quadratic coefficient, β_{ij} is the interaction coefficient and ε_i is the error).

The simplest quadratic equation for three variables is described in equation (2.15) (X. Vecino, May 2012).

$$Y=\beta_0+\beta_1X_1+\beta_2X_2+\beta_3X_3+\beta_{12}X_1X_2+\beta_{13}X_1X_3+\beta_{23}X_2X_3+B_{11}X^2_1+B_{22}X^2_2+B_{33}X^2_3 \quad (2.15)$$

The BBD with three variables for color removal of commercial biogas wastewater were coded as illustrated in Table 3.1.

Table 3.1 Coded and value of variables

Coded	Variables	Unit	Level of BBD		
			-1	0	+1
X_1	pH	-	3	4	6
X_2	$FeSO_4$	mM	0.89	17.98	35.07
X_3	H_2O_2	M	3.30	6.55	9.80

3.1.3 Experimental procedure

The experiment takes place at ambient temperature and pressure. Fenton process was conducted in a 250 mL glass bottle containing 20 mL sample. The pH of the sample is adjusted in the range of pH3 to pH6 using sulfuric acid. $FeSO_4$ concentrations are in the range of 0.89-35.07 mM and H_2O_2 concentrations in the range of 3.30-9.80 M. The calculated amount of $FeSO_4$ is added into the sample and stirred

for 15 minutes. Next, slowly add H_2O_2 and after finish adding the Fenton's reagent, stir sample for 24 hours at room temperature.

3.1.4 Analytical methods

3.1.4.1 Color measurement

Ministry of industry Thailand has prescribed in 2017 the new limit on effluent's color is not to exceed 300 ADMI and to use the ADMI method for measurement (Industry, 2017). Color in water is classified to two types; true color is the color after separating chemical substances which cause turbidity so to remain the true color in water and another one is the apparent color that is the color without isolation of suspended and colloid matters. The color measured by ADMI (American Dye Manufacturers Institute) method is a later standard developed after the platinum cobalt standard of the American Public Health Association (APHA). The Pt-Co has the main disadvantage in that it can be used to indicate only samples with yellow color. The ADMI color index is applicable to measure colored waters and wastewater that the characteristics of color are significantly different from the platinum-cobalt standard. The method investigates contaminants of dye, pigments in water and detect in three color dimensions are hue, chroma and value of color while the platinum-cobalt method measure only yellow color that appropriate for color in nature. The ADMI use spectrophotometer wavelength 400-700 nm for color measurement so that it can detect visible light spectrum from violet to red color. In standard method for examination of water and wastewater for color measurement is divided to two methods: the APHA 2120E ADMI TristimulusFilter method and the APHA 2120F ADMI Weighted-Ordinate Spectrophotometer (used in this experiments)

First, sample is prepared with 0.45 μm cellulose acetate syringe filters. Then the sample is filled into the rectangular cell and inserted into the compartment of Spectroquant Pharo 300 which has the standard method preloaded. The measurement results will be shown on display. The color removal efficiency (%) is calculated using the following equation (2.16).

$$(1 - ADMI/ADMI_0) \times 100 \qquad (2.16)$$

(where $ADMI_0$ and $ADMI$ represent are the initial and final values of color respectively.)

3.1.4.2 COD measurement

One of important parameters for industrial wastewater is the chemical oxygen demand (COD). COD is the amount of oxygen required to oxidize organic matters (biodegradable and non-biodegradable both dissolved and particulate). The COD measurement is conducted by refluxing a sample for 2 hours at 150°C in strong sulfuric acid and known excess potassium dichromate (D.B. Walker, 2019; L. Nazari*, 2018; Shmeis, 2018). A silver sulphate is used to catalyze the reaction, mercury nitrate is added to reduce the interference of chloride ions in the sample by forming complexes with them. After heating, the remaining unreduced potassium dichromate is titrated with ferrous ammonium sulphate (Bernhard Drosg, 2013). The more convenient COD measurement as COD cell utilizing a photometric method (Merck) was also used for convenience in usage, reducing chemicals preparation, increasing chemicals preservation time and enhancement of accuracy determination. Although the point of this study focuses on color wastewater, COD measurement is an important parameter and can indicate the total chemically oxidizable pollutants in wastewater hence COD and color are analyzed simultaneously. COD was analyzed as a total COD including both soluble COD and particulate COD (A. Tawfik, 2010; E. La Motta, January 2003; Mogens Henze, 2008; Sperling, 2006). The sample is mixed to be homogeneous before analyzing COD. In this research, COD analysis was carried out by standard method APHA 5220 D. closed reflux, colorimetric method. The sample was added to vials and digested for 2 hours at 150 °C in a Spectroquant TR 420 and cooled down to room temperature for 30 min. The COD concentration was then measured photometrically using the Spectroquant model Pharo 300. The COD removal efficiency (%) is calculated using formula equation (2.17).

$$(1 - C/C_0) \times 100 \tag{2.17}$$

(where C_0 and C represent are the initial and final COD concentration respectively.)

3.1.4.3 pH measurement

pH was measured with a EUTECH pH Tester 10.

3.2 Further color treatment by anion exchangers

The Fenton treated wastewater was further treated with anion exchangers to increase color removal. 20 mL of Fenton treated water with sediment separated by centrifuge at 4,000 rpm for 5-10 minutes. Prepare anion exchangers of 1, 2, 4, 8, 10 and 12% by weight corresponding to the anion exchangers of 0.2, 0.4, 0.8, 1.6, 2and 2.4 g for the sample volume of 20 mL. The anion exchangers are then immersed in the sample water and continuously stirred for 24 h at room temperature.

3.3 MFC for testing of COD removal from diluted biogas wastewater

3.3.1 Chemicals and materials

Commercial biogas wastewater is diluted to be an influent for MFC (Microbial fuel cell) system. The anaerobic microorganisms in the MFC are from a rice vermicelli factory presenting mixed culture anaerobic bacteria communities. MFC reactor components are two UFAF chambers, two cylindrical UBFC chambers, SS304 stainless mesh, stainless rods, coil, wires, copper, P120 sandpaper, plastic balls, silicone tube, fine bubble air diffuser, granular activated carbon (GAC), air filter, air pump, peristaltic pump and a data logger for measuring current and voltage connected with a computer.

3.3.2 Preparation

MFC component are divided two parts; the first section is pretreatment consisting of two UFAF columns (UFAF 1, UFAF 2). The second section consists of the vertically stacked UBFC chambers packed bed consisting of the cathode chamber placed on top of the anode chamber without any membrane between cathode and anode. The set-up is shown in the figure below. The cathode chamber is permanently attached with a glass tube-funnel which is placed between anaerobic and aerobic part for inhibit oxygen diffusion into the anode chamber besides on the bottom of the cathode chamber consists of the fine bubble air diffuser that connects with the air filter and air pump. The total capacity of the UBFC, UFAF 1 and UFAF 2 is 1 liter and made from glass. The

stainless rods connect with wire of the data logger to collect data. Eight plastic balls are soaked in ethanol 1 hour followed by distilled water. After that they are dried at room temperature. GAC is cleaned by tap water in order to eliminate dirty and purge air in pores then dried at 80 °C in a hot oven. SS304 stainless mesh is cut in length 16 cm×width 9 cm for anode part and length 12 cm×width 4 cm for cathode part. That meshes are polished by P120 sandpaper, cleaned with ultrasonic cleaner in acetone and ethanol each 2 hours, distilled water, respectively and dry at room temperature. Finally, the meshes are assembled into the anode and cathode chamber.
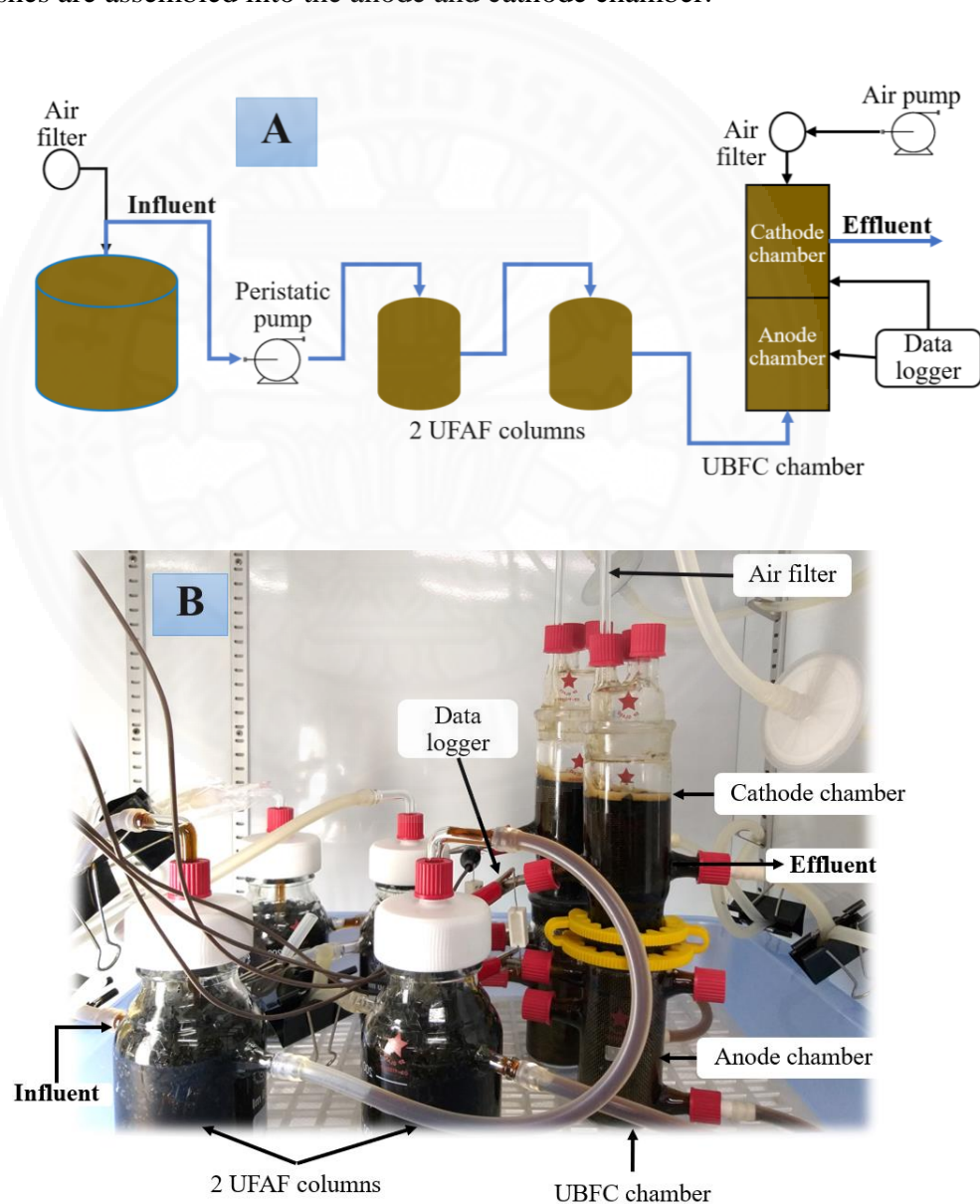
Figure 3.1 Schematic diagram (A) and experimental picture of MFC system (B)

3.3.3 Experimental procedure for MFC

First, anaerobic bacteria are cleaned by 10 mM phosphate buffer saline (PBS) 3 times then homogenized to reduce cell size by homogenizer after that homogeneity bacteria and GAC are mixed in ratio 30% w/w. The homogeneity bacteria and GAC are mixed in two UFAF columns, anode chamber and cathode chamber of 72: 240 grams, 18: 60 grams and 12: 40 grams, respectively. They are directly inserted into the anode and cathode chamber whereas they and the eight plastic balls are inserted in the two UFAF columns. A high vacuum grease is used to join the anode and cathode chamber in vertical to become a UBFC. The two UFAF columns and UBFC are combined by silicone tube. Diluted biogas wastewater of average COD concentration 5,640 mg/L is fed in batch mode into the anode chamber for inoculation stage 27 days at air flow 4.5 L/min, temperature 30 °C and an external resistance 100 Ω. After 27 days, the diluted biogas wastewater of COD 5,640 mg/L is fed at flow rate 2.7 rpm, air flow 4.5 L/min, temperature 30 °C into the anode chamber.

3.3.4 Electrochemical measurement of MFC

First parameter of MFC is cell voltage measured by data logger in every 5 minutes. Besides, the resistance will connect to the anode and cathode chamber of MFC from 100 M Ohm to 1000 Ohm to determine current density (mA/m^3) and power density (mW/m^3) of anode chamber 250 cm^3 by using equation (2.18)-(2.19).

$$I = V/R \tag{2.18}$$

$$P = I \times V \tag{2.19}$$

(where V is a cell voltage (V) and R is resistance (Ohm))

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Characteristic of commercial biogas wastewater

The quality parameters of commercial biogas wastewater from the ARW Co., Ltd. (Suphan Buri, Thailand) is analyzed as shown in Table 4.1. It appears that wastewater has extremely high concentration and seem to be a difficult task. The micro-EDXRF (micro-energy dispersive X-ray Fluorescence) results present major elemental composition of wastewater which are potassium (K) = 68.1%, sulfur (S) = 23.1, iron (Fe) = 5.1%and phosphorus (P) = 3.7% as illustrated in Figure 4.1. The appearance of the actual biogas wastewater is shown in Figure 4.2.

Table 4.1 Commercial biogas wastewater physical characteristics

Parameter	Concentration
COD	68,000±148 mg/L
Total solids	32,168 mg/L
Turbidity	6,430 NTU
Conductivity	56,000 μS
Color	203,600±3,920 ADMI
pH	8.0
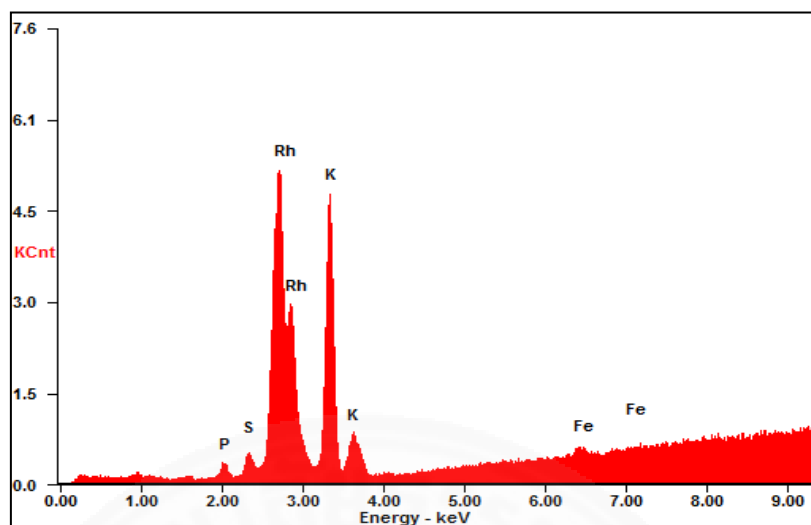
Figure 4.1 The result micro-EDXRF of commercial original wastewater

Figure 4.2 The picture of the actual commercial biogas wastewater

4.2 Feasibility study for color and COD removal of the diluted biogas wastewater using MFC

4.2.1 MFC performance

Both voltage and current across the 2 MFC units (UBFC 1 and UBFC 2, which are identical for duplicate measurements) were measured for 270 days by a data logger under the conditions of flow rate 2.7 rpm, influent average COD concentration 5,640 mg/L, color 21,200 ADMI, air flow 4.5 L/min and ambient temperature of 30 °C as shown in Figure 4.3. Their voltages slightly increase over time. Since electrochemically active microorganisms (EAMs) in anode chamber contribute to the discharge electrons from their cells to the electron acceptors (oxygen) in the cathode chamber. It illustrates that microorganisms can adjust to MFC system. The maximum voltage of UBFC 1 is 0.63V on date 145 while the maximum voltage of UBFC 2 is 0.66V on date 234. The

standard electrochemical methods of testing MFC performance are the polarization and power density curves obtained from connecting the variable load or resistors across the MFC terminals. Polarization curve shows the voltage output against the operating current density and the power density curve is a product between the voltage output and the current density. Polarization curve of UBFC 1 and 2 will fall according to increasing current densities; on the contrary, power density curve of UBFC 1 and 2 increase with increasing current densities until the maximum power density reached (at point where internal resistance matches with the external load resistance) and will slightly drop at higher current densities as shown in Figure 4.4-4.5. From observation of the final color of the diluted wastewater after MFC treatment, it was found that the color after the MFC was not much different from that of the initial color. So, it indicates that MFC is not appropriate to treat color nor COD of the diluted biogas wastewater. These reasons bring about using Fenton process to remove color and COD.
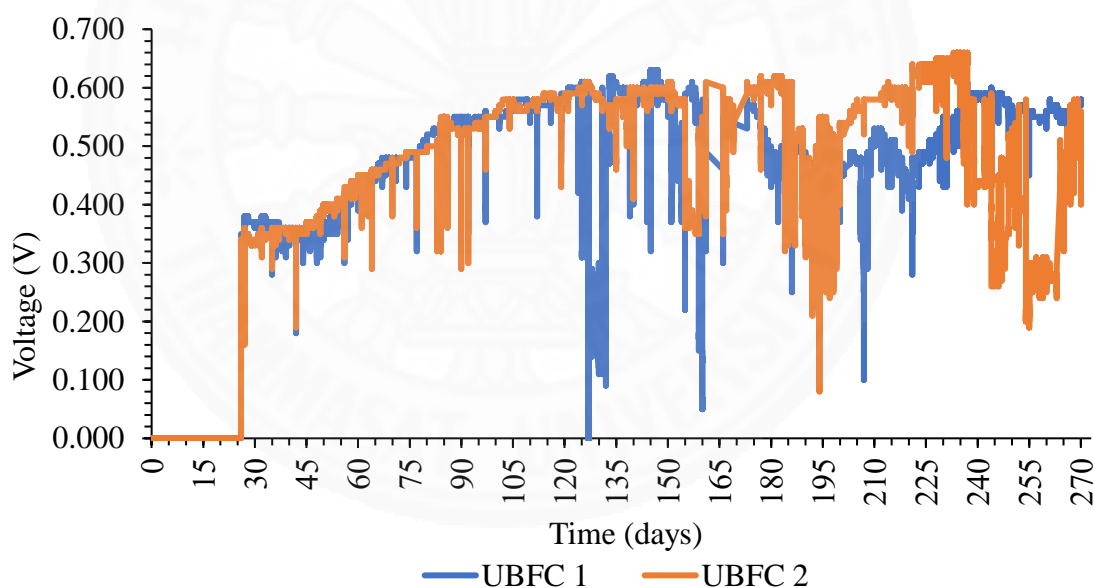
Figure 4.3 Open circuit voltage of UBFC 1 and 2 under flow rate 2.7 rpm of COD concentration 5,640 mg/L, air flow 4.5 L/min and temperature 30 °C
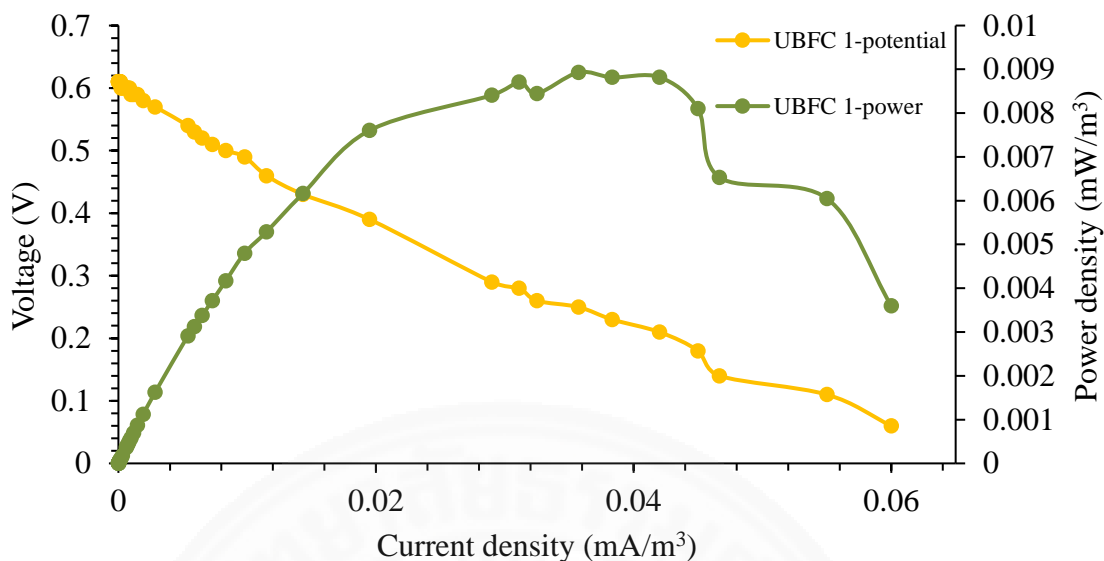
Figure 4.4 Polarization and power density curve of UBFC 1 under flow rate 2.7 rpm

of COD concentration 5,640 mg/L, air flow 4.5 L/min and temperature 30 °C
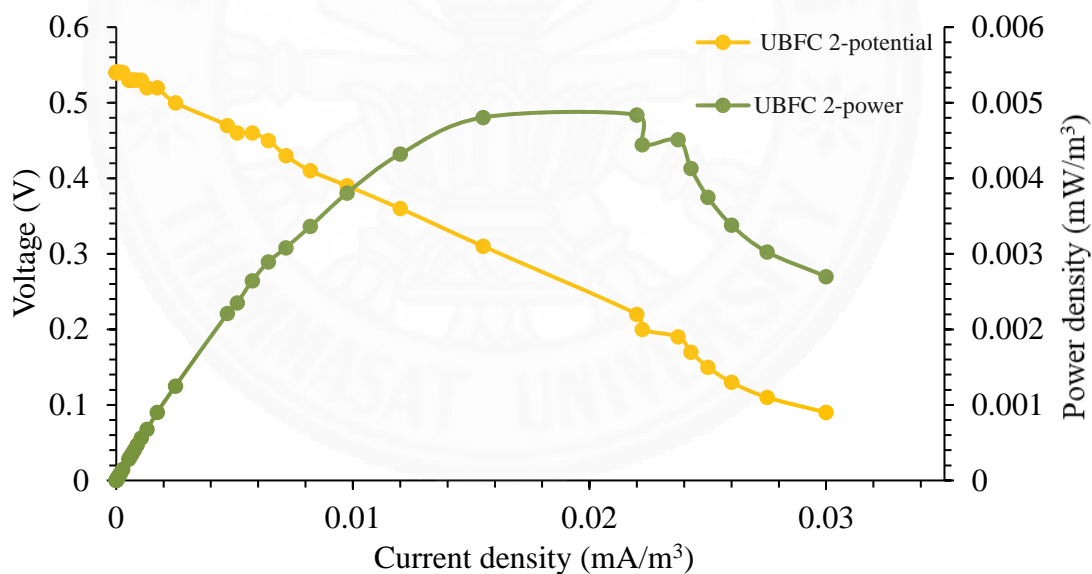
Figure 4.5 Polarization and power density curve of UBFC 2 under flow rate 2.7 rpm

of COD concentration 5,640 mg/L, air flow 4.5 L/min and temperature 30 °C

4.2.2 COD removal efficiency of diluted biogas wastewater by MFC

The objective of the preliminary MFC experiment is to study its performance in COD removal efficiency of the biogas wastewater that has been diluted to the level that the microorganisms may still be able to tolerate (5,000-6,000 mg/L). The effluent is periodically collected, and measured COD removal efficiency for 270 days as presented in Figure 4.6. From COD calculation, both UBFC 1 and 2 has low COD removal efficiency of 15.8%, 14.9% with the average COD removal of 15.4±2.2%. In the first period of operation has got higher COD removal efficiency resulting from feeding low COD concentration influent approximately 5,070 mg/L. But after that influent has higher COD concentration as 5,350 -5,870 mg/L. It contributes to the fluctuation in the COD removal efficiency of the system. The average COD concentration feeding is 5,640±308 mg/L under flow rate 2.7 rpm of, air flow 4.5 L/min and temperature 30 °C. The UBFC 1 and 2 have low COD removal efficiency whereas have high polarization and power density curve performance. Moreover, from observation found that the color effluent of MFC is not different and still dark brown color. The possible reasons causing low COD and color removal efficiency are antimicrobial and antioxidant properties of the biogas wastewater. These toxicity of wastewater affect to low cell activity of microorganisms. The key cell activity of microorganisms for COD and color removal is organic compounds degradation. If degradation is low, it will lead to low COD and color removal efficiency as well.
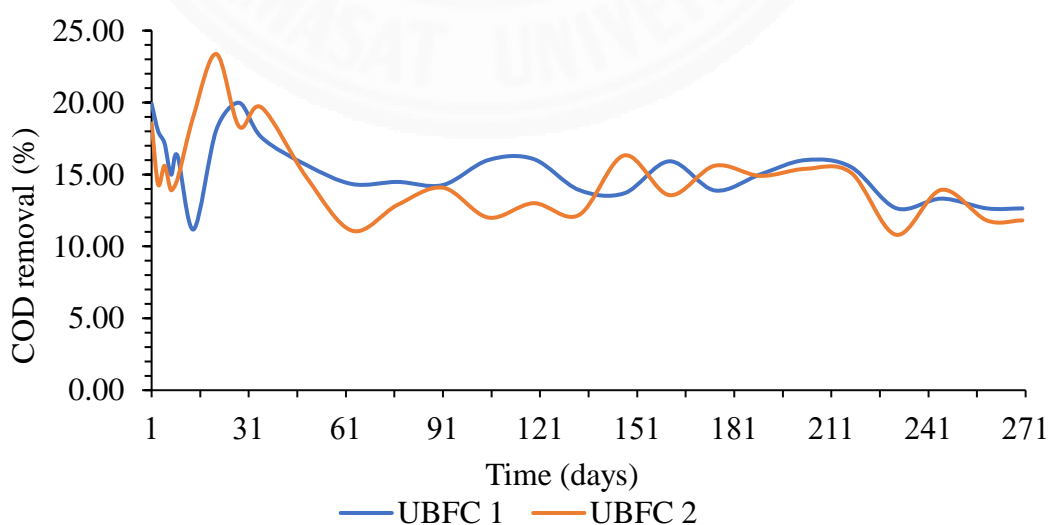
Figure 4.6 COD removal efficiency of UBFC 1 and 2 under flow rate 2.7 rpm of COD concentration 5,640 mg/L, air flow 4.5 L/min and temperature 30 °C

4.2.3 Scanning electron microscope (SEM) of MFC

After operation UBFC 1 and 2 for 270 days, GAC of anode and cathode from UBFC 1 and 2 were scanned by SEM in order to investigate the bacteria growing and colonization on the GAC support (Liang Zhang, 2011). SEM images illustrate the biofilm in both anode and cathode GAC surface at high magnification of 1,000X. Figure 4.7 shows coccus-shaped bacteria on the biofilm but bacterial genus could not be identified.

(a)

(b)

(c)

(d)
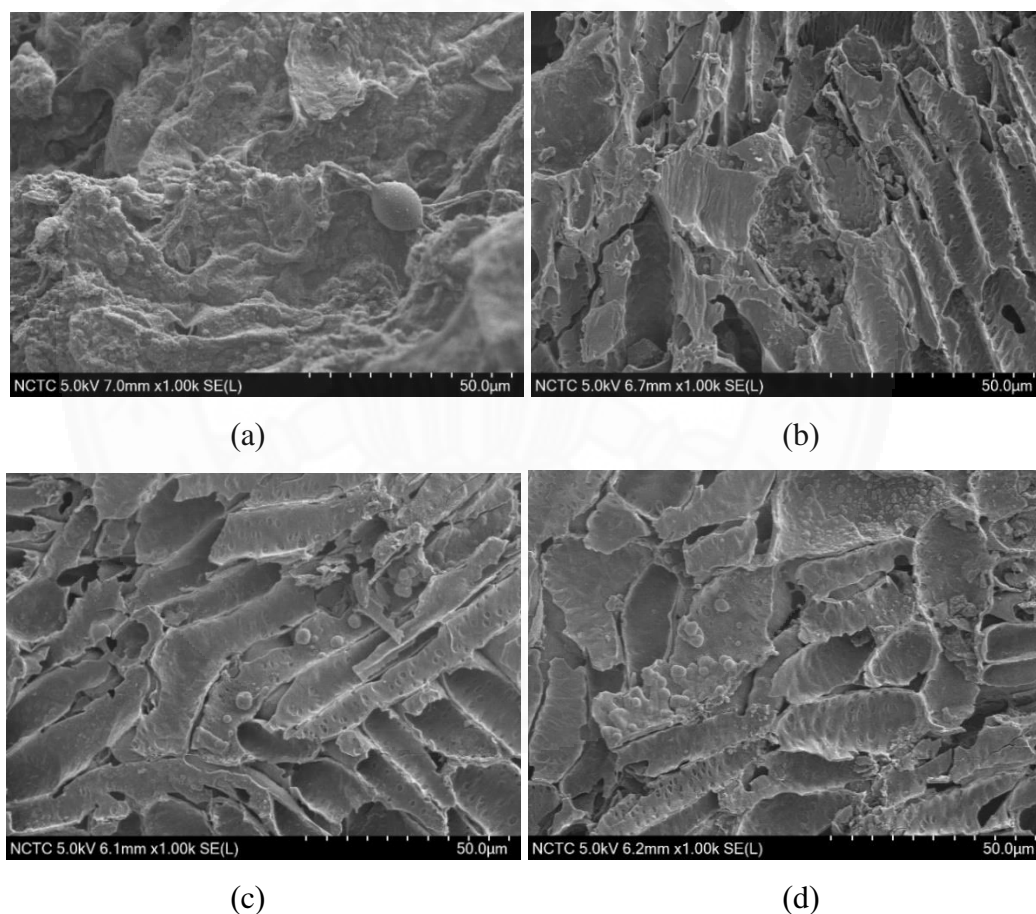
Figure 4.7 SEM image of biofilm formation from (a) anode of UBFC 1, (b) cathode of UBFC 1, (c) anode of UBFC 2, (d) cathode of UBFC 2 at higher magnification of 1000X

4.2.4 Energy dispersive X-ray spectroscopy (EDS) of MFC

Element compositions on GAC surface is observed by EDS spectrum. The EDS images in Figure 4.8 present that UBFC 1 and 2 mostly have elements of C and O respectively besides others are Na, Mg, Si, P, S, Cl, K and Ca.
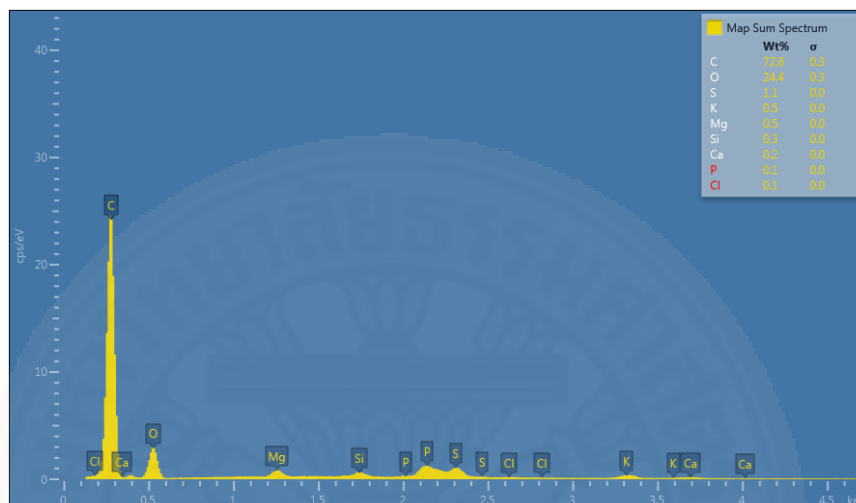
Figure 4.8 The representative EDS spectrum of anode and cathode from UBFC 1 and 2

4.3 Fenton process

From the previous experiment show that the MFC method is not effective to treat COD and color. So, it contributes to study Fenton process.

4.3.1 Preliminary experiment of vary amount of FeSO₄

In the preliminary experiments, potential of color removal by Fenton process was investigated to find the range of factors for further optimization. There have several factors. The first experiment aims to vary amount of catalyst as $FeSO_4$ with reaction pH 3.6, sample 10 mL and reactant H_2O_2 3 mL for 24 hours. Table 4.2 illustrates color removal efficiencies of $FeSO_4$ at 1, 5, 10, 20 and 30 mg which are 66.3±1.2%, 78.6±3.5%, 88.4±4.7%, 96.7±2.1% and 97.6±3.2% respectively. The condition of $FeSO_4$ concentration 1, 5 and 10 mg has low color removal efficiency. While $FeSO_4$ concentration of 20 and 30 mg have high efficiency. But higher $FeSO_4$ concentration

as 30 mg has slightly higher efficiency, so this condition is chosen. The optimum condition of this experiment will be $FeSO_4$ 30 mg and H_2O_2 3 mL in sample 10 mL at reaction time 24 hours. The pH after for $FeSO_4$ of 1, 5, 20 mg conditions are 2.6 whereas $FeSO_4$ 10 mg is 2.9 and $FeSO_4$ 30 mg is 2.2.

Table 4.2 The preliminary experiment of varying amount of $FeSO_4$ at H_2O_2 3 mL, sample 10 mL, reaction pH 3.6 and reaction time 24 hours

Vary $FeSO_4$ (mg)	Color removal efficiency (%)	pH after
1	66.3±1.2%	2.6
5	78.6±3.5%	2.6
10	88.4±4.7%	2.9
20	96.7±2.1%	2.6
30	97.6±3.2%	2.2
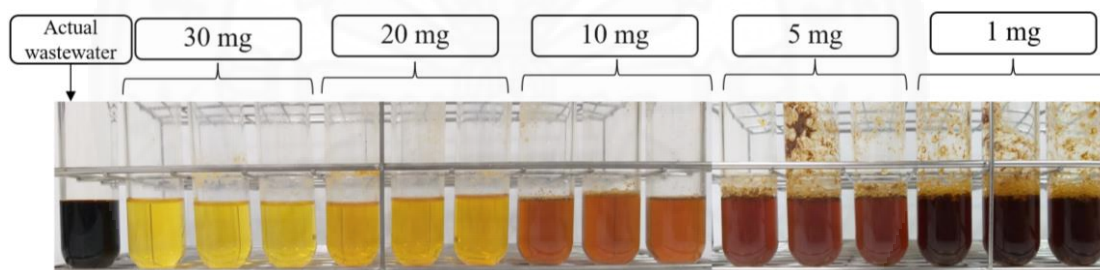
Figure 4.9 The preliminary experiment of vary amount $FeSO_4$ 1, 5, 10, 20 and 30 mg at H_2O_2 3 mL, sample 10 mL, reaction pH 3.6and reaction time 24 hours

4.3.2 Preliminary experiment of vary reaction pH

According to condition of Fenton process, it must be conducted in acidity. Therefore, this experiment aims to vary reaction pH until 1 to 6 by using $FeSO_4$ and H_2O_2 concentration from the optimal condition of previous experiment ($FeSO_4$ 30 mg and H_2O_2 3 mL in sample 10 mL at reaction time 24 hours, room temperature). The color removal efficiencies of reaction pH 1, 2, 3, 4, 5, 6 are 97.5±1.9%, 97.8±2.0%, 98±1.9%, 98±2.1%, 97.9±2.9% and 97.8±3.2% respectively in Table 4.3. It indicates that pH 4 is obtain the highest efficiency. If the reaction pH 3 and 4 are quite not different efficiency, so it should choose pH 4 due to it easily adjust from initial

wastewater pH of 8 and use less H_2SO_4. Therefore, the summary for optimum condition of this experiment is $FeSO_4$ 30 mg, H_2O_2 3 mL, sample 10 mL and reaction pH 4 at reaction time 24 hours. And pH after for pH reaction of 1, 2, 3, 4, 5, 6 are 1.5, 2.0, 2.2, 2,5, 3.0, 3.2 respectively. So, from pH after result indicate that when finish the Fenton reaction, pH will drop that is the reason to find out the method to increase pH before discharge.

Table 4.3 The preliminary experiment of vary reaction pH at $FeSO_4$ 20 mg, H_2O_2 3 mL, sample 10 mL and reaction time 24 hours

Vary pH reaction	Color removal efficiency (%)	pH after
1	97.5±1.9%	1.5
2	97.8±2.0%	2.0
3	98±1.9%	2.2
4	98±2.1%	2.5
5	97.9±2.9%	3.0
6	97.8±3.2%	3.2
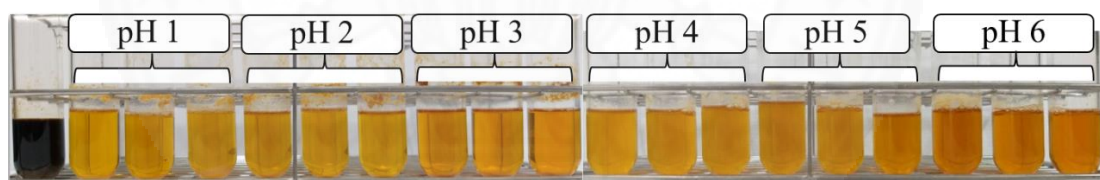
Figure 4.10 The preliminary experiment of vary reaction pH 1-6 at $FeSO_4$ 30 mg, H_2O_2 3 mL in sample 10 mL and reaction time 24 hours

4.3.3 Preliminary experiment of vary concentration of sample

The aim of this experiment is to increase volume of sample by using optimal condition of preliminary experiment ($FeSO_4$ 30 mg, H_2O_2 3 mL and reaction pH 4 at reaction time 24 hours). The efficiencies of the blank, the ratio 1 and 2 are 91.4±3.1%, 83.3±2.2% and 59.6±2.9% respectively at reaction time 24 hours. It illustrates that ratio 1 and 2 has low efficiency than blank hence sample 10 mL is optimum condition for $FeSO_4$ 30 mg, H_2O_2 3 mL and reaction pH 4 at reaction time 24 hours. The pH after of blank, ratio1 and 2 are 2.4, 2.2 and 2.3 respectively as shown in Table 4.4.

Table 4.4 The preliminary experiment of different concentration of sample at $FeSO_4$ 20 mg, H_2O_2 3 mL and reaction pH 4 at reaction time 24 hours

Ratio	Concentration of wastewater (mL)	Color removal efficiency (%)	pH after
Blank (initial water)	10	91.4±3.1%	1.9
Ratio 1:1	20	83.3±2.2%	2.1
Ratio 2:1	30	59.6±2.9%	2.5

Figure 4.11 The preliminary experiment of vary sample concentration of 10, 20, 30 mL at $FeSO_4$ 30 mg, H_2O_2 3 mL, reaction pH 4 at reaction time 24 hours

4.3.4 Preliminary experiment of measurement of iron and H_2O_2 concentration

$FeSO_4$ is added in Fenton process in order to react with H_2O_2 to generate $^\bullet OH$. This experiment aims to measure residue iron concentration in sample by the inductively coupled plasma-optical emission spectrometry (ICP-OES) which is an analytical technique used for measurement of composition of elements in sample. The results of ICP show that actual wastewater has an iron concentration of 153 mg/L. After Fenton process, Fenton treated wastewater of condition sample 10 mL, $FeSO_4$ 30 mg, H_2O_2 3 mL and reaction pH 4 at 24 hours has the iron of 471 mg/L. It indicates that remain residual iron in water. In facts, there have some adverse effects of high iron concentrations in water. Iron in water cause rusty/reddish color, metallic taste, odor, stains on clothes, corrode water pipe system (Hooser, 2018; Shalini Chaturvedi, 1 October 2012; Vipin Kumar, April 2017)and enhance growth of iron bacteria resulting in dark color slime layers inside water pipe system as well. However, it is not considered to cause health problems in human (Ityel, January–February 2011)and does

not have iron standard for industrial effluent standards (Industry, 2017). In term of residue H_2O_2, most Fenton process still have H_2O_2 remained approximately 100-300 mg/L determined using Quantofix® peroxide test strips. The adverse effects of H_2O_2 is irritation or burn on eyes and skin in case of higher concentrations (Tredwin C.J., 2006).

4.3.5 Optimization of commercial biogas wastewater by Fenton process using BBD tool

4.3.5.1 Optimization and relationship of color removal efficiency (%)

From all useful preliminary experiments, it can conclude that Fenton process is investigated to treat color wastewater under different operating variables of pH 2-6, $FeSO_4$ concentration of 5-195 mg, or 0.9-35.1 mM and H_2O_2 concentration of 2-6 mL, or 3.3-9.8 M in sample 20 mL at reaction time 24 hours using response surface methodology according to BBD for 45 experimental runs which also include 3 replicates as shown in Table 4.5.

Table 4.5 Experimental BBD matrix

Std.Order	RunOrder	pH	Fe (mM)	H_2O_2 (M)	Color removal efficiency (%)
31	1	2	0.9	6.55	80.7
29	2	4	18	6.55	96.6
36	3	6	18	3.30	59.0
16	4	2	0.9	6.55	79.5
44	5	4	18	6.55	96.4
22	6	2	18	9.80	97.9
2	7	6	0.9	6.55	61.5
43	8	4	18	6.55	96.5
42	9	4	35.1	9.80	94.1
28	10	4	18	6.55	96.3

Std.Order	Run Order	pH	Fe (mM)	H_2O_2 (M)	Color removal efficiency (%)
5	11	2	18	3.3	85.3
41	12	4	0.9	9.8	86.2
9	13	4	0.9	3.3	76.9
8	14	6	18	9.8	98.1
15	15	4	18	6.6	95.8
1	16	2	0.9	6.6	80.3
32	17	6	0.9	6.6	62.4
39	18	4	0.9	3.3	75.5
38	19	6	18	9.8	98.2
24	20	4	0.9	3.3	76.4
35	21	2	18	3.3	85.5
30	22	4	18	6.6	96.0
17	23	6	0.9	6.6	60.7
37	24	2	18	9.8	97.9
20	25	2	18	3.3	85.4
10	26	4	35.1	3.3	76.9
34	27	6	35.1	6.6	82.7
18	28	2	35.1	6.6	90.0
26	29	4	0.9	9.8	85.8
6	30	6	18	3.3	57.5
7	31	2	18	9.8	97.8
19	32	6	35.1	6.6	82.2
3	33	2	35.1	6.6	88.7
13	34	4	18	6.6	96.3
21	35	6	18	3.3	59.3
27	36	4	35.1	9.8	93.5
40	37	4	35.1	3.3	76.4
4	38	6	35.1	6.6	82.0
33	39	2	35.1	6.6	88.7

Std.Order	RunOrder	pH	Fe (mM)	H_2O_2 (M)	Color removal efficiency (%)
14	40	4	18	6.6	96.4
11	41	4	0.9	9.8	85.8
45	42	4	18	6.6	96.4
23	43	6	18	9.8	98.1
25	44	4	35.1	3.3	76.8
12	45	4	35.1	9.8	93.6

$$Y = 65.59 + 4.53X_1 + 0.935X_2 + 2.24X_3 - 2.020X_1^2 - 0.03395X_2^2 - 0.3039X_3^2 + 0.0864X_1*X_2 + 1.042X_1*X_3 + 0.0333X_2*X_3$$

(2.20)

After optimization, a quadratic model of color removal efficiency is obtained as show in the equation (2.20). The quadratic model between the color removal efficiency as the Y and the three variables is fit in regression equation in uncoded units. In addition, the regression equation has high coefficient of determination; $R^2 = 93.7\%$, adjusted-$R^2 = 92.1\%$ and predicted-$R^2 = 88.8\%$. The total degrees of freedom (DF) are total amount of information in experiment. Adjusted sums of squares (Adj SS) measure variation for different components of the model. Adjusted mean squares (Adj MS) calculate how much variation of the model explains. F-value determine the term involving with the response. Typically, the Adj SS, Adj MS and F-value (the F-value of 58.01 is more than F-critical of 3.26742) are used to calculate p-value which determine about statistical significance of the model. The statistical significance of the model is analyzed by p-value which is a probability of the observed results deviating from the null hypothesis. This model is statistically significant since the p-value of 0.000 is less than significance level of 0.05 which corresponds to a 95% confidence level as presented in Table 4.6.

Table 4.6 Analysis of variance for color removal efficiency (%)

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Model	9	6299.77	699.97	58.01	0.000
Linear	3	3875.72	1291.91	107.07	0.000
pH	1	1014.52	1014.52	84.08	0.000
Fe (mM)	1	540.93	540.93	44.83	0.000
H_2O_2 (M)	1	2320.27	2320.27	192.29	0.000
Square	3	1727.50	575.83	47.72	0.000
pH*pH	1	723.22	723.22	59.94	0.000
Fe (mM)*Fe (mM)	1	1089.37	1089.37	90.28	0.000
H_2O_2 (M)*H_2O_2 (M)	1	114.16	114.16	9.46	0.004
2-Way Interaction	3	696.54	232.18	19.24	0.000
pH*Fe (mM)	1	104.67	104.67	8.67	0.006
pH*H_2O_2 (M)	1	550.81	550.81	45.65	0.000
Fe (mM)*H_2O_2 (M)	1	41.07	41.07	3.40	0.074
Error	35	422.32	12.07		
Lack-of-Fit	3	414.93	138.31	599.07	0.000
Pure Error	32	7.39	0.23		
Total	44	6722.09			

The relationships between the independent variables and response are illustrated in 2D contour and 3D surface plots of color removal efficiency by Fenton process as shown in Figure 4.12. The concentration of Fenton's reagent in Figure 4.12 (a) H_2O_2 (M) and $FeSO_4$ (mM) indicates H_2O_2 concentration of 6-9 M and $FeSO_4$ concentration between 10 mM to below 35 mM are the most appropriate range dosage that used in Fenton process to achieve the highest color removal efficiency. Generally, dosage of H_2O_2 and $FeSO_4$ is increasing according to degradation rate (K. M. Arjunan Babuponnusami, March 2014; Dheeaa al deen A Aljuboury*, September 2014). Since, the wastewater has high color and COD value thus the reagents dosage is used in high concentration as well. The result from Figure 4.12 (b) H_2O_2 (M) and pH and (c) $FeSO_4$ (mM) and pH show that pH of H_2O_2 and $FeSO_4$ approximately 3-6 is achieved the highest color removal efficiency. With reference to requirement of Fenton process, the variables such as temperature, pH, H_2O_2 and $FeSO_4$ concentration need specific condition. For temperature, room temperature is used because higher temperature will increase rate of H_2O_2 decomposition into O_2 and H_2O and resulting in loss of forming •OH (Ruben Vasquez-Medrano, 2018).

In case of pH, high pH or alkaline solution will cause a ferrous ion to transform to be a floc of ferric oxyhydroxide ($FeHO_2$) and ferric hydroxide (Fe $(OH)_3$) which will then precipitate. Thereby, there contributes less free iron ions and will be lost as a consequence of •OH and its oxidation potential drop according to increasing pH (K. M. Arjunan Babuponnusami, March 2014). Furthermore, the H_2O_2 may decompose in alkaline solution into O_2 and H_2O, without •OH production (C, 2014). If lower pH at 2, iron will form complex hexaaquairon (II) ion [Fe $(H_2O)_6]^{2+}$ that it reacts slowly with H_2O_2 lead to produce less •OH (Xiang-Rong Xu*, 5 August 2009). Besides, H_2O_2 can solvate a proton (H^+) and generated oxonium ion [$H_3O_2]^+$ which brings about H_2O_2 electrophilic more stable and inhibits the reaction with ferrous ion affecting less •OH (Bum Gun Kwon, June 1999; V. Kavitha, August 2005) which is an crucial key to degrade pollutants. So, pH below 2 and above 6 are not appropriate for Fenton process and performance of Fenton process will decrease.
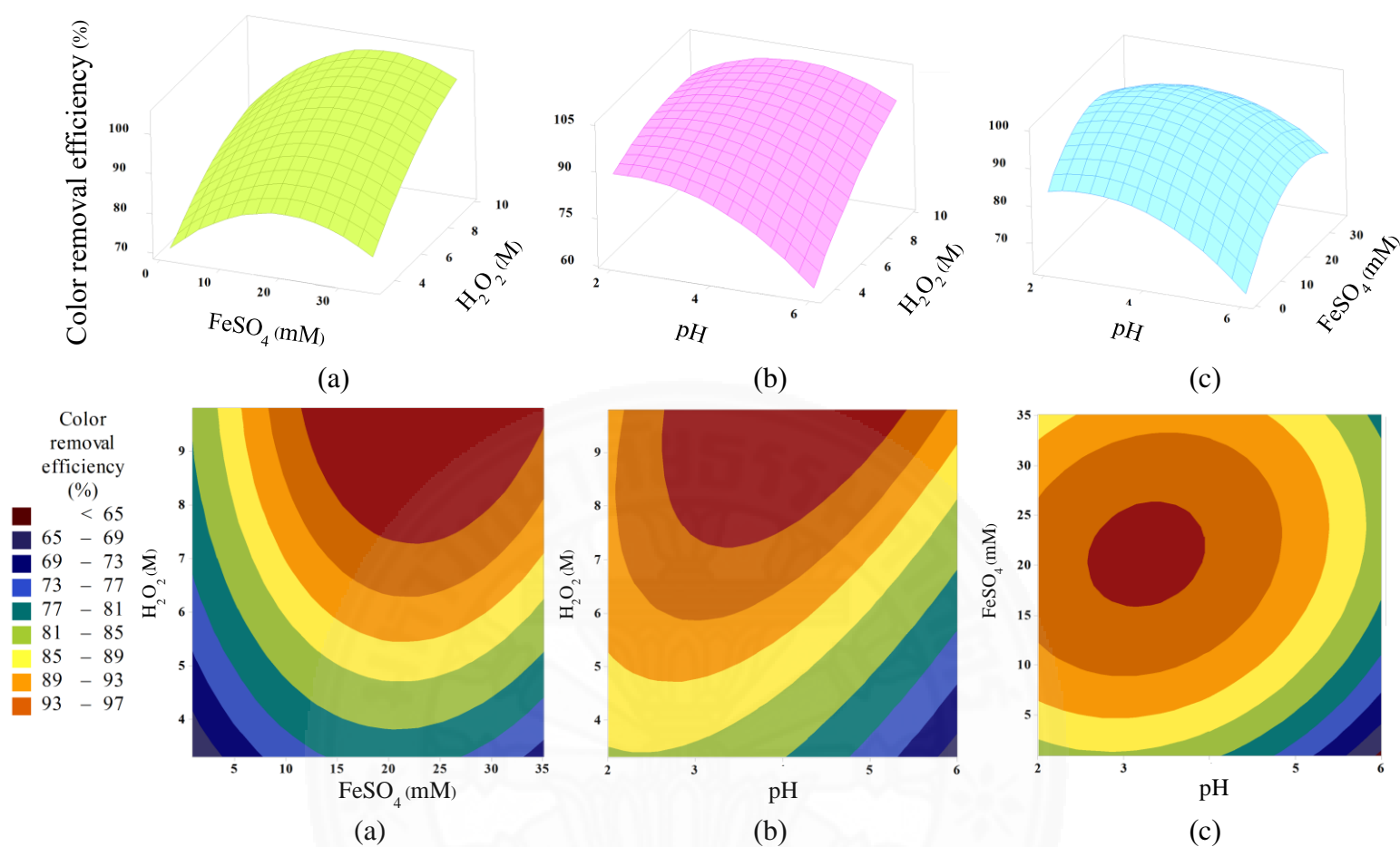
Figure 4.12 Color removal efficiency (**%**) of Fenton process in terms of two variables: (a) H_2O_2 (M) and $FeSO_4$ (mM), (b) H_2O_2 (M) and pH, (c) $FeSO_4$ (mM) and pH

4.3.5.2 Validation of BBD model

BBD has a response optimizer function. Therefore, it is used to validate the color removal efficiency (%) of this model by customization of desired values of inputs and outputs. After that randomly create five check points in order to validate and make confidence that the model predict accurate results. Check point at the maximization of color removal efficiency is preferred, which is 104% color removal at the approximate pH 4.1, the $FeSO_4$ concentration of 23.7 mM and H_2O_2 concentration of 9.8 M. Two customized targets of color removal efficiency are performed 100% and 97% at the same pH 5.5 and H_2O_2 9.8 M in $FeSO_4$ 22.3 and 15.7 mM respectively. And other check points are 89.4% at pH 3.0, $FeSO_4$ 9 mM and H_2O_2 4.9 M and 70% at pH 4.5, $FeSO_4$

4.2 mM and H_2O_2 3.3 M. These five check points from the model are determined by using initial color of 203,600±3,920 ADMI and COD 68,000±148 mg/L and included in Table 4.7. The five check points as 70%, 89.4%, 97%, 100% and 104% have color removal efficiency of 79.7±0.1%, 92±0.2%, 98.3±0.1%, 98.3±0.1% and 98.2±0.1% respectively. Then find how much difference between actual results from experiments and check points from the model. The experimental results are calculated the difference of the 70%, 89.4%, 97%, 100% and 104% check points at 12.2%, 2.8%, 1.3%, -1.8% and -5.9% respectively as presented in Figure 4.13. From the validation, experimental result of the check point of 104% exceeds values up to -5.9% whereas, experimental result of the check point of 100% and 97% are close to the model than others. Conclusion, from of all validation results shows that this model has high reliability. Therefore, it can be brought to use in lab scale experiment and can predict responses. In addition to color removal efficiency results, another important parameter as COD which identifies total chemically oxidizable pollutants are measured. The COD removal efficiency of the 70%, 89.4%, 97%, 100% and 104% check points are 32.5±0.1%, 48±0.2%, 64.5±0.1%, 71.8±0.9% and 71.8±0.3 respectively and show with color removal efficiency in Figure 4.14. The check point of 100% or condition 4 has the second highest color removal efficiency but has the highest COD removal efficiency in low amount of $FeSO_4$ and its experimental result is also close to that given by the model. For all reasons, the optimization condition of color removal of commercial biogas wastewater using Fenton oxidation process should be the condition 4 (pH 5.5, Fe 22.3 mM, H_2O_2 9.8 M) that achieve color removal efficiency 98.3±0.1% as final color 3,570±283 ADMI and COD removal efficiency 71.8±0.9% as final COD 17,500±590 mg/L.

Table 4.7 Validation of the model with five check points

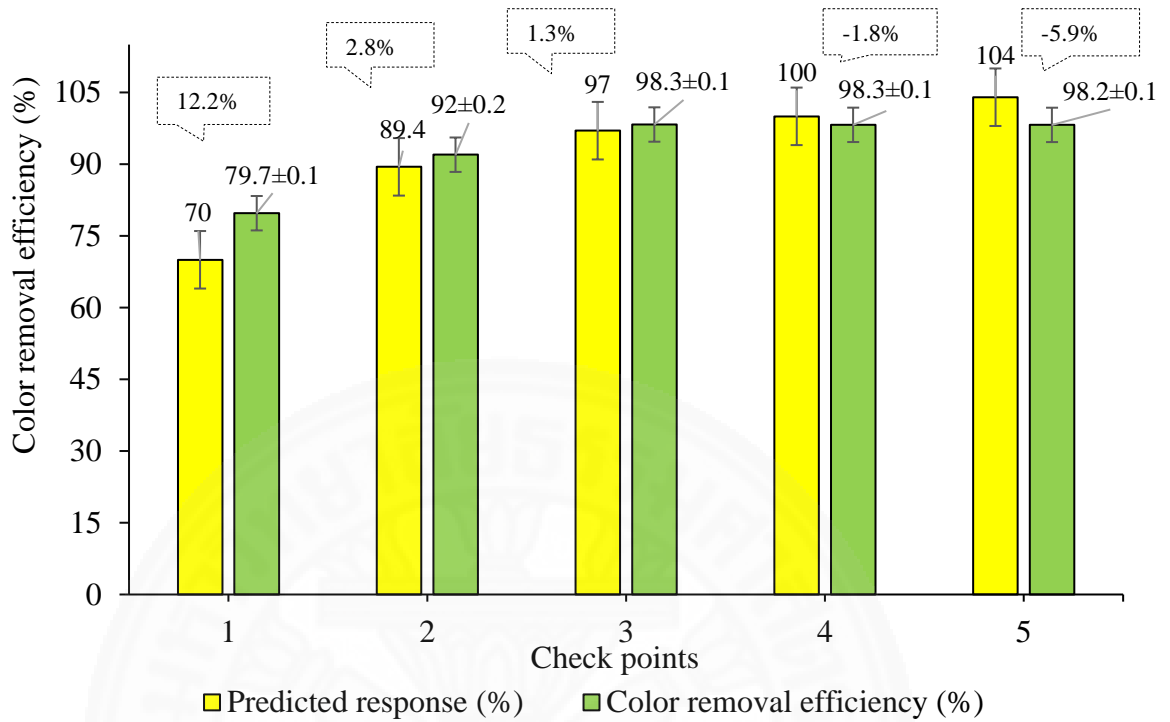| Check points	pH	Fe (mM)	H_2O_2 (M)	Experimental color removal efficiency (%)
1	4.5	4.2	3.3	70
2	3.0	9	4.9	89.4
3	5.5	15.7	9.8	97
4	5.5	22.3	9.8	100
5	4.1	23.7	9.8	104

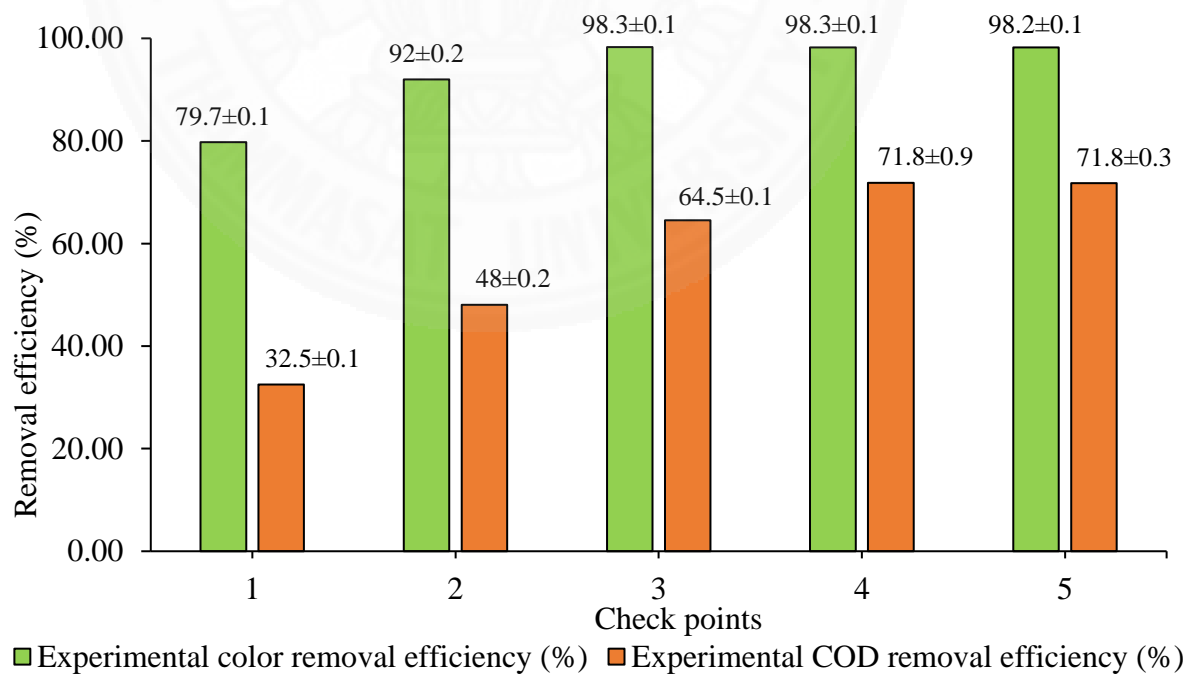**Figure 4.13** Comparison color removal efficiency (%) of the five check points

Figure 4.14 Color and COD removal efficiency (%) of the five check points
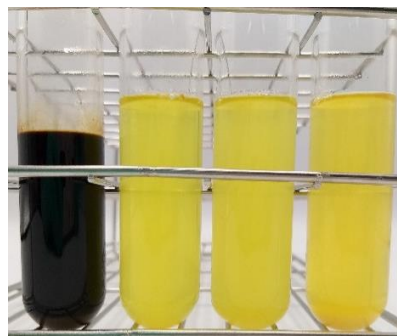
Figure 4.15 Comparison actual wastewater and 3 replications of optimum condition of Fenton process

4.3.5.3 Color and COD removal efficiency over time of optimum condition

According to, the optimum condition is received from the previous experiment. In this section aims to study of color and COD removal efficiency of the optimum condition (pH 5.5, Fe 22.3 mM, H_2O_2 9.8 M) over time by measure sample in 1, 2, 4, 8 and 24 hours to analyze how much efficiency is different by the time pass. The results show final pH after Fenton process is 2.3 from 5.5. In during Fenton process, pH will drop due to acidity of $FeSO_4$ (HIDER, 1994) and H_2O_2 (James Burckett St. Laurent, 2007). This strong acidity is a problem of Fenton treated wastewater. From the result found that in 1 hour of reaction time, color removal efficiency is extremely high up to 96.5±0.1% equivalent to the final color value of 7,110±73 , while COD removal efficiency has only 40.7±0.2% or 36,800±147 mg/L but when the time pass both removal efficiencies increase. It indicates that color removal experiment by Fenton process does not spend much time to achieve high efficiency whereas COD removal efficiency need more reaction time to reach high efficiency. Therefore, this information is useful for users to decide about how to operate. In this research, we use reaction time 24 hours in order to obtain high color and COD removal efficiency as 98.3±0.1% (3,540±95 ADMI) and 71.8±0.1% (17,500±68 mg/L) respectively. Reaction time 24 hours is a limitation boundary time for Fenton operation. If using reaction time more than 24 hours, it will spend too long time and have high operation cost. In Fenton process found that it is highly effective for color removal but lower COD removal since color is removed easily by breaking bond color molecules, but major fragments and some colorless pollutants still remain which shows up as small COD removal

efficiency. The color removal process in wastewater does not necessarily mean a total elimination of the molecules, just only that the visible light absorption becomes less (Oliver J. Hao, 2000).
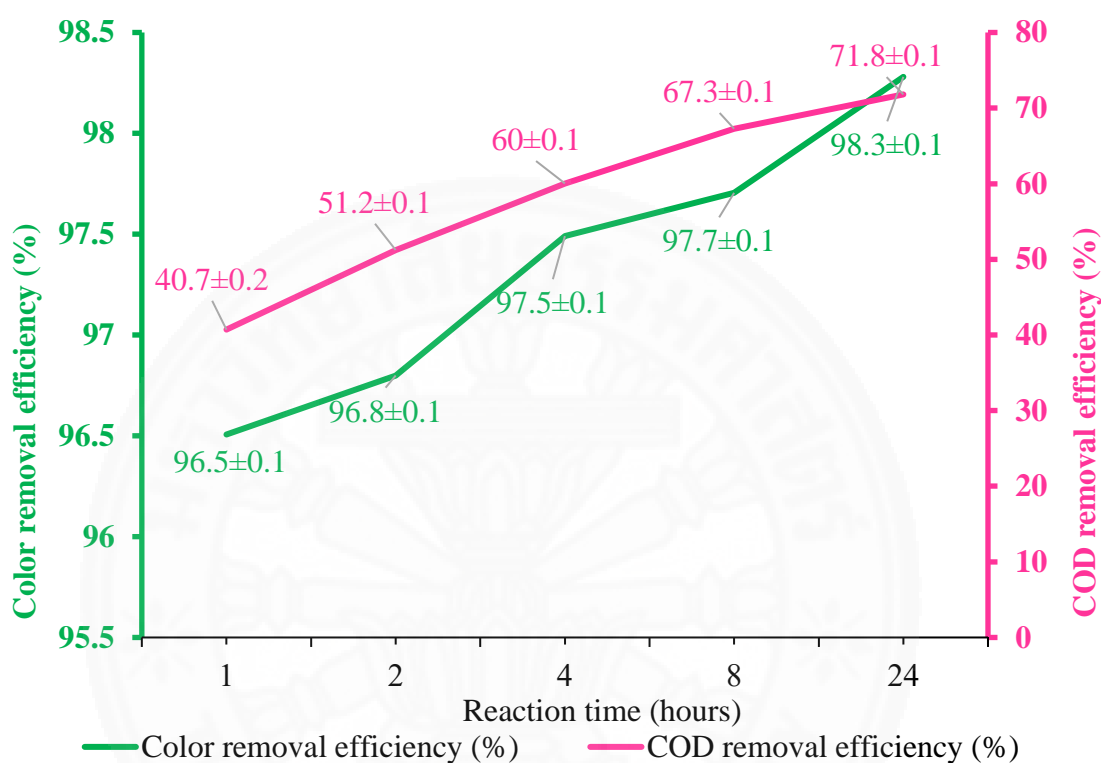
Figure 4.16 Color and COD removal efficiency (%) over time of optimum condition of Fenton process

4.4 The further color treatment by anion exchangers

Even though, the optimum condition of Fenton process at condition pH 5.5, Fe 22.33 mM, H_2O_2 9.80 M, 24 hours can achieve color removal efficiency up to 98.3±0.1% and COD removal efficiency 71.8±0.1% (final COD concentration of 17,500±68 mg/L). However, its final color value after Fenton treatment of 3,540±95 ADMI which still does not pass the color standard as not to exceed 300 ADMI (Leandro Janke*, 2015). A single technique may not be able to treat color to meet the standard. A combination may be able to treat the color until the desired value is obtained. Thus, further treatment is essential to remove the remaining color after the Fenton treated effluent to approach the color standard. The objectives of anion exchange experiment

are to investigate optimum ratio to treat color less than 300 ADMI and study color and COD removal efficiency of the optimum ratio in reaction time of 1, 2, 4 and 24 hours.

First, applying anion exchangers of 1, 2, 4, 8, 10 and 12% (w/v) in sample 20 mL at reaction time of 24 hours improve the color and COD removal efficiency after Fenton process treatment by using initial color of 3,490±31 ADMI with the COD of 17,400±45 mg/L.

The adsorption isotherm of the color adsorbed by the anion exchanger is also shown in Fig. 4.17. The plot is between the Qe (calculated as the difference between the initial and the final color value (ADMI) divided by weight of the anion exchangers in gram) and the Ce (taken as the final color value). Typically, as the amount of the anion exchanger is reduced (at high value of Ce), the Qe value should become higher and higher. However, this adsorption isotherm displays somewhat unexpected behavior, that is at high Ce value (low amount of the anion exchanger used, 1% loading), the amount of color adsorbed per gram of the exchanger seems to be reduced.

This is most probably caused by the presence of other non-color anion species in the solution being treated. The non-color anion species probably compete for the adsorption sites on the anion exchanger before the anionic dye color can be adsorbed. Hence at small amount of the anion exchanger used, the color almost did not change much, resulting in low amount of Qe calculated here. Only the non-color anionic species being adsorbed at low amount of anion exchanger used. The most likely non-color anionic species in this system is actually the sulfate group (SO_4^{2-}) coming from the use of the ferrous sulfate as Fenton's chemical reagent. . This non-color anions sulfate may bind to the anion exchangers better than color compounds causing reduction in color removal process at low amount of anion exchanger loading. However, at sufficiently high enough amount of the anion exchangers, both the non-color anion sulfate and the color compounds start to be adsorbed. As the amount of anion exchange resin is increased, more adsorption sites become available as we observed the change in the Q_e value. The Q_e value for color has the highest value at about 4% loading, and then decreases as the amount of resin used continues to increase, which is typical for adsorption isotherm.

Investigate optimum amount of the anion exchangers found that the anion exchangers 8% is the optimum ratio which is sufficient to treat the effluent color to pass the color standard. Although the anion exchangers 4% has the high Qe and thus efficient use of sorbent, the final color remains over the standard. The optimum ratio achieves the color removal efficiency of up to 92.9±0.6% equivalent to the final color value of 249±20 ADMI, which is now under the targeted standard color value of 300 ADMI. It also achieves a COD removal efficiency of 31.2±0.4% equivalent to the final COD value of 11,971±71 mg/L.

Second, the optimum ratio is studied for both color and COD removal efficiency at various reaction times of 1, 2, 4 and 24 hours by using initial color of 3,580±70 ADMI and COD 17,540±64 mg/L as presented in Figure 4.18. The reaction time 1 hour has the rapid increase for color removal efficiency 92.4±0.3% (corresponding to the final color of 272±11 ADMI), and COD removal efficiency of 31.3±0.3% (corresponding to the final COD value of 12,050±44 mg/L). As the contact time increases, the removal efficiencies of both color and COD do not increase much. This means that a contact time of 1 hour is suitable to treat the Fenton-treated water to meet the color standard.

In summary, the efficiency of the combined method, the Fenton process, and the anion exchange, has color and COD removal efficiency of actual biogas wastewater 99.9% and 82.3% respectively. And the final pH increases from 2.3 after the Fenton process to 4.4 after the anion exchanger because the anion exchanger exchanges some of its OH^- with the melanoidin making the water more base. After anion exchange process of Fenton treated wastewater, the residue H_2O_2 concentration was also measured by Quantofix® peroxide test strips and found that all conditions have a no detectable amount of H_2O_2 (the strips do not change any color, or they remain the same white color strips). The results indicate that after anion exchange treatment, the solution does not have detectable amount of remained H_2O_2 and the concern about the toxicity of remaining H_2O_2 in the effluent is minimal. The residue iron concentration in sample was determined by ICP in order to study how iron concentration changed after anion exchange treatment. The result shows sample has decreased iron concentration of 75.5 %. The residual iron of sample is not severe problem as mentioned in topic 4.3.4.
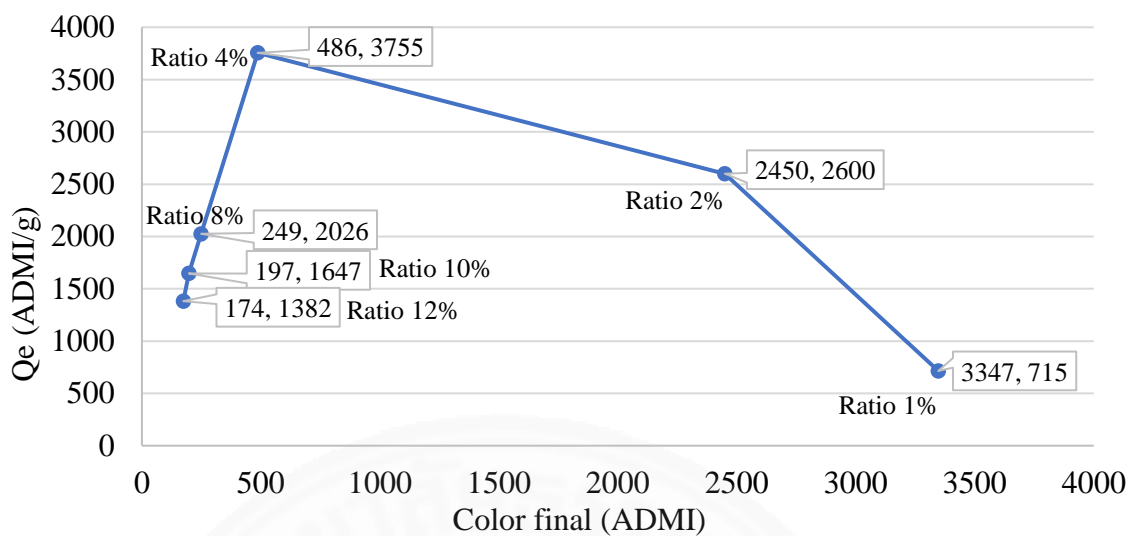
Figure 4.17 Adsorption isotherm of anion exchangers at 1%, 2%, 4%, 8%, 10% and 12% w/w and in the Fenton's treated water with the initial color of 3490 ADMI.
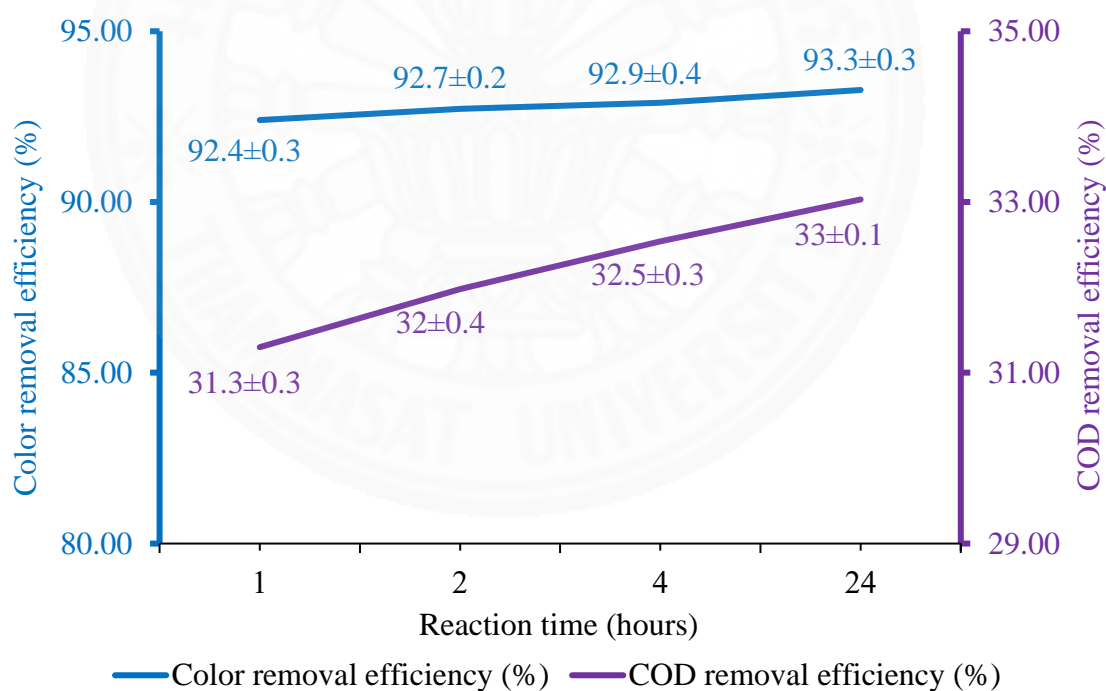

Figure 4.18 Color and COD removal efficiency (%) over time of optimum ratio (8%) of the anion exchangers
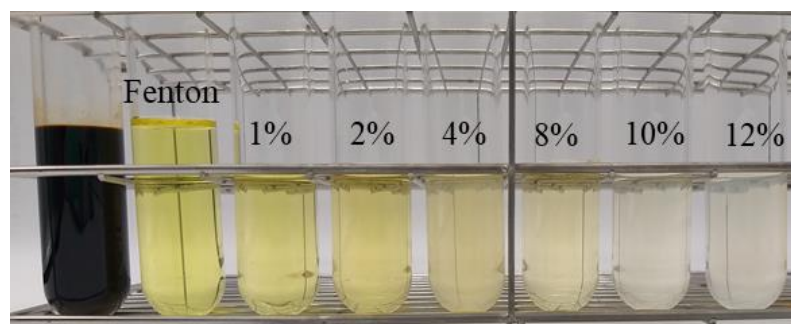
Figure 4.19 Comparison actual wastewater, the Fenton treated wastewater and various ratios of anion exchangers.

CHAPTER 5
CONCLUSIONS

The wastewater from the biogas industry utilizing molasses or vinasse as its feedstock is highly dark in color. The compounds causing this dark color are highly resistant to conventional wastewater treatment. Typical anaerobic process is insufficient to treat the effluent to meet the color standard. The Fenton process is used to solve this problem. The optimized Fenton conditions were obtained using BBD statistical experiment design tool in Minitab 18 software. The optimization of Fenton process was found to be at the pH 5.5, H_2O_2 9.8 M, $FeSO_4$ 22.3 mM and reaction time 24 hours resulting in high color removal efficiency of 98.3±0.1%, equivalent to the color value after Fenton treatment of 3,540±95 ADMI from the initial color value of 203,600±3,920 ADMI. The COD removal efficiency was achieved to be 71.8±0.1%, equivalent to the final COD value of 17,500±68 mg/L from the initial COD value of 68,000±148 mg/L.

However, this single treatment using Fenton process still cannot remove color wastewater to meet the new effluent color standard for Thailand (below 300 ADMI). The anion exchangers were employed following the Fenton process. The results indicate that 8% (w/v) of anion exchanger at reaction time 1 hour can remove color of the Fenton process effluent 92.4±0.3%. It results in the color value of approximately 272±11 ADMI passing the color standard from 3,580±70 ADMI. In addition, it can reduce COD further 31.3±0.3%, resulting in the final COD of 12,000±44 mg/L from 17,500±64 mg/L.

Using a combined Fenton and anion exchange method lead to the total color and COD removal efficiencies of 99.9% and 82.3% respectively. The residue COD concentration is still high and requires further COD treatment. A preliminary MFC set-up is used to treat COD of the diluted biogas wastewater. It was found that UBFC 1 and 2 of MFC has average COD removal efficiency of 15.4±2.2% under the flow rate of 2.7 L/min and the initial COD concentration of 5,640±308 mg/L, air flow 4.5 L/min and temperature 30 °C. The obtained maximum voltages are 0.66 V but there is no color

reduction in MFC. Therefore, MFC is not effective for COD and color removal of the effluent from this biogas effluent.

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