CHARACTERIZATION OF DISSOLVED ORGANIC MATTER IN TREATED TEXTILE WASTEWATER FROM MEMBRANE BIOREACTOR
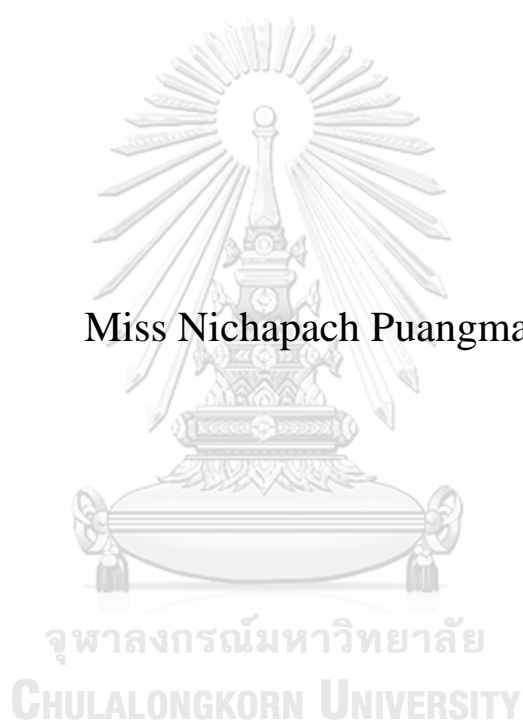
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จุฬาลงกรณ์มหาวิทยาลัย
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A Thesis Submitted in Partial Fulfillment of the Requirements
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การแยกชนิดของสารอินทรีย์ละลายน้ำในน้ำเสียสีย้อมผ้า
ที่ผ่านการบำบัดด้วยกระบวนการถังปฏิกรณ์ชีวภาพเมมเบรน

น.ส.ณิชพัชร พวงมาลัย

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรมหาบัณฑิต
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Thesis Title	CHARACTERIZATION OF DISSOLVED ORGANIC MATTER IN TREATED TEXTILE WASTEWATER FROM MEMBRANE BIOREACTOR
By	Miss Nichapach Puangmalai
Field of Study	Hazardous Substance and Environmental Management
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ฉิชพัชร พวงมาลัย : การแยกชนิดของสารอินทรีย์ละลายน้ำในน้ำเสียสีย้อมผ้า ที่ผ่านการบำบัดด้วยกระบวนการ
ถังปฏิกรณ์ชีวภาพเมมเบรน. (
CHARACTERIZATION OF DISSOLVED ORGANIC
MATTER IN TREATED TEXTILE WASTEWATER
FROM MEMBRANE BIOREACTOR) อ.ที่ปรึกษาหลัก : ผศ. ดร.ภาคภูมิ รักร่วม

    งานวิจัยนี้ มีวัตถุประสงค์เพื่อศึกษาประสิทธิภาพการกำจัดสารอินทรีย์ละลายในน้ำเสียสีย้อม โดยถังปฏิกรณ์ชีวภาพ
เมมเบรน ณ เวลาการกักเก็บตะกอน (SRT) ที่แตกต่างกัน นอกจากนี้ยังมีการศึกษาคุณลักษณะของสารอินทรีย์ละลายโดยใช้
เทคนิคการแยกแฟรคชันและเทคนิค *Fluorescence excitation-emission matrix (FEEM)* น้ำเสียสีย้อม
ผ้าที่ใช้ในการทดลองนี้เป็นน้ำเสียสังเคราะห์จากสีย้อมทั่วไป โดยน้ำเสียสังเคราะห์มีความเข้มข้นซีโอดีสูงถึง 2,000 มก. / ล.
ในขณะที่ความเข้มข้นของสารอินทรีย์ละลายน้ำเท่ากับ 466.1 mg / L ถังปฏิกรณ์ชีวภาพเมมเบรนเดินระบบภายใต้สภาวะ
ที่เวลากักเก็บน้ำ 2.5 วันและแปรเปลี่ยนค่าเวลาในการกักเก็บตะกอนที่ 15วัน, 30วัน และระยะอนันต์ ทำการเดินระบบจน
เข้าสู่สภาวะสมดุลโดยใช้เวลาประมาณ 60 วัน น้ำทิ้งที่ผ่านการบำบัดด้วยถังปฏิกรณ์ชีวภาพเมมเบรนจะถูกนำมาวัดพารามิเตอร์
ต่างๆ ได้แก่ซีโอดี สีและสารอินทรีย์ละลายน้ำ จากผลการศึกษาพบว่าถังปฏิกรณ์ชีวภาพเมมเบรนทุก SRT สามารถลดซีโอดี
ได้มากกว่า 95% อย่างไรก็ตามถังปฏิกรณ์ชีวภาพไม่สามารถลดค่าสีให้อยู่เกณฑ์มาตรฐานน้ำทิ้งได้ (300 ADMI)
ถึงแม้ว่าจะมีประสิทธิภาพในการลดค่าสีมากกว่า 80% โดยการปรับพีเอชของน้ำและไม่ปรับพีเอช ให้ค่าสีที่ไม่แตกต่างกัน
อย่างมีนัยยะสำคัญ นอกจากนี้ถังปฏิกรณ์ชีวภาพเมมเบรนมีประสิทธิภาพในการกำจัดสารอินทรีย์ละลายสูงกว่า 80%
ถังปฏิกรณ์ชีวภาพเมมเบรนนี้มีประสิทธิภาพสูงในการกักกันสารแขวนลอย (SS) และสารแขวนลอยที่ระเหยได้ (VSS)
โดยมีประสิทธิภาพสูงถึงร้อยละ 99 ในส่วนของการลดโอกาสในก่อตัวของสารไตรฮาโลมีเทน พบว่าถังปฏิกรณ์ชีวภาพเมม
เบรนสามารถลดโอกาสในก่อตัวของสารไตรฮาโลมีเทนได้ซึ่งเกิดมาจากการลดสารตั้งต้นในการเกิดสารไตรฮาโลมีเทนคือ
สารอินทรีย์ โดยโอกาสในก่อตัวของสาร ไตรฮาโลมีเทนมีค่าเพิ่มขึ้นเมื่อเดินระบบที่เวลาการกักเก็บตะกอนสูงขึ้น จากผล
การศึกษาคุณลักษณะของสารอินทรีย์พบว่าโอกาสในก่อตัวของสาร ไตรฮาโลมีเทนไม่ได้ขึ้นกับปริมาณสารอินทรีย์ละลายอย่าง
เดียว แต่ยังขึ้นกับคุณลักษณะของสารอินทรีย์ละลายด้วย จากผลการศึกษาโอกาสในก่อตัวของสารไตรฮาโลมีเทนจำเพาะพบว่า
สารอินทรีย์ที่ถูกกำจัดโดยถังปฏิกรณ์ชีวภาพเมมเบรนมีความสามารถในการก่อตัวของสารไตรฮาโลมีเทนต่ำ อย่างไรก็ตาม
โอกาสในก่อตัวของสาร ไตรฮาโลมีเทนในน้ำที่บำบัดแล้วมีค่าลดลงเนื่องจากปริมาณของสารอินทรีย์ละลายที่ถูกกำจัดออกไป

สาขาวิชา	การจัดการสารอันตรายและสิ่งแวดล้อม	ลายมือชื่อนิสิต ....
ปีการศึกษา	2562	ลายมือชื่อ อ.ที่ปรึกษาหลัก ....

5987539620 : MAJOR HAZARDOUS SUBSTANCE AND ENVIRONMENTAL MANAGEMENT
KEYWORD: Textile wastewater, Membrane bioreactor, Dissolved organic matter

Nichapach   Puangmalai   :
CHARACTERIZATION OF DISSOLVED ORGANIC
MATTER IN TREATED TEXTILE WASTEWATER
FROM MEMBRANE BIOREACTOR. Advisor: Asst. Prof. Pharkphum
Rakruam, Ph.D.

This research aims to investigate the DOM removal efficiency in textile wastewater by MBR at different sludge retention time. In addition, the characteristics of DOM was investigated by using resin fractionation and fluorescent excitation-emission matrix techniques. Textile wastewater was synthesized by using commercial dyes and used in all experiment. The characteristics of synthesis textile wastewater showed that the COD concentration was high as 2,000 mg/L. In addition, the DOC concentration in synthesis textile wastewater was also high at 466.1 mg/L. MBR was conducted under HRT 2.5 days and SRT was varied at 15 days, 30 days and infinite, respectively. MBR was operated continuous until it reaches steady state (60 days). The effluent of MBR were collected and measuring various parameters including COD, colour and DOC concentration. From the result, it was found that MBR at all SRT conditions can provided the high percent COD reduction (>95%). However, MBR cannot reduced colour to meet the standard of discharge wastewater; nevertheless, the high percent colour reduction was obtained (>80%). Trends of colour value was not significantly different for non-adjusted pH and adjusted pH to 7. Furthermore, MBR has provided high percent DOC reduction more than 80% for all SRT conditions. MBR has very high efficiency for retained suspended solid (SS) and volatile suspended solids (VSS) in the reactor with 99%. In term of trihalomethane formation potential, MBR can reduced the formation potential of THMs by reduced the organic matter. The formation of THMs was increased with the increasing of SRT conditions. The obtained results of DOM characteristics confirmed that the formation of THMs not only depend on the organic matter concentration but also the characteristics of organic matter. The specific THMFP revealed that the organic matter that removed by MBR was low ability to form THMs. However, the THMFP was decreased due to the amount of organic matter was removed.

Field of Study:	Hazardous Substance and Environmental Management	Student's Signature ....
Academic Year:	2019	Advisor's Signature ....

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ABBREVIATIONS AND SYMBOLS

BDCM	Bromodichloromethane
BF	Bromoform
BOD	Biological Oxygen Demand
CF	Chloroform
COD	Chemical Oxygen Demand
DBCM	Dibromochloromethane
DBPs	Disinfection by – Products
DOC	Dissolved Organic Carbon
DOM	Dissolved Organic Matter
FEEM	Fluorescence excitation – emission matrices
F/M	Food to Microorganism ratio
HA	Humic Acids
LD50	lethal dose 50%
MBR	Membrane Bioreactor
MF	Microfiltration Membrane
MLSS	Mixed Liquor Suspended Solids
MLVSS	Mixed Liquor Volatile Suspended Solids
SRT	Solid Retention Time
THMs	Trihalomethanes
TOC	Total Organic Carbon
UF	Ultrafiltration Membrane
UV-254	Ultraviolet absorbance at Wavelength 254 nm.

CHAPTER 1

INTRODUCTION

1.1 Backgrounds

At the present time, environmental issues, especially water pollution which caused by the growth of the industry has increasingly intensified. The textile industry is another high growth industry, improving both the manufacturing process and the competition to increase the volume of products. Moreover, it is a highly popular industry in the north, particularly for tourist destinations such as Chiang Mai, Lamphun, Phrae and Lampang; due to the products of the textile industry, such as cotton and silk fabrics, are the main income generating products for the villagers. The texture and color of the woven fabrics are important to attracting a lot of tourists. The patterns indicate the identity of the place; therefore, the dyeing and bleaching industry is an indispensable industry in the processing of products. Bleaching dyeing and finishing industries are the final process of fabric production to consumers or garment factories. Hence, the dyestuff is required to be a part of the dyeing industry. There are many types of dyes which use in textile industry. Direct dyes is one of the dyes that commonly used in the northern industry. Most of these dyes are azo compounds which has high molecular weight contain the sulfonic acid, and negative charge. The most important component which consequential use in every process production is water. Water is one of factors that must be applied in all production lines, whether spinning, knitting, and bleaching process.

Consequently, the water quality which discharge from these processes was changed based on the types of dyes and chemical used. When discharge wastewater form dyes process to water not only makes the natural water source unattractive but also reduces the oxygen intake to the surface of the water. As a result, the amount of sunlight cannot pass through surface water, causing plants unable to photosynthesis, resulting in reduced oxygen in water and damage to aquatic organisms. In addition, the textile wastewater contains

more organic matter. The discharge of textile wastewater which untreated can increased the organic matter remaining in natural water. When utilized the natural water for the raw water sources for water supply, the remaining organic matter can react with chlorine to form disinfection by products as trihalomethane (THMs). The dyes used nowadays have various types of dyes and difficult to biodegrade. Currently, the technology used to treat wastewater from both physical and chemical method has been reduced because there are many limitations, such as the cost of treatment and the sludge from the treatment system. Biological treatment processes such as activated sludge is normally used to treat wastewater. Although different chemical, physical, and biological treatment alternatives have been studied to remove dyes from textile wastewaters, biological methods are commonly considered to be the most effective and environmentally safe (Cirik et al., 2013; Ozdemir et al., 2013).

Membrane Bioreactor (MBR) is a combination of biological process and membrane filtration process which has become increasingly recognized and accepted in the current year for various types of wastewater treatment. Moreover, MBR technology can be used in cases of the need for quality effluent exceeds the capacity of the conventional activated sludge (CAS). However, there are several factors that may contribute to the lower organic carbon content of MBR effluents as compared to CAS processes, like longer retention times, smaller floc sizes, etc. Many experiments claim that the operations parameters such as, sludge retention time has impact on the removal performance of membrane bioreactor. Moreover, various components such as mixed liquor suspended solids (MLSS), colloids, and dissolved organic matter (DOM) can result in membrane fouling during the filtration operation (Liang et al., 2008). Although the concentration of DOM is normally lower than that of MLSS, it can induce significant fouling resistances in MBRs. Furthermore, DOM also performs as a significant precursor of DBPs. During chlorination, the chlorine can react with DOM present in water to create DBP mainly trihalomethanes (THMs), haloacetic acids (HAAs) and haloacetonitriles (HANs). Nevertheless, the appropriate advanced technology for remove DOM in treated textile wastewater depends on the DOM

characteristics. Thus, the characteristics of DOM in treated textile wastewater should be investigated.

Resin fractionation technique has been widely applied to investigate various properties of DOM. It has been shown that it greatly facilitates subsequent studies associated with DOM and the formation of disinfection by-products (DBPs). Presently, Three-dimensional excitation–emission matrix (EEM) fluorescence spectroscopy which is a rapid, selective and sensitive technique has been proposed by many researches as another promising technique for characterizing the organic compositions of DOM. It has been proven to be a useful technique to differentiate the changes and transformations of organic matters in natural environments (Baker, 2001; Lu and Jaffe, 2001; Peuravuori et al., 2002). On the other hand, the report to characterize DOM in MBRs by using resin fractionation and EEM fluorescence spectroscopy technique could hardly be found in the literature. Information on DOM in MBRs obtained by these techniques should be very useful for understanding the role of DOM in MBR effluent. The purposes of this study were, therefore, to obtain the DOM characterization by using resin fractionation and fluorescence characteristics to contribute to a better understanding of organic compositions in MBRs effluent. Additionally, the MBRs operational parameters such as SRT should be determined for study the effect on DOM characteristics.

1.2   **Objective:**

The objectives of this research were aims to investigate the DOM removal efficiency by MBR at different sludge retention time. In addition, the DOM characterization was investigating by resin fractionation and fluorescent excitation-emission matrix.

1.3   **Hypothesis:**

Operating MBR with longer SRT have higher efficiency in term of organic removal.

1.4   Scopes of the Study:

1)   Synthetic textile wastewater was used as raw water sample. The characteristics of raw water were analyzed by measuring various parameters such as pH, BOD, COD and color. Furthermore, the dissolved organic matter concentration and characteristics was analyzed by measuring dissolved organic carbon (DOC).

2)   Continuous experiment of MBR was conducted with 0.01 microns hollow-fiber ultrafiltration membrane. The volume of MBR reactor was 31.25 liters with working volume 15 liters. Seed sludge was collected from aerator tank from the Chiang Mai University wastewater treatment plant. The SRT of MBR was varied at 15, 30 and infinite. The MBR experiment was operated under room temperature. The effluent of MBR was collected and measuring various parameters including COD, THMFP and DOC. The effect of operating condition to DOM concentration and characteristics was investigated.

3)   DOM in wastewater and treated wastewater was fractionated into 2 groups as hydrophilic (HPI) and hydrophobic (HPO) by using resin fractionation technique and DOM characteristic was determined by FEEM.

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CHAPTER 2

THEORETICAL BACKGROUND AND LITERATURE REVIEW

2.1   Textile Industry

The textile industry plays an important role in the northern part of Thailand. It is one of the most popular industries in the tourist area such as Chiang Mai, Lamphun, Phrae and Lampang. The products of the textile industry are artistic, unique and reflects the Lanna (northern part) culture. Therefore, textile products are popular for tourists and be the main business which is earn money for villagers and communities. Creating beautiful art for textile products, the important things are the colors and patterns on the product. In order to attract the attention of consumers, dyes are so important and indispensable in the textile industry.

2.1.1   Dyestuff

Dyeing industry is an intermediate industry in the textile industry. It is the process of changing the textile material in the form of yarn or calico into ready-made materials that can be produced or sold to consumers. Dyestuffs are one of the colors which used to dye the fibers of the fabric. It may be organic or inorganic. The qualities look like Crystal or fine powder. Some dyes are water solubility some cannot be soluble in water but can dissolve in organic solvents. There are two types of dyes. First, natural dyestuffs, dyes from natural sources especially flora and fauna. The dye comes from the plant components such as stem, flower, shelled leaves. Second, synthetic dyestuffs are dyes produced by chemical processes. There are many types of dyes which use in textile industry such as reactive dye, acid dye, basic dye, direct dye, vat dyes, disperse dye etc.

2.1.2   Direct Dyes

Direct dyes are colorants that can dye cellulose fibers without the need for a pre-treatment of the fibers with mordant. Despite their existence for over 100 years, direct dyes continue to be one of the most important groups of dyes for the textile industry. Since the development of new dyes, direct dyes are also used for dyeing cellulose fibers because of favorable characteristics such

as intense colors, hue, bright shades, high substantively, ease of synthesis and low cost. The direct dyes derived from benzidine, owing to their excellent substantively towards cellulose fibers, have gained considerable importance.

However, due to carcinogenic behavior, the production of dyes was forbidden. Most direct dyes are azo compounds, mostly bisazo and trisazo in naturehaving sulfonate group for making it water soluble which is important for dyeing.

2.2   Textile wastewater

Current environmental problems particularly water pollution which caused by industrial growth have intensified. Especially the textile industry, which have high growth industry improve both production process and competition to increase product volume. Water is an important factor that must be used with raw materials in all line of production whether, fiber production, spinning, weaving, knitting and bleaching by used dyes, fabrics and chemicals as a raw material. It transforms the water into a wastewater: for example, temperature increase, odorous, color and aquatic animals die due to high levels of organic substances in the water, caused lack of oxygen.

Furthermore, the effect of this wastewater is also inhibited by various microorganisms in the biological treatment process. Dyeing industry is an industry that uses a lot of water and chemicals. The main problem which effect on the environment is discharge wastewater from industry. Discharge wastewater which contain color, BOD, COD, Acid-Base, suspended solids and heat have impact on aquatic life, destroy the scenery and offensive. Most of contaminants that contaminated in the wastewater came from dyeing and finishing process. In most cases, these substances and some colors can be treated in a physical and chemical way, but some colors cannot be treated by such methods.

Damage caused by dyes not only makes the natural source of water is not beautiful, but also reduce the import of oxygen into the surface of the water source. As a result, the amount of sunlight that falls on the surface of the water is obscured, making water plants unable to synthesize by light; this will reduce the amount of oxygen in the water and menace to aquatic life.

Thereby, factory environmental management planning is needed to prevent pollution at the source and saves wastewater treatment costs by study about wastewater treatment technology to achieve the quality of wastewater according to the standard criteria. According to the basics, the contaminated dyes in the effluent, even with a small amount, it is clearly visible and annoys consumers. The dye which is using nowadays have many types of dyes and difficult to biodegrade.

2.3   Organic matter treatment for textile wastewater

Organic matter represents the main emission load for textile wastewater suggesting treatment based on biological processes (M. Brik, P. Schoeberl, B. Chamam, R. Braun, W. Fuchs, 2006). Because of the poor-biodegradability and sometimes even toxicity of the textile wastewater components, an advanced treatment technology is necessary. Especially if reuse of treated wastewater is the objective, extensive removal of organic contents as well as almost complete decolorization is required (Rott U, Minke R., 1999).

Currently, the technology used in wastewater treatment from dyeing plants both physical and chemical are less treated color from the water. There are several limitations, such as the cost of treatment and sludge from the treatment system. Water discharged from the dyeing industry is generated by the water and chemicals used in the dyeing process. It contains toxic substances, suspensions, oils and waste, whether organic or inorganic contaminated in effluent. Biological treatment processes such as activated sludge is normally used to treat wastewater.

Although different chemical, physical, and biological treatment alternatives have been studied to remove dyes from textile wastewaters, biological methods are commonly considered to be the most effective and environmentally safe (Cirik et al., 2013; Ozdemir et al., 2013). Aerobic treatment of azo dyes is quite difficult due to its recalcitrant nature and toxicity to microorganisms.

2.4   Membrane Bioreactor Technology (MBR)

Membrane Bioreactor Technology (MBR) is one of technologies which combine membrane filtration and biological treatment processes has become increasingly famous, various, and has been recognized in current years for treated many wastewater types. In the meanwhile, the conventional activated sludge

(CAS) process cannot handle with wastewater composition or mutability of wastewater flow rate. Therefore, MBR technology can be used in cases of the need for quality effluent exceeds the capacity of the CAS. The first membrane bioreactors (MBRs) were developed commercially by Dorr-Oliver in the late 1960s (Bemberis, Hubbard, &Leonardet, 1971), combining UF with a conventional activated sludge process (CASP), for application to ship-board sewage treatment (Bailey et al., 1971).

2.4.1   Ultrafiltration Processes

In an MBR system, the membranes are submerged in an aerated biological reactor with the use of micro- or ultra-filtration membranes (pore size: 0.05-0.4 microns) (Yurtsever 2016). This filter allows the water to pass out of the filter media is high quality and reduces the sedimentation and filtration steps, which are typically used for wastewater treatment. Ultrafiltration (Ultrafiltration: UF) is a micro porous membrane process with a pore size of about 2-20 nm (20-200 A). Driving pressure between 100-800 kPa or 1-8 atm is used to separate colloidal particles, bacteria, viruses from the water, and organic compounds with large molecules such as proteins. Typical types of membrane filters are Cellulose acetate, Polyacrylonitrile and Polyester. etc.

2.4.2   Wastewater Treatment by Membrane Bioreactor Process

Côté et al. attributed the improved COD removal to the avoidance of biomass washout problems commonly encountered in activated sludge process, as well as to complete particulate retention by the membrane. In a study of Al-Malack et al., COD removal efficiency in immersed MBR was found to increase significantly with increase in MLSS concentration, however, the effect of SRT on permeate COD became insignificant for MLSS concentrations above of 3 g L–1 , which probably means that the organic loading rate was not high enough to show a significant difference at higher biomass concentrations. Since typical sludge concentrations for immersed MBRs are between 1 5 and 2 5 g L–1 , elimination of organic matter and turbidity is almost independent on SRT, and average removals normally achieved for COD and SS are over 9 0 and nearly 1 0 0 % , respectively. An

important feature of MBRs is the possibility to employ high sludge ages facilitating the growth of specialized microorganisms and in such a way promoting improved degradation of refractory organics (Stephenson T, Judd S, Jefferson B, Brindle K., 2000). This makes MBR technology a highly promising technique for industrial wastewater purification. Therefore, MBR effluents can be of a quality suitable for direct recycling or after further purification by additional post-treatment steps (Malpei&, Bonomo&, Rozzi ,2003) (Brik &, Chamam&, Scho¨berl&, Braun &, Fuchs 2004).

The use of MBR may also open the opportunity of water reuse, which is important especially in industries consuming high quantities of wastewater, like textile industry (Hoinkis et al., 2012). MBR has been proved to be very effective to remove COD and BOD from textile wastewater (Schoeberl et al., 2004).

2.4.3 General characteristics of membrane bioreactor

There are two types of Membrane reactor system. First, the membrane is submersed MBR. Another type of membrane is side stream MBR as shown in Figure 1.

(a) **Submersed / Immersed** is the type of membrane that is submerge in wastewater without draining out of the water. This type of membrane is more expensive depend on optional as shown in Figure 1(a). Water is pumped into the bioreactor to contact the biomass and filtered with membrane. The air is released from the bottom of the membrane set to remove the clogged surface of the membrane with the airlift effect. Crossflow and bubbles help prevent sediment residues that clog the surface of the membrane. Moreover, air is also used for oxidation substances and internal metabolism of microorganisms the treated water flows out of the tank by suction through the membrane. At present, the use of both MF and UF membrane uses this type.

(b) **Side Stream** is a membrane that extract wastewater to treat the membrane outside as shown in Figure 1(b). The water flows into the bioreactor which is contact with biomass. This mixture is pumped from the reactor under pressure to be filtered through the membrane. Then, water passing through the

membrane will flow out of the system. While all biomass is returned to the reactor, excess sludge is pumped out to control the sludge time and the membrane is cleaned by backwashing, chemical cleaning or bubbling (Antony et al.).
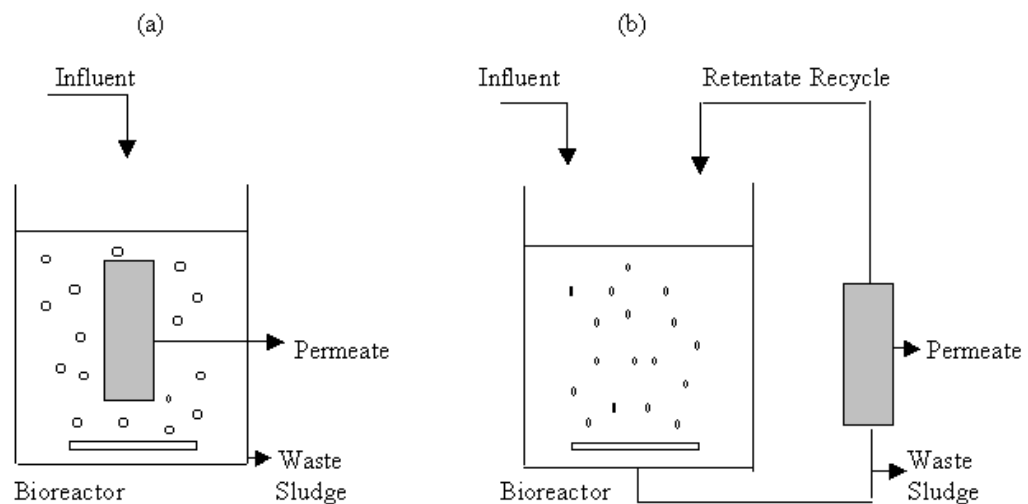
source:http://www.wioa.org.au/conference_papers/01/paper8.htm

Figure 1. Type of membrane bioreactor system
(a) Submersed/Immersed MBR (b) Side Stream MBR

2.4.4. Membrane bioreactor operation parameters

There are several factors that may contribute to the lower organic carbon content of MBR effluents as compared to CAS processes, like longer retention times, smaller floc sizes, etc. Membrane rejection of a significant amount of soluble organic molecules and colloids makes their removal more effective due to a higher lyses activity in the reactor induced by elevated concentrations of these compounds. Higher sludge ages that are achieved by long SRTs allow more complete mineralization of biodegradable raw water organics, but also an adaptation of microorganisms to less biodegradable compounds. Therefore, biomass can acclimatize to wastewater without being restricted to fast-growing and floc-forming microorganisms.

2.5   Natural organic matter: NOM

The major problem of wastewater is often caused by organic matter contained in the water, causing biological wastewater treatment to occur, because organic matter is often biodegradable and therefore requires oxygen to allow microorganisms to digest. Decompose organic matter by using oxygen to breathe. The amount of organic matter that is too high makes the dissolved oxygen in nature inadequate, resulting in an air deficiency condition that has an effect. Causing the decay of water sources and the deaths of various aquatic animals that lack oxygen by finding that contaminants in the water are also caused by dirt suspended in water such as soil particles of various sizes, minerals Water, algae, protozoa and bacteria, including both pathogenic and non-pathogenic species, will cause water color, odor and turbidity. Water-soluble impurities include gases. Such as oxygen, nitrogen, hydrogen sulfide, carbon dioxide, methane, ammonia, chloride, nitrite, nitrate, and colloidal substances in the water are the smallest particles of silica, clay and organic matter rotting in the form of a colloidal precipitation.

2.5.1.   Dissolved organic matter: DOM

Dissolved organic matter (DOM), comprising the partial decomposition products of plant and other biological materials, is ubiquitous in surface, soil and ground waters (Perdue and Gjessing, 1990; Kullberg et al., 1993; Hessen and Tranvik, 1998). It has numerous ecological and geochemical functions, including light absorption, pH buffering, interactions with metals and organic contaminants, adsorption to surfaces and photochemical activity. It plays a role in the terrestrial and aquatic carbon cycles, so that monitoring its concentrations and fluxes can aid in understanding the effects of land-use change, acidification reversal and climatic warming (Pastor et al., 2 0 0 3 ; Worrall et al., 2004; Monteith et al., 2007).

There are two major sources of DOM in lake water: (1) autochthonous DOM, that is, photosynthetic inputs from the littoral and pelagic flora through secretions and autolysis of cellular contents, and (2) allochthonous DOM, composed largely of terrestrial humic substances refractory to rapid bacterial

degradation (Wetzel, 1983). Effluent DOM originated from biological wastewater treatment schemes may include organic compounds of different groups, from carbohydrates and proteins to more biologically resistant components known as fulvic and humic materials (Rebhun and Manka, 1971; Manka et al., 1974; Ma et al., 2001; Imai et al., 2002; Ilani et al., 2005).

DOM is a heterogeneous mixture of aromatic and aliphatic organic compound containing oxygen, nitrogen, and sulfur functional groups (e.g., carboxyl, phenol, enol, alcohol, carbonyl, amide, and thiol). It has been found that the relative contribution of DOM to membrane fouling was in the range of 26–52% (Bouhabila et al., 2001; Lee et al., 2003; Wisniewski and Grasmick, 1998). In MBRs, various components such as mixed liquor suspended solids (MLSS), colloids, and dissolved organic matter (DOM) can result in membrane fouling during the filtration operation (Liang et al., 2 0 0 8). Although the concentration of DOM is normally several orders of magnitude lower than that of MLSS, it can induce significant fouling resistances in MBRs.

DOM also acts as an important precursor of DBPs and enables the micro-organism to grow in the water treatment plant and the distribution system. During chlorination, the chlorine reacts with DOM present in water. The reaction produces various DBP mainly trihalomethanes (THMs), haloacetic acids (HAAs) and haloacetonitriles (HANs).

The reaction is reflected in the following equation:

Chlorine + DOM → THMs + HAAs + HANs + Chloral hydrate + halopropanones + Cyanogen halides + chloropicrin
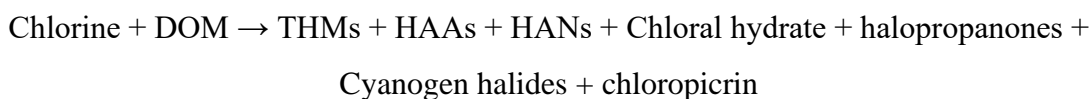
2.5.2. Origin of natural organic substances

Organic matter in water plays an important role in environmental engineering. (Sinsin Tanthulwet, 2004) In general, the organic substances that occur are divided into 4 types as follows.

1) Organic substances caused by degradation of organic matter, carcasses in natural water, called Natural Organic Matter (NOM), formed as a small molecule of organic matter until it can dissolve in water such as the humic

group And fluvic, both of which also contribute to the color of water (Light brown or tea color)

2)   Organic substances produced by microorganisms composed of microbes, protozoa, bacteria, fungi and single-celled algae Organic within the cells dissolve in water. For example, micro-cystins that are caused by blue-green algae Microcytin Aeruginose These are some of the toxic blue-green algae called Ooze La Vitoria limonene can be produced compounds resulting from the metabolism in the cells of the substance Methylisorneol. Which is a substance that causes water to have unpleasant odors etc.

3)   Organic substances caused by community wastewater, agricultural and industrial activities, as well as excretion, cleansing the human body, causing organic contaminants to be waterproof, including chemicals, pesticides and fertilizers, etc.

4)   Organic substances caused by wastewater treatment systems and water conditioning systems such as sedimentation accelerators in wastewater treatment systems. In addition, biological wastewater treatment systems, which often contain organic substances that microorganisms cannot be degraded throughout Until the remains of the residual microorganisms contaminated in the water through the treatment system, through the chlorine disinfection system may cause these substances to become organic substances that are toxic The more such compounds, resulting in methane tri Haro. (Trihalomethanes: THMs), a type of carcinogen.

2.5.3. DOM measurement

Normally, the quantity of DOM can be evaluated by measuring DOM surrogate parameters including dissolved organic carbon (DOC), UV absorbance at wavelength 254 nm (UV-254) and trihalomethane formation potential (THMFP).

1)   **Total Organic Carbon (TOC)**

All organic carbon is an agent index to measure the concentration of natural organic substances in water. The total amount of organic carbon

concentration in natural water sources has a very wide range which is shown in Figure 2.
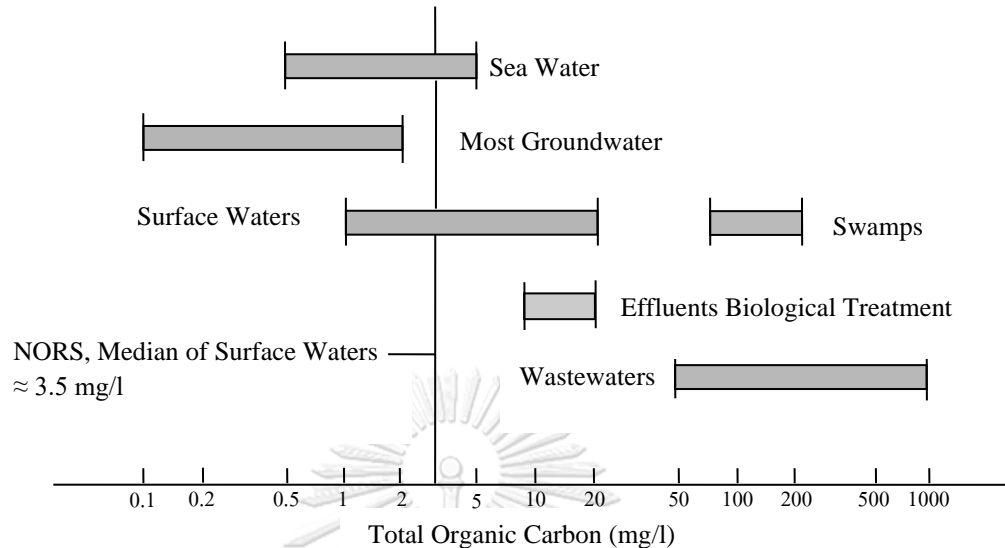
Figure 2. *The Total Organic Carbon in natural water sources*
Source: (Kavanaugh, 1978)

2)   **Dissolved organic carbon (DOC)**

Dissolved organic matter (DOM) commonly expressed by its content (DOC) is an important component in secondary water resources. DOC is used to represent the presence of dissolved organic matter such as humic substance and non-humic substance (Julie, Minhan and Robert, 2004) Aquatic humic substances (AHS), which are typical naturally occurring recalcitrant DOM, constitute 30–80% of DOM as dissolved organic carbon (DOC), and they constitute the largest fraction of natural organic matter in waters (Thurman, 1985). They are straw-colored, polar, hydrophobic organic acids derived from soil humus, terrestrial and aquatic plants, and plankton.

TOC and DOC were analyzed in accordance with Standard Methods 5310 (Total Organic Carbon, TOC) and section 5310 D (Wet-Oxidation Method). Water samples were filtered through glass-fiber filters (GFC) of nominal pore size (1.2micron) prior to analyzing TOC. Water samples were filtered through a prewashed 0.45micron cellulose acetate membrane prior to analyzing DOC. A TOC Analyzer (OI analytical 1010) was used to measure both TOC and DOC.

Analytical methods DOC measurements were conducted as non-purgeable DOC with a Shimadzu TOC-5000 total-organic-carbon analyzer equipped with a Pt catalyst on quartz wool. At least three measurements were made for each sample, and analytical precision was typically less than 1%. Potassium hydrogen phthalate (Kanto Chemical Co., Tokyo) was used as a standard.

3) **Dissolved Organic Nitrogen (DON)**

Water soluble organic nitrogen is a parameter that indicates the amount of dissolved organic nitrogen contained in water.

4) **UV Absorbance at Wavelength 254 nm. (UV-254)**

Qualitative information about DOM is commonly sought from UVe visible absorption and fluorescence spectroscopy. For example, specific UV absorbance (SUVA), measured at 254 or 280 nm, is a measure of aromaticity (Chin et al., 1994; Weishaar et al., 2003), absorbance slopes and slope ratios provide information about DOM sources and properties (Helms et al., 2008; Loiselle et al., 2009).

UV-254 is used to provide an indication of the aggregate concentration of UV-absorbing organic constituents, such as humic substances and various aromatic compounds (APHA, AWWA, WEF, 1995). The first surrogate parameter that utilizes to determine the organic matter in raw water is UV absorbance at a wavelength of 254 nm. Organic matter including humic aromatic compounds and molecules with conjugated double bonds can absorb UV light whereas the simple aliphatic acids, alcohol, and sugars do not absorb (Edzwald et al. 1985). Hence, the UV-254 absorbance can be used to indicate the presence of aromatic compounds of organic matter in natural water. Eaton (1995) found that the UV absorbance of organic matter in water is very useful to indicate the concentration of DOC and THMs in water because the humic substrates strongly absorb ultraviolet radiation.

5) **Specific Ultraviolet Absorption (SUVA)**

The specific violet absorption rate is a measure of the humic organic matter that is in the water, which can be calculated from the ultraviolet absorption at the 254 nm wavelength (in units per centimeter) divided by

Water soluble organic carbon (in milligrams per liter), sample water with low specific light absorption rate, consisting of non-humic organic matter and not suitable for This process coaxial regulator steep reduction in organic matter. For the sample water, the light absorption rate, high specific violet rate, can generally be used in the coagulation process to reduce organic matter well (USEPA, 1999).

6) **Fluorescence excitation-emission matrices (FEEM)**

FEEM is used as a technique to classify and differentiate between various types of humic compounds in nature (Chen et al., 2003). This technique is often used to classify different types of compounds such as differentiation of Humic compounds (humic acid, fulvic acid, including humin) or other components of natural organic substances (Hua et al., 2007). Excitation-Emission Matrices (EEM) techniques are derived from the scanning of both excitation wavelength and emission wavelength at the same time slowly. Several times, the data of the EEM technique is in the form of fluorescence contour plot Which is obtained from the point of measurement at the same wavelength and then connected to the terrain map Which can be used to differentiate the sample with many components from the same place But cannot directly identify the components of the sample from many places (Hertz and McGown, 1992). In addition, FEEM peak intensity can measure the characteristics of organic substances dissolved in both water and soil. And can also monitor changes in organic matter in natural water

2.5.4. Composition of natural organic substances

Natural organic substances in general water sources consist of hydroponic and hydrophilic. Depends on the size and characteristics of the compounds present in the water (Marthaba et al., 2003). The hydroponic group, which is a humic compound, is humic acid and fluvic acid. In the past, it was found that more than 50% of the natural hydroponic substances are Dissolve Organic Carbon: DOC which is caused by the decomposition of plant or animal matter. If the water has a DOC concentration greater than 5 mg / L,

the water in the water source will be colored. The composition of natural organic materials can be divided into 6 groups as shown in Table 1.

Table 1. *Composition of natural organic substances in general water sources (Swietlik et al., 2005)*

Sample	Parameter	
	$UV_{254}(cm^{-1})$	DOC (mg/l)
Humic Acids (HA)	0.321	5.81
Hydrophobic Acids (HOA)	0.162	4.81
Hydrophobic Neutrals (HON)	0.170	5.54
Hydrophilic Acids (HIA)	0.154	4.98
Hydrophilic Bases (HIB)	0.166	5.02
Hydrophilic Neutrals (HIN)	0.114	4.84

For dissolved organic matter in the surface water, there will be organic components as shown in Figure 3, while the hydrophilic group will have the size of the molecular weight cut-off. (MWCO) 300 to 3000 Darton contains carbohydrates Proteins and amino acids, etc.
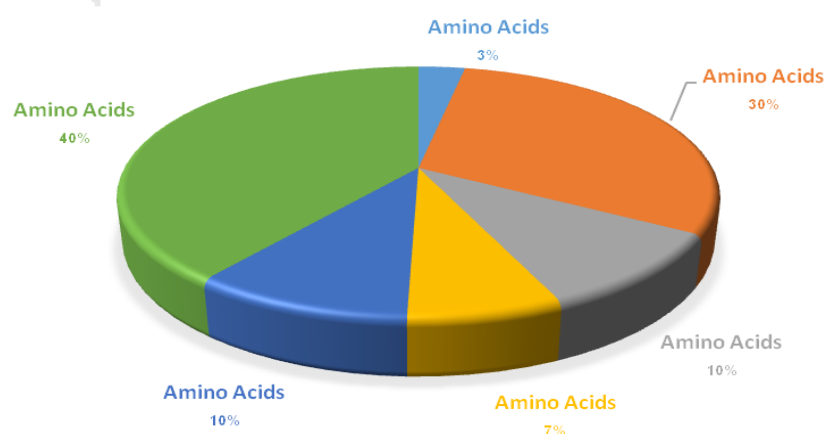
Figure 3. Organic elements in surface water

General dissolved organic components It was found that about 30% of hydrophilic acid is called "Hydrophilic Humic Substance". Humic compounds can be divided into 3 types:

1) Insoluble humic acid at pH equal to 1, with MWCO between 10-300 kDt.

2) Fulvic acid, water soluble, every pH has MWCO is between 3-100 kilowatts.

3) Insoluble humin (Swift, 1985) in which humic and fluic acids can be eliminated by the separation process.

Which in general, natural organic substances shown in Figure 4
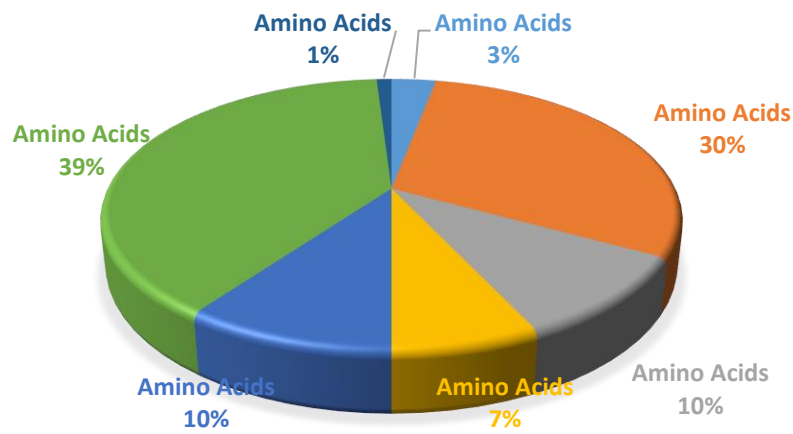
Figure 4 .Composition of common organic substances with DOC 5 mg/l

2.5.5. Classification of natural organic substances

In the removal of natural organic matter, it is important that we know the properties of the substances contained in the water in order to properly extract the homogeneous substances.

1) Particulate / Dissolve Organic Carbon Separation To separate particles from dissolved organic substances, can be separated by filter paper with a pore size of 0.45 microns, but filtration with filtered paper with a 0.45 micron pore size cannot eliminate the particles of Small soluble colloids or organic matter with particles smaller than 450 nm

2) Fluoric acid and humic acid humic acid can be precipitated at lower pH. 1.0 While fluoric acid remains in the water, every pH, fluoric acid dissolved in water is found more than humic acid (Rasyid et al., 1992).

3) Molecular size and weight, size and weight of particles are important to the characteristics of treated water, ie, affecting the diffusion coefficient and particle movement. Based on previous studies, it was found that 50-60% of

Fluid is larger than 10 kDa (Legube et al., 1990) and the molecular weight of fluvic is between 650-950 darton. The molecular weight of the humic is between 2,000-3,000 Darton.

4)   Hydrophilic / Hydrophobic Fractionation For hydrophilic substances that are dissolved in water (Cotsaris et al., 1988), it is found that about 58-74% of organic matter is dissolved in water, while hydroponic or hyaluronic acid Insecticides are insoluble substances.

2.6   Disinfection by-products (DBP)

The formation of DBPs depends on the quantity and characteristics of DOM. The factors for DBPs formation do not limit to the chlorination condition, the DOM concentration and characteristics is the one of the major factors (Gang et al., 2003; Zhang et al., 2009).

The increase in organic matter presents a challenge to utilities as chlorine, the most common disinfectant, reacts with a fraction of the DOM to form halogenated organic compounds, termed disinfection by-products (DBP), some of which are of health concern and regulated in many countries.(Katherine M. H. Beggs, R. Scott Summers, Diane M. McKnight, 2009).

Chlorine disinfection is generally required to prevent the potential transmission of pathogenic microorganisms in reclaimed water (USEPA, 2004).

Thus, the remaining organic matter in treated wastewater has a risk to human health when it faces with chlorine during disinfection process and produce DBPs. Chlorine is commonly used for disinfection of MBR effluent due to the low-cost (USEPA, 2004; Xia et al., 2016).

2.7   Trihalomethanes (THMs)

During chlorination, the chlorine reacts with DOM present in water. The reaction produces various DBP mainly trihalomethanes (THMs), haloacetic acids (HAAs) and haloacetonitriles (HANs) (Lim Fang Yee, Md. Pauzi Abdullah, Sadia Ata, Basar Ishak, 2006). Special concerns are associated with the trihalomethanes (THMs) because they have been recognized as potentially hazardous and are the major by-products of chlorination (Bull et al.,1995). In the case of THMs, EPA relied primarily on studies conducted by the National Cancer Institute (NCI) that

demonstrated the carcinogenicity of chloroform in both rats and mice (Joseph A. Cotruvo 1981).

Ma et al., (2013a) reported that total trihalomethane formation potential (THMFP) of the MBR treated municipal wastewater was high as 665 ug/L, which was high enough to be concerned for human health security.

2.8   Trihalomethane formation potential (THMFP)

The trihalomethane formation potential (THMFP) is influenced by the amount and chemical characteristics of the DOM present in the sample. THMFP was found to be directly related with dissolved organic carbon (DOC) content. However, when different source waters were compared, poor relationships between DOC and THMFP have been observed (EPA, 1981).

2.9   Effects of natural organic substances

2.9.1.   Produce by-products from disinfectants

Production of byproducts caused by the use of Disinfection by-products (DBPs) occurs during the reaction of chemicals used to kill germs such as chlorine and natural organic substances in the water. Produce the by-products from the use of disinfectants first detected in the year. 1974 From the introduction of chlorine-containing sample water, it was found that trihalomethane (Trihalomethanes; THMs) in the water in the process of producing tap water, chlorine is added to kill germs and when chlorine is left from the disinfection process. This group of chlorine will react with natural organic substances causing the trihalomethane (Rook, 1974). Later in 1975, the United States Environmental Protection Agency (USEPA) brought water samples from 80 The cities in the United States of America were examined for the presence of trihalomethane (Symons et al., 1975). In 1976, the National Cancer Institute found that chloroform found in tap water was a substance. Cancer and in 1979 the United Environmental Protection Agency America has issued a rule to control the amount of trihalomethane in drinking water to a maximum value of not more than 0.1 milligrams per liter at a time. Produce byproducts caused by the use of disinfectants such as Trihalomethane, halo acetic acid Chlorite and bromate are at levels that affect the human body. So,

in the year 1998 The United States Environmental Protection Agency has set a new standard of maximum contaminant level (MCL). In the first phase, the value of trihalomethane is set at 80 micrograms per liter and phase 2 is reduced. 40 micrograms per liter (USEPA, 1998)

2.9.2. Trihalomethanes (THMs)

Trihalomethane is a halogenated compound. (Organohalogen), which is called as part of methane the general structure of the formula is CHX_3. When X is an atom of a halogen element from a structural formula, there is 1 atom of hydrogen and the other 3 atoms are halogenated atoms, such as fluorine, chlorine, bromide, iodine, etc. The four types of trihalomethane consist of chloroform (Chloroform; CF), bromidochloromethane. (Bromodichloromethane; BDCM), dibromolomethane (Dibromochloromethane; DBCM) and bromoform (Bromoform; BF) The molecular formula name and structure of trihalomethane are shown in Table 2.

Table 2. *Molecular formula name and structure of trihalomethane*

Name	Molecular formula	Structure
Chloroform (CF) or Trichloromethane	$CHCl_3$	$$Cl-\underset{\underset{Cl}{\vert}}{\overset{\overset{Cl}{\vert}}{C}}-H$$
Bromodichloromethane (BDCM)	$CHBrCl_2$	$$Br-\underset{\underset{Cl}{\vert}}{\overset{\overset{Cl}{\vert}}{C}}-H$$
Dibromochloromethane (DBCM)	$CHBr_2Cl$	$$Cl-\underset{\underset{Br}{\vert}}{\overset{\overset{Br}{\vert}}{C}}-H$$
Bromoform (BF) หรือ Tribromomethane	$CHBr_3$	$$Br-\underset{\underset{Br}{\vert}}{\overset{\overset{Br}{\vert}}{C}}-H$$

Factors affecting the occurrence of trihalomethane can be shown as in Table 3

Table 3. Factors affecting the occurrence of trihalomethane

Factors	affecting the occurrence of trihalomethane1
1. The amount of organic water	The amount of trihalomethane produced will vary according to the amount of organic matter in the water.
2. Chlorine content	The reaction of chlorine and disinfectants will increase as the amount of chlorine increases.
3. Water temperature	When the water temperature is high, the reaction of trihalomethane causes faster.
4. pH of the water.	If the water has a high pH value, the reaction will occur faster. And pH is also related to changing the function of organic matter in water
5. Chlorine contact time	The amount of trihalomethane depends on the duration of chlorine contact time in the disinfection process.

The toxicity of trihalomethane in lab rats, which are animals with metabolic patterns similar to humans, were found to have LD50 (lethal dose 50%) as shown in Table 4. Is the amount of chemicals that are given to all experimental animals only once And causing 50% (half) of the experimental animals to die and the health effects of trihalomethane.

Table 4. *Toxicity of Trihalomethane*

	LD50 (mg / kg)	Health effects
Chloroform	908	- If exposed to vapors of this material for a long time or frequently exposed to chemicals may cause the central nervous system, heart, liver and kidneys to be destroyed. - The effect of contact with the liquid will cause fat to be destroyed May cause chronic skin irritation Causes dry skin and can cause dermatitis This chloroform is suspected to be carcinogenic to humans.
Bromodichloromethane	916	- affecting tumor and cancer in the liver and kidneys
Dibromolomethane	848	- affects the central nervous system Affecting the occurrence of tumors in the intestines, liver and kidneys
Bromoform	1,147	- prolonged or repeated skin contact will cause dermatitis, liver and kidneys, lungs - This substance is classified as a carcinogen of type B2 according to the list of EPA / IRIS and is a carcinogen of type 3 according to the IARC list.

Source (Pohanish, 2012)

2.10   Characteristics DOM

2.10.1. Resin fractionation

In order to further understand the role and chemistry of DOM in surface water, it is often necessary to fractionate DOM. A wide range of procedures has been used to fractionate DOM from surface water (Thurman, E.M. & Malcolm, K.L. ,1981.) (Spark & D.W. Page. ,1999.).   Various methods have been used to fractionate DOM from natural water. The ordinary methods are using the macroporous resins (Vance, G.F. & David, M.B. ,1991.), by ultrafiltration (Kainulainen, T., Tuhkanen, T., Varitianien, T., Heinonen, H. &Kalliokoski, P. ,1994.) and by gel filtration (Shaw, P.J., De Haan, H., & Jones, R.I. ,1994.) (Bruchet, A., Rousseau, C. &Mallevialle, J. ,1990.). Adsorption techniques utilizing various resins have been proven to be useful in the fractionation analysis (Leenheer, J.A. Croue, J.P., Benjamin, M., Korshin, G.V., Hwang, C.J., Bruchet, A., & Aiken G.R. ,2000.). An extraction protocol that utilizes sequential hydrophobic and ion exchange resin sorption steps has been developed that simultaneously extracts and concentrates DOM into hydrophobic acid (HPOA), hydrophobic base (HPOB), hydrophobic neutral (HPON), hydrophilic acid (HPIA), hydrophilic base (HPIB) and hydrophilic neutral (HPIN) fractions (Leenheer, J.A. ,1981).

Resin fractionation of dissolved organic materials (DOM) in water is a technique to concentrate and categorize the water organic complex into structurally more specific, physicochemically more analogous subgroups by retaining DOMs onto a series of types of resin followed by eluting with eluants. By applying this technique, DOMs of natural water can be characterized into hydrophobics, which mainly consist of fulvic and humic acids, and hydrophilics, which comprise of carbohydrates with low molecular weight, proteins and amino acids. Hydrophobics are more structurally aromatic than hydrophilics and more prone to conventional treatment. This technique has been widely applied to investigate various properties of DOM. It has been shown that it greatly facilitates subsequent studies associated with DOM, such as the formation of disinfection by-products (DBPs).

2.10.2. Fluorescence excitation and emission matrix (EEM) spectroscopy

Presently, Spectro fluorometry analysis (fluorescent excitation-emission matrix, FEEM) has been proposed by many researches as another promising technique for characterizing the organic compositions of DOM.

Fluorescence spectroscopy, which measures a subset of chromophoric compounds in natural waters, has been successful in measuring how the DOM character varies spatially and temporally, and may be useful in evaluating source waters for drinking water treatment (Katherine et al., 2009). Fluorescence excitation and emission matrix (EEM) spec-troscopy has been applied to identify and track terrestrial, marine and anthropogenic components of DOM (Coble,1996; Yan et al., 2000; Baker, 2001; Stedmon et al., 2003; Cory and McKnight , 2005).

The FEEM can be conducted by using fluorescent spectrometry (excitation and emission coordinate) and its simplicity with low amount of sample, minimal pretreatment and low analysis time requirement (Musikavong, 2006). The FEEM provides information on the putative origin of fluorescent organic matter in water; it may identify the matter as a tyrosine-like substance, tryptophan-like substance, humic and fulvic acid-like substance, and so on (Coble 1996; Nakajima *et al*. 2002; Chen *et al.* 2003; and Sierra *et al.* 2005).

2.11   Process for the removal of natural organic substances

In the removal of natural organic substances, the objective is to eliminate the color, odor and organic matter from the water. By the general process Which is commonly used to eliminate natural organic substances such as adsorption with activated carbon (nano-fusion) (Nanofiltration) and coagulation. At present, Ion Exchange Resin is used as a method to reduce the amount of natural organic materials before entering the chlorine disinfection system (Morran et al., 1996) or using the microfiltration process (Microfiltration) or ultrafiltration (Ultrafiltration) instead of disinfecting with chemicals

Qin et al. (2006) studied the removal of natural organic substances from reservoirs in Singapore by coagulation process by using alum to create sediment.

It was found that the concentration of alum 5 mg / L at pH Equal to 5.2, able to eliminate 45% of natural organic substances in the form of DOC and eliminate turbidity by 97%, while pH is equal to 7.2, can remove natural organic substances in the form of DOC by 35% for Leiknes et al. (2004). g Process of micro-filtration together with coagulation process in the production of drinking water to eliminate natural organic matter. It can reduce turbidity to less than 0.2 NTU. Eliminate more than 95% color. Eliminate UV254 85 % And eliminating the reduction of natural organic substances in the form of TOC about 65-75% when using poly-alumina chloride at a concentration of 5 mg / L as a coagulant and ultrasound flow through the membrane Membrane equal to 180 liters per evil hour

In addition, Siddiqui et al. (1997) studied the removal of natural organic substances with ozone in raw water from four sources: (1) Silver Lake (SLW) (2) Barker Lake (BLW) (3) Boulder Reservoir (BRW) and (4) The Colorado River (CRW) in the United States with DOC in the range of 2.8-7.0 is very high, passing through the 0.45 micron membrane. DOC is reduced by 40-50%, while Aldehyde decreases by 90-100% and tria. Lethane decreases by 40-60%, respectively. It is also found that the removal of natural organic materials by ion exchange using Cyclodextrin polyurethanes. Is an ion exchange device, effective in the removal of 6-33% natural soluble organic matter (Nkambule et al., 2009) and when using an ion exchange process with ozone, it can eliminate more than 88% of the natural soluble organic matter.

2.11.1   Air-degradation process

Air degradation process Is a biological wastewater treatment system that uses a group of bacteria that rely on dissolved oxygen or free oxygen to decompose organic matter into organic waste disposal. Organic matter is decomposed into carbon dioxide and there is a lot of microbial cell formation. (About 50 percent of organic matter in wastewater that is converted to microorganisms). Reaction to decomposition of organic matter by bacteria group that uses air (aerobic bacteria) can be classified   into 2 steps in the following order.

Step 1 is the process of bringing organic substances or nutrients into the cell, where the microorganism sends enzymes to decompose organic matter that adheres to the cell wall to change to form a small molecule that can absorb. Through the microbial cell as the equation

$$OHNS + O_2 + bacteria \rightarrow CO_2 + H_2O + NH_3 + Products + energy \tag{4.1}$$
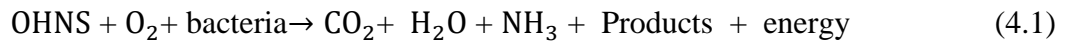
Step 2 is a biochemical process within microbial cells in order to produce energy for various activities and to create new cells.

$$CHONS + O_2 + energy + bacteria \rightarrow C_5H_7NO_2 \quad \text{(New bacterial cells)} \tag{4.2}$$
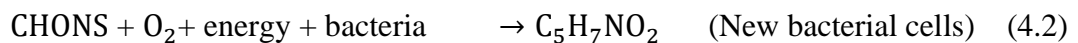
By writing in the form of the overall equation as follows

$$C_5H_7NO_2 \text{ (New bacterial cells)} + 5CO_2 \rightarrow 5CO_2 + 2H_2O + NH_3 + energy \tag{4.3}$$
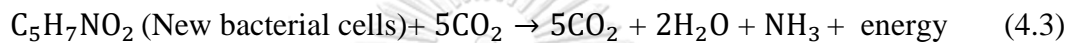
When organic substances in the wastewater are transformed into microorganisms, the new cells will form biological flocculation, which will result in more weight and easily separated from the wastewater by settling the air-wastewater treatment process. Can be classified into 2 main types:

1)   Suspended systems such as Aerobic Pond, Aerated Lagoon and Activated Sludge etc.

2)   fixed film systems such as Trickling Filter and Rotating Biological Contactor etc.

2.11.2. Factors affecting oxygen degradation

In biological treatment, the factor of decomposition is oxygen gas due to the microorganisms that decompose organic matter, need to use oxygen gas to decompose in order to get the product is a new microorganism, carbon dioxide and water. The amount of oxygen in the water is sufficient for microorganisms to be used to decompose organic matter in the wastewater. It can treat wastewater efficiently. The image can reduce the amount of waste water in the form of Biological demand oxygen by 80-95 percent by using the principle of microorganisms under the condition that there is oxygen with an aerator which in addition to acting Increasing oxygen in the water also causes the mixing of water, causing the decomposition of organic matter thoroughly.

In addition, the time value must be considered 2 times as the water retention time (Hydraulic Retention Time, HRT) and Solid Retention Time (SRT). Water retention time must be sufficient to produce metabolism in the cell. Has value in the hour level While the sludge age must be large enough to increase the amount of microorganisms in the day level The air treatment system uses less retention time, resulting in a smaller volume of the reaction tank, which helps to save construction space because the growth rate of microorganisms is faster. Making it faster to start the system (startup)

Oxygen removal systems must have an appropriate environment for the growth of important microorganisms. Important factors that affect Summarized as follows

1) pH is a pH value indicating pH value of 7 is considered neutral if less than 7 is considered acidic. And if more than 7 is considered alkaline Microorganisms grow well at pH values between 6.5 - 8.5. If the pH is less than 6.5 mold (Fungi) will grow better than microorganisms, resulting in lower efficiency and poor sedimentation. As for the pH value High will cause phosphorus to separate from the water (Precipitate) and microorganisms cannot be utilized. Makes the system work poorly as well but if the pH is very low or very high, the microorganism will die out, unable to continue to live

2) Temperature is an important factor in the work and growth of microorganisms in the process. Generally, increasing the temperature every 10 degrees Celsius will double the growth of microorganisms. Until the temperature is about 37 degrees Celsius. Then the temperature becomes too hot until the microorganisms grow less

3) Microbiological supplements need Nutrients, which are nitrogen, phosphorus and iron in addition to various organic substances. Which is used as normal energy These minerals are present in domestic wastewater but may not be enough in industrial wastewater. Lack of these important supplements Will cause the microorganisms that produce floppy grow poorly Until the filamentous microorganisms grow more Which makes it difficult to precipitate and causes a sluggish sediment layer in the tank And may overflow with water until the system cannot continue to work In addition, many microorganisms

grow poorly, resulting in lower system performance. Normally controlling 100 kilograms of BOD, 5 kg of nitrogen, 1 kg of phosphorus and 0.5 kg of iron

4) Oxygen dissolved in the air in the aeration tank must have dissolved oxygen values between 1 to 2 mg / l which the amount of air or oxygen used to maintain the concentration of this dissolved oxygen depends on The temperature, if the temperature is high, microorganisms can work a lot, they will need a lot of oxygen. In addition, at high temperatures, oxygen will have low solubility and therefore need to add more oxygen to the system. When the water temperature in the tank is high Similarly, if the water temperature is low, there is less demand for air at high temperatures. In order to maintain the level of dissolved oxygen concentrations equal

5) Proper agitation within the aeration tank must be thoroughly stirred to prevent sediment, sediment, microorganisms and to allow microorganisms to experience the wastewater sent into treatment by using food and reducing various pollutants. Including being able to catch himself as a good lock the correct agitation will prevent the water from flowing short-circuits and make the system effective in the removal of high pollutants. Completely mixed must have sediment solids (MLSS) and the dissolved oxygen concentration uniformly throughout the tank.

2.11.3. Nitrification

Previously, the nitrification process was beneficial to the industry because this process gave nitrates to gunpowder production. Until the end of the 19th century, this process became a necessity in the process of improving soil quality and played an important role in environmental technology. (Vandenabeele and Verstraete, 1989) Nitrification process is an oxidation process that occurs in biology. To change the nitrogen compounds in the form of ammonia into nitrates This reaction is caused by nitrifying microorganisms. It consists of 2 steps. The first step will change the ammonia into nitrite by the main Nitrosomonas microorganism. Nitrobacter microorganisms are shown as equations (4.4) to (4.6)

Nitrosomone:

$$2NH_4^+ + 3O_2 \rightarrow 2NO_2^- + 4H^+ 2H_2O \tag{4.4}$$

Nitro Backer:

$$2NO_2^- + O_2 \rightarrow 2NO_3^- \tag{4.5}$$

Total reactions:

$$NH_4^+ + 2O_2 \rightarrow NO_3^- + 2H^+ + H_2O \tag{4.6}$$
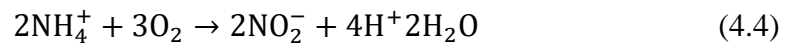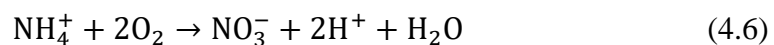
But some ammonium ions will be synthesized or created with new microbial cells as the equation (4.7) Microbial cell reaction:

$$4CO_2 + HCO_3^- + NH_4^+ + H_2O \rightarrow C_5H_7O_2N + 5O_2 \tag{4.7}$$
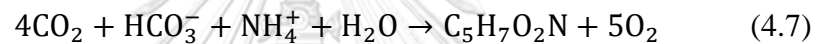
Total reactions of oxidation and microbial cell formation:

$$NH_4^+ + 1.83O_2 + 1.98HCO_3^- \rightarrow 0.021C_5H_7O_2N + 0.98NO_3^- + 1.041H_2O + 1.88H_2CO_3 \tag{4.8}$$

In the process of nitrification, it was found that in the first step, ammonia was transformed into nitrite by nitrosomes. The pH value will decrease as the hydrogen ion reaction occurs. Resulting in the growth of nitro batters Causing the growth of nitroglycerin to decrease or inhibit growth the reduction of nitrite into nitrates is therefore lower, causing the process of nitrification to decrease or slower than before. Therefore, it is necessary to control the pH level. To be suitable for microbial growth to complete the nitrification process Which the appropriate pH value for the work and the growth of microorganisms should be in the range of 7.2–8.0

2.11.4. Denitrification reaction

Although ammonium nitrogen is eliminated by nitrifying reactions, which reduces the effect of ammonia in wastewater that is already on the

water source, but the nitrate generated by the nitrification reaction is still delivered. The impact on water sources can cause carcinogens, Nitrosamines, or cause disease to infants who consume contaminated water called "Blue baby". Therefore, complete nitrogen removal is recognized. Want to get rid of nitrates, which caused the reaction nitrification applications by eliminating biological nitrate with 2-way

1)   Assimilatory Nitrate Reduction is caused by microorganisms in the treatment system using nitrates instead of ammonia in cell synthesis.

2)   Dissimilatory Nitrate Reduction, also known as "Denitrification" This nitrification reaction is a reduction reaction where nitrate with an oxidation number plus 5 is converted to nitrogen gas, which has an oxidation number of 0, with nitrite, nitrogen oxide and nitrogen dioxide as the substance that occurs between reaction

$$NO_3^- \rightarrow NO_2^- \rightarrow NO\ (g) \quad \rightarrow \quad N_2O \rightarrow N_2\ (g) \qquad (4.9)$$

The reaction takes place under conditions without oxygen. Which causes bacteria to use nitrate as the final electron receptor instead of oxygen. The bacteria that cause the reaction are called "Denitrifiers" or "Denitrifiying Bacteria", most of which are Heterotroph bacteria, using organic carbon as both energy sources and carbon sources. The condition that causes the reaction is called "Anoxic Condition"

2.11.5. Factors affecting the nitrifying reaction

1)   The type of carbon source or electron body There are many types of carbon source for bacteria that cause nitrite reaction. Which each type gives energy to different bacteria, causing the rate of occurrence of nitrifying reactions to be unequal as well

2)   The temperature from the previous study found that the nitrification reaction can occur in a wide temperature range and can also occur at high temperatures. Li (1988) research said that the optimum temperature for the nitrification reaction is 40 °C and can still occur at temperatures between 0 - 50 °C. Bitton's research (1994) found that the reaction can occur at a temperature of 35 - 50 °C and the reaction rate will be slower when the temperature is between 5 - 10

℃. The research of Henze and McGown (1996) states that the nitrification reaction can occur even at temperatures up to 50 - 60 ℃. The nitrate removal rate is higher at 35 ℃ to 50%. WEF (1998) said that the temperature range that makes D nitrification grow well is 5 –25 ℃.

3) dissolved oxygen in the system, which has both oxygen and nitrate as the last electron receptor The microorganism will use the oxygen in the system as the last electron receptor because it gives the energy to sustain microorganisms that are higher than the use of nitrates as the last electron receptor. Therefore, in systems that require nitrate removal, there should be no dissolved oxygen in the system at all. Because oxygen will use carbon sources for the reaction, resulting in more carbon source waste and reduced reaction rate (McCarty, 1969)

4) pH from the previous study found that the optimum pH value for nitrifying compounds is in the range of 6.0-9.0.

5) Other elements Bitton's research (1994) found that molybdenum (Mo) and selenium (Se) have an impact on enzymes responsible for the nitrification reaction.

2.12   Control of membrane bioreactor system

There will be an Aeration or Gas Scouring system which will fill the air to enter oxygen to the microorganisms to stir the liquids and sediments and to clean the membrane by causing shear, resulting in high flux and solid retention time (SRT) control. Of the sludge age in the system by adding SRT will increase MLSS and reduce the formation of sludge that needs to be pulled out but will cause clogging and cause poor oxygen transfer

Control of clogging for membrane bioreactor systems before treatment should use a feed pretreatment, such as using a trap to prevent clogging of the membrane or Use physical cleaning, such as the method of flushing, or using the release method together, or there may be a reduction in flux by the flow rate and movement characteristics of the feeder within the membrane. Which increases the flux and can reduce the occurrence of clogging or fouling. Due to the turbulent movement with high shear, the diffusion of particles at the

surface of the membrane has increased. Therefore, decreasing the volume (Thapanee, 2005) and increasing the aeration rate to allow the bubbles to distribute bubbles better to help reduce clogging, resulting in a higher flux. In addition, the liquid may be adjusted in the tank. In addition, the condition of the water membrane bioreactor tank is adjusted by flocculation process (coagulation / flocculation) by using alum and ferric chloride, which ferric chloride is more effective but more expensive or may be added to iron compounds to sub-sulphide-coated bacteria by membrane The ferric hydroxide is added to the absorbent by adding PAC (powder activated carbon) to allow the bacteria to bind and absorb organic matter. It helps to reduce the occurrence of clogging. In addition, zeolite and cationic polymer may be found. That is effective more (Chan Songkol, 2007)

- Control method for food-to-microbial ratio (F / M ratio method) Sludge of microorganisms that have working capacity must have adequate amount of food Which can be controlled by maintaining the ratio of the weight of the organic material delivered to treat the weight of the sludge which is measured in the form of Mixed liquor suspended solids (MLSS), Mixed liquor volatile suspended solids (MLVSS)to the desired value And call this control The food to microorganism ratio, F / M ratio can be written as the equation as follows:

-

Food to microbial ratio = <u>weight of organic substances that enter the system per day</u>
Microbial weight in aeration tank

= <u>The weight of the BOD entered (Kg per day)</u>
The weight of MLSS in aeration tank (kg)

= <u>Flow rate of wastewater (Min. Per day) x BOD (Mg per liter)</u>
Air tank volume (m3) x MLVSS (milligrams per liter)

In controlling the operation of the system using the F / M value, it can be seen that the food value (F) or the BOD value in the incoming water is less controllable. Therefore, the F / M value must be maintained by changing the weight of the microorganism (M) which is measured in the form of MLSS or MLVSS by increasing or decreasing the excess sludge. For example, if F / M is high, it means that M has the small amount must be reduced by removing the micro-sludge so that the M is higher and vice versa. If F / M is low, then the micro sludge must be added to reduce the M value.

- How to control the sludge age Sludge Age refers to the mean time that the microorganisms in the system (Mean cell residence time) are important in the design and control of the system. There is a direct relationship with the ratio of microorganisms (F / M) to the control of the sludge age to be constant to make the ratio of microorganisms or Organic Loading values are constant as well. Which these control values will determine the quality of waste. The control must find the appropriate sludge age by determining the relationship between the sludge age value and the quality of wastewater such as BOD, OOD and suspended sediment. And choose the value that is best seen from the definition of age, the sludge can be written as this equation.

Sludge Age   =   <u>weight of microorganisms in aeration tank</u>
                           The weight of microorganisms that leave the system per day

= <u>Volume of aerator tank (m3) x MLSS (kg / l)</u>
(Amount of sludge discharged (minus m / day) x The concentration of suspended solids (kg / l)) + (water discharge rate (m3 / day) x suspended solids concentration In the water out (kg / l)))

How to control the operation by using the sludge age is the best way. Because it controls the organic loading in the body and can calculate the value of the sludge that is dumped correctly. In addition, the method of control is simple and does not require complicated analysis. Table 5. shows the age of sludge during various work periods, which means controlling the sludge age, controlling the growth of microorganisms. And is the selection of the type of microorganisms in the system as well If lowering the sludge age to below 7-10 days will cause microorganisms that cause Nitrification Growing behind and leaving with excess sediment that is left behind Until making it impossible Nitrification

Table 5. Age of sludge at various work periods

Organic Loading	Sludge age, day
High rate	< 3
Conventional rate	5 - 15
Low rate	> 20

Controlling or changing the sludge age Can be done by adjusting the rate of excessive microbial sludge disposal If discarded, the sludge will decrease. And if disposing less, the sludge age will increase to adjust the age of each sludge, it takes about 1-3 times the sludge age. To allow the system to adjust to a constant state and must track the weight of the MLVSS used to treat wastewater and sludge, microorganisms that must be dumped every day Until the value does not change much

2.13   Factors affecting the operation of the membrane

2.13.1. Concentration Polarization

High concentration accumulation is the phenomenon of accumulation of organic matter or particles near the surface of the membrane until the concentration is higher than the average value of that substance in water

several times, causing the flux to be reduced by the water pressure. Reverse cleaning, chemical or filtration, parallel to cross flow, enough to allow flux to last longer. (Rattana, 1998)

2.13.2. pH and oxidizing temperature

The temperature increased by 1 degree Celsius, the flux will increase by 3 - 5%, but the organic membrane will often decompose by hydrolysis reaction which occurs slowly at temperatures below 30 degrees Celsius, pH 3 - 7. Good resistance to oxidizing substances such as chlorine, while inorganic membranes are not resistant to oxidizing substances but are resistant to pH in a wider range, ie 2 - 11 and the working temperature at a higher limit is 45 degrees. The euthanasia (Porntip and Supaluck, 2552).

2.13.3. Pressure

Increasing pressure increases the membrane flux and the water quality that is produced, but if the pressure exceeds the limit (Critical Pressure) will cause the structure and particles that accumulate on the surface of the surface. The membrane is compressed tightly so that the flux is reduced and may damage the internal structure of the membrane so that the water cannot be restored again (Thapanee, 2005).

2.13.4. Membrane dirt

As a result of the accumulation of organic matter and various dirt particles in the membrane gap holes, the permeability rate decreases, the operating pressure increases and cannot be restored to the new state by using pressure, water or chemicals, with the following factors involved.

1) The nature of the raw water that is used by the secondary membrane through the water that is very high with the membrane is usually a lot of organic additives, depending on whether the water that will be used as a secondary type of water. Each type of organic organism has different effects on pollutants according to the size, structure of the molecule, and the force between the membrane surface and itself when many organic substances are combined in the same solution or have The transport height would cause contamination over a single or low concentrations, respectively.

2)   Membrane material, including the size and distribution of holes, gap on the membrane also affects the rate of filth.

3)   Initial water adjustment such as removal of large suspended particles, organic substances, pH adjustment and temperature and oil removal, etc., can increase the permeability rate of the membrane and alleviate the problems of the system Longer working time (Chan Song Acid, 2007)

2.14   Advantages of the membrane process in biological reactor tanks

The most important advantage of this system is the quality of treated water because the system has the ability to treat biology and remove pathogens in water. Complete separation during hydraulic retention time (Hydraulic Retention Time: HRT) and Solid Retention Time (SRT) lead to appropriate and most cost-effective biological control and high stability in the use of sludge age control. It is an important point that can increase the number of microorganisms that grow slowly, such as Nitrifying bacteria. Higher biomass concentrations will lead to the ability of bioreactors more than conventional AS systems that use force separation. Gravity, because of this reason, the membrane bioreactor system is smaller. Membrane can maintain high molecular weight soluble substances. Biodegradation in reactor (Tanith Act, 2552).

The advantages of the membrane in the bioreactor compared to the traditional accelerator sludge system can be described as follows. (Chan Songkol, 2007)

1)   can completely eliminate suspended solids and the quality of treated water does not depend on the stability of the sediment

2)   Bacteria and viruses are eliminated by the membrane itself by the dynamic membrane properties.

3)   Microorganisms that grow slowly can be preserved in the reactor with a long sludge age.

4)   Microorganisms that can degrade special substances can grow and live.

5)   The greater the amount of MLSS, the higher the treatment capacity and the less excess sludge.

The disadvantage of the MBR system is that the system has higher operating costs than the general system.

1) The power that is used to pump perimeter out of the system

2) Energy used to fill the air

Chavalit (2003) reports the energy consumption of MBR systems used to treat wastewater from large offices to reuse water that requires energy from 3.0-5.5 kWh / m3. And comparing the energy consumption of the MBR system using various membrane plates, it was found that when the concentration of the suspended solids of the system increased, the electrical energy used in the treatment was also increased. More than 15,000 mg / l. The energy required for pipe-type membranes is 2.5-3.5 kWh / m3 And equal to 1.0-2.0 kWh / m3 For hollow fiber membranes and sheets and when the concentration is increased to 25,000 mg / l, energy consumption of 3.0 kWh / m3 for hollow fiber membranes and sheets (Energy that is used specifically for filtering and aeration)

2.15   Control variables

What should be considered in the membrane process in the bioreactor is

1) Separated liquids due to a mixed system containing microorganisms, organic molecules with a variety of molecules and inorganic substances

2) The characteristics of the mix will change over time due to the consumption activity of microorganisms.

3) The water that passes through the membrane should be of quality because the water is filtered through the membrane. Therefore, the membrane is treated with water.

The control parameters of the membrane process are the operating conditions (such as filter pressure), crossflow velocity, and biological treatment conditions. (Such as the concentration of microorganisms), the characteristics of the ingredients in the wastewater, especially the concentration of the soluble microorganisms that form into the surface coating layer of the membrane

Transmembrane pressure is the driving force of the filtering process as the equation can be used to predict the flow that is proportional to the resistance for the hydraulic system. The flux membrane represents the amount of material passing through the area. The unit of membrane per unit of time

and can analyze the driving force on the membrane surface and the resistance to the flow of the membrane.

$$J = \frac{\Delta P}{\mu(R_{m+}R_f+R_c)}$$ (4.10)

J: Perimeter flux (L / m^2.H)

ΔP: Pressure difference (kPa)

μ: Viscosity of Perry (Pa.s);when Pa = N / m^2

R_m: the resistance of the membrane Rc: Resistance to fouling from the cake formation (reversible fouling)

R_f: Resistance to the formation of fouling in the case of the solution being absorbed into the porous membrane (irreversible fouling)

This equation shows that the difference in the variables influencing hydraulic resistance: Rm is the characteristic of the membrane, which depends on the specific characteristics of each membrane. Resistance sheet with permanent blockage (Irreversible fouling resistance: Rf) which is the result of increased resistance to filtration and can be caused by many reasons related to the porosity of the resistance membrane of the Rc. The result of the relationship of concentration and residues of suspended solids and hydraulic conditions (Chan Songkol, 2009; Pornthip and Supaluck, 2009)

2.16   Microbial growth equations in the system

The increased amount of sludge is an indicator that the microorganisms are growing in the system. Which can be expressed in the form of mathematical equations (Metcalf and Eddy, 1991)

$$\mu = \frac{\mu_m s}{K_s+s}$$ (4.11)

μ = specific growth rate of microorganisms (Mg per mg. Day)

μ_m = Maximum growth rate of microorganisms (Mg per mg. Day)

s = concentration of organic substances in the system (Mg per liter)

K_s = the concentration of organic substances in the system at the point of 0.5 micrometers (mg per liter)

Mean Cell Residence Time or Sludge Age, θ_x is the period in which the sludge is in the system. But how long it will take depends on the removal of the sludge from the system. The θ_x equation from the dumping of the sludge from the tank in the sediment system accelerates as

$$\theta_x = \frac{VX}{X_w Q_w + (Q - Q_w)X_e} \tag{4.12}$$

θ_X = Age of sludge (day)

X = concentration of the sludge that needs to be controlled in the system is usually used (MLVSS) (mg per liter MLSSS)

X_w = the concentration of sludge contained in the system (Milllarum per liter, MLS)

V = volume of aeration tank (cubic meter)

Q_w = The amount of sludge needed to be discarded (Cubic meters per day)

Q = rate of inflow of wastewater (Cubic meters per day)

X_e = The concentration of the sludge that flows away from the effluent   that flows from the second sedimentation tank. (Mg per liter TSS)

For the membrane bioreactor system, $X_e = 0$ and if $X_w = X$ can find the amount of sludge that needs to be dumped as the equation is

$$Q_w = \frac{V}{\theta_x} \tag{4.13}$$

In choosing the sludge age depends on the degradation of the organic matter of the wastewater. From the relationship between the number of microorganisms and the degradation of organic matter in wastewater, the following equations are obtained.

$$Y_{obs} = \frac{Y}{1 + k_e \theta_x} + \frac{f_d k_e Y \theta_x}{1 + k_e \theta_x} \tag{4.14}$$

Y_{obs} = Observed Yield

Y = mass of cells created / mass of food being eaten (G.VSS per G.BOD)

k_e = Death rate constant = 0.040-0.075 days$^{(-1)}$ for general sludge activation systems and 0.050-0.32 days$^{(-1)}$ for general membrane bioreactor systems

θ_x = age of sludge (days$^{(-1)}$)

f_d = Proportion of microorganisms that are cell debris = 0.1-0.15 grams VSS / g Substrate

In the bioreactor system, the membrane can control the sludge age so that the yield is low until there is no need to pull out the sludge.

2.17 Literature review

Ueda et al., (1997) studied the effects of aeration and the use of suction pressure on sludge removal. By using a bioreactor system model with a submerged membrane, It was found that aeration is an important factor controlling the filter conditions. By considering the air flow when the air flows at speed and has a relatively high flow rate will cause turbulence in the membrane reactor. This agitation will increase the efficiency of the cake removal. The membrane permeability rate will increase and use less suction pressure. From the results of the experiment, it can be concluded that to get rid of the cake for good performance Should do one of the following. 1) Increase the air flow rate (speed and wind strength) 2) Increase the density of the air flow rate per area (control the tank volume appropriately)

Galil et al., (2003) conducted a study to improve the existing sewage treatment system in paper mills. With the need to separate solids from wastewater Therefore, the study and experiment to use the membrane bioreactor system to compare with the existing Attitude Sludge system. During the 90 day processing period after the system is in a stable state The results obtained from the study can be concluded that the membrane bioreactor system Can effectively treat suspended solids contained in wastewater Which is clearly better than the Attila Sludge system The suspended solids value of the treated water of the membrane bioreactor system was 2.5 milligrams per liter. While the suspended solids of the Athlete Sludge system were measured at 37 milligrams per liter. In addition, when comparing the COD values of both systems, which are 129 and 204 milligrams per liter and the BOD 7.1 and 83 milligrams per liter respectively. It was found that the membrane bioreactor system was more efficient in treating wastewater. Therefore, able to meet the need to separate solids from the wastewater of the factory very well

Zheng et al., (2006) conducted a study on the use of membrane bioreactor for treating wastewater from dyeing and printing processes of wool factories without the use of chemicals to assist in the treatment for a period of time. 135 days. The results showed that the water quality after treatment has passed the standards used in China. The average concentration of COD = 36.9 milligrams per liter, BOD 5 = 3.7 milligrams per liter, turbidity = 0.2 NTU and the color value = 21 dilution times (DT). The average COD removal rate = 80.3. %, BOD 5 = 95.0%, turbidity = 99.3% and color = 58.7%, where the flux of the membrane will increase according to the density and pressure of the aeration of the system Statistical analysis shows that the pressure from the aeration increases at the acceptable level of the membrane, in addition to providing sufficient air to the system. Also causes shear force on the surface of the membrane Makes the membrane not easily clogged and the flux obtained is high and satisfactory

Shane et al., (2006) conducted a wastewater treatment experiment from the community by using a submerged membrane bioreactor with a membrane model. Ultrafiltration, pore size 0.035 microns and with a constant membrane flux value of 30 liters per square meter per hour. By controlling sediment aging (SRT) at different values, 10, 5, 4, 3 and 2 days and the ratio of food to microbes or F / M is 0.34, 0.55, 0.73, 0.84 and 1.41 grams. ODS per gram VSS per day respectively. The results show that the system can remove COD effectively (COD in 345 mg / L, COD out 23-34 mg / L). The total suspended solids values can be measured to standards (less than 2 Milligrams per liter) and found that the fouling rate of the membrane increases with the increasing F / M. At the steady state of the system, the foaming value increases to 20. Times the default and more than four times the F / M ratio. The rising rate of fouling is related to the concentration of the products obtained from microbes or Soluble Microbial Products (SMP). And affects the COD removal of the system as the membrane is unable to filter the soluble COD

Lerner et al., (2007) conducted a study on the efficiency of wastewater treatment with the Activated Sludge Wastewater Treatment System of an existing paper mill. Compare with the membrane bioreactor system. The results show that the membrane bioreactor system can treat suspended solids better than the Attitude

Sludge system. In which the suspended solids were measured less than 1 milligrams per liter While the Attitude Diet Salad System measures 12 milligrams per liter. While other parameters such as COD, BOD, nitrogen, phosphorus or ammonia Not different until significant

Yigit et al., (2009) conducted a study on the treatment of highly concentrated wastewater from the fabrication process of a denim fabrication factory using a submerged membrane bioreactor system model. By requiring aeration of the system at all times and a continuous flow rate of wastewater for a period of 3 months, with the system being operated in two different stages: 1) no emptying of the sediment at all System operation And set the flux constant to 20 liters per square meter per hour. 2) Set the SRT value to 25 days with the same flux as the first. From the experimental results, it was found that during the operating period Even with a high number of suspended solids but the efficiency of wastewater treatment of the system is still good. Not affected by the change in the F / M ratio, the load rate for

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CHAPTER 3

METHODOLOGY

3.1 Synthetic textile wastewater

The synthetic textile wastewater used in the study was prepared from direct dye as shown in Figure 5. The method for synthesis was followed the recommend method of commercial color by dissolved 15 grams of dye in the 20 liters of distilled water. The final concentration of dye in synthetic textile wastewater was 750 mg/l. However, the membrane bioreactor system is a microbial working system to decompose organic matter. Therefore, the addition nutrients were added for microorganism growth. The nutrient added was followed by the study of Sahinkaya (2013) and Yurtsever (2017). The list of nutrients that added to the system are shown in Table 6.

Table 6. *Concentration of ingredients in the synthetic textile wastewater (adapted from Sahinkaya,2013 and Yurtsever,2017).*

Chemical	Chemical formula	Concentration (mg/l)
Starch	$C_6H_{10}O_5$	1000
Acetic acid	CH_3COOH	200
Sucrose	$C_{12}H_{22}O_{11}$	600
Sodium Hydroxide	$NaOH$	500
Sulfuric acid	H_2SO_4	300
Sodium Carbonate	Na_2CO_3	500
Sodium Chloride	$NaCl$	300
SLS (Sodium Lauryl Sulphate)		100

Figure 5. Direct dye

3.2   Equipment

3.2.1) Feed tank volume 10 liters for stored synthetic textile wastewater before feed into the membrane bioreactor system

3.2.2) Solenoid-Driven Beta® water pump, as shown in Figure 6, with a pumping range of 0.74-32 liters per hour for pumping water into the membrane bioreactor tank.

Figure 6. Solenoid-Driven Beta®

3.2.3) MBR reactor was made of clear acrylic with size 0.25 * 0.25 * 0.5 meters^3 with a 0.01 micrometer pore size of polytetrafluoroethylene (PTFE) or Teflon hollow fiber ultra-filtration membrane as shown in Figure 7.

Figure 7. *MBR tank and hollow fiber ultra-filtration membrane*

3.2.4) Air pump as shown in Figure 8. was used to supply the oxygen in the MBR for microbial growth.

Figure 8. *Air pump*

3.2.5) The float switch as shown in Figure 9. was used to controls the water level in the membrane bioreactor.

Figure 9. *The float switch*

3.2.6) Masterflex® L / S® pumps as shown in Figure 10. was used to pumping treated water from the membrane bioreactor.

Figure 10. Masterflex® L/S®

3.3 Membrane bioreactor (MBR)

The diagram of MBR is illustrated in Figure 11. The synthetic textile wastewater was contained in 10 liters of feed tank. Then, the synthetic wastewater was pumped into the membrane bioreactor tank which operate under aerobic condition with a 0.01 microns of hollow-fiber ultrafiltration membrane. The operating condition was varied SRT at 15 days, 30 days and infinity, respectively. At SRT 15 days and 30 days, the system was controlled by remove sludge from the aeration reactor about 1 and 0.5 liter per day, respectively. About 1 liter Treated water was sucked pass through membrane by Masterflex® L/S® Series Peristaltic Pump. Treated water was collected and analyzed for various parameters. Treated water from the MBR system was pumped through the membrane in a volume of 1 liter per time, 3 days a week in order to maintain the nutrients in the sludge, it has to be maintained in the system for a while until become stable. The used membrane in MBR was clean with chlorine as shown in Figure 14, by soaked with chlorine concentration 66 grams per liter for 2 days and soaked in clean water for 3 days. The membrane cleaning was conducted once a week.
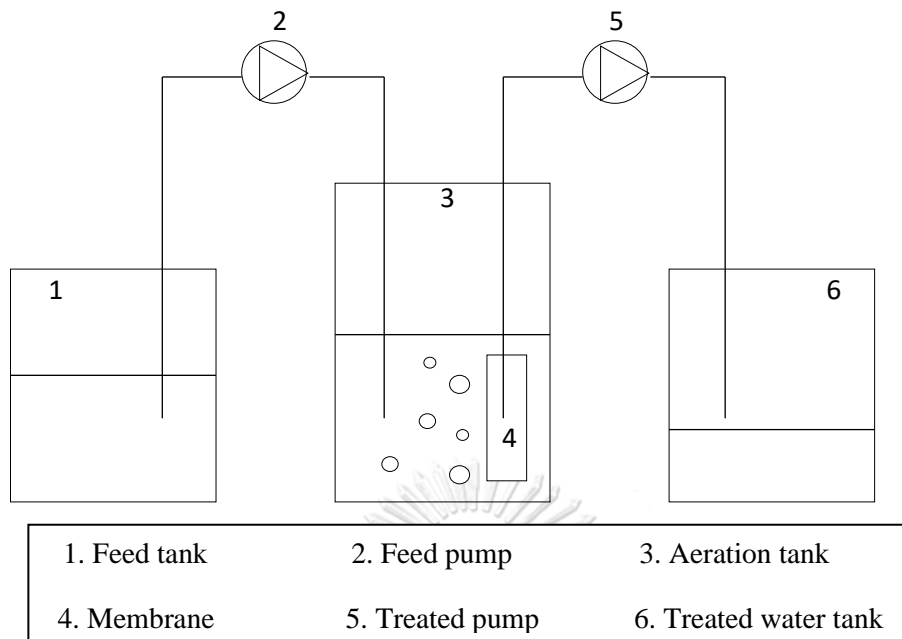
Figure 11. Diagram of MBR system
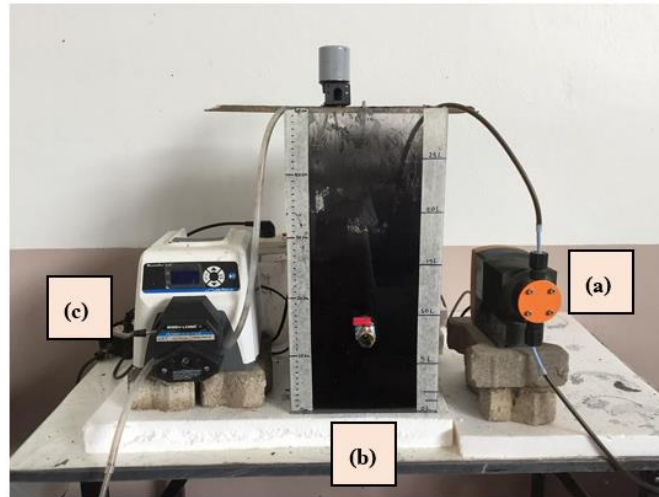
Figure 12. Membrane Bioreactor system
(a) *feed pump,* (b) *aerobic tank,* (c) *treated pump*

Figure 13. Chemicals used to clean the membrane

(a) Membrane before cleaning   *(b) Membrane after cleaning*

Figure 14. Before and after cleaning the membrane

3.5   Seed sludge

Seed sludge used to start up the MBR process was collected from the aerator tank of Chiang Mai University wastewater treatment plant, 110 Intrawarr Road, Sri Phum, Muang, Chiang Mai. Seed sludge was collected two times. First, it was collected on July 2018 and used for startup MBR at SRT infinity. The concentration of MLSS and MLVSS were 2,096 mg/l and 1,466 mg/l, respectively. Second, it was collected on October 2018 and used for startup MBR at SRT 15 days and 30 days. The concentration of MLSS and MLVSS were 1,773 mg/l and 1,173 mg/l, respectively.

Figure 15. *Seed sludge used in experiments*

3.6   Experimental diagram

The experimental diagram of this study is shown in Figure 16. First, synthetic textile wastewater was prepared. Then, the characteristics of synthetic textile wastewater was measured including COD, MLSS, MLVSS, pH, Color, TOC, and THMFP. Next, the MBR was startup by adding seed sludge and synthetic textile wastewater. MBR experiment was conducted by varying SRT and fix the volume of water in aerobic tank at 15 liters. The MBR process was operated until it reaches the steady state. The treated water was collected and analyzed for COD, MLSS, MLVSS, pH, Color, TOC, and THMFP. Moreover, the DOM characterization was investigated by using FEEM and resin fractionation.

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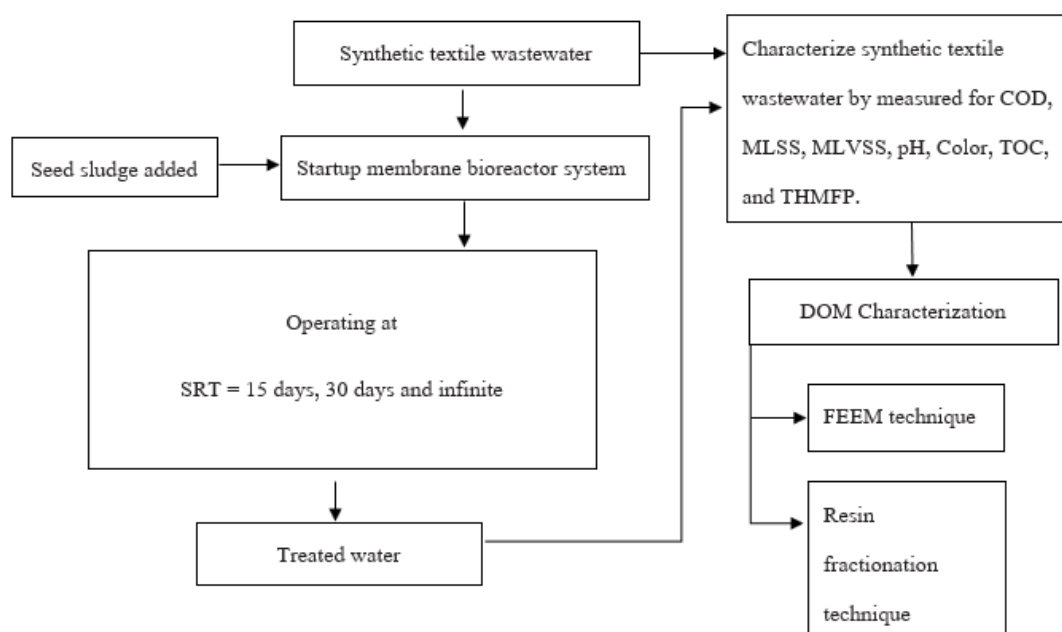
Figure 16. *Experimental diagram.*

3.7 DOM Characterization

3.7.1. Resin fractionation

DOM in raw water sample and treated water from MBR was fractionated by using resin fractionation method. The resin fractionation was conducted with DAX-8 resin to separate DOM into hydrophilic (HPI) and hydrophobic (HPO) fraction. Water sample was filtered through a pre-combusted (550°C) GF/F 0.7 μm filter before fractionation.

Resin adsorption procedure was employed to fractionate three liters of water sample into two organic fractions by using a series of DAX-8 resin (Leenheer, 1981). First, water sample was acidified to pH 2 and pass through the column which containing DAX-8 resin with a flow rate of less than 12 BV/h (0.33 ml/s). The effluent water from DAX-8 resin column was contained the HPI fraction. While the HPO fraction was adsorbed on the DAX-8 resin which can be eluted from resin by using 0.1 N of NaOH (5 BV or 50 ml) and 0.01 N of NaOH (25 BV or 250 ml), respectively with flow rate of less than 2 BV/h (3.3 ml/min). Fractionated samples of each fraction were adjusted pH to 7 and filtrated with 0.45 μm GF/C filter paper

before analyzed for their organic fractions in term of DOC. The diagram of resin fractionation is shown in Figure 17.
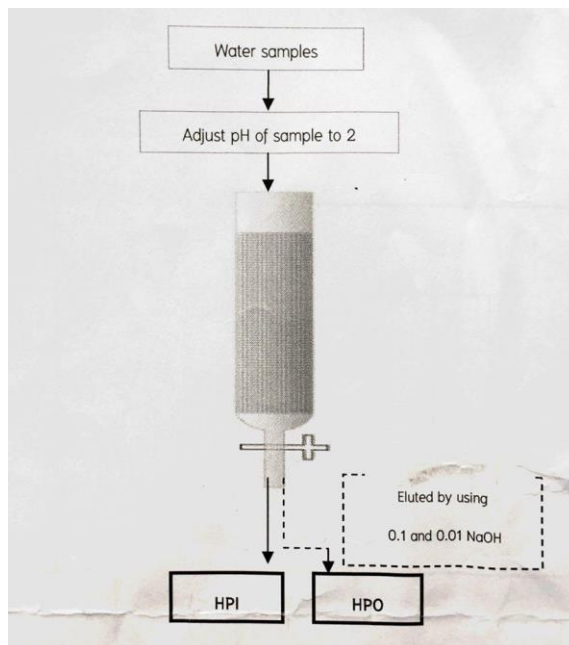
Figure 17. Diagram of resin fractionation method

3.7.2. Fluorescence excitation and emission matrix (EEM) spec-troscopy

All the three-dimensional EEM spectra was measured using a luminescence spectrometry (F-4500 FL spectrophotometer, Hitachi, Japan). EEM spectra are a collection of a series of emission spectra over a range of excitation wavelengths, which can be used to identify the fluorescent compounds present in complex mixtures.

In this study, influent and effluent wastewater of MBR were adjusted pH to 7 ± 0.2 and analyzed for DOM characteristics by spectrofluorometer. Influent wastewater was filtered through a pre-combusted (550 °C for 2 h) Whatman GF/F (nominal pore size 0.7 μm). In case of DOM fractions, concentrated HPO from resin fractionation process was with Milli-Q water to their original DOCs which calculated by using the mass balance from the resin fractionation results. A JASCO FP-6200 spectrofluorometer was used to measure Fluorescent excitation-emission wavelengths, FEEM of all water samples in this study using the proposed operated condition of Musikavong, 2006.

3.8   Analytical methods

The analytical methods for various parameters are shown in Table 7

Table 7. Analytical method for parameter measurement

Parameters	Analytical method
COD	Open Reflux Method
DOC	Standard Method 5310 section C, Persulfate-Ultraviolet Oxidation Method, aj-Analyzer multi N/C 3100; multiWin 4.09
THMFP	Standard Method 5710B, Agilent Gas Chromatography-6890 with an electron capture detector (ECD)
pH	pH meter Horiba LAQUA F-71
MLSS	Total Suspended Solid Dried at 103-105°C
MLVSS	Fixed and volatile Solids Ignited at 550°C
Color	American Dye Manufacturers Institute (ADMI)

3.8.1. COD Measurement

Open Reflux Method suitable for analyzing COD values in various wastewater samples by using a large sample of water samples, reduce sampling errors. And sample pipettes (Use an analysis sample of about 50 ml). Metals are also used in many reactions, such as Silver Sulfate, Ag_2SO_4 and Mercuric Sulfate; $HgSO_4$ (Phitoon, 2012).

3.8.2. DOM Measurement

Normally, the quantity of DOM can be evaluated by measuring DOM surrogate parameters including dissolved organic carbon (DOC), UV absorbance at wavelength 254 nm (UV-254) and trihalomethane formation potential (THMFP).

3.8.2.1. Dissolved organic carbon (DOC)

Standard Method 5310 section C, Persulfate-Ultraviolet Oxidation Method will be selected to measure DOC in water sample in form of total organic carbon (TOC). This experimental use aj-Analyzer multi N/C 3100; multiWin 4.09 for TOC measurement. Firstly, filter sample and a reagent water blank through 0.45-µm filter. To determine nonpurgeable organic carbon, transfer 15 to 30 mL sample to a flask or test tube and acidify to a pH of 2. Next, check efficiency of inorganic carbon removal for each sample matrix by splitting a sample into two portions; to one of the portions, add inorganic carbon to a level like that of the sample. The TOC values should agree. Then, sample injection and prepare an organic carbon standard series over the range of organic carbon concentrations in the samples.

3.8.2.2. Trihalomethane formation potential (THMFP)

THMFP measurements will be conducted according to Standard Method 5710B. The phosphate solution will be used as buffer solution before incubation at 25 $\pm$ 2 ˚C in amber bottles with PTFE liners. At the end of 24-hour reaction period, the remaining free chlorine in water samples should between 3 to 5 mg/L. The residual chlorine will be measured according to the Standard Method 4500-Cl G. The chlorine concentration will be represented by the light absorbance at 515 nm using a spectrophotometer with matched quartz cells that provided a path length 10 mm. THMs will be extracted with pentane in accordance with Standard Method 6232B. Agilent Gas Chromatography-6890 with an electron capture detector (ECD) will be utilized for measure THMs in water samples under the operating conditions. THMFP analysis will be conducted with two replications for each samples and Milli-Q water will be used for dilutions, chemical preparation and final glassware cleaning.

CHAPTER 4

RESULTS AND DISCUSSION

Membrane bioreactor was conducted with varied sludge retention time (SRT) at 15 days, 30 days and infinity. The synthesis textile wastewater and treated water were collected and analyzed for various parameters. In addition, the DOM characteristic was investigated. The obtained results were illustrated in this chapter.

4.1 Synthesis textile wastewater characteristics

In this experiment, synthesis textile wastewater was used as raw wastewater. The characteristics of raw wastewater were investigated. The results are shown in Table 8.

Table 8. Characteristics of raw wastewater

Parameter	Concentration	Average ± Standard deviation	unit
DOC	400 – 500	466.1 ± 7.6	mg/l
COD	1,633 – 2,122	1,867 ± 174.1	mg/l
VSS	105 – 263	248 ± 68.5	mg/l
SS	133 – 282	266 ± 64.2	mg/l
Color (pH= 8-9)	5,720 – 11,205	9,378 ± 2,054	ADMI
Color (pH= 7)	6,120 – 10,760	9,497 ± 1,626	ADMI
pH	8.49 – 9.23	9.12 ± 0.31	

From Table 4.1, the average COD concentration in raw wastewater was 1,867 mg/L which higher than the wastewater standard. In the study of Adem Yurtsever (2017) claim that the feed COD concentration was 2000 mg/L. The MBR reduced COD of mixed textile wastewater from 1380–6033 to 130–900 mg/l (Brik et al., 2006). Furthermore, the research about synthetic textile wastewater by Serkan Sahinkaya (2013) reported that COD of the synthetic wastewater before treatment was 2575 mg/L. In addition, the color of raw wastewater was higher than 5,000 ADMI

which higher than the wastewater standard (<300 ADMI). On the other hand, the average ADMI value was 1956 ADMI (De Jager et al., 2014).

Dissolved organic carbon (DOC) which represented the organic matter content showed that the raw wastewater was contained high DOC concentration at 466.1 mg/L. The result from the analysis presence average concentrations of DOC in domestic wastewater was approximately 70 mg/l (Katsoyiannis et al., 2007). The influent wastewater from the central wastewater treatment plant of the Northern-Region Industrial Estate have value of DOC at 10.3 mg/l (Water sample was collected in June 24, 2004). Thus, DOC in textile wastewater has higher concentration than domestic wastewater, hence; the wastewater treatment process of textile wastewater is necessary before discharge into natural water resources.

4.2 Membrane Bioreactor experiment

The membrane bioreactor was conducted with different SRT at 15 days, 30 days and infinity. The experiment was run continuous until it reaches the steady state. The organic matter removal efficiency by MRT at different SRT was investigated. The measured parameters along the experiment was separately explain in the following section.

4.2.1. MLSS and MLVSS

MLSS and MLVSS was measured in MBR reactor. The MLVSS was represented the bacteria community in the MBR reactor. The results of average MLSS and MLVSS are shown in Table 9. And 10., respectively.

Table 9. Average Mixed liquor suspended solids (MLSS)

SRT	Average ± Standard deviation (mg/L)	
	Aerobic	**Permeate**
Infinite	2,350.58 ± 1,037.80	21.25 ± 22.07
30 days	1,740.46 ± 408.87	11.40 ± 5.86
15 days	2,442.69 ± 547.99	7.57 ± 4.34

From Table 9, the average MLSS in reactor at steady state was fluctuation depend on the SRT. From the experimental, the concentration of MLSS before treatment has high concentration at all SRT. After pass membrane, MLSS in permeate water were reduced to 7.57-21.25 mg/L at all SRT. It can be concluded that the MBR was high efficiency to reduce MLSS in aeration tank. On the other hands, MLSS in aeration tank at all SRT tends to increase with longer operation period as shown in Figure 18. to 20.
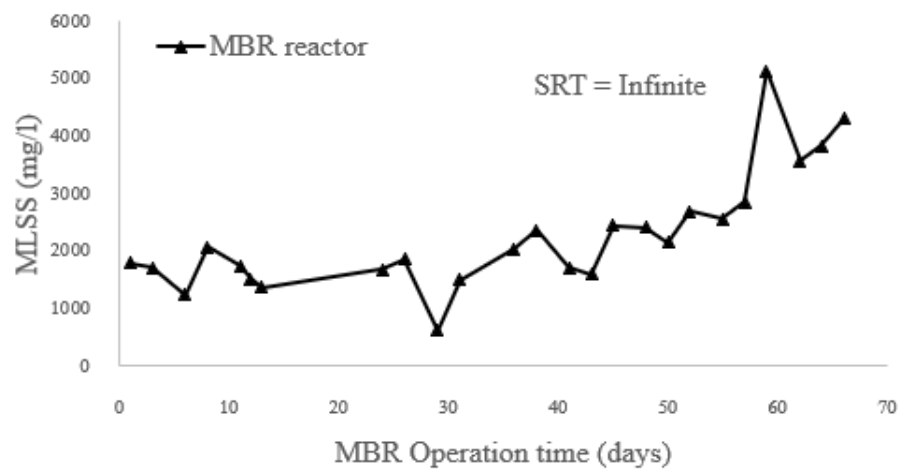
Figure 18. MLSS at SRT infinite
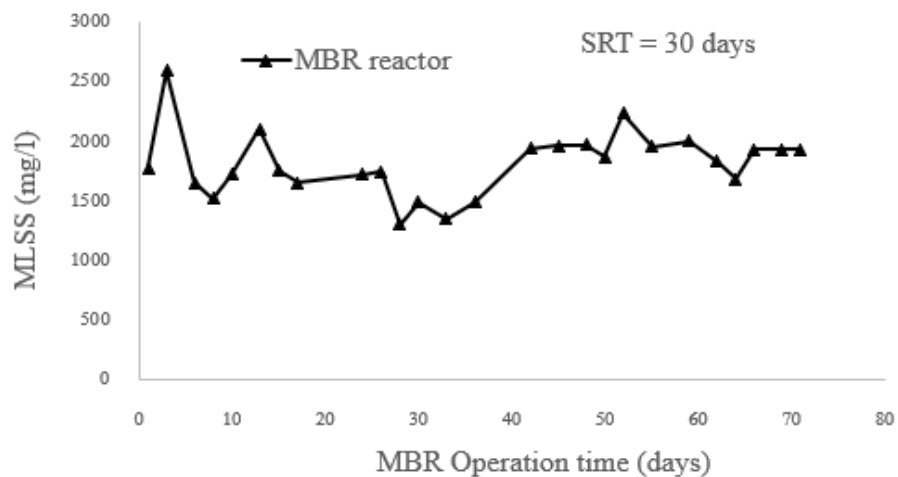
Figure 19. MLSS at SRT 30 days
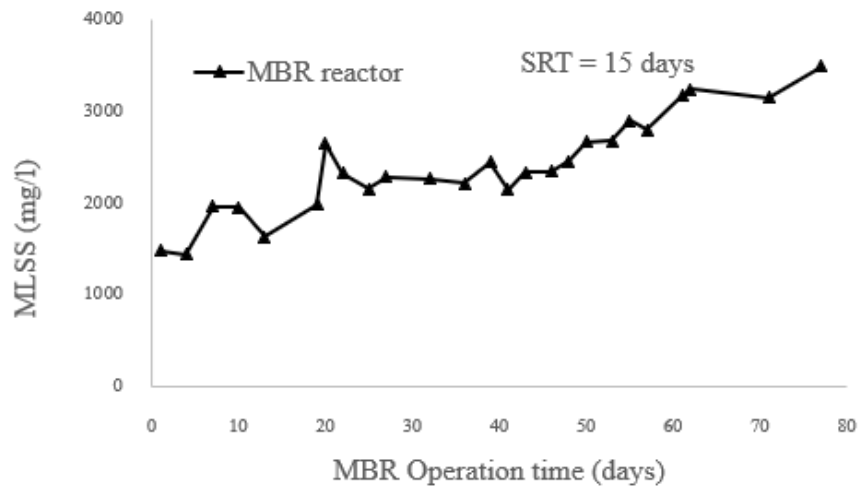
Figure 20. MLSS at SRT 15 days

The average MLVSS which represent the amount of microorganism in aeration tank and permeate water are shown in Table 10. and MLVSS at different operating times of all SRT are illustrated in Figure 21-23.

Table 10. Average Mixed liquor volatile suspended solids (MLVSS)

SRT	Average± Standard deviation (mg/L)	
	MBR reactor	Treated water
Infinite	1,556.80 ± 673.24	41 ± 149.76
30 days	1,154.8 ± 286.90	2.2 ± 2.36
15 days	1,744.23 ± 407.72	4.04 ± 2.58
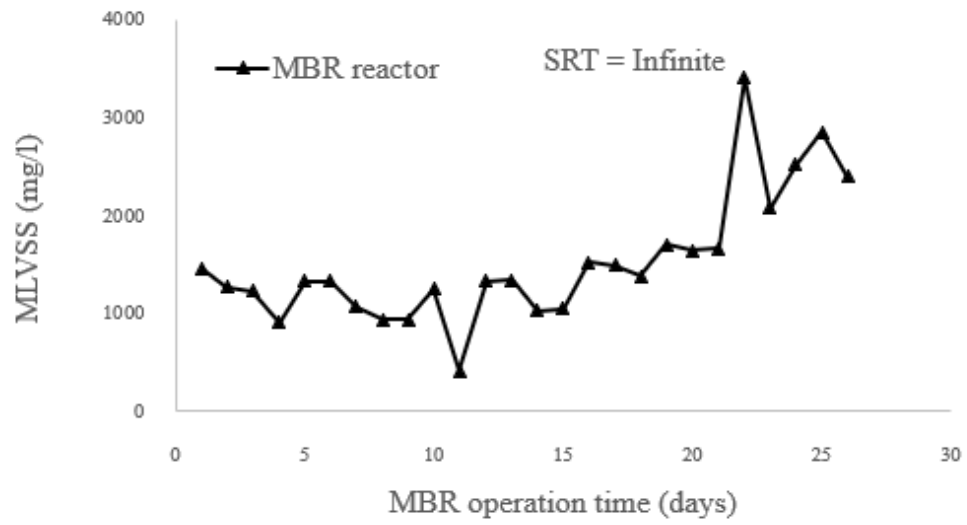
Figure 21. MLVSS at SRT infinite
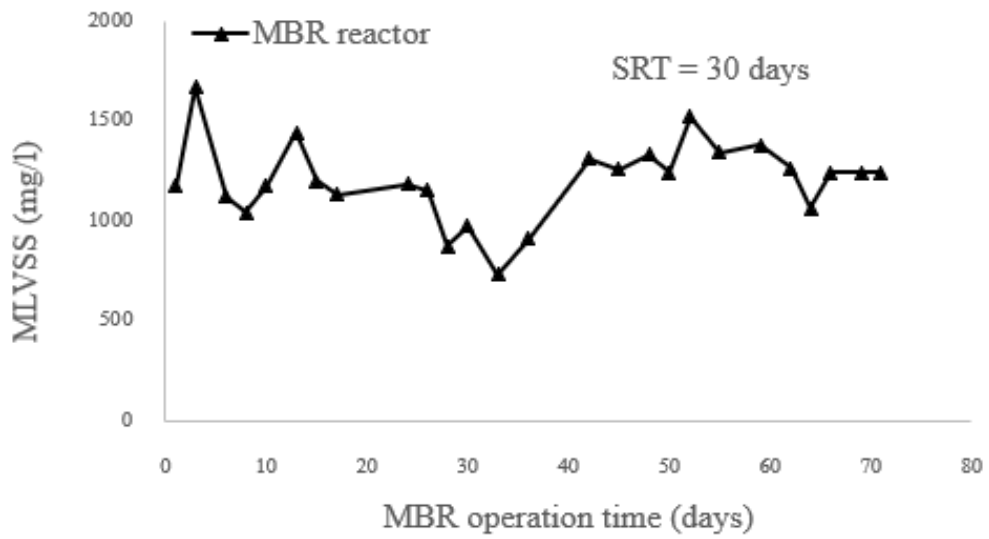
Figure 22. MLVSS at SRT = 30 days
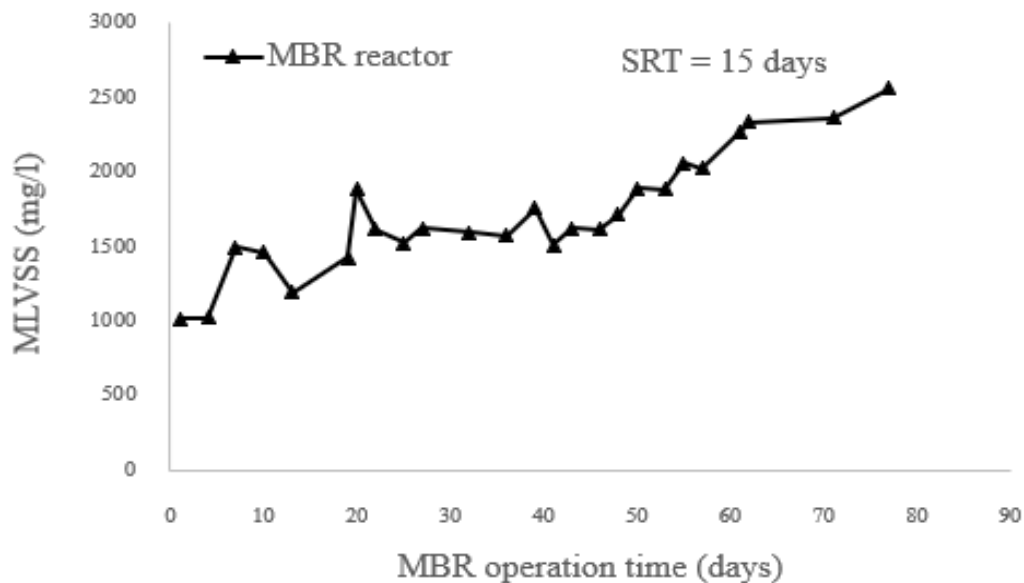
Figure 23. MLVSS at SRT = 15 days

According to the MLSS and MLVSS, it can be indicated that the MLSS and MLVSS at all SRT were the same trends which increased in the beginning stage. After that it was stable at steady state. In generally, the ratio between MLVSS and MLSS should be equal to 0.8, which is used in the design of the aerated tank volume. The higher of MLSS causing the F/M Ratio (ratio of organic matter to the amount of microorganism) was inappropriate.

Average MLSS and MLVSS in treated water were 14.97 mg/L and 11.14 mg/L, respectively, at all SRT which lower than those in reactor. Because the MBR used small pore size membrane, all the suspended solids were retained in the reactor. Thus, the advantages of the membrane bioreactor system were well reduced suspended solids in wastewater without a sedimentation tank required.

4.2.2. Chemical Oxygen Demand (COD)

COD concentration in raw wastewater, reactor and treated water were measured as shown in Table 11.

Table 11. The average Chemical Oxygen Demand in water samples

SRT	Average ± Standard deviation (mg/L)		
	Raw water	**MBR reactor**	**Treated water**
Infinite	1,911.57	551.98 ± 624.98	91.22 ± 28.60
30 days	1,867.35	$1,835.03 \pm 340.47$	63.31 ± 22.87
15 days	2,000.00	$2,197.39 \pm 37123$	41.78 ± 14.03

From Table 11, average COD concentration in raw wastewater was in the range of 1,800-2,000 mg/L at all SRT. Average COD concentration in MBR tank was 551.98 mg/L, 1,835.03 mg/L and 2,197.39 mg/L at SRT infinite, 30 days and 15 days, respectively. After wastewater treated by MBR, average COD in permeate was 91.22 mg/L, 63.31 mg/L and 41.78 mg/L at SRT infinite, 30 days and 15 days, respectively. The COD concentration during the operation period was illustrated in Figure 24-26.

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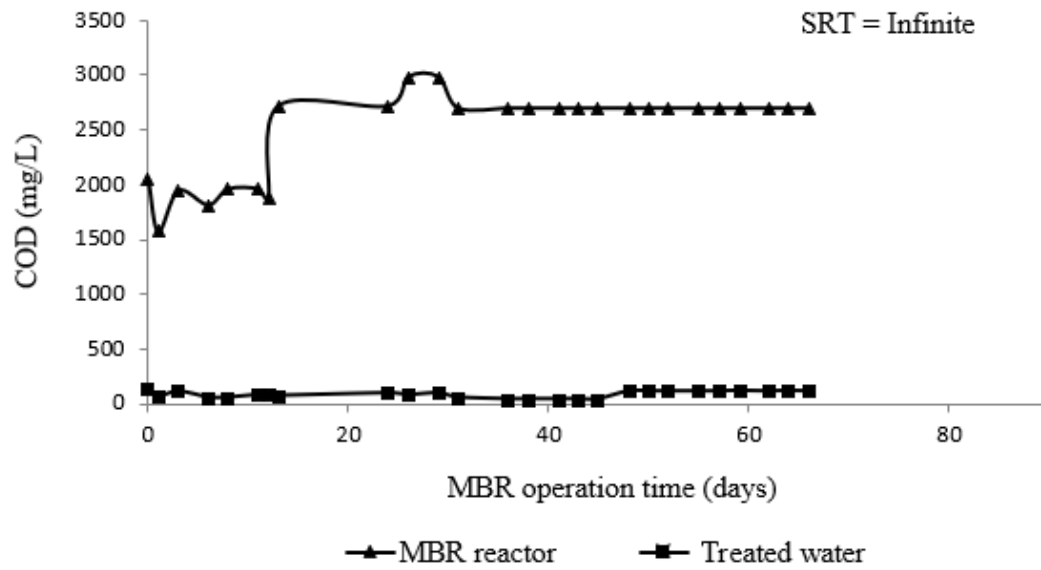
Figure 24. *COD concentration at SRT Infinite*
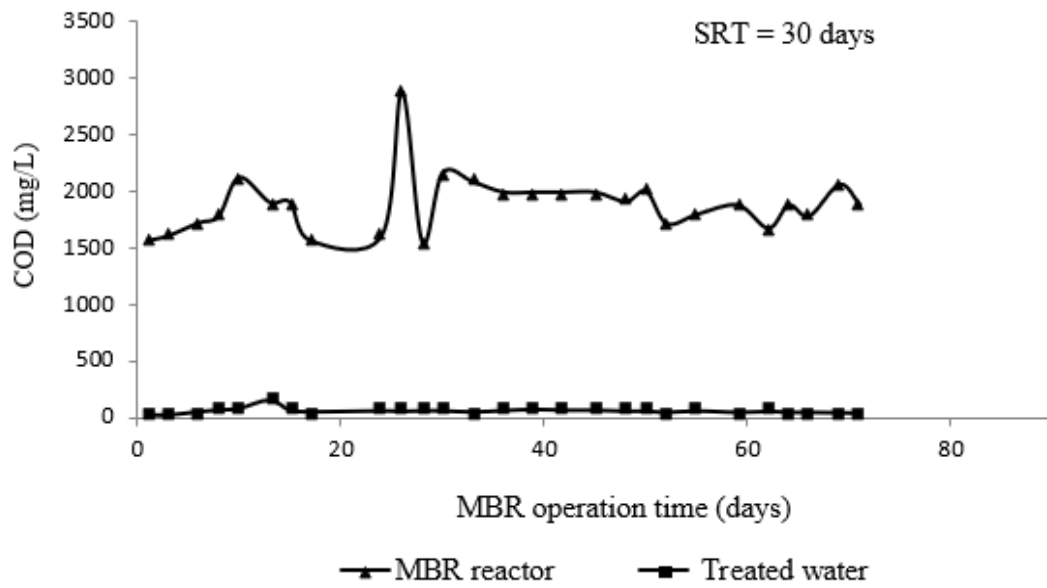
Figure 25. *COD concentration at SRT 30 days*
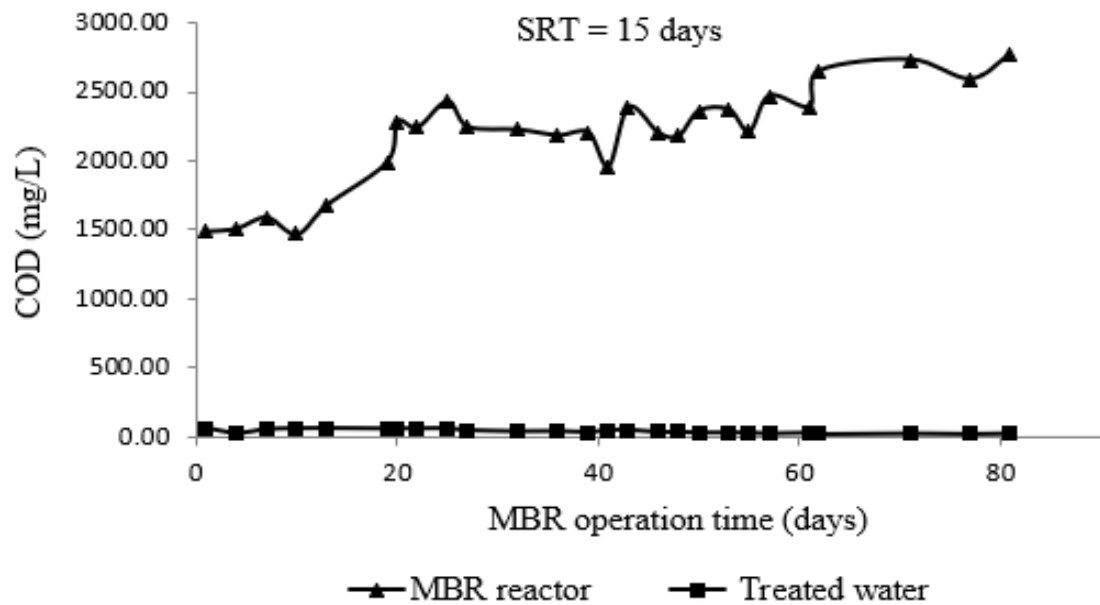
Figure 26. COD concentration at SRT 15 days

The obtained COD results indicated that MBR reactor had high efficiency to remove COD from raw wastewater. COD concentration in treated water at all SRT were met the standard of COD concentration in wastewater (<120 mg/L). When compared the COD reduction in each SRT, it was found that the MBR operation at SRT 15 days provided the highest COD reduction at 97.9%. While the COD reduction of SRT 30 days and infinity were 96.6% and 95.2%, respectively, as shown in Figure 4.3.4.
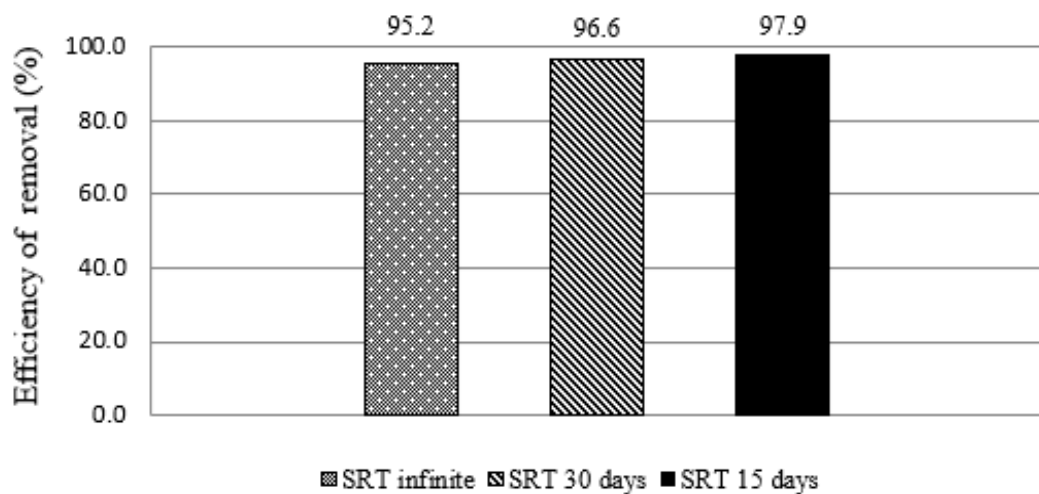
Figure 27. Average percent COD reduction

The COD reduction of all SRT were not significant different. However, the different of SRT resulted in different sludge extraction. The high amount of sludge extraction was conducted in SRT 15 days, follow by 30 days and infinity. When the sludge was extracted from the reactor, seed was added to the reactor at the same volume to maintain the working volume in the reactor. Thus, it might affect the COD reduction in MBR. However, the results of COD removal did not relate with the MLVSS concentration in reactor. Thus, it can be indicated that the COD removal in MBR not only from the biodegradation but also filtration of membrane. From the obtained result, the filtration of membrane acts as the major role for remove COD.

COD reduction in MBR caused by the transformation of organic matter into carbon dioxide and microbial cell in the decomposition process. In particular, the membrane bioreactor system which has less SRT, the sludge was rolled out from system which mean that a nutrient was circulation in the system. Yurtsever (2017) reported that the average COD removal performance (86–65%) and it was decreased at shorter SRT due to the decreased biomass concentration in reactor. Operating condition with good nutrients circulation causing microorganisms to grow up better and increased the degradation (Wagner and Rosen, 2000).

4.2.3. Color removal

The color of the synthetic textile wastewater is a substance with high intensity. Therefore, even if the color in the water is only a small amount, it can cause the water to be a color that is disgusting to the witness. Moreover, the color founded in wastewater is colloidal particles that will obscure the sunlight that passes through the surface affecting the water synthesis process of plants and causing the amount of oxygen in the water to decrease, resulting the aquatic life in the water. Therefore, the color of wastewater must be removed before discharge into public water sources. Color values and color removal efficiency are shown in Figure 28 - Figure 35.
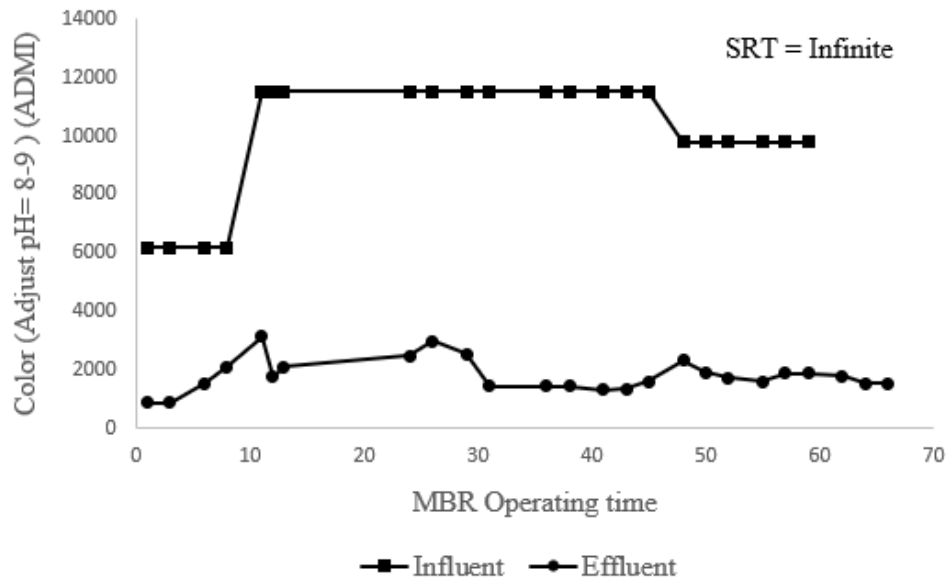
Figure 28. *Color concentration values of influent and treated water before adjusting the acid-base (pH = 8-9) at SRT = infinite*
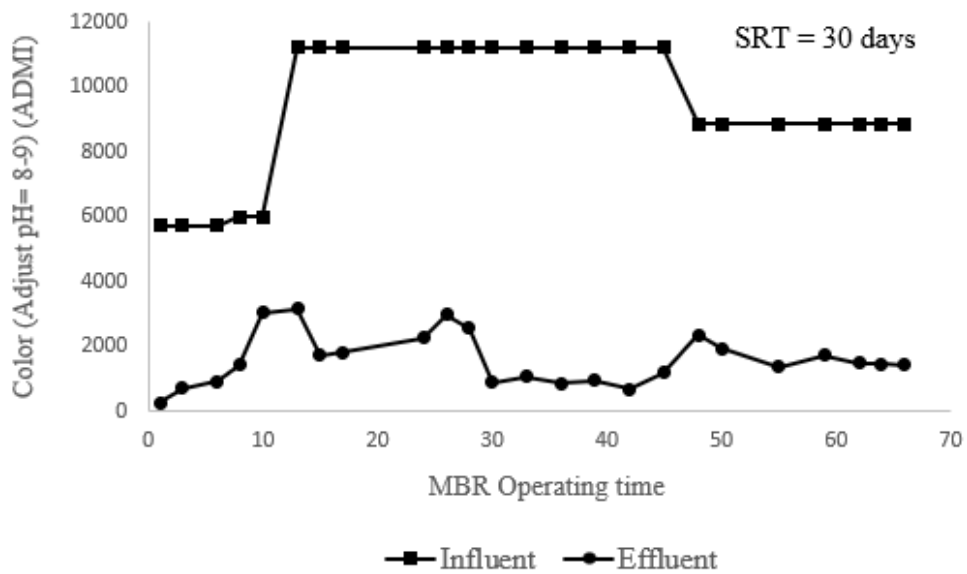
Figure 29. *Color concentration values of influent and treated water before adjusting the acid-base (pH = 8-9) at SRT = 30 days*
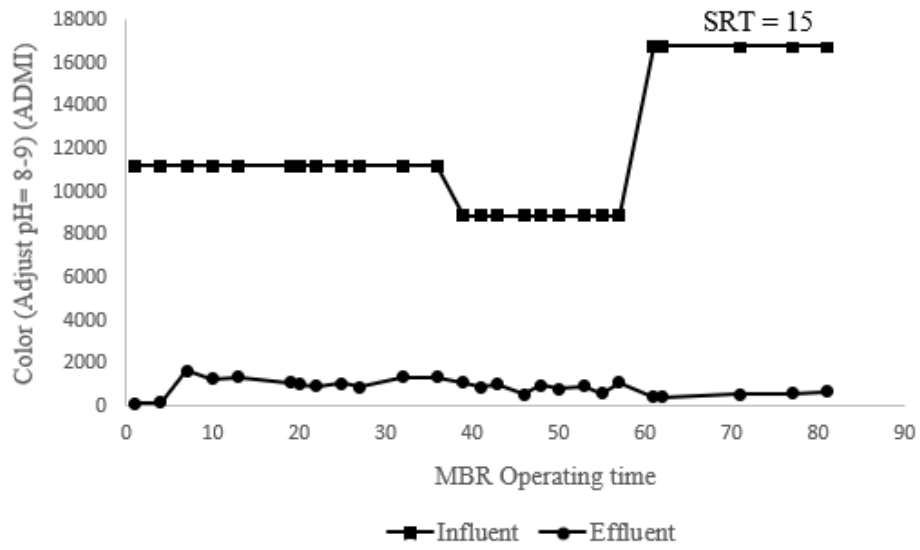
Figure 30. *Color concentration values of influent and treated water before adjusting the acid-base (pH = 8-9) at SRT = 15 days*
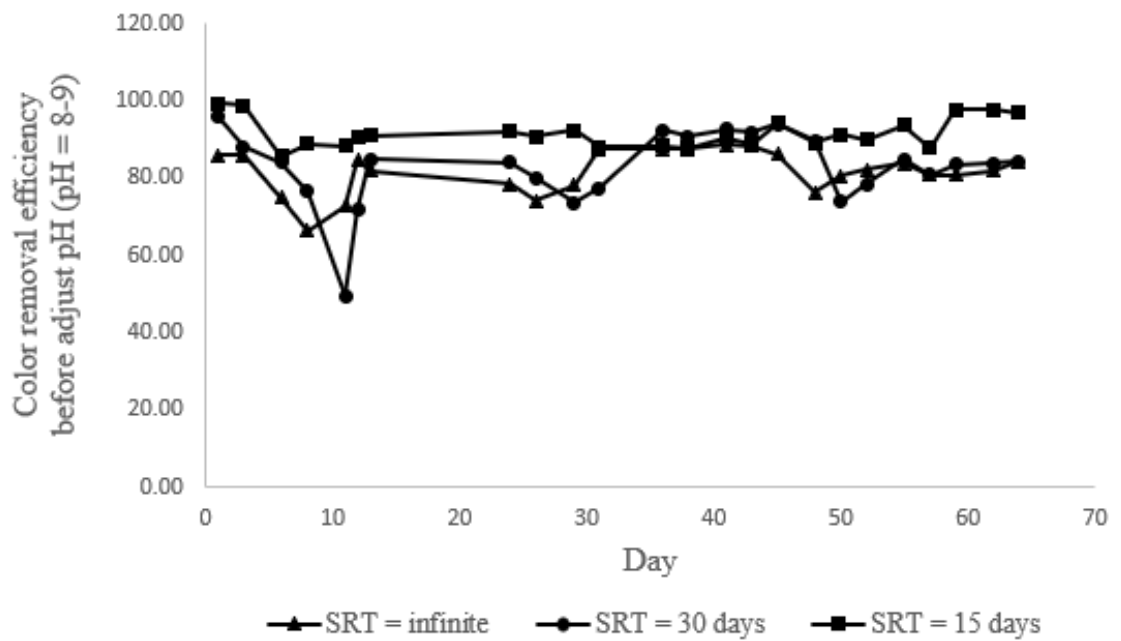
Figure 31. *Color removal efficiency (pH = 8-9) at all SRT condition*
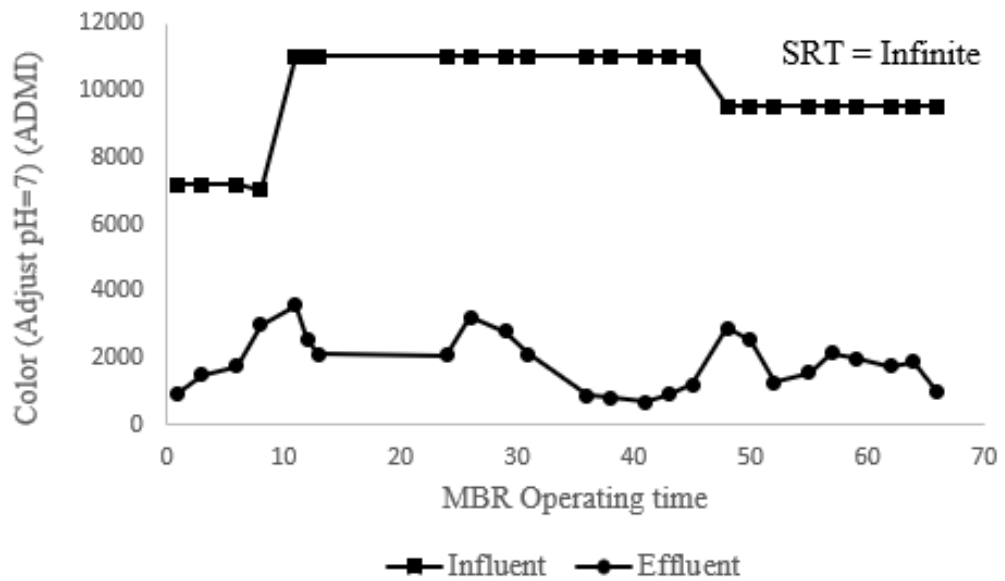
Figure 32. *Color concentration values of influent and treated water after adjusting the acid-base (pH = 7) at SRT = Infinite*
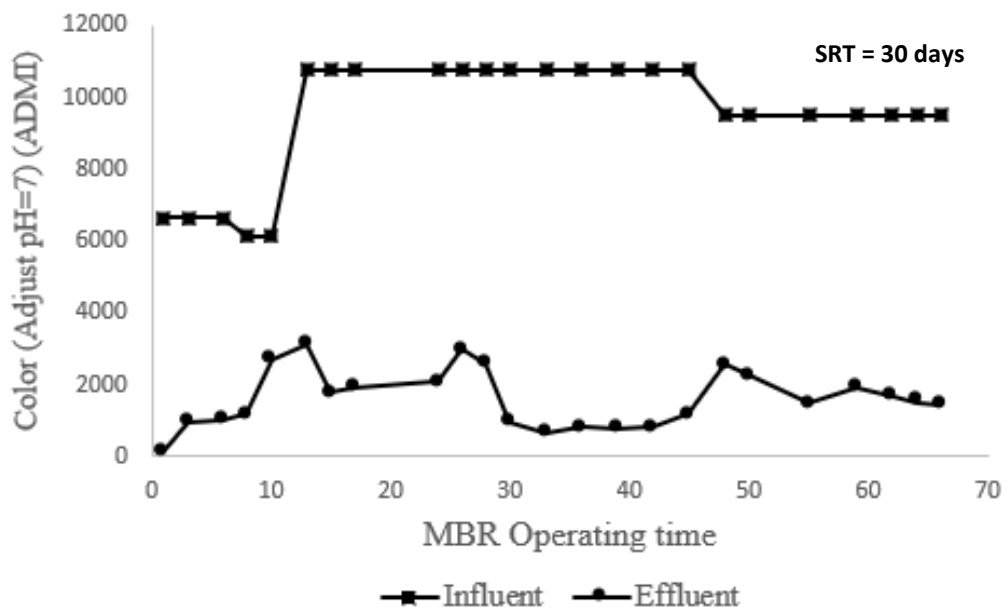
Figure 33. *Color concentration values of influent and treated water after adjusting the acid-base (pH = 7) at SRT = 30 days*
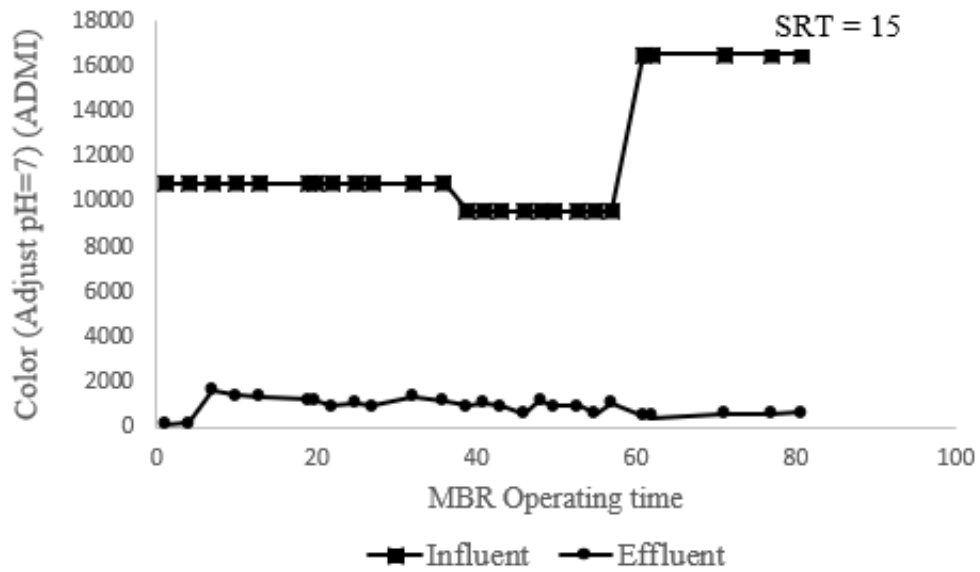
Figure 34. *Color concentration values of influent and treated water after adjusting the acid-base (pH = 7) at SRT = 15 days*
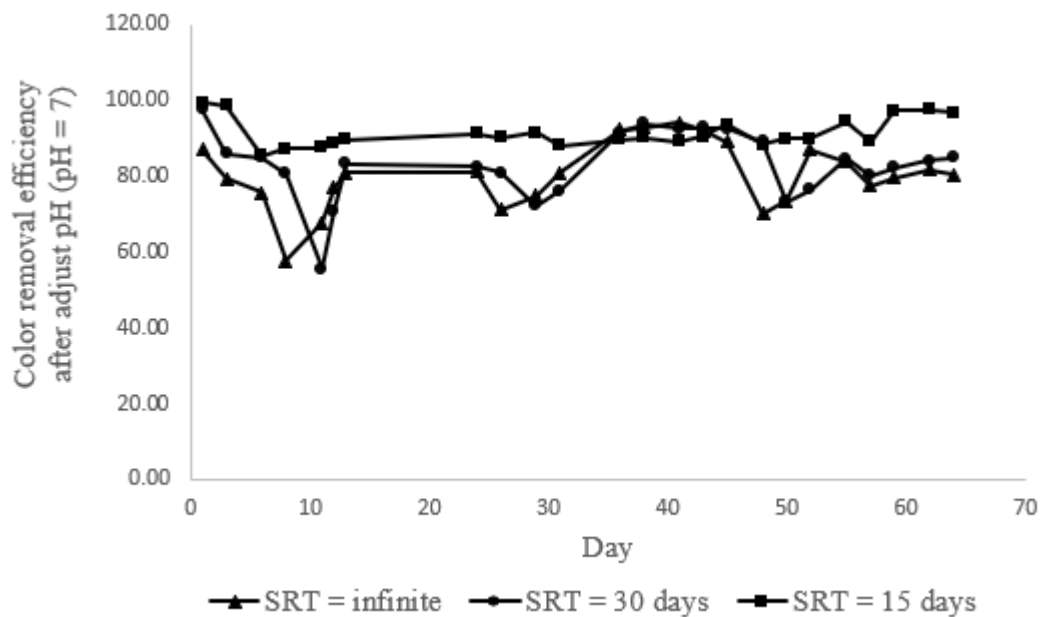
Figure 35. *Color removal efficiency (pH = 7) at all SRT condition*

According to Figure 28 - 31 represented color concentration values and percent color removal of influent and treated water. The average color of influent water at pH in the range of 8-9 was 10,040, 9,400 and 11,469 ADMI at SRT 15 days, 30 days and infinite, respectively. Moreover, the average efficiency of color removal

by MBR were 81.61%, 82.66% and 91.91% at SRT 15 days, 30 days and infinite, respectively.

Water is composed of a positively charged hydrogen ion and a negatively charged hydroxide ion. In acidic (pH<7) water, there is a high concentration of positive hydrogen ions. While in neutral water, the concentration of hydrogen and hydroxide ions is balanced. Basic (pH>7) water contains an excess of negative hydroxide ions.

Besides the color of actual pH, the color value when pH of water change to 7 was investigated. The color values at pH 7 was important because when discharge textile wastewater to natural water sources, the pH was change to 7 or nearly 7. Thus, the color values at pH 7 should be determined. Figure 32-35 showed color concentration values and percent color removal after adjusted pH to 7. The average color values of influent were 9,845 ADMI at SRT = 15 days, 9,496 ADMI at SRT = 30 days and11,431 ADMI at SRT = infinite. The efficiency of color removal equal to 80.54% at SRT = 15 days, 82.70% at SRT = 30 days, and 91.67% at SRT = infinite. The results were correlated well with the results of Badani (2005) which reported that MBR can removed color with efficiency higher than 70%.

Color values can be changed according to the pH value. Before discharge, wastewater need to adjust the pH value to close to pH of natural water sources for check the color intensity value when wastewater is released into natural water sources. Relation of color values between adjusting the pH value and not adjusting the pH value shown in Figure 36.
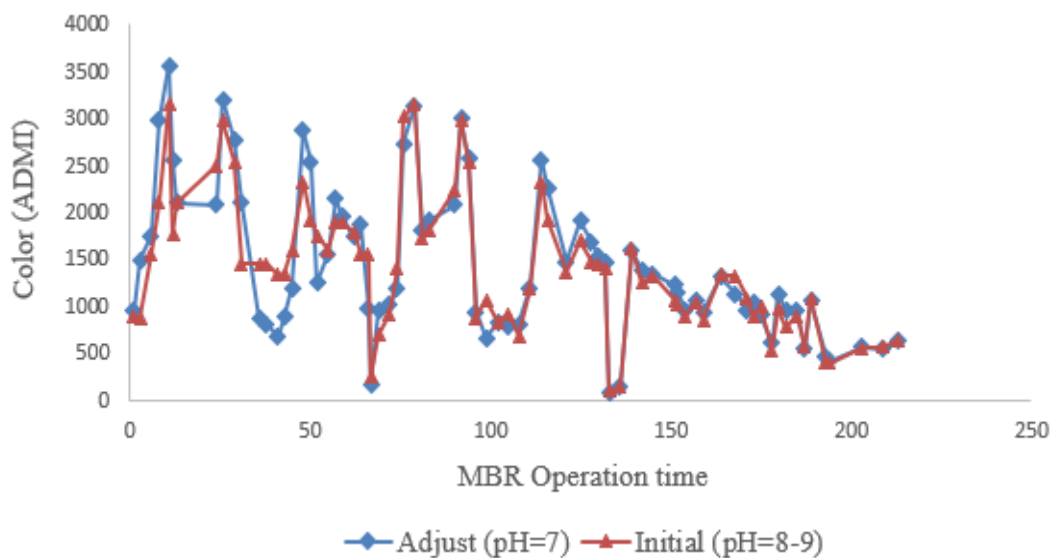
Figure 36. *Relation of color values between adjusting the pH value and not adjusting the pH value*

According to Figure 36, the relationship of color intensity values by adjusting acidity and not adjusting was not related with the theory that described that the color values increased with increasing pH. The result showed that the average color in influent was 10,283 ADMI at the initial pH (pH = 8-9) at all SRT. On the other hands, the adjusted pH at 7.023 ± 0.03 has an average color value 10,330 ADMI at all SRT. Moreover, the average color values were 1,450 and 1,408 ADMI at the initial pH (pH = 8-9) and at the adjusted pH (pH = 7), prospectively. Thus, it can be concluded that the color of non-adjusted and adjusted pH not different. When discharge the wastewater to natural sources, the color values not influent by the pH. However, the color value was not meet the standard criteria of color in wastewater.

4.2.4. Dissolved Organic Carbon (DOC)

Dissolved organic carbon (DOC) is the amount of carbon found in an organic compound and is often used as a non-specific indicator of water quality or cleanliness of pharmaceutical manufacturing equipment. The term of dissolved is represent the organic matter that pass through the filter pore size 0.45 um. The DOC concentration of water samples is shown in Table 12.

Table 12. *Average dissolved organic carbon in water samples*

SRT	Average ± Standard deviation (mg/L)	
	Raw water	**Treated water**
Infinite	484.15 ± 0.00	95.77 ± 31.61
30 days	462.65 ± 0.00	33.41 ± 30.71
15 days	451.5± 0.00	13.67 ± 4.56

From Table 12, average DOC concentration in raw water was in the range of 451.5-484.15 mg/L at all SRT. After treatment, the remained average DOC concentration in treated water were 95.77 mg/L, 33.41 mg/L and 13.67 mg/L at SRT infinite, 30 days and 15 days, respectively. It indicated that the short SRT provided highly efficient for DOC removal. However, the remained DOC concentration in treated water was high when compared to DOC concentration in natural water sources which commonly lower 10 mg/L.
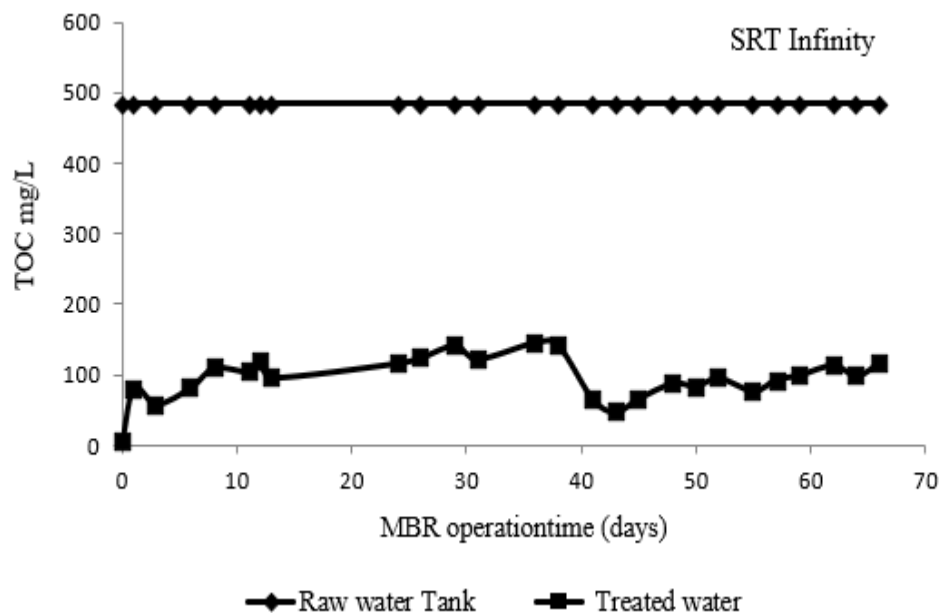
Figure 37. *DOC concentration at SRT infinity*
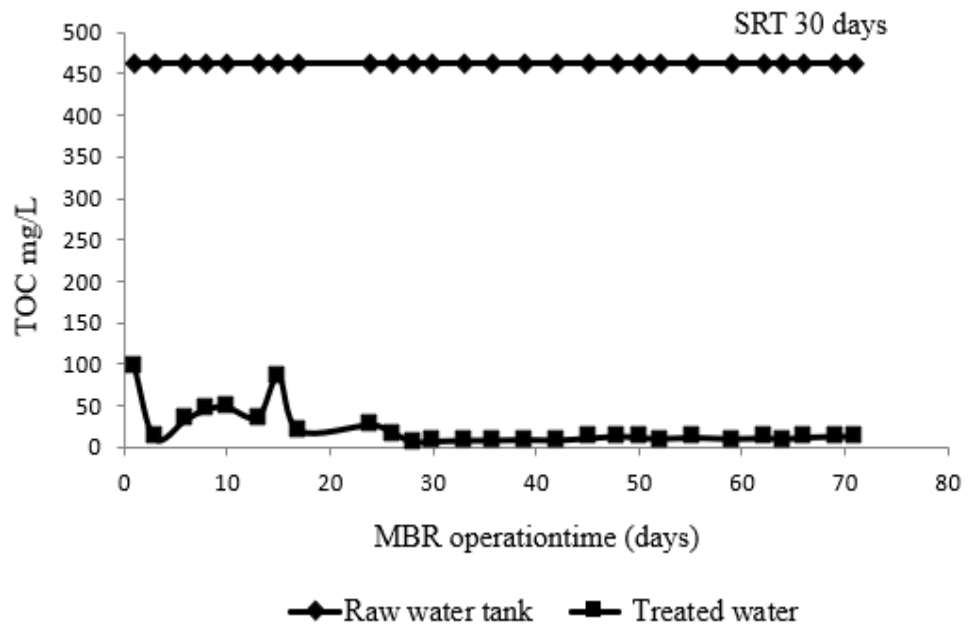
Figure 38. *DOC concentration at SRT 30 days*
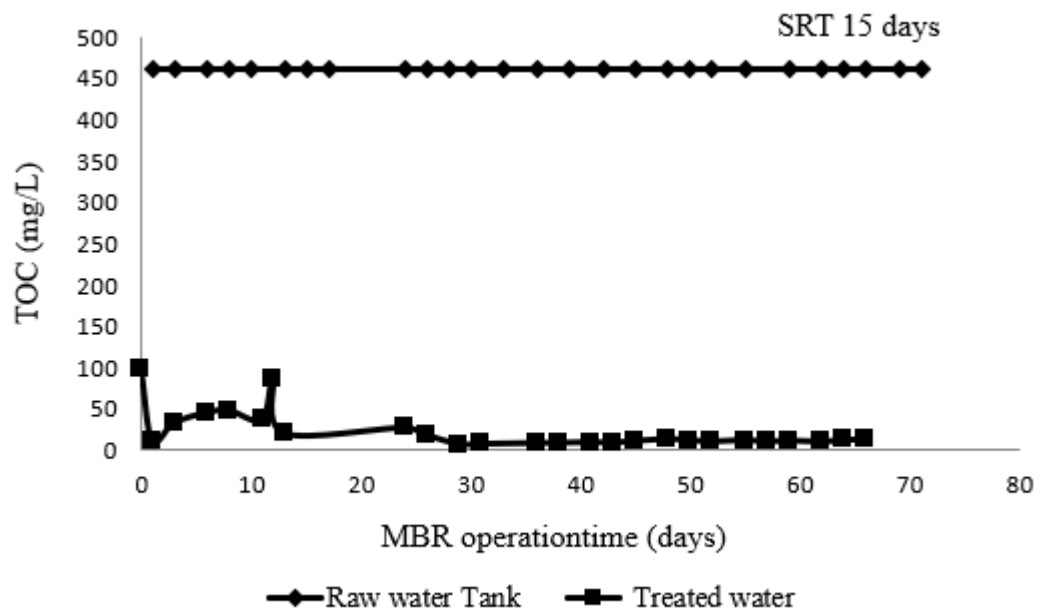
Figure 39. *DOC concentration at SRT 15 days*
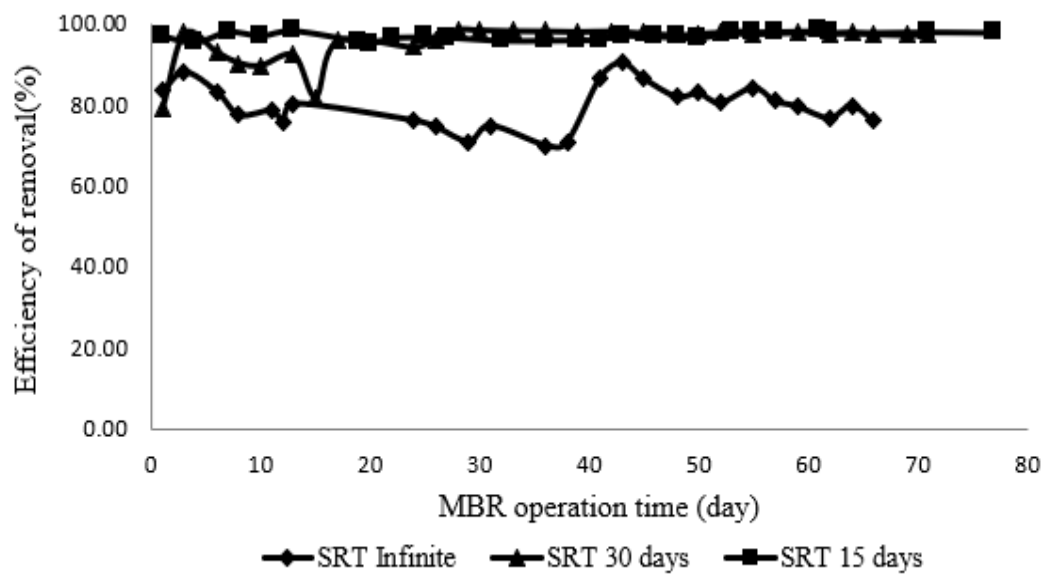
Figure 40. *The efficiency of DOC reduction*

The efficiency of DOC removal of MBR at infinite SRT was 80.22 %, at 30 days SRT is 92.77 % and at 15 days SRT is 96.97 %. It founds that the trend of dissolved organic carbon removal efficiency increased when decreasing SRT. As shown in the Figure 4.2.2, at SRT = 15 days has the highest efficiency of dissolved organic carbon. The result was the same trend with COD reduction which found that the MBR operation at SRT 15 days had provided the highest COD reduction.

4.2.5. Trihalomethanes formation potentials (THMFPs)

Trihalomethanes (THMs) is presence from the reaction between DOM and residue chlorine. Trihalomethanes formation potentials (THMFPs) was the formation potential of DOM to form THMs in case of excess chlorine. The results of THMFP in influent wastewater and after treated by MBR at different SRT was shown in Figure 41. THMFP in influent synthetic wastewater were 5,473.95 μg/L. Only $CHCl_3$ and $CHBrCl_2$ can be found in influent water at concentration 5,088.68 μg/L and 385.27 μg/L, respectively. Compare with other research the influent wastewater from the central wastewater treatment plant of the Northern-Region Industrial Estate have an average THMFP value of 1233.9 μg/L. This value came from the summation of the $CHCl_3$ -FP at 1,097.6 μg/L, $CHCl_2Br$-FP at 114.3 μg/L, $CHClBr_2$ -FP at 21.3 μg/L and $CHBr_3$ -FP at 4.0 μg/L. (Water sample was collected in June 24, 2004)

The World Health Organization (WHO, 1996) has set the health-related guideline values (GV) of 200, 60, 100 and 100 μg/L for $CHCl_3$, $CHCl_2Br$, $CHClBr_2$ and $CHBr_3$, respectively.

After treated with MBR, the THMFP was decreased to 1,515.40 μg/L, 705.11 μg/L and 1,555.70 μg/L at SRT 15 days, 30 days and infinity, respectively. It can be stated that MBR at SRT 30 days can reduced more THMFP from influent water. In addition, only chloroform can be found in treated water at SRT 30 days. The THMFP in each species in each SRT was illustrated in Figure 41.
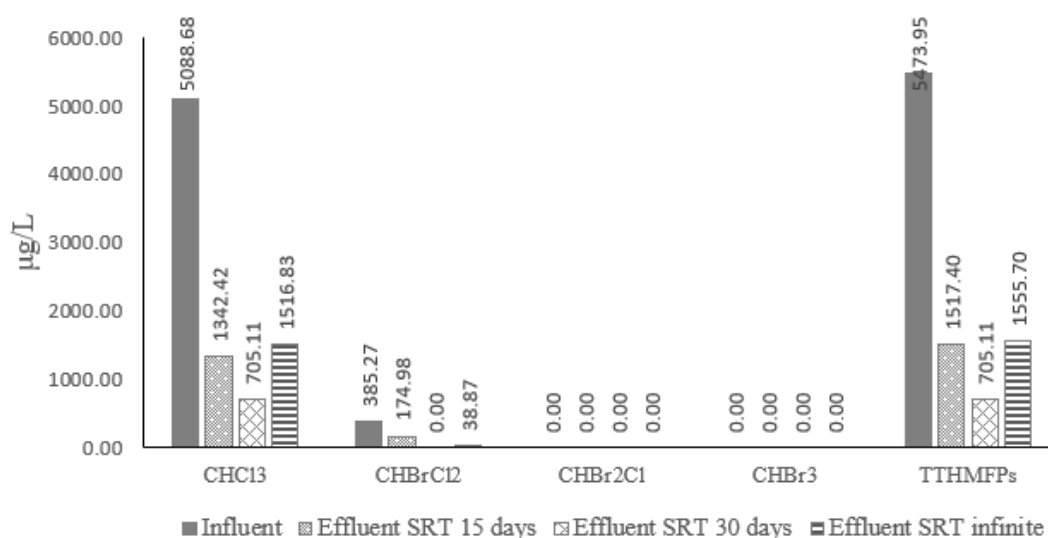
Figure 41. *The formation of THMFPs in influent and effluent at different SRT*

Specific THMFP is the ratio between THMFP and DOC of each water sample and use to indicate the potential of organic matter to react with chlorine to form THMs. The specific THMFP of influent water and treated water was shown in Table 13.

Table 13. *Specific THMFP of raw surface water and treated water*

Water samples	THMFP (ug/L)	DOC (mg/L)	Specific THMFP (ug/mg)
Influent	5,473.95	567.2	9.65
Treated water at SRT 15 days	1,517.4	26.62	57.00
Treated water at SRT 30 days	705.11	12.03	58.61
Treated water at SRT infinite	1,555.7	22.89	67.96

From the obtained results of specific THMFP, it was found that DOM in influent has low ability to form THMs. However, after treated by MBR, the remaining DOM in treated water has high ability to form THMs. It can be indicated that DOM the remove by MBR has low ability to form THMs. However, the total THMs was decreased due to the high amount of DOM was removed.

4.2.6. Fluorescent excitation-emission matrix, FEEM

FEEM was used to characterize the DOM in water samples. All water samples were analyzed for their characteristics by using FEEM techniques. The results of FEEM of all samples were shown separately in Figure 42 – 45. According to the studies about spectrofluorometry analysis, the water sample was collected during June 24, 2004 at the central wastewater treatment plant of the Northern-Region Industrial Estate reported that in influent wastewater have Tyrosine-like substance at peaks A and B, Tryptophan-like substances at peaks C and D and Humic and fulvic acids-like substances at peaks G and H.
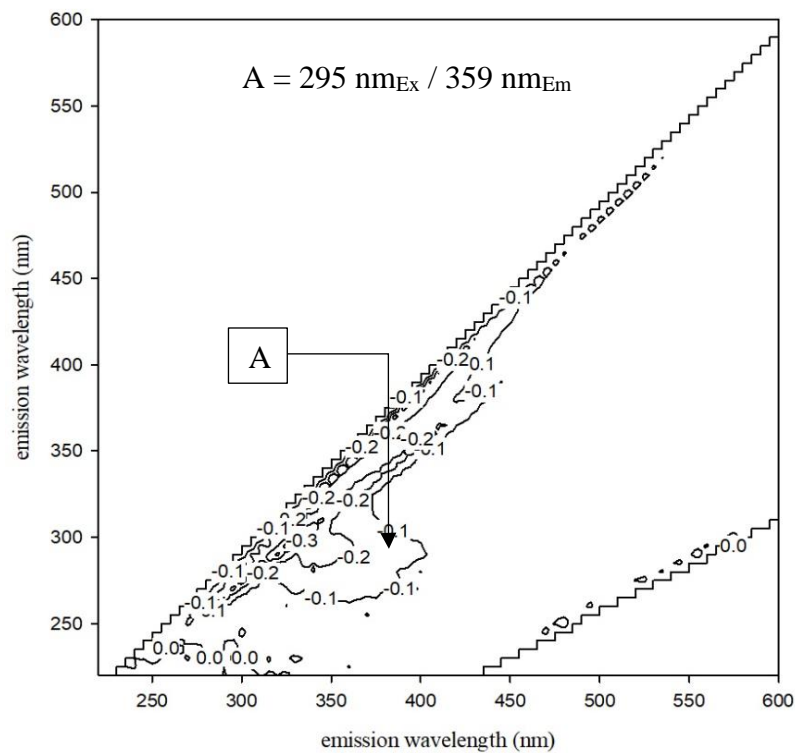
Figure 42. FEEM of influent water

According to Figure 42 when analyzing FEEM of synthetic textile wastewater before entering the membrane bioreactor tank, it was found the Peak at point A which in the range of 275-300 nm_{Ex} / 325-375 nm_{Em} It can be indicated that DOM in influent water was Tryptophan-like and protein-like substances (Leenheer et al., 2003).
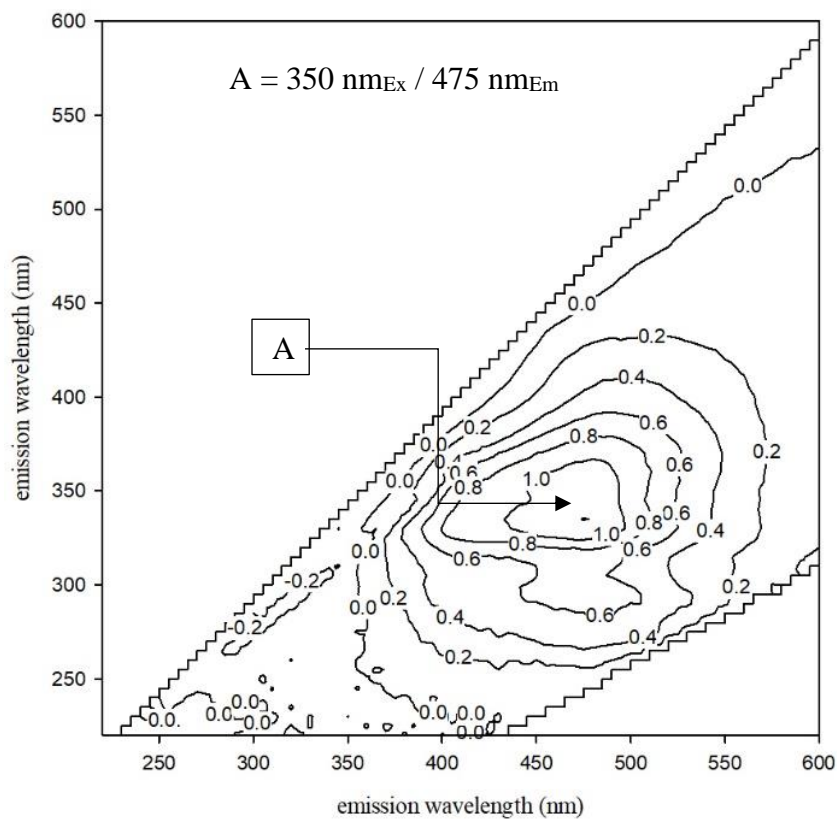
Figure 43. *Synthetic textile wastewater after treatment at SRT 15 days*

After treated with MBR at SRT 15 days, the results of FEEM in Figure 43 showed that only one peak was found at point A which in the range of 325-365 nm_{Ex} / 425-475 nm_{Em} .It can be indicated that the remaining DOM in treated water was Humic acids and humic-like substances. The Tryptophan-like and protein-like substances that found in influent water did not found in treated water.
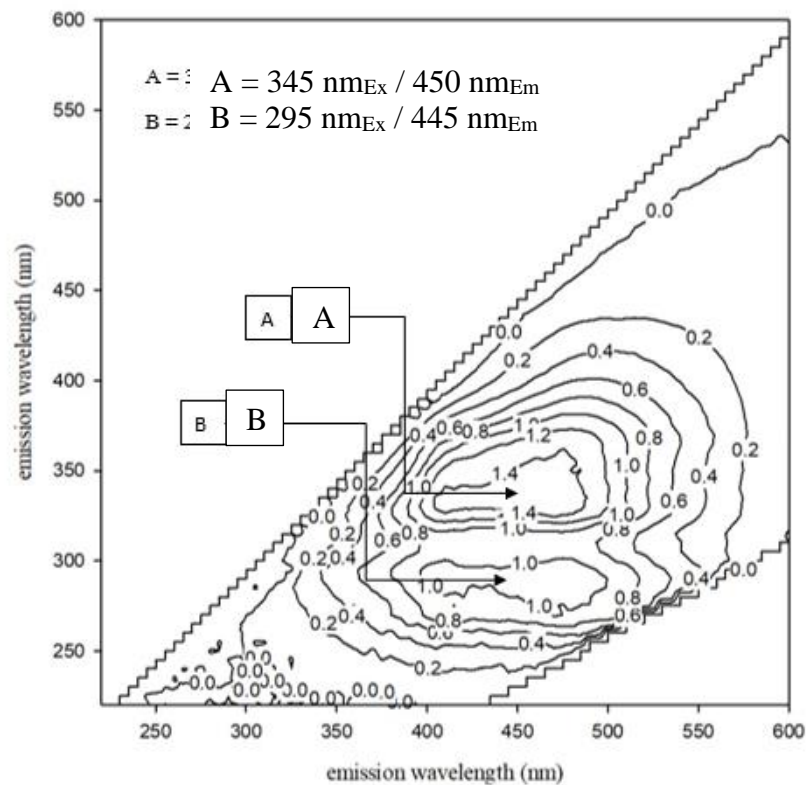
Figure 44. *Synthetic textile wastewater after treatment at SRT 30 days*

After treated with MBR at SRT 30 days, the results of FEEM in Figure 4.4 showed that two peaks were found. The first peak was found at peak A in the range of 345-365 nm$_{Ex}$ / 415-485 nm$_{Em}$ which defined as Humic acids and humic-like substances. The second peak was found at peak B in the range of 265-295 nm$_{Ex}$ / 400-500 nm$_{Em}$ which defined as Fulvic acids and fulvic-like substances. The Tryptophan-like and protein-like substances that found in influent water did not found in treated water.
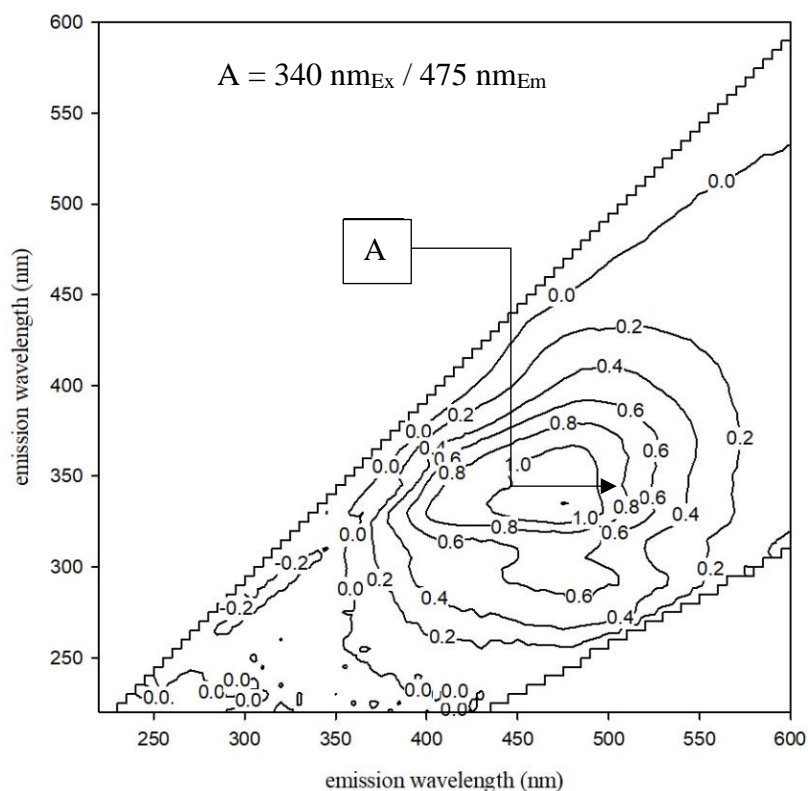
Figure 45. *Synthetic textile wastewater after treatment at SRT infinite*

As showed in Figure 45 when analyzing FEEM of synthetic textile wastewater aftertreatment by the membrane bioreactor tank under infinite SRT condition, it was found that Peak at point A is in the range $=325\text{-}365$ nm_{Ex} / $425\text{-}500$ nm_{Em}. It can be indicated that the remaining DOM in treated water was Humic acids and humic-like substances. The Tryptophan-like and protein-like substances that found in influent water did not found in treated water.

4.3   DOM characterization by resin fractionation

4.3.1. Mass distribution of DOM

Raw water and treated water at SRT 15 days, 30 days and infinity was collected and fractionated to HPI and HPO fractions. All water samples were collected and analyzed for their DOC and THMFP concentration. The results of DOM fractionation are shown in Table 14 and Figure 46.

Table 14. *DOC mass distribution in water samples*

			DOC
Influent	Raw water (μg/L)	Unfraction	567.2
		HPI	156
		HPO	64.2
Effluent	SRT = 15 days (μg/L)	Unfraction	26.62
		HPI	22.21
		HPO	36.05
	SRT = 30 days (μg/L)	Unfraction	12.03
		HPI	17.03
		HPO	7.458
	SRT = Infinite (μg/L)	Unfraction	22.89
		HPI	21.19
		HPO	6.92
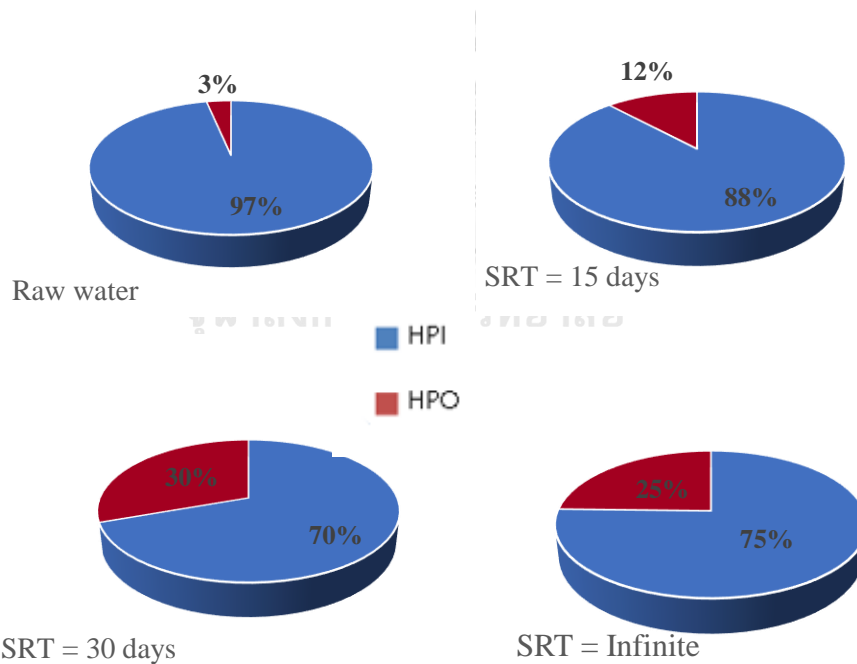
Figure 46. *Percentage distribution of HPI and HPO in raw water and treated water at all conditions*

As shown in Figure 46, raw water contained most of HPI with 97%. After treatment at all SRT, the percent distribution of HPI was decreased from those in raw water. The HPO fraction in treated water was increased in the range of 12-30% at all

SRT. from before treatment. It can be concluded that HPI in raw water was removed during MBR experiment. According to literature research, the study in the THMFP distribution sequences and percent THMFP distribution of six DOM fractions of influent wastewater reported that in influent wastewater present HPOA (42%), HPIA (17%), HPON (16%), HPIB (13%), HPIN (11%) and HPOB (2%).

4.3.2. Mass distribution of Trihalomethanes formation potentials (THMFPs)

The formation of trihalomethane has been studied in synthetic textile wastewater before treatment and after treatment with membrane bioreactor process at SRT = 15 days, SRT = 30 days and SRT = infinite. In addition, the formation of trihalomethane includes the study of the formation of chloroform ($CHCl_3$), the formation of bromodichloromethane ($CHBrCl_2$), the formation of dibromochloromethane ($CHBr_2Cl$), the formation of bromoform ($CHBr_3$) and the formation of all TTHMFPs trihalomethane, a combination of $CHCl_3$, $CHBrCl_2$, $CHBr_2Cl$ and $CHBr_3$, as shown in Table 15. and Figure 47.

Table 15. Formation of trihalomethane in all experiments

			$CHCl_3$	$CHBrCl_2$	$CHBr_2Cl$	$CHBr_3$	TTHMFPs
Influent	Raw ($\mu g/L$)	Unfraction	5088.68	385.27	0.00	0.00	5473.95
		HPI	10318.59	1875.26	0.00	0.00	12193.86
		HPO	2093.06	0.00	0.00	0.00	2093.06
Effluent	SRT = 15 days ($\mu g/L$)	Unfraction	1342.42	174.98	0.00	0.00	1517.40
		HPI	72.07	226.53	0.00	0.00	298.60
		HPO	997.97	168.59	0.00	0.00	1166.56
	SRT = 30 days ($\mu g/L$)	Unfraction	705.11	0.00	0.00	0.00	705.11
		HPI	112.34	419.86	0.00	0.00	532.20
		HPO	4085.34	466.97	0.00	0.00	4552.31
	SRT = Infinite ($\mu g/L$)	Unfraction	1516.83	38.87	0.00	0.00	1555.70
		HPI	0.00	792.92	0.00	0.00	792.92
		HPO	1430.77	295.10	0.00	0.00	1725.88

The results in Table 15 showed that the percent THMFP of unfractioned was lower than percent THMFP of HPI fraction combined with HPO fraction. It might due to the separation of HPI and HPO can increased the availability of DOM in term of both fractions can easily to react with chlorine to form THMFP. The percent distribution of THMFP in each DOM fraction was analyzed and showed in Figure 47.
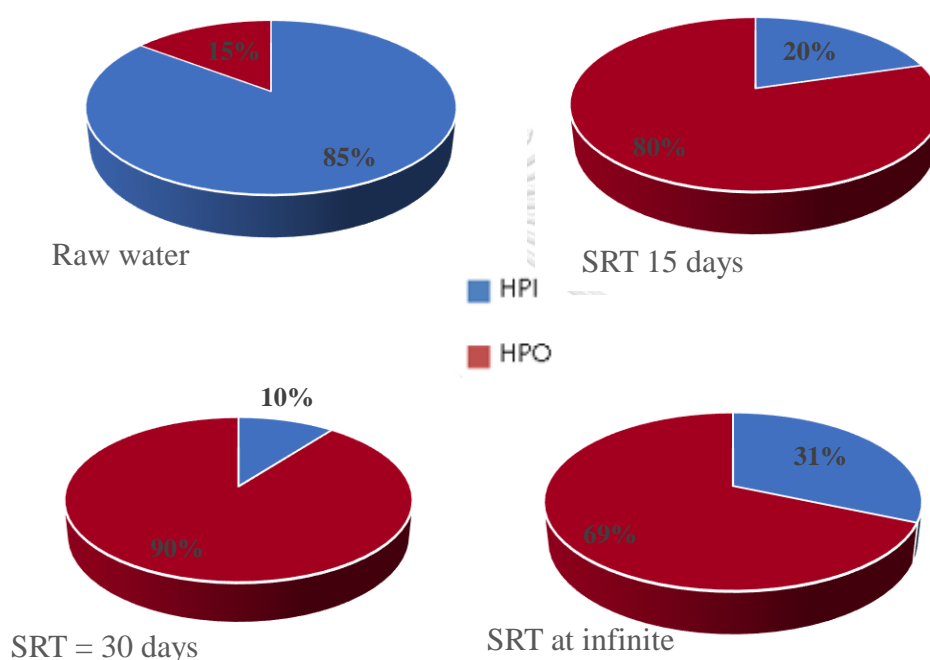
Figure 47. *Percentage of THMFP in term of HPI and HPO in raw water and treated water at all conditions*

According to Figure.47, THMFP has created from HPI fraction more than HPO fraction in raw water. About 85% of THMFP was from HPI fraction in raw water. However, after treated with MBR at all conditions, THMFP has found in HPO fraction than HPI fraction. More than 69% of THMFP was from HPO fraction. The results related to the percent distribution of DOM which found that most of HPI fraction was removed by MBR process. According to literature research, the study in the specific THMFP sequences and specific THMFP values of unfractionated water samples and of theirs six DOM fractions of influent wastewater reported that in influent wastewater present HPOA (144), HPON (93), HPIA (90), HPOB (86), HPIB (67) and HPIN (42) THMFP value, µg THMFP/mg DOC.

Figure 48. showed the results of THMFPs in term of HPI fraction. Most of THMFP was found in raw water with total 12,193.86 μg/L and only $CHCl_3$ and $CHBrCl_2$ was found at concentration of 10,318.59 μg/L and 1,875.26 μg/L, respectively.

After treated by MBR process, the effluent MBR, THMFP was reduced to 298.60 μg/L, 532.2 and 792.92 μg/L at SRT 15 days, 30 days and infinity, respectively. It can be seen that MBR operated at SRT 15 days provided the highest percent THMFP reduction (98%). In addition, only $CHCl_3$ and $CHBrCl_2$ were found in treated water by MBR.
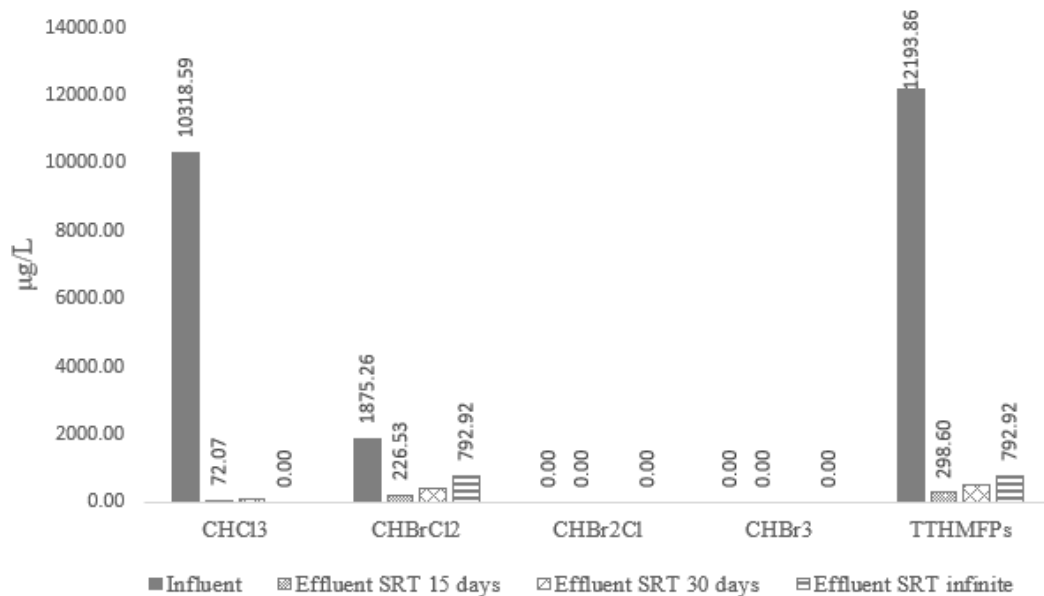
Figure 48. *The formation of THMFPs after resin fractionation in term of HPI at each SRT*

Figure 49. showed the results of THMFPs in term of HPO fraction. The THMFP in term of HPO in raw water was 2,093.06 μg / L and only $CHCl_3$ species was found in HPO fraction. After treated by MBR process, THMFP in term of HPO fraction was reduced only SRT 15 days and infinity. While the THMFP in term of HPO fraction of SRT 30 days was increased to 4,552.31 μg / L.
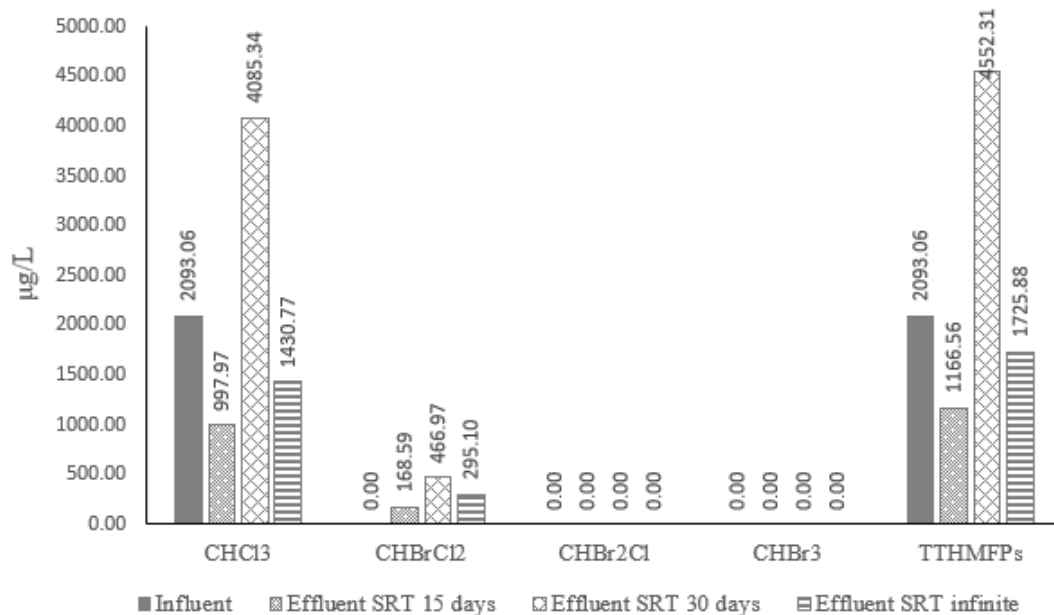
Figure 49. *The formation of THMFPs after resin fractionation on HPO term at each SRT*

Specific THMFP of both HPI and HPO fraction for all water samples was analyzed and showed in Table 16 and Figure 50.

Table 16. *Specific THMFP of raw surface water and treated water in term of HPI and HPO*

Water samples	Specific THMFP in HPI (ug/mg)	Specific THMFP in HPO (ug/mg)
Raw water	78.16	32.60
Treated water at SRT 15 days	13.44	32.36
Treated water at SRT 30 days	31.24	610.39
Treated water at SRT infinity	37.40	249.52
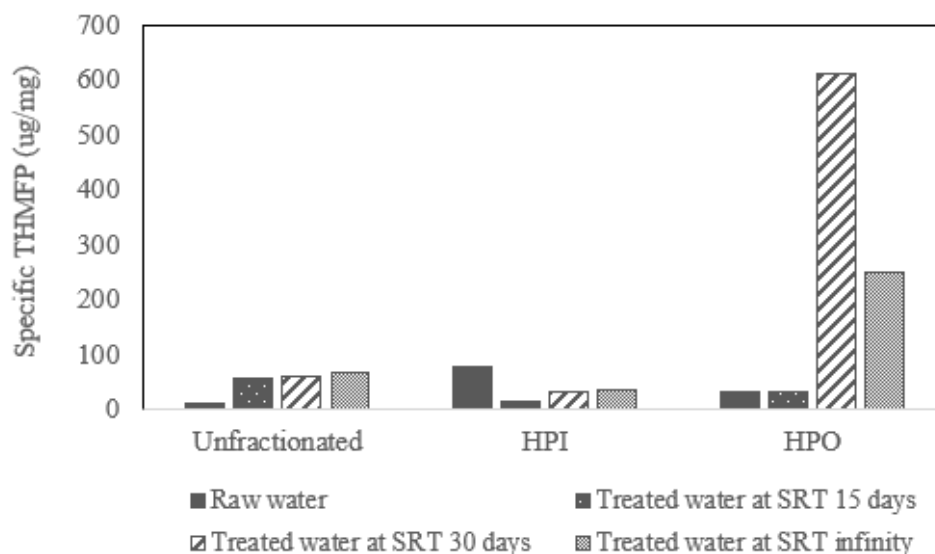
Figure 50. *The Specific THMFP (ug/mg) at each SRT*

The results of specific THMFP showed that the specific THMFP of unfractionated was increased after treated by MBR. It means that DOM that removed by MBR was low ability to form THMs. When fraction DOM into DOM fraction, the specific THMFP of DOM in term of HPI fraction showed that the specific THMFP of raw water was higher than treated water at all condition. It can be indicated that the MBR process can remove DOM in term of HPI fraction that has high ability to form THMs. While in term of HPO fraction, the specific THMFP showed that the specific THMFP in raw water was lower than treated water. It can be indicated that the DOM in term of HPO fraction that removed by MBR has low ability to form THMs.

4.3.3. Fluorescent excitation-emission matrix, FEEM

All water samples were analyzed for DOM characteristics by using FEEM technique and the results were shown in Figure. 51 – 58

As shown in Figure 51, it cannot find the peak of DOM in HPI fraction of raw water. For HPO fraction, only one peak was found at point A which in the range of 275-300 nm$_{Ex}$ / 325-375 nm$_{Em.}$ It can be indicated that DOM in influent water was Tryptophan-like and protein-like substances (Leenheer et al., 2003).
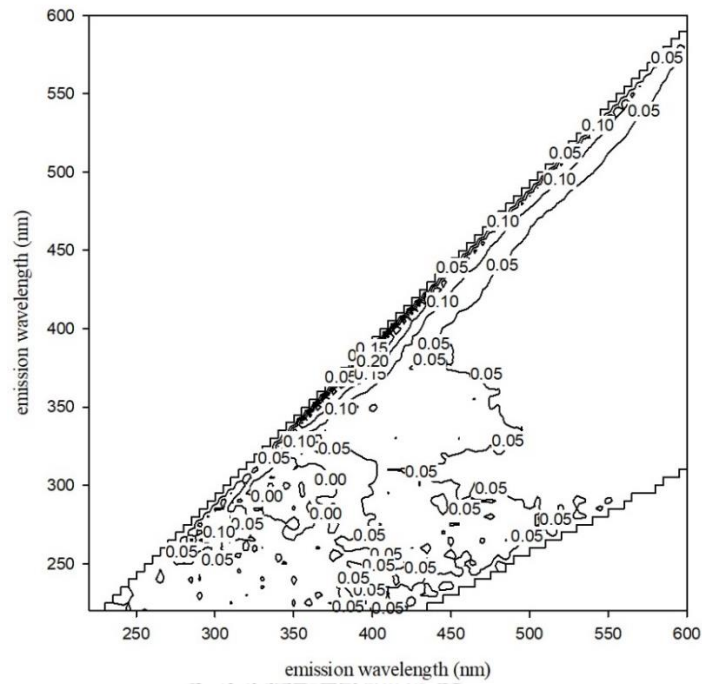
Figure 51. Synthetic textile wastewater before treatment (hydrophilics)
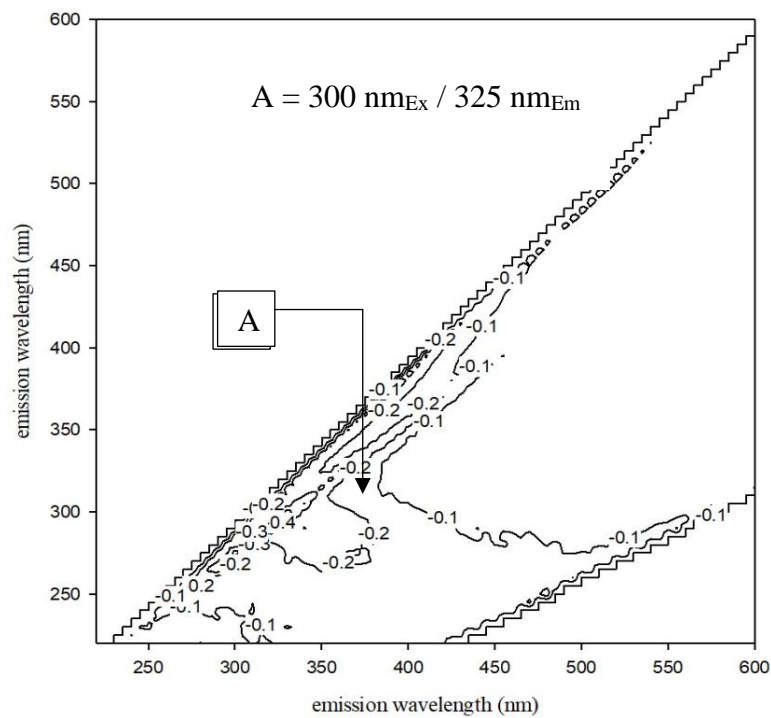
Figure 52. Synthetic textile wastewater before treatment (hydrophobics)

After treated with MBR at SRT 15 days, it cannot find the peak of DOM both in HPI and HPO fraction. It might due to the low amount of DOM concentration in

water. Thus, it cannot define the DOM characteristics of DOM in treated water from MBR at SRT 15 days.
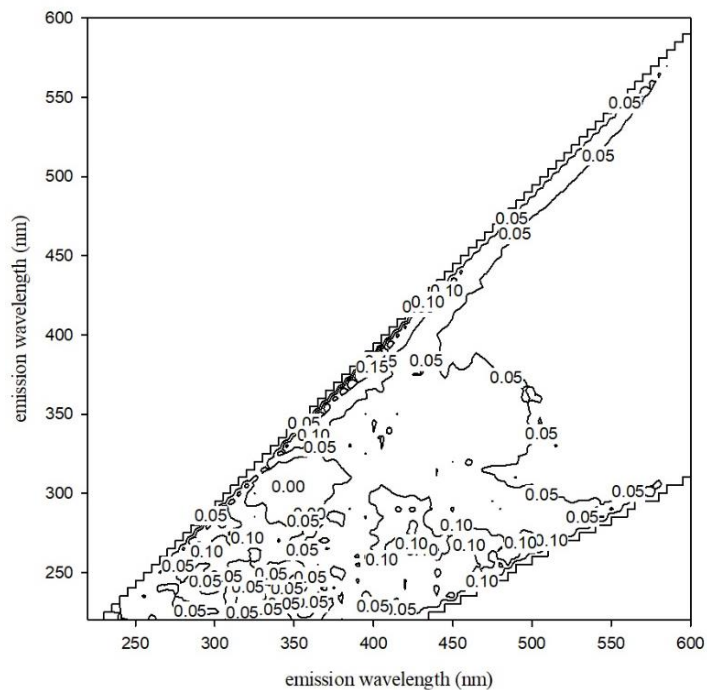
Figure 53. *Synthetic textile wastewater after treatment at SRT 15 days (hydrophilics)*
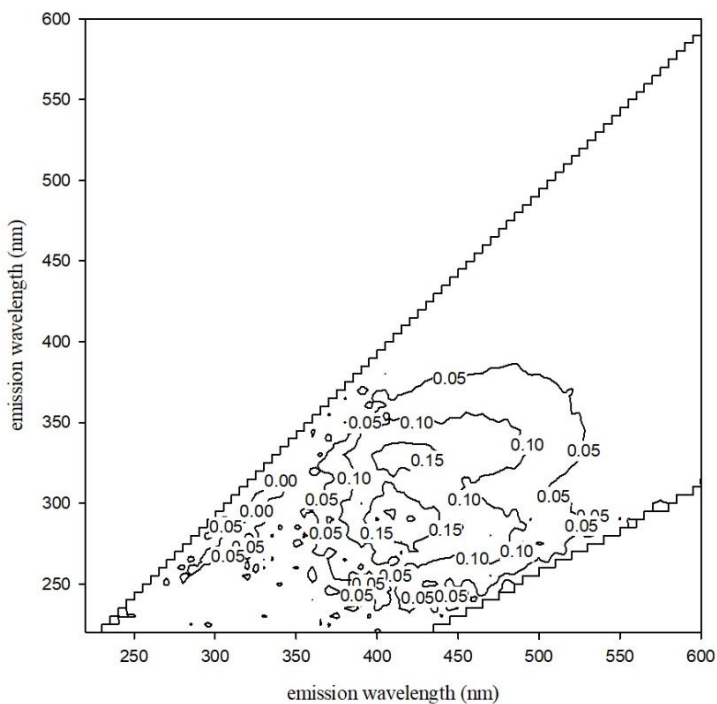
Figure 54. *Synthetic textile wastewater after treatment at SRT 15 days*

(hydrophobics)

After treated with MBR at SRT 30 days, it cannot find the peak of DOM in HPI fraction. For HPO fraction, it only one peak was found at point A which in the range of 340 nm_{Ex} / 425 nm_{Em} which defined as Humic acids and humic-like substances.
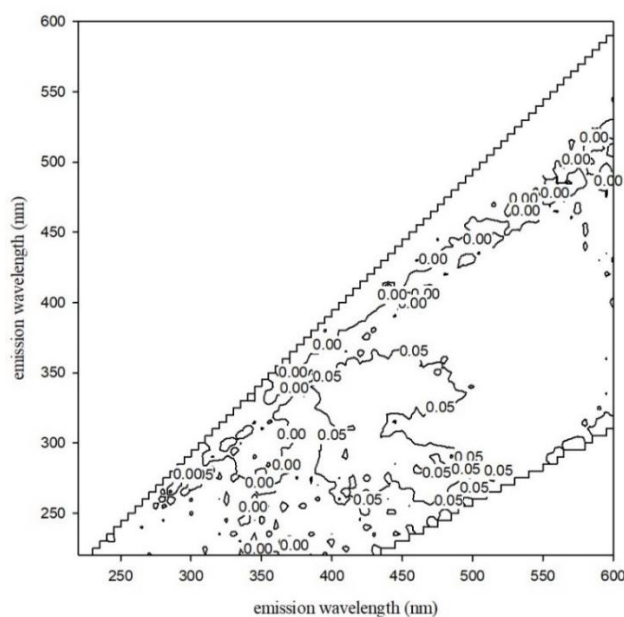
Figure 55. Synthetic textile wastewater after treatment at SRT 30 days (hydrophilics)
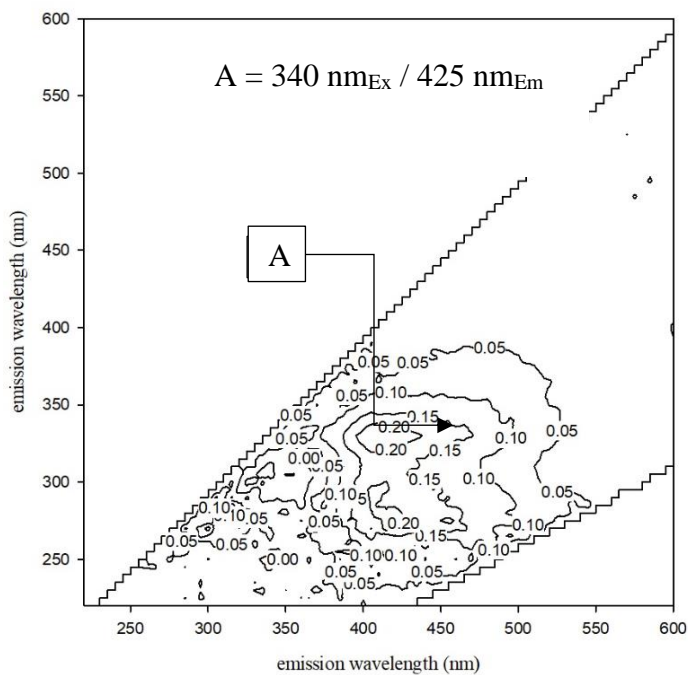
Figure 56. Synthetic textile wastewater after treatment at SRT 30 days (hydrophobics)

After treated with MBR at SRT infinity, it cannot find the peak of DOM in HPI fraction. For HPO fraction, it only one peak was found at point A which in the range of 325 nm$_{Ex}$ / 450 nm$_{Em}$ which defined as Humic acids and humic-like substances.
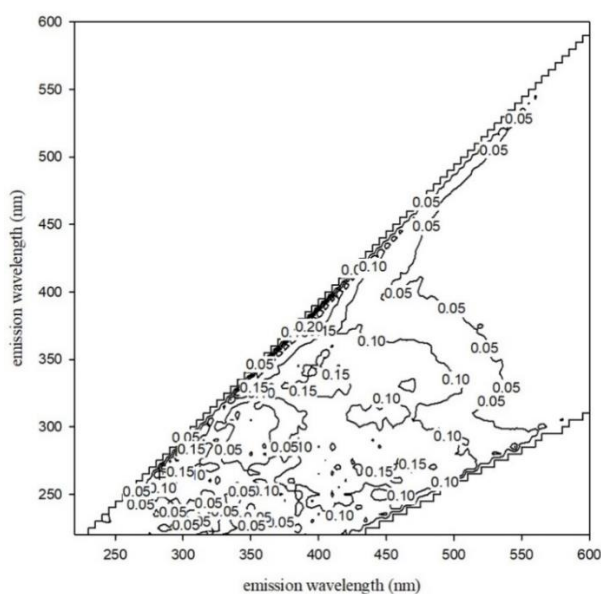
Figure 57. Synthetic textile wastewater after treatment at SRT infinite (hydrophilics)
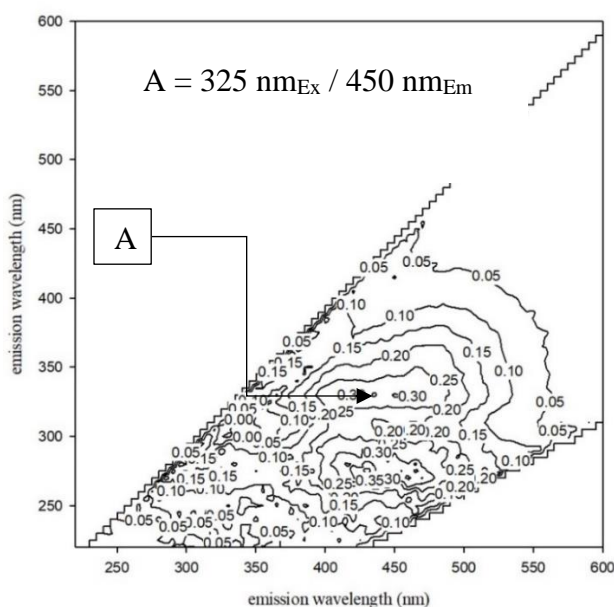
Figure 58. Synthetic textile wastewater after treatment at SRT 15 days (hydrophobics)

According to the classified of characteristics of organic substances, classified by the range of Excitation / Emission values, it was found that Peak A is a

representative of the fulvic acid group. (Baker and Curry, 2004) And position B is a representative of humic acid organic (Chen et al., 2003).Humic acid and fulvic acid are a precursor of chloroform in making chlorine, which is a substance in the THMs group (Babcock and Singer, 1979).

The results showed the trend of the removal of organic compounds, fluvic acid and humic acid organic matter not much different when changing duration of sludge age.

Table 17. *Fluorescent excitation-emission matrix, FEEM*

	Before Treatment	After Treatment		
	Raw	15 days	30 days	Infinity
A	-	350 nm$_{Ex}$ / 475 nm$_{Em}$	345 nm$_{Ex}$ / 450 nm$_{Em}$	340 nm$_{Ex}$ / 475 nm$_{Em}$
B	295 nm$_{Ex}$ / 359 nm$_{Em}$	-	295 nm$_{Ex}$ / 445 nm$_{Em}$	
HPI (A)	-	-	-	-
HPI (B)	-	-	-	-
HPO (A)	-	-	340 nm$_{Ex}$ / 425 nm$_{Em}$	325 nm$_{Ex}$ / 450 nm$_{Em}$
HPO (B)	300 nm$_{Ex}$ / 325 nm$_{Em}$	-	-	-

จุฬาลงกรณ์มหาวิทยาลัย

CHULALONGKORN UNIVERSITY

CHAPTER 5

CONCLUSION AND SUGGESSION

5.1   Conclusion

The study of characterization of dissolved organic matter in treated textile wastewater from bioreactor by operating under different solid retention time was conducted at 15, 30 days and infinite (no transfer of sediment). From the obtained resulted, it can be summarized as follows.

1.   Membrane bioreactor can remove COD from textile wastewater with high efficiency more than 95% at all SRT conditions. However, the COD removal efficiency did not relate with MLVSS concentration in reactor. Therefore, the present of high COD removal in this system caused by the high performance of UF membrane by filtration process.

2.   The color value without adjusted pH and adjusted pH to 7 has not significantly different. The synthetic textile wastewater has the color value higher than 9000 ADMI which higher than standard of color in discharge wastewater. MBR has provided high efficiency for color removal (>80%) at all SRT conditions. However, the remaining color in treated water still higher than the standard.

3.   In term of organic matter removal, MBR has high efficiency for DOC removal (>80%) for all SRT conditions.

4.   Comparing the efficiency of reducing the formation of trihalomethane in MBR, it was found that the efficiency values were not significantly different at all SRT. The increasing of SRT can enhanced the reduction of THMFP.

5.2   Suggestion

1.   The microbial community in reactor should be controlled to ensure the biodegradation of COD in MBR by frequently measuring MLVSS and seed sludge should be collected one times and used for all experiment.

2.   Measuring parameter with more frequent or daily measurements.

3. The nutrient such as nitrogen and phosphorus should be added to the reactor to enhance the microbial growth.

4. The soluble COD should be measured to confirm the biodegradation of COD.

REFERENCES

Antony H Robinson Wehrle Environmental, Witney, Oxfordshire, UK, New Developments in the Application of Membrane BioReactors (MBR) for Industrial Wastewater Treatment.

Avagyan, A., et al. (2014). "Application of high-resolution spectral absorbance measurements to determine dissolved organic carbon concentration in remote areas." Journal of Hydrology **517**: 435-446.

AWWA. (1993). "Characterization of natural organic matter and its relationship to treatability." AWWA Research Foundation American Water Work Association Printer in the U.S.A.

Babcock, D. a. S., P. (1977). "Chlorination and Coagulation of Humic and Fulvic Acid.In : 97th Annual Conference Proccedings paper 16 – 6." Journal of American Water WorksAssociation.

Badani, Z., et al. (2005). "Treatment of textile waste water by membrane bioreactor and reuse." Desalination **185**(1-3): 411-417.

Beggs, K. M. H., et al. (2009). "Characterizing chlorine oxidation of dissolved organic matter and disinfection by-product formation with fluorescence spectroscopy and parallel factor analysis." Journal of Geophysical Research **114**(G4).

Belin, C., et al. (1993). "Characterization by fluorescence of the dissolved organic matter in natural water. application to fractions obtained by tangential ultrafiltration and XAD resin isolation." Environmental Technology **14**(12): 1131-1144.

Bisutti, I., et al. (2004). "Determination of total organic carbon – an overview of current methods." TrAC Trends in Analytical Chemistry **23**(10-11): 716-726.

Brik, M., et al. (2006). "Advanced treatment of textile wastewater towards reuse using a membrane bioreactor." Process Biochemistry **41**(8): 1751-1757.

Carter, H. T., et al. (2012). "Freshwater DOM quantity and quality from a two-component model of UV absorbance." Water Res **46**(14): 4532-4542.

Drumond Chequer, F. M., et al. (2013). Textile Dyes: Dyeing Process and Environmental Impact. Eco-Friendly Textile Dyeing and Finishing.

El Bouraie, M. and W. S. El Din (2016). "Biodegradation of Reactive Black 5 by Aeromonas hydrophila strain isolated from dye-contaminated textile wastewater." Sustainable Environment Research **26**(5): 209-216.

Fan, J., et al. (2014). "Dissolved organic matter removal using magnetic anion exchange resin treatment on biological effluent of textile dyeing wastewater." J Environ Sci (China) **26**(8): 1567-1574.

Fenu, A., et al. (2010). "Activated sludge model (ASM) based modelling of membrane bioreactor (MBR) processes: a critical review with special regard to MBR specificities." Water Res **44**(15): 4272-4294.

Hsu, C. H., et al. (2001). "Estimation of potential lifetime cancer risks for trihalomethanes from consuming chlorinated drinking water in Taiwan." Environ Res **85**(2): 77-82.

Jegatheesan, V., et al. (2016). "Treatment of textile wastewater with membrane bioreactor: A critical review." Bioresour Technol **204**: 202-212.

Labanowski, J. and G. Feuillade (2011). "Dissolved organic matter: precautions for the study of hydrophilic substances using XAD resins." Water Res **45**(1): 315-327.

Li, W., et al. (2015). "Characterization of fluorescent-dissolved organic matter and identification of specific fluorophores in textile effluents." Environ Sci Pollut Res Int **22**(6): 4183-

4189.

Li, X.-y. and H. P. Chu (2003). "Membrane bioreactor for the drinking water treatment of polluted surface water supplies." Water Research **37**(19): 4781-4791.

Luukkonen, T., et al. (2014). "Removal of total organic carbon (TOC) residues from power plant make-up water by activated carbon." Journal of Water Process Engineering **3**: 46-52.

Ma, D., et al. (2014). "Influences of dissolved organic matter characteristics on trihalomethanes formation during chlorine disinfection of membrane bioreactor effluents." Bioresour Technol **165**: 81-87.

Marhaba, T. F., et al. (2003). "Modified dissolved organic matter fractionation technique for natural water." Journal of Hazardous Materials **101**(1): 43-53.

Marrot, B., et al. (2004). "Industrial wastewater treatment in a membrane bioreactor: A review." Environmental Progress **23**(1): 59-68.

Meric, S., et al. (2004). "Color and COD removal from wastewater containing Reactive Black 5 using Fenton's oxidation process." Chemosphere **54**(3): 435-441.

Mosteo, R., et al. (2009). "Evaluation of trihalomethane formation potential in function of oxidation processes used during the drinking water production process." J Hazard Mater **172**(2-3): 661-666.

Mutamim, N. S. A., et al. (2013). "Membrane bioreactor: Applications and limitations in treating high strength industrial wastewater." Chemical Engineering Journal **225**: 109-119.

Ng, A. N. L. and A. S. Kim (2007). "A mini-review of modeling studies on membrane bioreactor (MBR) treatment for municipal wastewaters." Desalination **212**(1-3): 261-281.

Nicholas, A. a. J. (2004). "Risk analysis of drinking water microbial contamination versus disinfection by-products (DBPs)." Toxicology 198(1–3): 255-262.

Pearce, C. (2003). "The removal of colour from textile wastewater using whole bacterial cells: a review." Dyes and Pigments **58**(3): 179-196.

Rodrigues, C. S. D., et al. (2014). "Synthetic textile dyeing wastewater treatment by integration of advanced oxidation and biological processes – Performance analysis with costs reduction." Journal of Environmental Chemical Engineering **2**(2): 1027-1039.

Safa, Y. and H. N. Bhatti (2011). "Adsorptive removal of direct textile dyes by low cost agricultural waste: Application of factorial design analysis." Chemical Engineering Journal **167**(1): 35-41.

Saroj, D. P., et al. (2008). "Modeling and simulation of membrane bioreactors by incorporating simultaneous storage and growth concept: an especial attention to fouling while modeling the biological process." Desalination **221**(1-3): 475-482.

Soni, B. D. and J. P. Ruparelia (2013). "Decolourization and Mineralization of Reactive Black-5 with Transition Metal Oxide Coated Electrodes by Electrochemical Oxidation." Procedia Engineering **51**: 335-341.

Visvanathan, C., et al. (2000). "Membrane Separation Bioreactors for Wastewater Treatment." Critical Reviews in Environmental Science and Technology **30**(1): 1-48.

Wintgens, T. (2003). "Modelling of a membrane bioreactor system for municipal wastewater treatment." Journal of Membrane Science **216**(1-2): 55-65.

Wu, Q., et al. (2016). "Removal of fluorescent dissolved organic matter in biologically treated textile wastewater by ozonation-biological aerated filter." Journal of the Taiwan Institute of Chemical Engineers **59**: 359-364.

Xue, S., et al. (2008). "Trihalomethane formation potential of organic fractions in secondary

effluent." Journal of Environmental Sciences **20**(5): 520-527.

Yigit, N. O., et al. (2009). "Treatment of a denim producing textile industry wastewater using pilot-scale membrane bioreactor." Desalination **240**(1-3): 143-150.

You, S. J., et al. (2010). "Degradation of Reactive Black 5 dye using anaerobic/aerobic membrane bioreactor (MBR) and photochemical membrane reactor." J Hazard Mater **177**(1-3): 1112-1118.

Yurtsever, A., et al. (2017). "Impact of SRT on the efficiency and microbial community of sequential anaerobic and aerobic membrane bioreactors for the treatment of textile industry wastewater." Chemical Engineering Journal **314**: 378-387.

Appendix

A-1 Raw data from MLSS and MLVSS SRT 15 days

Day	SS (mg/l)		VSS (mg/l)	
	MBR reactor	Treated water	MBR reactor	Treated water
1	1480.0	9.0	1015.0	7.0
4	1445.0	7.0	1020.0	5.0
7	1970.0	2.0	1490.0	2.0
10	1950.0	7.0	1460.0	4.0
13	1630.0	5.0	1190.0	0.0
19	1990.0	9.0	1425.0	1.0
20	2645.0	16.0	1880.0	8.0
22	2330.0	2.0	1610.0	4.0
25	2160.0	8.0	1520.0	6.0
27	2290.0	8.0	1620.0	3.0
32	2270.0	1.0	1590.0	2.0
36	2220.0	0.0	1570.0	3.0
39	2450.0	8.0	1750.0	3.0
41	2150.0	1.0	1510.0	1.0
43	2340.0	10.0	1620.0	4.0
46	2350.0	12.0	1610.0	3.0
48	2460.0	0.0	1710.0	0.0
50	2670.0	9.0	1890.0	6.0
53	2680.0	11.0	1880.0	6.0
55	2900.0	6.0	2060.0	6.0
57	2800.0	11.0	2020.0	7.0
61	3170.0	10.0	2260.0	5.0
62	3240	9	2330	6
71	3150	11	2360	1
77	3500	14	2560	9

A-2 Raw data from MLSS SRT MLVSS 30 days

Day	SS (mg/l)		VSS (mg/l)	
	MBR reactor	Treated water	MBR reactor	Treated water
1	1773.3	4.0	1120.0	2.0
3	2593.3	4.0	1040.0	0.0
6	1650.0	1.0	1170.0	5.0
8	1520.0	2.0	1440.0	3.0
10	1720.0	8.0	1200.0	2.0
13	2100.0	6.0	1130.0	6.0
15	1750.0	12.0	1180.0	2.0
17	1650.0	15.0	1150.0	1.0
24	1720.0	11.0	870.0	0.0
26	1740.0	13.0	970.0	6.0
28	1300.0	18.0	730.0	0.0
30	1490.0	18.0	910.0	2.0
33	1350.0	18.0	185.0	2.0
36	1490.0	20.0	1310.0	3.0
39	305.0	14.0	1255.0	8.0
42	1935.0	13.0	1330.0	1.0
45	1965.0	26.0	1240.0	1.0
48	1970.0	9.0	1520.0	0.0
50	1870.0	11.0	1340.0	0.0
52	2230.0	11.0	1380.0	1.0
55	1950.0	10.0	1260	0
59	2000.0	8.0	1060	6
62	1830	9	1240	4
64	1680	14	1240	4
66	1930	10	1240	4

A-4 Raw data from COD SRT 15 days

Day	COD (mg/l)		
	*Raw water	Treated water	%Removal
1	2000.0	30.7	98.5
4	2000.0	54.9	97.3
7	2000.0	59.8	97.0
10	2000.0	61.0	97.0
13	2000.0	58.5	97.1
19	2000.0	58.9	97.1
20	2000.0	59.3	97.0
22	2000.0	59.8	97.0
25	2000.0	48.4	97.6
27	2000.0	41.3	97.9
32	2000.0	42.9	97.9
36	2000.0	36.6	98.2
39	2000.0	49.6	97.5
41	2000.0	49.0	97.0
43	2000.0	37.1	98.1
46	2000.0	37.0	98.0
48	2000.0	33.1	98.3
50	2000.0	32.9	98.4
53	2000.0	32.5	98.4
55	2000.0	27.7	98.6
57	2000.0	31.0	98.4
61	2000.0	23.5	98.8
62	2000.0	27.0	98.6
71	2000.0	24.1	98.8
77	2000.0	27.5	98.6

*Raw water uses the average value

A-5 Raw data from COD SRT 30 days

Day	COD (mg/l)		
	*Raw water	**Treated water**	**%Removal**
1	1867.4	31.5	98.3
3	1867.4	29.5	98.4
6	1867.4	56.5	97.0
8	1867.4	73.5	96.1
10	1867.4	85.7	95.4
13	1867.4	159.2	91.5
15	1867.4	69.4	96.3
17	1867.4	57.1	96.9
24	1867.4	65.0	96.5
26	1867.4	61.0	96.7
28	1867.4	65.3	96.5
30	1867.4	65.3	96.5
33	1867.4	55.2	97.0
36	1867.4	67.6	96.4
39	1867.4	77.6	95.8
42	1867.4	70.5	96.2
45	1867.4	70.5	96.2
48	1867.4	62.2	96.7
50	1867.4	62.2	96.7
52	1867.4	52.0	97.2
55	1867.4	64.0	96.6
59	1867.4	52.0	97.2
62	1867.4	60.0	96.8
64	1867.4	52.0	97.2
66	1867.4	52.0	97.2

*Raw water uses the average value

A-6 Raw data from COD SRT infinite

Day	COD (mg/l)		
	*Raw water	**Treated water**	**%Removal**
1	1911.6	65.6	96.6
3	1911.6	114.8	94.0
6	1911.6	57.4	97.0
8	1911.6	57.4	97.0
11	1911.6	82.0	95.7
12	1911.6	82.0	95.7
13	1911.6	73.8	96.1
24	1911.6	98.4	94.9
26	1911.6	82.0	95.7
29	1911.6	98.4	94.9
31	1911.6	57.4	97.0
36	1911.6	41.0	97.9
38	1911.6	0.0	0.0
41	1911.6	0.0	0.0
43	1911.6	0.0	0.0
45	1911.6	0.0	0.0
48	1911.6	0.0	0.0
50	1911.6	0.0	0.0
52	1911.6	0.0	0.0
55	1911.6	0.0	0.0
57	1911.6	116.9	93.9
59	1911.6	121.0	93.7
62	1911.6	116.9	93.9
64	1911.6	121.0	93.7
66	1911.6	116.9	93.9

*Raw water uses the average value

A-7 Raw data from TOC SRT 15 days

Day	TOC (mg/l)		
	*Raw water	Treated water	%Removal
1	451.5	9.22	97.96
4	451.5	13.6	96.99
7	451.5	8.06	98.21
10	451.5	20.29	95.51
13	451.5	22.53	95.01
19	451.5	16.16	96.42
20	451.5	15.31	96.61
22	451.5	15.53	96.56
25	451.5	19.13	95.76
27	451.5	19.04	95.78
32	451.5	18.58	95.88
36	451.5	17.96	96.02
39	451.5	13.54	97.00
41	451.5	14.67	96.75
43	451.5	15.33	96.60
46	451.5	16.69	96.30
48	451.5	8.85	98.04
50	451.5	9.48	97.90
53	451.5	9.31	97.94
55	451.5	8.57	98.10
57	451.5	10.69	97.63
61	451.5	9.66	97.86
62	451.5	10.24	97.73
71	451.5	8.3	98.16

*Raw water uses the average value

A-8 Raw data from TOC SRT 30 days

Day	TOC (mg/l)		
	*Raw water	Treated water	%Removal
1	462.65	98.12	78.79
3	462.65	11.13	97.59
6	462.65	33.22	92.82
8	462.65	45.71	90.12
10	462.65	48.25	89.57
13	462.65	36.33	92.15
15	462.65	84.98	81.63
17	462.65	20.22	95.63
24	462.65	27.19	94.12
26	462.65	18.1	96.09
28	462.65	7.07	98.47
30	462.65	7.56	98.37
33	462.65	8.55	98.15
36	462.65	8.82	98.09
39	462.65	9.51	97.94
42	462.65	8.91	98.07
45	462.65	11.16	97.59
48	462.65	13.4	97.10
50	462.65	11.88	97.43
52	462.65	10.62	97.70
55	462.65	11.98	97.41
59	462.65	10.55	97.72
62	462.65	11.37	97.54
64	462.65	10.4	97.75
66	462.65	12.14	97.38

*Raw water uses the average value

A-9 Raw data from TOC SRT infinite

Day	TOC (mg/l)		
	*Raw water	Treated water	%Removal
1	484.15	81	83.27
3	484.15	57.75	88.07
6	484.15	82	83.06
8	484.15	109.75	77.33
11	484.15	104.25	78.47
12	484.15	119	75.42
13	484.15	95.75	80.22
24	484.15	116.25	75.99
26	484.15	124	74.39
29	484.15	142	70.67
31	484.15	122.5	74.70
36	484.15	146.25	69.79
38	484.15	142	70.67
41	484.15	64.8	86.62
43	484.15	46.2	90.46
45	484.15	65.6	86.45
48	484.15	87.8	81.87
50	484.15	83.4	82.77
52	484.15	95.2	80.34
55	484.15	76.6	84.18
57	484.15	93	80.79
59	484.15	99.2	79.51
62	484.15	113.6	76.54
64	484.15	98	79.76
66	484.15	117	75.83

*Raw water uses the average value

A-10 Raw data from THMFPs at SRT 15 days

SRT 15 days	Raw	Out	Raw (HPO)	Out (HPO)	Raw (HPI)	Out (HPI)
$CHCl_3$	5088.68	1342.42	2093.06	997.97	10318.59	72.07
$CHBrCl_2$	385.27	174.98	0.00	168.59	1875.26	226.53
$CHBr_2Cl$	0.00	0.00	0.00	0.00	0.00	0.00
$CHBr_3$	0.00	0.00	0.00	0.00	0.00	0.00
	5473.95	1517.40	2093.06	1166.56	12193.86	298.60

A-11 Raw data from THMFPs at SRT 30 days

SRT 30 days	Raw	Out	Raw (HPO)	Out (HPO)	Raw (HPI)	Out (HPI)
$CHCl_3$	5088.68	705.11	2093.06	4085.34	10318.59	-
$CHBrCl_2$	385.27	0.00	0.00	466.97	1875.26	-
$CHBr_2Cl$	0.00	0.00	0.00	0.00	0.00	-
$CHBr_3$	0.00	0.00	0.00	0.00	0.00	-
	5473.95	705.11	2093.06	4552.31	12193.86	0.00

A-12 Raw data from THMFPs at SRT infinite

SRT infinite	Raw	Out	Raw (HPO)	Out (HPO)	Raw (HPI)	Out (HPI)
$CHCl_3$	5088.68	1516.83	2093.06	1430.77	10318.59	0.00
$CHBrCl_2$	385.27	38.87	0.00	295.10	1875.26	792.92
$CHBr_2Cl$	0.00	0.00	0.00	0.00	0.00	0.00
$CHBr_3$	0.00	0.00	0.00	0.00	0.00	0.00
	5473.95	1555.70	2093.06	1725.88	12193.86	792.92

A-13 Raw data from resin fractionation

Sample	Parameter	Fractionated water		HPI + HPO	Unfractionate water	%Diff
		HPI	HPO			
Raw	DOC (mg/L)	156	64.2	220.2	567.2	-251.53
	Mass DOC (mg)	468	16.05	484.05	1701.6	
	% Mass DOC	96.7	3.3	100		
	THMFP (mg/L)	12193.9	2093.1	14286.9	5474.0	
	% THMFP	85.3	14.7	100.0		
SRT 15	DOC (mg/L)	22.215	36.05	58.265	26.62	-5.55
	Mass DOC (mg)	66.645	9.0125	75.6575	79.86	
	% Mass DOC	88.1	11.9	100		
	THMFP (mg/L)	298.6	1166.6	1465.2	1517.4	
	% THMFP	20.4	79.6	100.0		
SRT 30	DOC (mg/L)	17.035	7.458	24.493	12.03	50.88
	Mass DOC (mg)	51.105	22.375	73.48	36.09	
	% Mass DOC	69.5	30.5	100		
	THMFP (mg/L)	532.2	4552.3	5084.5	705.1	
	% THMFP	10.5	89.5	100.0		
SRT infinie	DOC (mg/L)	21.195	6.91667	28.11167	22.89	18.57
	Mass DOC (mg)	63.585	20.75	84.335	68.67	
	% Mass DOC	75.4	24.6	100		
	THMFP (mg/L)	792.9	1725.9	2518.8	1555.7	
	% THMFP	31.5	68.5	100.0		

จุฬาลงกรณ์มหาวิทยาลัย

CHULALONGKORN UNIVERSITY

A-14 Calibration table from THMFPs

```
========================================================================
                          Calibration Table
========================================================================



Calib. Data Modified   :       Wednesday, February 27, 2019 11:14:45 AM


Rel. Reference Window :        5.000 %
Abs. Reference Window :        0.000 min
Rel. Non-ref. Window  :        5.000 %
Abs. Non-ref. Window  :        0.000 min
Uncalibrated Peaks     :        not reported
Partial Calibration    :        Yes, identified peaks are recalibrated
Correct All Ret. Times:        No, only for identified peaks

Curve Type             :        Linear
Origin                 :        Included
Weight                 :        Equal

Recalibration Settings:
Average Response       :        Average all calibrations
Average Retention Time:        Floating Average New 75%

Calibration Report Options :
    Printout of recalibrations within a sequence:
        Calibration Table after Recalibration
        Normal Report after Recalibration
    If the sequence is done with bracketing:
        Results of first cycle (ending previous bracket)
```

```
Signal 1: ECD1 A,

RetTime   Lvl    Amount       Area      Amt/Area  Ref Grp Name
 [min] Sig         [ppb]
-------|--|--|----------|----------|----------|---|--|---------------
  1.450  1  1    25.00000    69.33199 3.60584e-1         Chloroform
            2    50.00000   224.04796 2.23167e-1
            3   100.00000   275.94226 3.62395e-1
            4   200.00000   634.59235 3.15163e-1
            5   300.00000   927.57709 3.23423e-1
            6   400.00000  1093.48145 3.65804e-1
            7   500.00000  1297.78552 3.85272e-1
  1.988  1  1    25.00000   375.88925 6.65090e-2         Bromodichloromethane
            2    50.00000  1475.38184 3.38895e-2
            3   100.00000  1855.84705 5.38838e-2
            4   200.00000  4299.59229 4.65160e-2
            5   300.00000  5504.00732 5.45057e-2
            6   400.00000  8239.62695 4.85459e-2
            7   500.00000  8681.64844 5.75927e-2
  2.729  1  1    25.00000   406.49368 6.15016e-2         Dibromochloromethane
            2    50.00000  1540.97778 3.24469e-2
            3   100.00000  1963.83716 5.09207e-2
            4   200.00000  4529.42041 4.41558e-2
            5   300.00000  5647.82129 5.31178e-2
            6   400.00000  8573.57910 4.66550e-2
            7   500.00000  9243.19922 5.40938e-2
  3.633  1  1    25.00000   194.42650 1.28583e-1         Bromoform
            2    50.00000   677.48615 7.38022e-2
            3   100.00000   854.47711 1.17031e-1
            4   200.00000  1886.57239 1.06012e-1
            5   300.00000  2311.64746 1.29778e-1
            6   400.00000  3488.33130 1.14668e-1
            7   500.00000  3759.67749 1.32990e-1
```
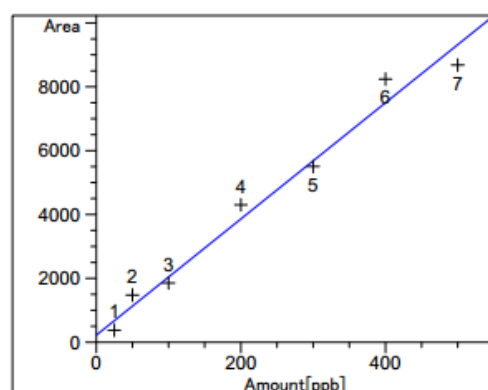
A-15 Calibration curves from THMFPs

==
                      Calibration Curves
==
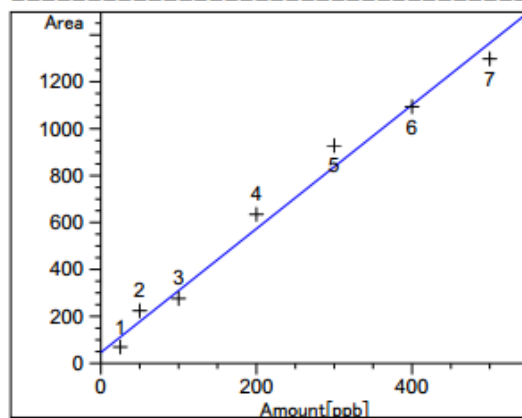
Chloroform at exp. RT: 1.450
ECD1 A,
Correlation: 0.99309
Residual Std. Dev.:   62.76523
Formula: y = mx + b
        m: 2.63977
        b: 45.63937
        x: Amount
        y: Area

Bromodichloromethane at exp. RT: 1.988
ECD1 A,
Correlation: 0.99100
Residual Std. Dev.:   494.94180
Formula: y = mx + b
        m: 18.20739
        b: 219.42021
        x: Amount
        y: Area
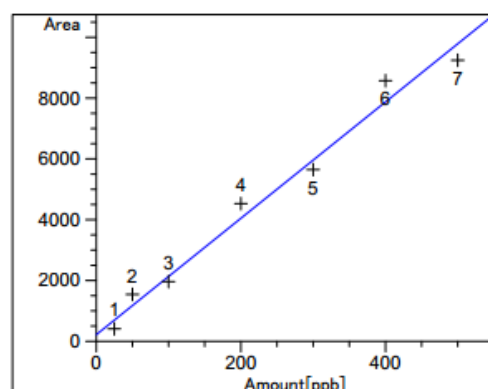
Dibromochloromethane at exp. RT: 2.729
ECD1 A,
Correlation: 0.99217
Residual Std. Dev.:   484.96980
Formula: y = mx + b
        m: 19.14649
        b: 218.70043
        x: Amount
        y: Area

Bromoform at exp. RT: 3.633
ECD1 A,
Correlation: 0.99145
Residual Std. Dev.: 204.55011
Formula: y = mx + b
      m: 7.72198
      b: 126.31224
      x: Amount
      y: Area
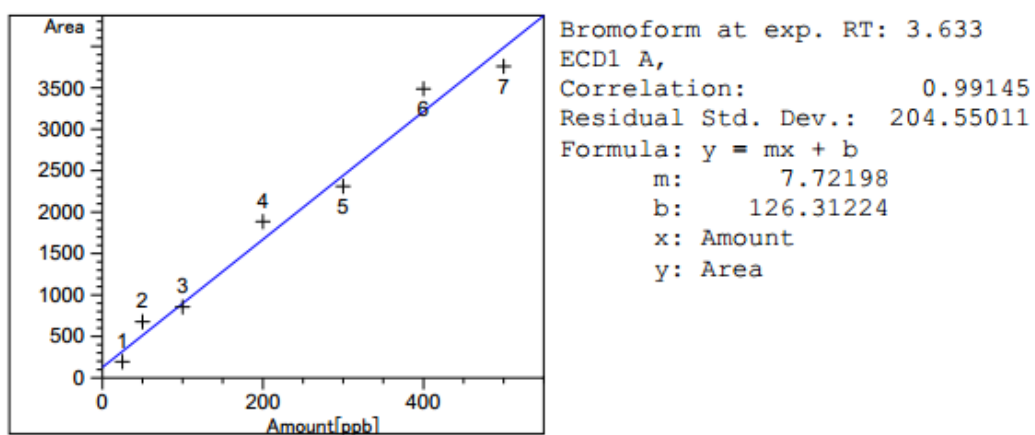
A-16 Flux membrane during operated under SRT 15 days

				SRT 15 days
Day	Time	ml/s	Q (L/hr) = V/t	Flux (L/hr/m2) = Q/Am
1	43.35	0.92	3.32	17.21
3	40.54	0.99	3.55	18.40
6	37.47	1.07	3.84	19.91
8	40.68	0.98	3.54	18.34
11	38.06	1.05	3.78	19.60
12	39.71	1.01	3.63	18.79
13	40.3	0.99	3.57	18.51
24	39.75	1.01	3.62	18.77
26	40.86	0.98	3.52	18.26
29	38.76	1.03	3.72	19.25
31	42.06	0.95	3.42	17.74
36	41.68	0.96	3.45	17.90
38	40.85	0.98	3.53	18.26
41	38.96	1.03	3.70	19.15
43	39.85	1.00	3.61	18.72
45	39.29	1.02	3.67	18.99
48	35.59	1.12	4.05	20.96
50	38.95	1.03	3.70	19.16
52	40.28	0.99	3.57	18.52
55	41.67	0.96	3.46	17.91
57	40.43	0.99	3.56	18.45
59	39.35	1.02	3.66	18.96
62	37.06	1.08	3.89	20.13
64	39.18	1.02	3.68	19.04
66	40.72	0.98	3.54	18.32

A-17 Flux membrane during operated under SRT 30 days

SRT 30 days				
Day	Time	ml/s	Q (L/hr) = V/t	Flux (L/hr/m2) = Q/Am
1	38.58	1.04	3.73	19.34
3	40.75	0.98	3.53	18.31
6	40.52	0.99	3.55	18.41
8	44.69	0.90	3.22	16.70
11	42.17	0.95	3.41	17.69
12	42.76	0.94	3.37	17.45
13	43.14	0.93	3.34	17.30
24	44.38	0.90	3.24	16.81
26	43.98	0.91	3.27	16.96
29	43.35	0.92	3.32	17.21
31	40.23	0.99	3.58	18.55
36	41.88	0.96	3.44	17.82
38	39.46	1.01	3.65	18.91
41	41.3	0.97	3.49	18.07
43	41.82	0.96	3.44	17.84
45	40.97	0.98	3.51	18.21
48	38.4	1.04	3.75	19.43
50	40.75	0.98	3.53	18.31
52	37.52	1.07	3.84	19.89
55	41.78	0.96	3.45	17.86
57	40.85	0.98	3.53	18.26
59	43.46	0.92	3.31	17.17
62	37.96	1.05	3.79	19.66
64	37.62	1.06	3.83	19.83
66	37.36	1.07	3.85	19.97

VITA

NAME   Nichapach Puangmalai

DATE OF BIRTH   16 January 1994

PLACE OF BIRTH   Phayao, Thailand

INSTITUTIONS   International Programs in Hazardous Substance and
ATTENDED   Environmental Management
HOME ADDRESS   114 Moo 12, Bantom, Muang, Phayao, Thailand 56000