SHANGHAI JIAO TONG UNIVERSITY

OPTIMIZATION OF MEMBRANE FABRICATION PROCESS AND EXPERIMENTAL CONDITIONS FOR THE REMOVAL OF NATURAL ORGANIC MATTER

A Major Qualifying Project Report

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Abstract

Membrane Ultrafiltration (UF) is a great alternative for treating Natural Organic Matter (NOM) in drinking water that might be harmful for human health. However, membrane fouling is an important factor that restricts its widespread application. This project worked on reducing membrane fouling and improving membrane NOM removability by optimizing the membrane fabrication and the experimental conditions of ultrafiltration. By distributing an additional layer of titanium dioxide (TiO_2) photocatalyst on the TiO_2 doped polyvinylidene fluoride (PVDF)-polyethylene glycol (PEG) membrane. Results indicated the membrane fouling was reduced from 40% to less than 10% and the membrane NOM rejection rate increased from around 80% to above 93%.

Acknowledgments

I would like to thank my advisor Professor Zhou, co-advisor Professor DiBiasio of Worcester Polytechnic Institute and co-advisor Professor Shao of Shanghai Jiao Tong University for this great research opportunity in Environmental Engineering Department of Shanghai Jiao Tong University Minghang Campus. Additional thanks are owed to PHD student Hassan Younas who helped me with membrane preparations and running the experiments. Special thanks to Xiuwen Chen and Shuai Du who helped me a lot with everything around campus when I was staying in Shanghai.

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Nomenclatures

Variable	Definition
R (%)	Membrane rejection rate
C_P	Concentrations of HA in the permeate Stream
C_F	Concentrations of HA in the Feed Stream
J	Permeate flux (L m^{-2} h^{-1})
A	Effective membrane filtration area
V	Total volume of the permeate
t	Total ultrafiltration time (min).
J_0	Initial flux at steady state
J	Permeate flux at a certain time

1 Introduction

Having access to clean water is a particularly acute problem in China today. The water supply in China is less than that of the U.S., yet it must meet the needs of a population of nearly five times as large. [1] High population density, a poor ratio of available water to demand, and regional imbalances in available water supplies are serious challenges for China in managing its usable water supply. On top of the water shortage problem, water pollution has got severe over the years. Starting from early 1990s, the major water contamination source has slowly shifted from microorganisms into natural organic matters (NOM). [2] NOM can cause problems to drinking water and generate harmful disinfection by-products (DBPs) during chlorination. To ensure the quantity and quality of drinking water, China has been focused on the investigation of appropriate water treatments for NOM removal.

A possible solution for treating the NOM is membrane ultrafiltration (UF), which is an effective and economical way for purifying and concentrating macromolecular solutions. However, membrane fouling is the most important factor that restricts the wide application of UF technology to water NOM treatment. Membrane fouling is the blockage of membrane pores during filtration by the sieving and adsorption of particulates and compounds onto the membrane surface or within the membrane pores [3]. Pore blockage not only reduces the permeate flux and affect the efficacy of membrane filtration but also causes cracks on the membrane surface and shorten the membrane life spam which lead to high expense. Minimize membrane fouling is the key to make UF into a sustainable MON treatment.

Polyvinylidene fluoride (PVDF) is an organic polymer material commonly used for UF process. Despite its good tensile strength and proper asymmetric structure, PVDF can be easily fouled by water contaminants. [4] Over the past decay, several studies have been done to improve PVDF membrane fouling. [5] Among all the approaches, developing a more hydrophilic membrane surface seems to the most effective one. [6] Previous researches have found that polyethylene glycol (PEG) additives can be physically blended with PVDF to enhance membrane hydrophilicity thus reduce membrane fouling. [7] Recent investigations on nanotechnology also suggest better membrane performance can be achieved by combining PVDF membrane with suspended titanium dioxide (TiO_2) nanoparticles. TiO_2 is commonly used for photocatalystic water contaminants degradation under ultraviolet (UV) light. Combining TiO_2 with PVDF will help degrade some of the NOM during UF thus reduce PVDF membrane fouling. [8] However, such process is a lot more complex and expensive compared to single ultrafiltration process, plus the unrecycled TiO_2 nanoparticles in water might also lead to environmental problems. [3] An alternative is to immobilize TiO_2 by blending it with PVDF in the membrane casting solution to fabricate organic-inorganic composite membranes. [9] This approach integrates the membrane separation and photocatalystic degradation into a single operation. The pre-treated membrane will not only have the ability to degrade NOM and reduce membrane fouling during UF process under UV light, but also prevent the TiO_2 nanoparticles from moving into the water and causing more problems. [10] To testify and optimize this process, students in Shanghai Jiao Tong University (SJTU) have fabricated membranes using various concentrations of TiO_2 P25 (average size of 20–30 nm (Degussa Corp)) doped PVDF (SOLEF® 6020, Solvay Ltd.)-PEG (molecular weight of 600 Da) casting solution and performed experiments in a cross flow ultrafiltration system under ultraviolet (UV) light. [3] Results indicated that membrane fouling was successfully reduced and over 60% of the NOM was rejected.

This MQP is a continuation of previous research. The goal is to further reduce membrane fouling and improve the NOM removal ability to the next level. To achieve that, a layer of TiO_2 photocatalyst was evenly developed on the membrane surface in addition to the casting solution.

The semi-permeate side of the membrane that allows molecules to pass through the membrane selectively through osmosis is also known as the selective layer. During the modified process, the direction of the selective layer of the membrane was turned from facing the UV light to back against the UV light. The permeate flux and the NOM rejection were compared between modified

membranes and unmodified membranes. Results indicate that membrane fouling was significantly reduced to less than 10% and up to 93% of the NOM was remove by the modified membranes under UV light. The detailed methodology, results and conclusions along with recommendations for future experiments are discussed here.

2 Background Information

2.1 Water Situation in China

In 2012, the World Health Organization (WHO) estimated that one out of four (300 million) Chinese do not have daily access to clean water, and that one out of two (700 million) are forced to consume water below WHO standards. [1] In 2013, about 200 million of Chinese were reported sick from drinking contaminated water. [11]

Aware of the severity, Chinese government has placed great emphasis on cleaning up the country's water supply in its 12th Five-Year Plan that began in 2011. [1] During this period, the country will spend a total of $536 billion on water purification and wastewater treatment plants, irrigation systems and flood control projects. By the year of 2015, the government intended to increase its urban wastewater treatment rate to 85 percent by adding 42 million tons of daily NOM treatment capacity. [1] To achieve such water purification duty, the country must come up with long-term and sustainable water treatments with low cost and high efficiency. The most obvious solution to enhanced wastewater treatments would be to improve the performance of existing processes. [12] Membrane filtration is currently used as a refining phase of conventional water treatments to remove the untreated residuals. It has been recognized for its superior outcome quality and low cost. With proper modification, it might become the appropriate water treatment for China's water situation.

2.2 Water Purification

2.2.1 Natural Organic Matters in Water

Natural Organic Matters (NOM) has historically been a concern at some water treatment plants. [13] It can be derived from both internal (autochonous) aquatic and external (allochthonous) sources. The factors influencing NOM levels in surface water can be classified into natural and human-related factors. [14] Examples of natural factor are the climate, the typography, the geology, and soils. Areas with wet climate and high precipitation events are subject to soil detachment and mobilization. Areas with steep slopes and have tendency of natural erosion. Organic particulate materials, sediments, debris and nutrients are then introduced into the source water. [15] The increased nutrient loading will cause algae and weed growth, which contributes to the levels of NOM in source water. [16] Human-related factors include land development, forest management, agricultural, dairies, feed lots and urban run off which also lead to surface erosion and introduce nutrient into source water. [17] In the past century, society growth and technology developments have brought great changes to human beings lives. However, due to the rapid increasing population and over deforestation, the amount of dissolved NOM source water also increased. [12] NOM is a complex mixture of both aliphatic and aromatic molecules with a wide variety of chemical compositions and molecular sizes. It is created from the decomposition process of living or growing organisms, such as animals, plants and microorganisms after their death. It is responsible for giving the water a distinct yellow-brown color. NOM causes problems in the production of drinking water. [12] Not only does it have an adverse effect on the aesthetic water quality and may result in biofouling of pipelines with negative hygienic consequences, [18] but it has also been demonstrated that NOM is the basis for the production of potentially hazardous disinfection by-products (DBPs). [19] Thus, NOM must be removed from source water efficiently to prevent drinking water contamination.

NOM molecule generally contains aromatic carbon rings, which make it relatively stable and thus hard to break down. There are both humic and non-humic fractions of NOM [20]. The humic substance is a major fraction of NOM in surface water therefore humic acid (HA) were commonly used to test NOM removal rate in laborites. [3]

2.2.2 Conventional Treatments for NOM

NOM can be removed from water by a number of different treatment processes. [21] Some of the common NOM removal treatments are coagulation and activated carbon (AC) filtration. [12]

Coagulation is a process where the repulsive potential of electrical double layer of colloids is reduced so that micro-flocs can be produced. The micro-flocs collided with each other and form larger structures (flocs) in flocculation process. [22] Chemical coagulation can be achieved by addition of inorganic coagulants such as aluminum or iron salts. [12] In the process of coagulation, NOM is removed through a combination of charge neutralization, entrapment, adsorption and complexion with coagulant metal ions into insoluble particulate aggregates. These micro-particles are then further agglomerated to form the flocs. [23] The hydrophobic fraction of NOM with high molar mass (HMM) can be removed from water effectively by the chemical coagulation process. However, the hydrophilic fraction of NOM with intermediate and low molar mass (LMM) can pass through the process and remain in source water. Although NOM removal can be achieved by optimizing the processes, the increased coagulant doses will result in higher costs. Some studies show that the removal of the lowest molar mass organic compound is not improved even when coagulation of optimized. [24] [25]

Activated carbon (AC) adsorption is an effective absorbent that commonly used in micro pollutants. [26] LMM compounds can be absorbed by AC filtration more efficiently than HMM compounds because their surface area are more accessible. [27] [28] Smaller molecules can easily enter the nanopores that would separate them from macromolecules. Thus, AC filtration is an effective way to reduce the DBP precursor compounds. [29] However, like all the other absorbents, AC absorbent has limited capacity and it need to be replaced or recharged. [30] The most common way to regeneration AC is thermal reactivation at temperature above 700C. [31] [32] However, degradation of AC particles has been found after going through several regenerations. [33] The absorbent then need to be completely replaced which make AC a relatively expensive water treatment process.

Overall, AC absorption process is expensive and demand some process modifications. But economically feasible process like coagulation is not able to remove LMM organic matters completely. [12] Other NOM removal processes include ion exchange resin filtration, chlorine-based disinfection, ozonation and membrane filtration. [12] However, chlorine-based disinfection and ozonation process can lead to the formation of trihalomethanes (THMs) and other harmful DBPs. [34] [35] Both of the processes need to be combined by with other treatments for further purification, which also make the process expensive.

2.3 Membrane Ultrafiltration

Although membrane filtration technology has been available for several decades, it wasn't until recent when membranes were used for NOM removal. [15] Pressure driven membrane processes include reverse osmosis (RO), nanofiltration (NF), ultrafiltration (UF) and microfiltration (MF). [18]

UF is a cross-flow separation process. It is typically used to remove high molecular-weight substances, colloidal materials, and organic/inorganic polymeric molecules. [36] The feed stream is caused to flow under pressure across a membrane surface, thereby producing two streams. Solutes and colloids are rejected at the semi-permeable membrane barrier while solvents and micro solutes below the molecular weight cut-off (MWCO) pass through the membrane. [28] The stream of liquid that comes through the membrane is called permeate and the other stream is called concentrate. UF was first observed to be superior as the refining phase after conventional treatment. [29] UF process can significantly improve the removal of LMM organic matter, which can avoid high cost of using extra coagulation agents and other chemicals. [30] In spite of the excellent NOM removal capacity, the problems in the use of UF in surface water treatment include: membrane fouling which leads to the need of rapid membrane replacement, low process yields in comparison with conventional processes, and need for raretentate and cleaning solution disposal. [31]

Much of the research has focused on a greater understanding of the membrane fouling potential of surface water constituent. [32] [32] [34] Several studies indicate that NOM, especially the hydrophobic and HMM fraction of the NOM is somewhat responsible for membrane fouling. [35] [36] [37] Improving the membrane surface hydrophilicity is critical for increase the membrane anti-fouling ability during UF process.

2.4 Enhanced Ultrafiltration Membranes

The hydrophilicity of the membranes and its porous structure play an essential role in membrane separation processes. High surface porosity and proper pore structure of membranes are extremely important to obtain high membrane permeability during ultrafiltration process. [38] Among all organic macromolecule polymer materials, polyvinylidene fluoride (PVDF) is one of the ideal materials for ultrafiltration because it forms asymmetric structured membranes that are excellent for separation (refer figure 1).

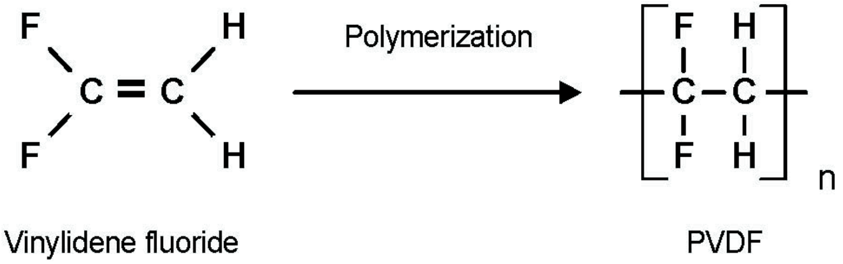

Figure 1 Structure of PVDF

PVDF-based membranes show outstanding oxidative, thermal and hydrolytic stability as well as good mechanical and film-forming properties. [8] [40] That is the reason why PVDF membranes are widely used in many ultrafiltration processes. However, due to the hydrophobic nature of PVDF polymer, a neat PVDF membrane can be easily fouled by NOM. The fouled membrane will lead to permeate flux decline hence lower NOM removal efficiency and less process yield. [7] The fouled containments can also build up on membrane surface causing cracks and making the membrane less durable over time.

Several additives can be used to enhance the hydrophilicity of polymeric membranes such as glycols, lithium chloride and lithium perchlorate. [41] Polyethylene glycol (PEG) stands out because its low cost and good biocompatibility. [10] [11] .PEG is soluble in many organic solvents including aromatic hydrocarbons. [42] Hence PEG has been reported as a pore former to enhance the permeation properties for not only hydrophilic membranes but also hydrophobic [membrane like PVDF. [43] PEG can be easily dissolved in casting solution to fabricate enhanced PVDF membranes while obtain the pore size and high porosity. The graft copolymers with PEG side chains often show an enhanced hydrophilicity and anti-fouling ability compared with the hydrophobic polymeric backbones alone. [44]

Recent research shown photo degradation process can be combined with UF to increase NOM removal rate because it can degrade bulky molecules blocked on membrane surface and reduce membrane fouling. [45][46] A photo degradation process is an oxidation reaction in the presence of light and oxygen, and, the photocatalyst is the agent that is capable of combining light and oxygen (reactants). [47] Titanium dioxide (TiO_2) is an excellent photocatalyst that has been used to degrade water contamination for the past few years. Not only it is photoactive, non-toxic and stable but also very easy to generate and inexpensive [5] TiO_2 can be physically blended into the casting solution with PVDF and PEG to fabricate TiO_2-doped PVDF-PEG membranes. The TiO_2-doped PVDF-PEG membranes shown smaller pore size, increased hydrophilicity and anti-fouling abilities in preliminary tests. [3] Although TiO_2 is excitable under both visible and UV light, TiO_2-doped PVDF-PEG membrane shown better self-cleaning ability, anti-bactericidal and anti-fouling abilities under UV light exposure.

2.5 Goal and Significance

To optimize the membrane ultrafiltration experiments, the following goal were set to be achieved within 7 weeks.

(1) To study the effect of the addition layer of TiO_2 on top of the TiO_2-doped PVDF-PEG membranes membrane surface under natural light.

(2) To study the effect of the addition layer of TiO_2 on top of the TiO_2-doped PVDF-PEG membranes membrane surface under UV light.

(3) To study the effect of the membrane selective layer direction of the TiO_2-doped PVDF-PEG membranes membrane surface under UV light.

(4) Select the membranes with the lowest membrane fouling and highest HA removal rate and see if the result if repeatable.

(5) Select the best performing membrane with constantly low membrane fouling and high HA removal rate for future studies.

In the research point of view, the results of this project will be helpful for those who is interested in continue working on optimizing membrane ultrafiltration process. The conclusion of this project can be used to conduct future researches on improving the membrane ultrafiltration process for NOM removal.

In the society point of view, this project will significantly reduce membrane fouling thus maximize the process yield and NOM removal rate. The modified membranes will have better self-cleaning ability and therefore, require less frequent maintenance and replacement. The membranes will also have longer life spans because the damages caused by water containments will be effectively prevented. Hence the cost of membrane ultrafiltration process will be significantly lower.

Over all, the optimized the membrane ultrafiltration process will be a more efficient and economically feasible treatment in water NOM removal. It can be used to replace some of the conventional NOM treatment. The same technology can be applied into other water purification process such as water bacterial removal and oil removal.

3 Experimental Method

3.1 Previous Research Summary

The modifications and experiments of this project were conducted based on the theories and results of previous studies as following.

- Humic acid (HA) is the major fraction of NOM. The concentration of HA in drinking water is roughly 2ppm (particles per million=mg/L).
- The membrane with maximum NOM rejection is 15w.t. %PVDF-1w.t. %PEG-0.5 w.t. %TiO_2. The membrane with high NOM rejection and high permeate flux is
- 12%w.t. % PVDF-2w.t. %PEG-1.5 w.t. %TiO_2 (summarized in table.1).

Table 1 Best performing Membrane Fabrication Parameters

Constituents	PVDF	PEG	TiO_2
Optimized	12%	2%	1.5%
Maximum rejection	15%	1%	0.5%

- The NOM absorbance can be measured with spectrophotometer at a wavelength λ=254nm.
- The maximum NOM rejection rate is 65%, and the membrane fouling was reduced to about 40%

3.2 Fabrication of the membrane

To compare the membrane performance during UF/photocatalysis, both unmodified and the modified membranes were prepared based on previous best performing fabrication parameters (refer table 1). Due to the 7-week time constraint, all the membranes are pre-made by Hassan Younas, a first year PHD student in Professor Shao's lab, SJTU.

3.2.1 Fabrication of Unmodified Membranes

Twelve PVDF membranes with different polymer concentration were prepared by the phase inversion process (PIP) method. The casting solution were blended with different concentrations of PVDF (SOLEF® 6020, Solvay Ltd.), additive PEG (molecular weight of 600 Da) and TiO2 particles P25 with average size of 20–30 nm (Degussa Corp.) in N, N-dimenthylacetamide (DMAc) solvent. With a casting knife of 200µm space, the solution was casting on a glass plate at a speed of 1.2m/min. The membranes were immediately immersed in the water coagulation bath at room temperature. After the coagulation, the membranes were then placed into a deionized water bath for 24 hours to remove the remaining solvent. [3]

Table 2 Fabrication Parameters for unmodified membranes

Membrane	PVDF	PEG	TiO_2
1	12%	1%	—
2	12%	2%	—
3	15%	1%	—
4	15%	2%	—
5	12%	1%	0.5%
6	12%	2%	0.5%
7	12%	1%	1.5%
8	12%	2%	1.5%
9	15%	1%	0.5%
10	15%	2%	0.5%
11	15%	1%	1.5%
12	15%	2%	1.5%

3.2.2 Modification of the membrane fabrication process

Twelve more PVDF membranes were made using the same method above. However, a layer of TiO_2 was also developed on the membrane surface in addition to the casting solution. This is to ensure the even distribution of the TiO_2 nanoparticles on membrane surface and prevent partial membrane fouling.

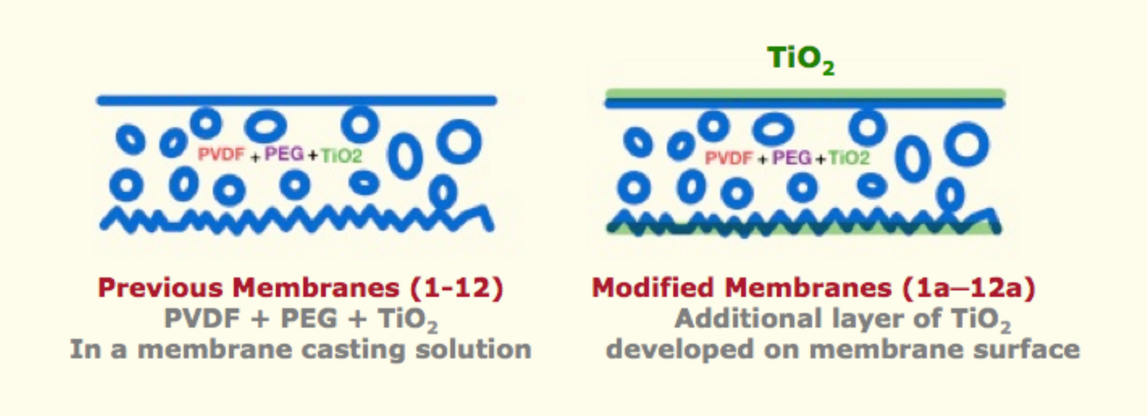

Figure 2 Modified Membranes

3.3 Modifications of Experimental Conditions

In the process of membrane separation, the semi-permeate side of the membrane that allows smaller molecules to pass through is also known as the selective layer. The blockage of the selective layer is the reason for membrane fouling and permeates flux declining. Although the NOM blockage can be degraded with the help of TiO_2 photo degradation, the rate of degradation is relatively slow when the membrane selective layer is directly facing up. This is because the bulky NOM molecules on top of the membrane surface will hinder the reaction between TiO_2 and UV light. In the modified process, the direction of the selective layer of the membrane was turned from facing the UV light to back against the UV light (refer figure 2). Such modification will speed up the photo degradation process because the NOM blockage will no longer be on the top of the membrane surface thus the rate of TiO_2 degradation will not be effected.

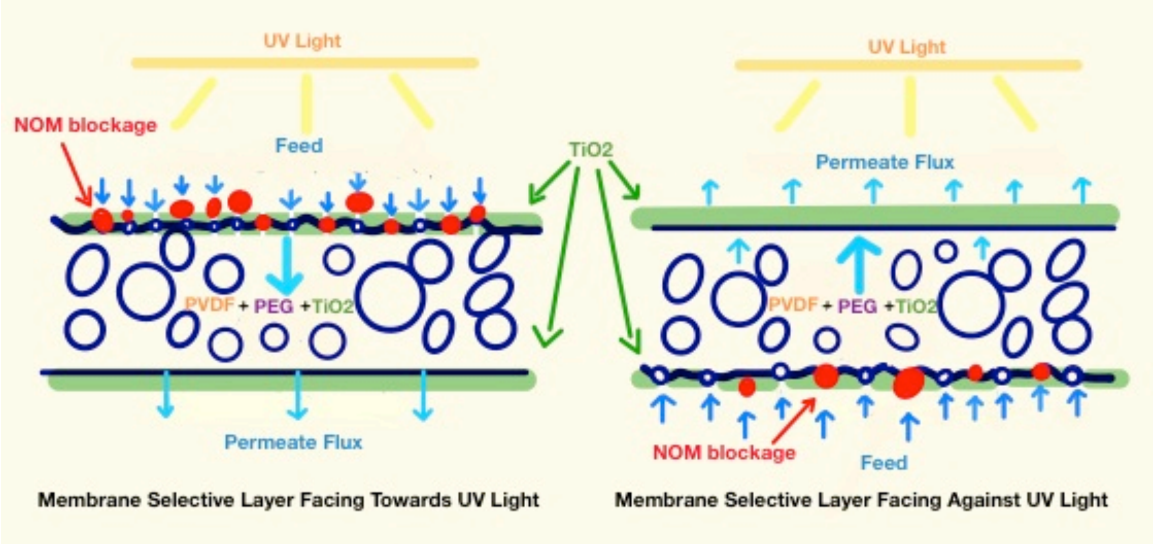

Figure 3 Membrane Selective Layer Direction During UF/photocatalysis

Higher photo degradation rate will result in less NOM blockages on the membrane surface and allow more permeate flux pass through the membrane. Hence membrane fouling will be reduced and the NOM removal rate will be increased as well as the process yield.

3.4 Preparation of humic acid Solution

Since the major fraction of NOM is humic, humic acid (HA) was used to represent NOM for the experiments. HA is prepared by dissolving 0.01g of solid Humic Acid Sodium Salt (Sigma Aldrich) into 5000ml of DI water which would create a HA concentration of 20ppm (particles per million= mg/L). The 20ppm HA was then was diluted to 2ppmHA by adding 20mg of the 20ppm HA into 2000ml of DI water.

3.5 Ultrafiltration Process

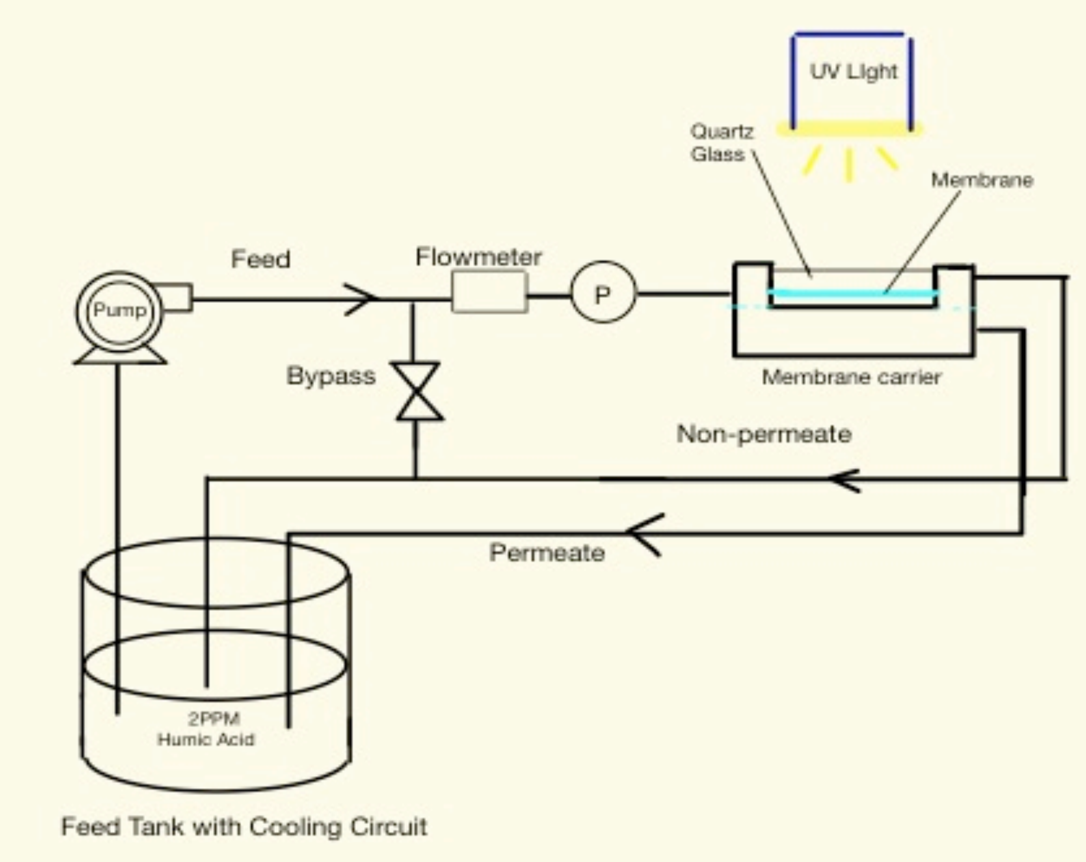

Figure 4 Schematic Diagram of cross-flow UF/Photocatalysis experiment

The Cross-flow ultrafiltration coupled with photocatalysis (UF/photocatalysis) was conducted in a lab scale custom-made filtration unit. In this unit, humic acid solution was held in a 10L reservoir and fed to the membrane carrier by a pump.

Inside the membrane carrier, the effective membrane area was 48 cm^2 (8cm× 6cm). A piece of quartz glass was embedded on the top of the membrane carrier. When conducting experiments with UV light, a 100W high-pressure mercury UV lamp (Bilon Corp, China) would be placed on top of the quartz glass and irradiated the membrane surface. After coming out of the membrane carrier, both the permeate stream and non-permeate stream would return to the reservoir to keep the feed concentration constant. The feed tank of the unit is connected to a cooling circuit to maintain the solution at a constant temperature of 25° C. The operation pressure was controlled at

0.1 MPa using a pressure gage. And the cross-flow rate was controlled at 0.5 L/min by a flow meter. The peak wavelength of UV lamp was 365 nm, and the light intensity at membrane surface was 1.2 mW/cm2. (Bilon Corp., China). [3]

3.6 Running the Experiments

In this phase, each of the membrane was cut into four 6cm × 8cm pieces (refer figure 5). There were three experimental conditions:

1. Cross-flow UF under natural light.
2. Cross-Flow UF under UV light with the membrane selective layer face forward the light.
3. Cross-flow UF with UV light while the membrane selective layer back against the light.

The forth piece of membrane was simply served as a spare. The previously prepared 2mg/L HA will be used as the initial feed of the system.

Figure 5 TiO_2 doped PVDF-PEG Membranes

Starting the preparation work by turn on the spectrophotometer and let the system pre-heat for 20mins.

Figure 6 The spectrophotometer

During this period of time, rinse the Cross-Flow membrane Ultrafiltration Unit and the PVDF membrane, the quartz cell holder and all the containers that are going to be used with DI water.

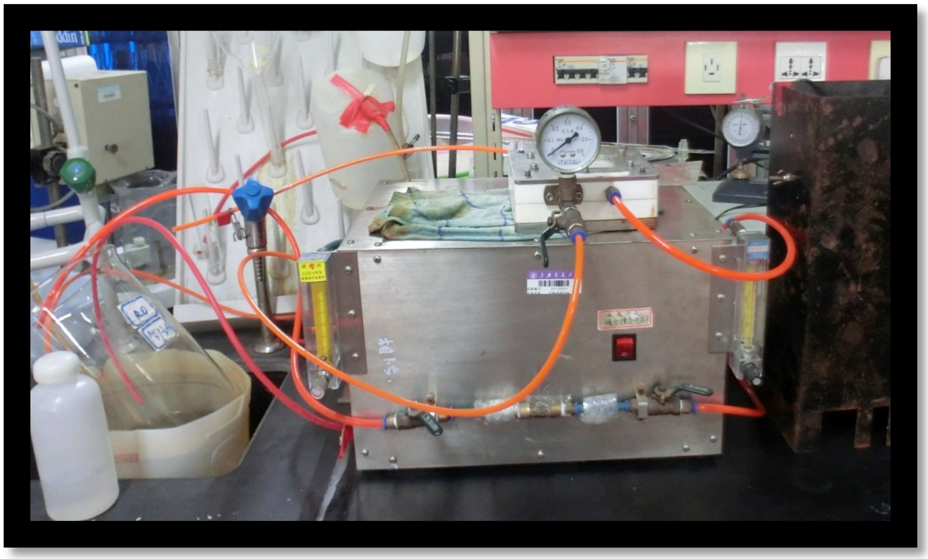

Figure 7 The cross-flow UF/photocatalysis Unit

After the system is heated, set the wavelength of the spectrophotometer to 254nm. Fill one of the cleaned cell holders with DI water. Place it in the spectrophotometer as reference absorbance then set the measure to zero.

Figure 8 The quartz cell holders

Fill the other cell holder with the same DI water and measure the absorbance to identify the spectrophotometer system error. Take one of the cell holder our and use the spectrophotometer to measure the absorbance of initial inlet stream and record it. Measure the weight of 20 clean 5ml tubes and record the weight accordingly for later use.

Put the cleaned PVDF membrane into the membrane carrier, secure the membrane by fasten the screws on the edges of the carrier. Turn on the cooling water and place the UV Light on top

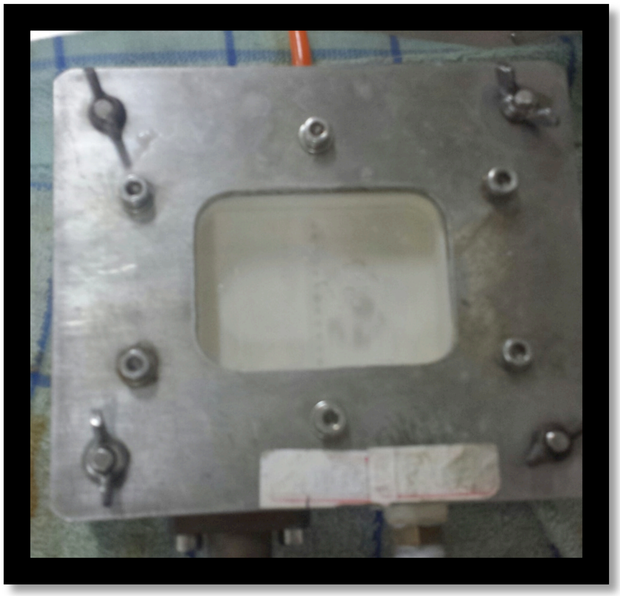

Figure 9 The Membrane Carrier

of the membrane carrier when running experiments with UV light and turn on the ultrafiltration Unit. Adjust the operating pressure to 0.1 MPa and the flow rate to 0.5ml/h. Set a timer to 10min and start it once the permeate stream come out of the system.

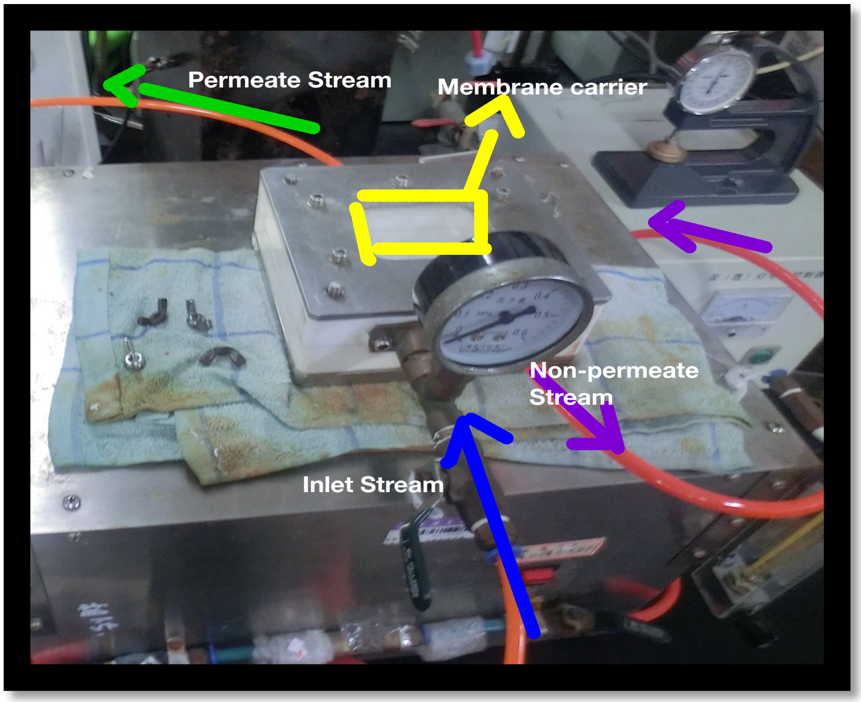

Figure 10 Membrane Ultrafiltration System

Meanwhile use one of the prepared small glass tubes to take the permeate steam for 30s then measure and record the weight. If the weight of the permeate stream is less than 4grams, increase the sampling time by 15s. After measuring the weight. Use the spectrophotometer to measure the absorbance of the permeate stream and record it. After ten minutes, repeat the steps to measure the weight and the absorbance of the permeate stream. At the same time, collect the reservoir (what's left in the tank) with a pipet and measure the absorbance. Repeat the same process for 90 minutes and record all the data.

In this phase, a total of 96 PVDF membranes were tested to gather all the data.

3.7 Data Analysis

After collecting all the data, calculations were done in excel to determine the membrane performance.

The permeate flux at any time J (L/m^{2}h) can be calculated with:

$$J = \frac{1}{A}\frac{dV}{dt} \qquad (1)$$

Where $\frac{dV}{dt} = \dot{v}$ (L/h) is the volumetric flow rate of the permeate stream that can be calculated with:

$$V = \frac{M}{\rho} \qquad (2)$$

$$\dot{v} = \frac{V}{t} \qquad (3)$$

Where M (g) is the mass and ρ (g/L) is the density of the permeate stream and t is the sampling time (h).

The permeate flux recovery can be calculated by:

$$\frac{J}{J_O} \times 100\% \qquad (4)$$

Where J_0 (L/m^{2}h) is the initial permeate flux.

The membrane NOM rejection rate is calculated by:

$$R(\%) = 1 - \frac{C_P}{C_F} \qquad (5)$$

Where C_F is the absorbance of the reservoir and the C_P is the permeate absorbance.

The detailed sample calculation is included in the appendix.

4 Results and Discussion

4.1 The Effect of Additional TiO_2 Layer on Membrane Surface under Natural Light

The membrane NOM rejection and flux recovery of two membranes with 15wt.%PVDF, 2wt. % PEG, and 0.5wt.%TiO_2 in the casting solution, one with a additional layer of TiO_2 on the membrane surface were compared. Both experiments were conducted under natural light. Where J/Jo is the permeate flux recovery and the R is the membrane NOM rejection rate.

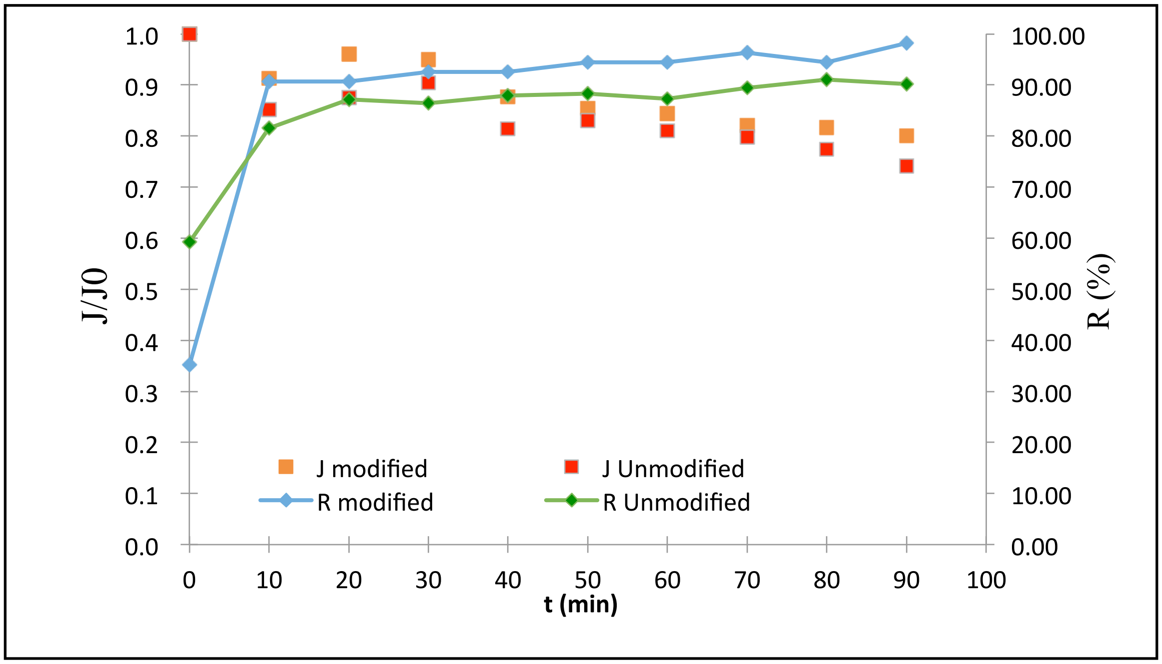

Figure 11 Flux Recovery and Membrane NOM Rejection Unmodified vs. Modified

By applying an additional layer of TiO_2 on the membrane surface, both the membrane NOM rejection rate and the permeate flux recovery was increased. The average NOM rejection rate increased from 85% to around 90%.The average permerate flux of the modified membrane was $159\frac{L}{m^2 \cdot h}$ where the average permeate flux of the unmodifed membrane was only $71\frac{L}{m^2 \cdot h}$. The average permeate flux was more thant doubled with the additional layer of the TiO_2.The results indicated that membrane fouling is better reduced by disturbuting an even layer of TiO_2 on the membrane surface. Ahtough the modified membrane shown improvements on membrane fouling and NOM removal rates. However, the permeate flux recovery shown decreasing trend over time which means the bulky NOM molecule was still building up on the membrane surface even with the addtion layer of TiO_2. This is because the experiment was conducted under natural light. Although TiO_2 photocatatlysist can be excited by visible light, it is not as effiencit as it would be under UV light.

4.2 The effect of the additional TiO_2 and UV Light

The membrane NOM rejection and permeate flux recovery of two identical membranes with 15wt.%PVDF, 2wt.%PEG, and 0.5wt.%TiO_2 in the casting solution, and additional layers of TiO_2 on the membrane surface were compared. One experiment was conducted under the UV light and another was not. Where J/Jo is the permeate flux recovery and the R is the membrane NOM rejection rate.

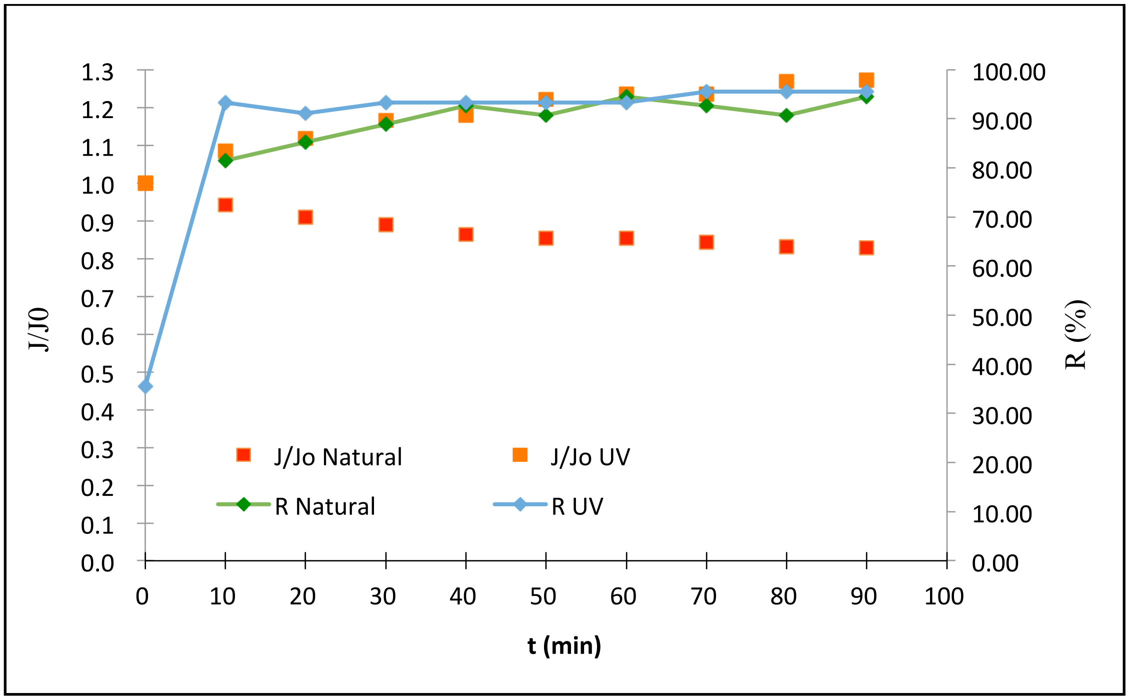

Figure 12 Flux Recovery and Membrane NOM Rejection with vs. without UV

With the presence of the UV light, the average membrane NOM rejection increased from 90% to about 93% and the average permeate flux increased from 159$\frac{L}{m^2 \cdot h}$ to 168$\frac{L}{m^2 \cdot h}$. Both of the data shown slightly increase that was not very obvious. However, the permeate flux recovery shown significant improvement and it was no longer decreasing overtime. This is because TiO_2 is an excellent photocatalyst and it will react with the UV light a lot better than natural light and produce strong hydroxyl radicals that can degrade most of the complex organic compound. The effect of photocatalysis will provide the PVDF membrane self-cleaning property which would make the membrane last longer.

4.3 The Effect of Membrane Selective Layer Direction During Ultrafiltration Under UV light

The membrane NOM rejection and permeate flux recovery of two identical membranes with 15wt.%PVDF, 2wt.%PEG, and 0.5wt.%TiO_2 in the casting solution, and additional layers of TiO2 on the membrane surface were compared. Both of the experiments were on conducted under the UV light, with one membrane facing towards and the other facing against the UV light. Where J/Jo is the permeate flux recovery and the R is the membrane NOM rejection rate.

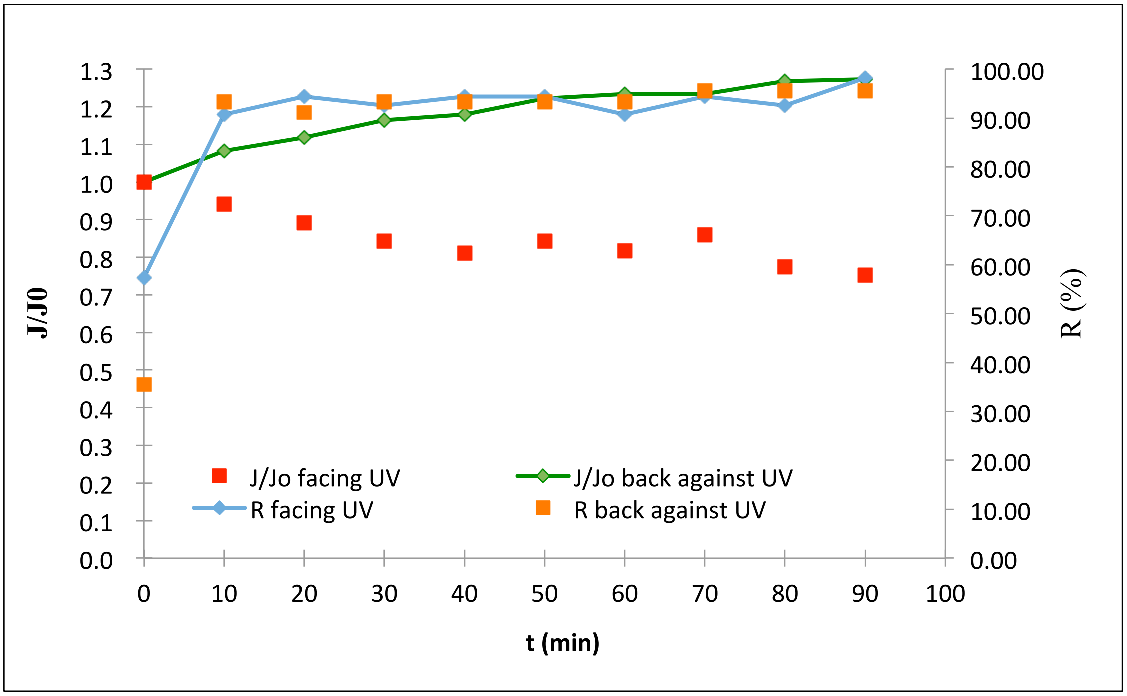

Figure 13 Flux Recoveries and Membrane NOM Rejection Selective Up vs. Down

When the memebrane selective layer was back againsting he UV light, the permeate flux recovery increased from 85% to above 90 %. This is because the modified membrane had self-cleaing abaility uder the UV light. The membrane NOM rejection rate increased from 90% to 93%. The average permeate flux increasd from 83 $\frac{L}{m^2 \cdot h}$ to 168$\frac{L}{m^2 \cdot h}$.Which indicates that the membrane fouling is a lot more reduced when the selective layer is facing against the UV light. This is because the bolky NOM molecule was no longer on top of the membrane surface hindering the photo reaction between UV light and photocatalyst TiO_2 after the selective layer is turned back against UV light. Hence the photo degradation process will be faster and more of the NOM molecules will be degraded thus recude membrane fouling.

4.4 Selective Best Result

The best performing membrane is the one with 15wt.% PVDF, 2wt.% PEG, and 0.5 wt.% TiO_2 in the casting solution; A layer of TiO_2 on membrane surface under the UV light with membrane selective layer facing against the UV light. To testify if the membrane's performance is consistent, this experiment was conducted three times. The average performance is shown blow.

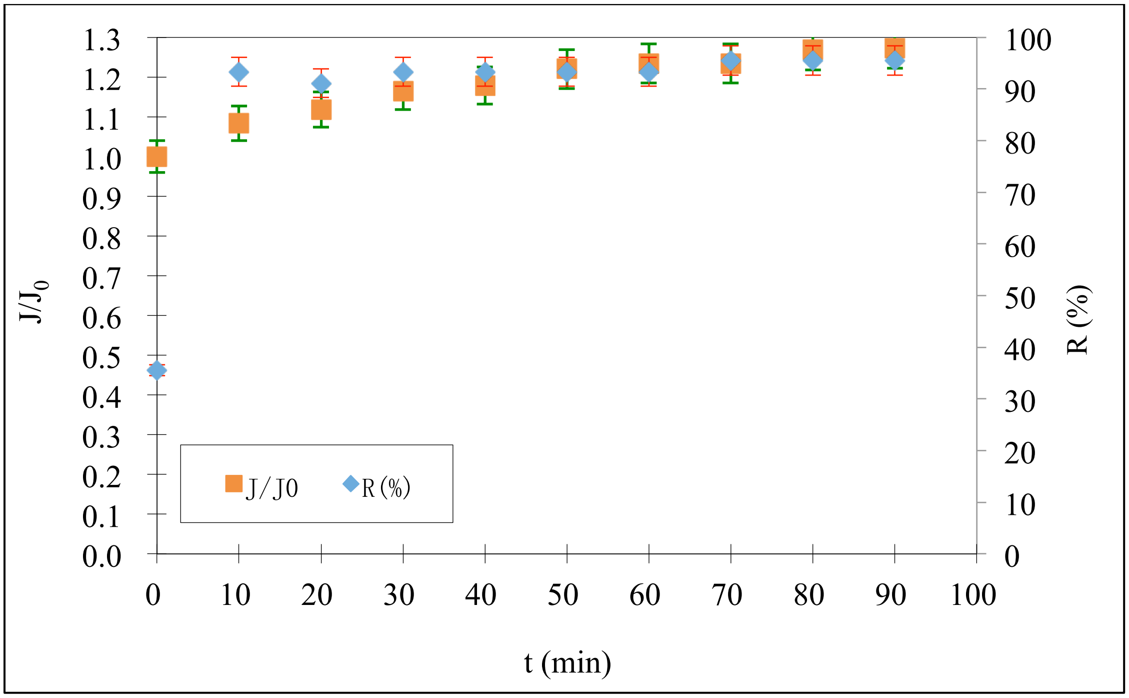

Figure 14 Best Performing Membrane

From the graph above, the membrane NOM rejection was consistently high above 93% and the permeate flux slightly increased overtime due to the UV light degradation. The result is repeatable with less than 5% of error. The modified membrane reduced membrane fouling significantly, the average permeate flux rate is 168$\frac{L}{m^2 \cdot h}$ and only less than 10% of the membrane is fouled. This result also agreed with previous studies on PVDF membrane modification in regards of the correlation between casting solution polymer concentration and the NOM removability.

Overall the results indicated that the modified membrane fabrication process and the updated experimental condition significantly reduced membrane fouling and improved membrane NOM rejection. The modified membranes also showed better self-cleaning ability that requires less maintenance and replacement. Hence the process efficiency will be increased and process cost will be reduced.

5 Conclusions and Recommendations

5.1 Conclusions

Based on the results of this project, it can be concluded that: The best polymer concentration for the casting solution is 15% PVDF-2%PEG- 0.5%TiO_2. Membrane with an additional layer of TiO_2 on top can significantly reduce membrane fouling and improve NOM removability under UV light with the selective layer facing back. With the modified membrane and experimental condition, less than 10% of the membrane was fouled and more than 90% of the HA was removed from water. This result is repeatable with less than 5% of error.

5.2 Recommendations

Although this project got promising results on modifying the membrane fabrication process, there are still a lot of the aspects of UF that was not covered by the project. For people who are interested to continue working on this project, here are some of things recommended.

Due to the time constraints, most of the membranes were only tested once under each condition. Conducting more experiments on the membranes with high flux recovery and membrane NOM rejection rate to see if the results are repeatable is highly recommended. In this MQP the cross-flow UF/photocatalysis process was continued for 90 minutes for each membrane. However, the process could be longer to find out if the membrane to find out the membrane performance after a few hours.

In this project, the effect of the UV light and the effect of the membrane selective layer direction are considered. There are a lot more experimental conditions that can be tested and modified to improve membrane performance such as the operating pressure, HA concentration, pH value and the feed flow rate etc. Researchers could also consider taking water samples from nearby rivers instead of using HA solutions.

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7 Appendix

7.1 Sample Calculations

P= 1MPa C_{HA}=2mg/L m_{In}=500ml/min

The density of HA is too small to be consider therefore assume

$$\rho_{HA} = \rho_{Water} = 1g/cm^3 = 1g/mL^3$$

From experiment, measure the mass of the permeate flow for 1minute M_p=10g, then

$$V_P = \frac{M_P}{\rho_{HA}} = \frac{10g \bullet mL}{1g} = 10mL$$

Then, the permeate flow rate is 10ml/min. Knowing the effective membrane area is 48cm^2

Converting the flow rate into permeate flux **(L m^{-2} h^{-1})**

$$J = \frac{10mL \bullet 60\min \bullet 1L \bullet 10000cm^2}{\min \bullet h \bullet 1000ml \bullet 48cm^2 \bullet 1m^2} = 125\frac{L}{m^2h}$$

Given the initial permeate flux $J_O = 152\frac{L}{m^2h}$

$$\frac{J}{J_O} = \frac{125}{152} = 0.82$$

From experiments Abs Reservoir C_F=0.051, Abs Permeate C_P=0.01

The membrane NOM rejection rate is

$$R(\%) = (1 - \frac{C_P}{C_F}) \times 100\%$$

$$= (1 - \frac{0.01}{0.051}) \times 100\%$$

$$= 81.48\%$$

7.2 Selective Preliminary Data

Membranes with highest permeate flux recoveries and NOM rejection rates are shown in this section.

7.2.1 Unmodified Membranes

Membrane 4-1 Without UV

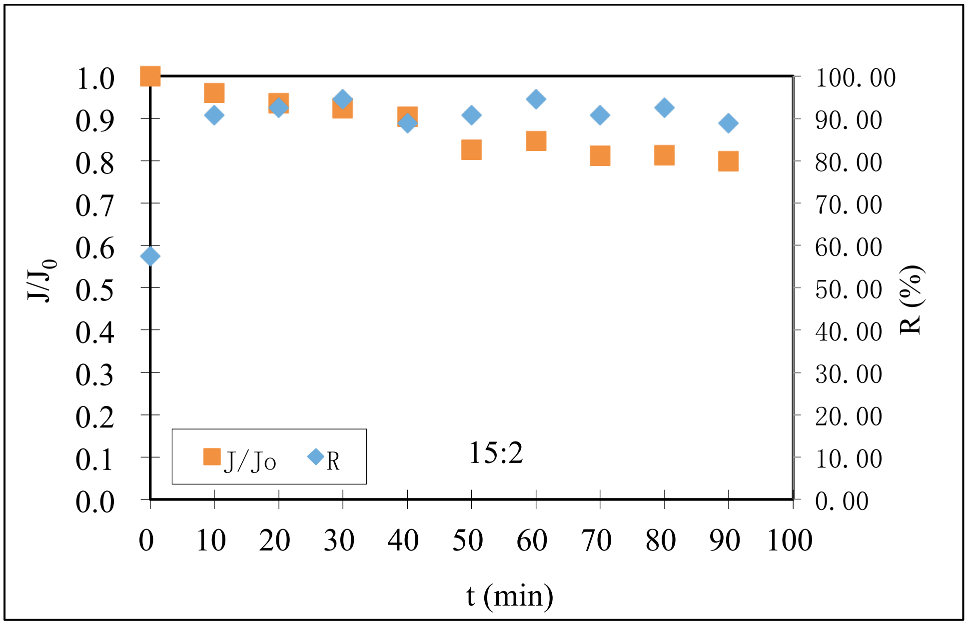

Figure 15 Membrane 4-1 Without UV

Membrane 9-1 without UV

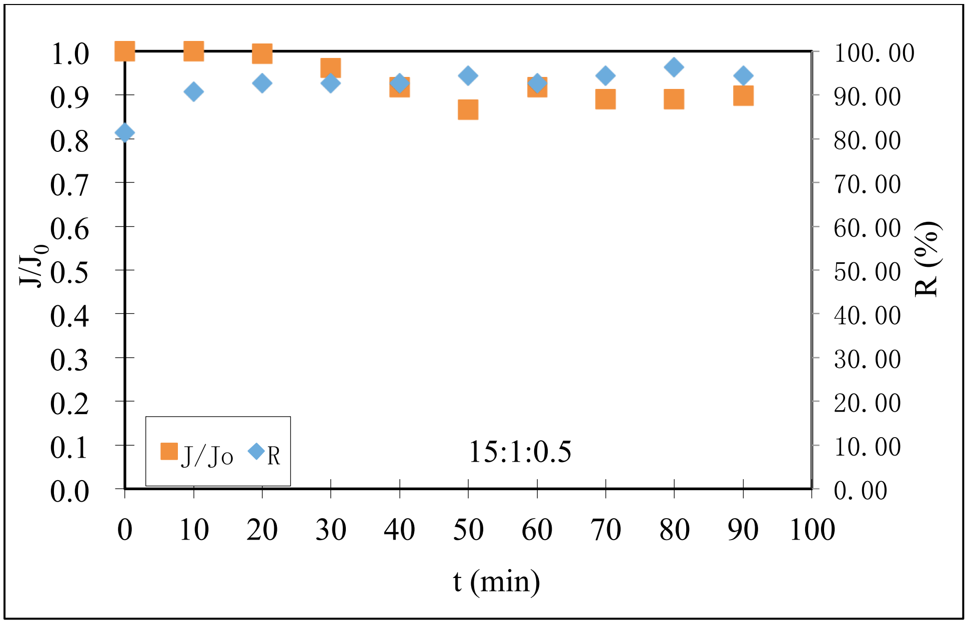

Figure 16 Membrane 9-1 without UV

7.2.2 Modified Membranes

Membrane 7a-3 Without UV

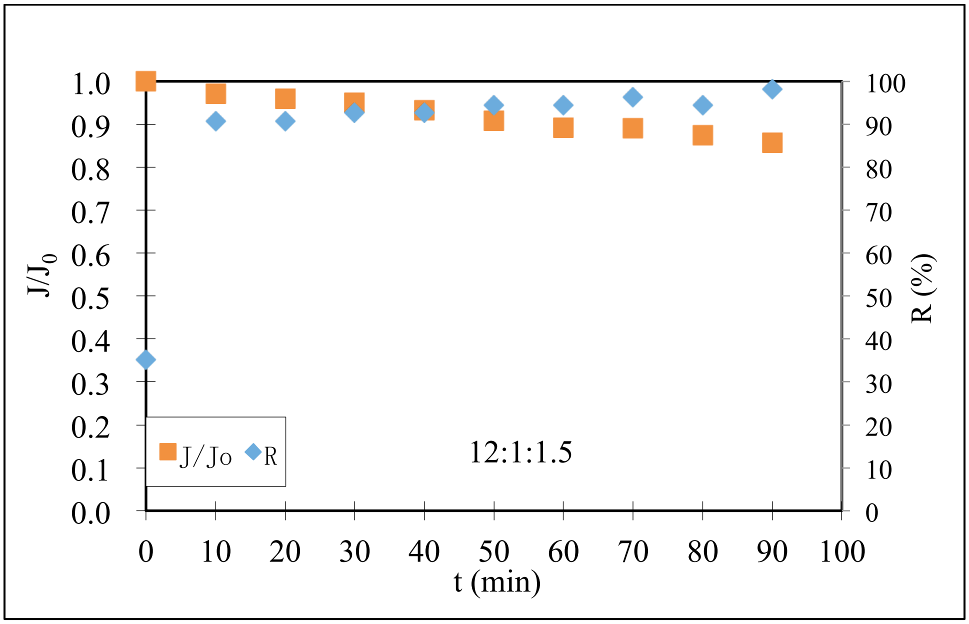

Figure 17 Membrane 7a-3 without UV

Membrane 9a-4 Without UV

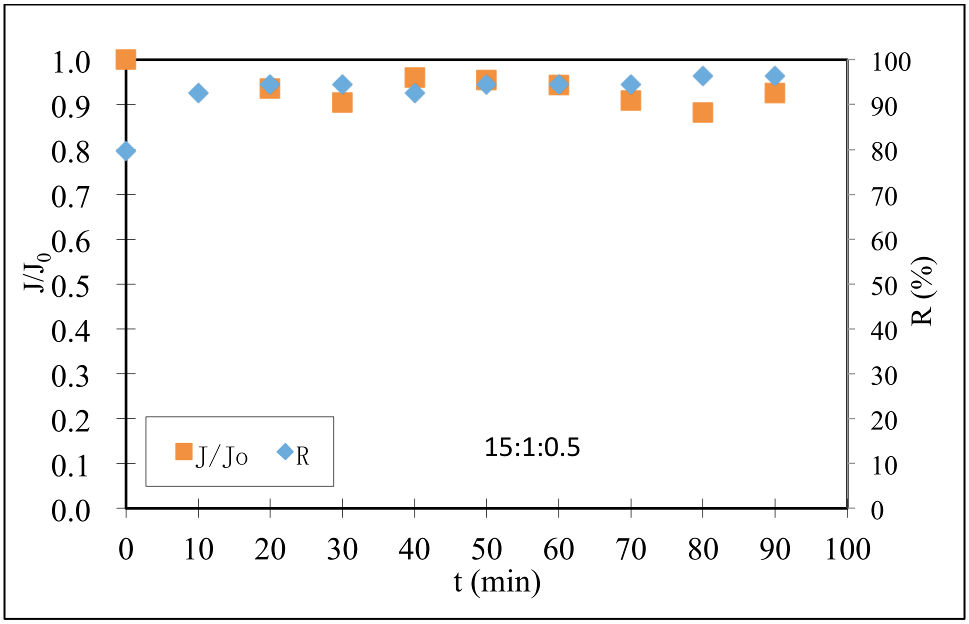

Figure 18 Membrane 9a-4 without UV

Membrane 12a-1 Without UV

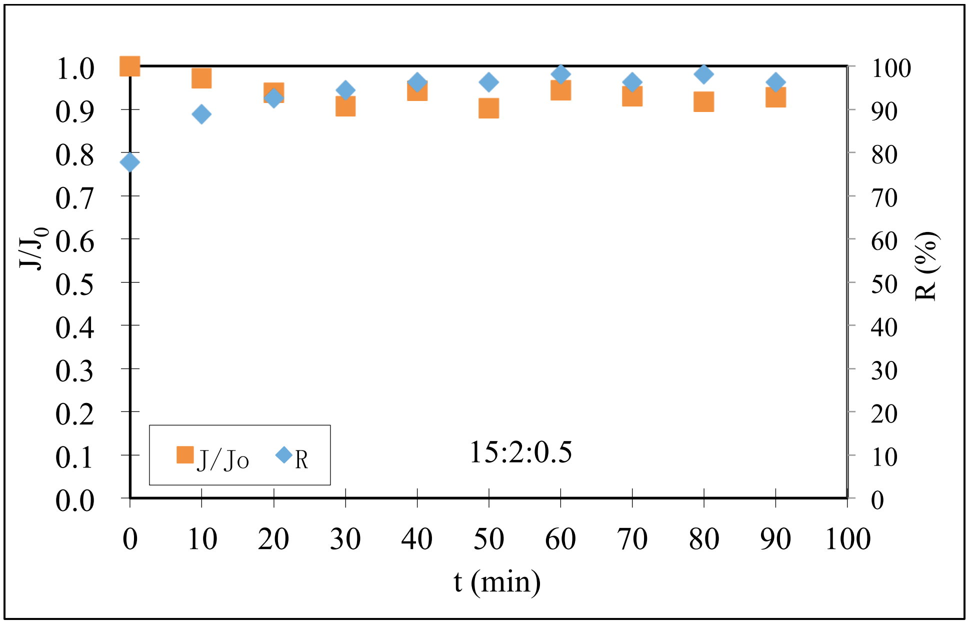

Figure 19 Membrane 12a-1 without UV

7.2.3 Unmodified Membranes with Selective Layer Facing Up

Membrane 6-4 Back With UV

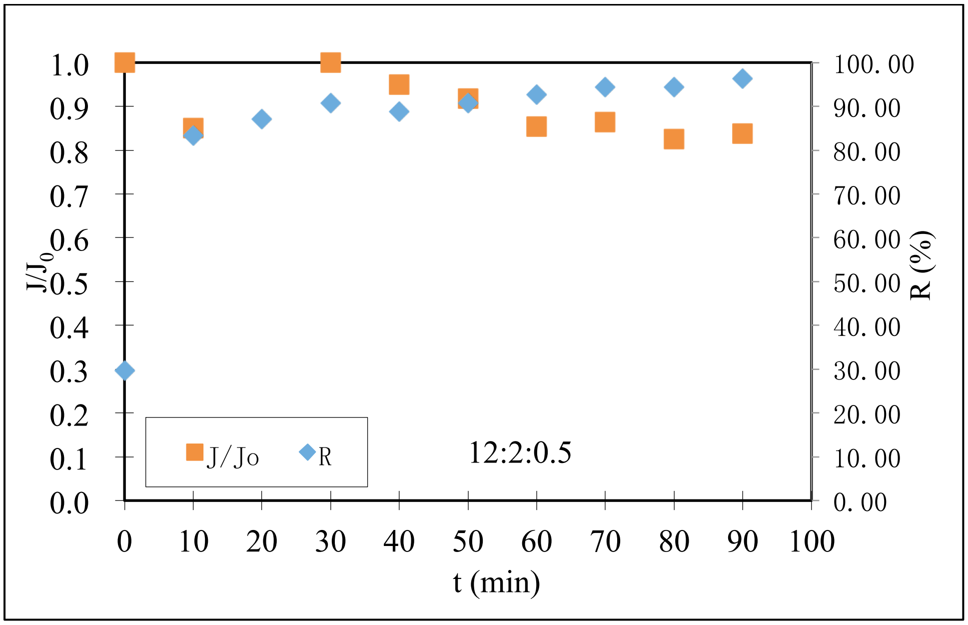

Figure 20 Membrane 6-4 back with UV

Membrane 10-4 Back With UV

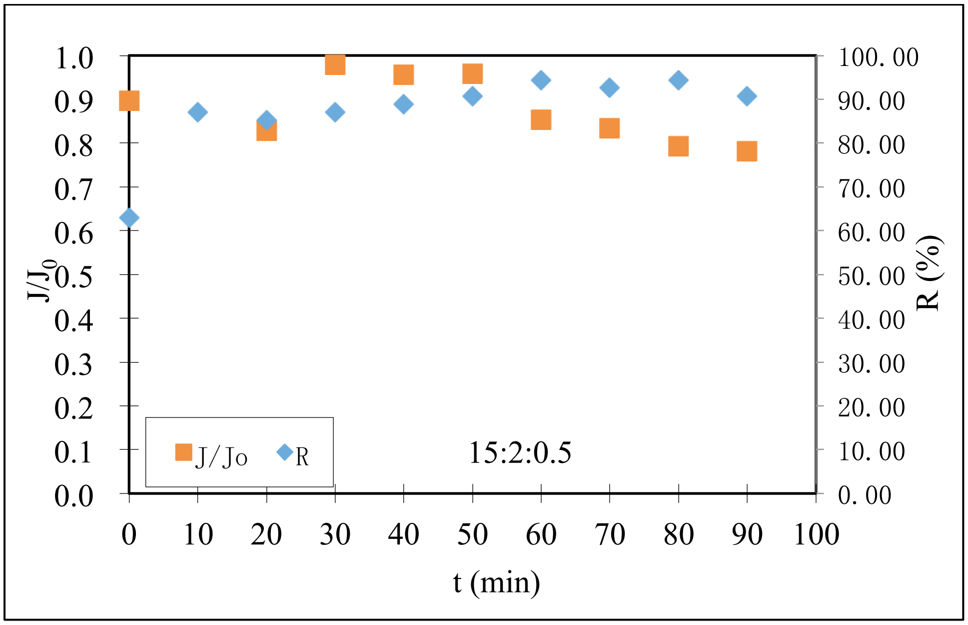

Figure 21 Membrane 10-4 back with UV

7.2.4 Modified Membranes with Selective Layer Facing Up

Membrane 4a-4 Back With UV

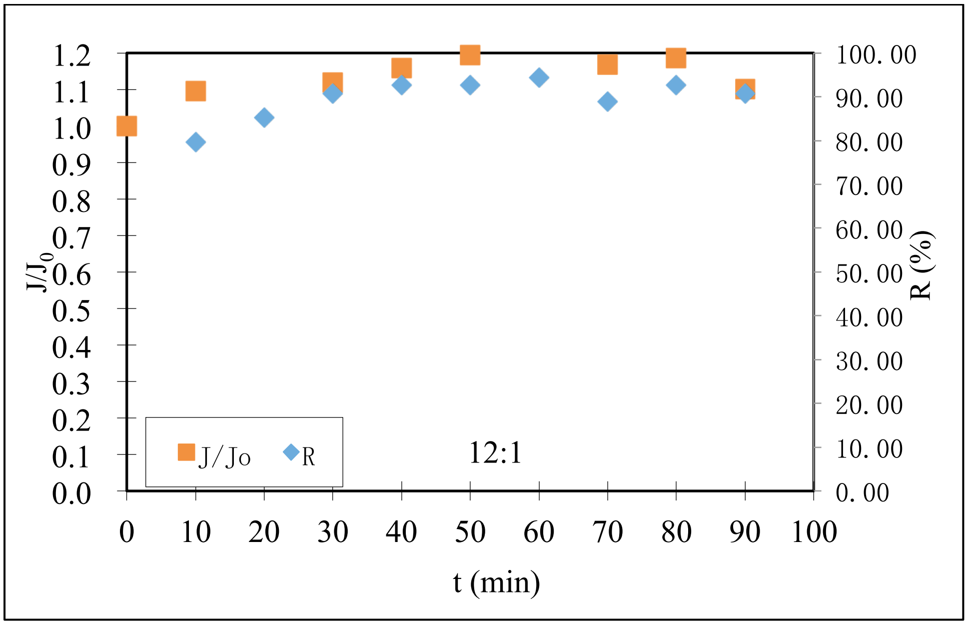

Figure 22 Membrane 4a-4 Back With UV

Membrane 8a-4 back With UV

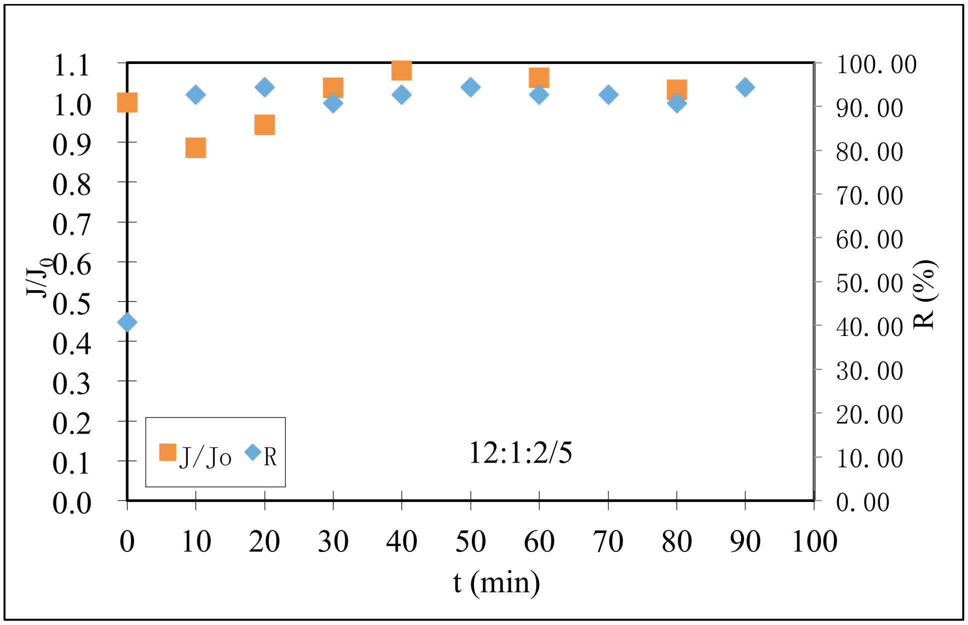

Figure 23 Membrane 8a-4 back with UV