โครงการ
การเรียนการสอนเพื่อเสริมประสบการณ์

ชื่อโครงการ **Hydrophilic hollow fiber polyvinylidene fluoride (PVDF) membrane enhancement by graphene oxide nanoparticles via plasma-induced grafted polymerization**

ชื่อนิสิต **Miss Pitsinee Laohapakdee**

ภาควิชา **Environmental Science**

ปีการศึกษา **2019**

คณะวิทยาศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย

การเพิ่มคุณสมบัติความชอบน้ำของเมมเบรนเส้นใยกลวงโพลีไวนิลไอดีนฟลูออไรด์โดยเคลือบนาโนแกรฟีนออกไซด์ที่ผ่านการกระตุ้นด้วยพลาสมา

นางสาวพิชญ์สินี เลาหภักดี

โครงการการเรียนการสอนเสริมประสบการณ์นี้เป็นส่วนหนึ่งของการศึกษา

ตามหลักสูตรวิทยาศาสตรบัณฑิต สาขาวิทยาศาสตร์สิ่งแวดล้อม

คณะวิทยาศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย

ปีการศึกษา 2562

Hydrophilic hollow fiber polyvinylidene fluoride (PVDF) membrane enhancement by graphene oxide nanoparticles via plasma-induced grafted polymerization

Pitsinee Laohapakdee

A Senior Project Submitted in Partial Fulfillment of the Requirements for the Bachelor's Degree of Science Program in Environmental Science

Department of Environmental Science

Faculty of Science, Chulalongkorn University

Academic Year 2019

Title **Hydrophilic hollow fiber polyvinylidene fluoride (PVDF) membrane enhancement by graphene oxide nanoparticles via plasma-induced grafted polymerization**

Name Miss Pitsinee Laohapakdee Student ID 593 33337 23

Project adviser Sermpong Sairiam, Ph.D.

Department Environmental Science

Academic year 2019

Accepted by Department of Environmental Science, Faculty of Science, Chulalongkorn University in Partial Fulfillment of the Requirements for the Degree of Bachelor of Science.

Wanida Jinsart ..... Head of Department of Environmental Science

(Professor Wanida Jinsart, Ph.D.)

SENIOR PROJECT COMMITTEE

Supawin Watcharamul ..... Chairman

(Supawin Watcharamul, Ph.D.)

Roonghan Nuisin ..... Committee

(Assistant Professor Roongkan Nuisin, Ph.D.)

Sermpong Sairiam ..... Project Advisor

(Sermpong Sairiam, Ph.D.)

หัวเรื่อง การเพิ่มคุณสมบัติความชอบน้ำของเมมเบรนเส้นใยกลวงโพลีไวนิลไอดีนฟลูออไรด์โดยเคลือบนาโนแกรฟีนออกไซด์ที่ผ่านการกระตุ้นด้วยพลาสมา

โดย นางสาวพิชญ์สินี เลาหภักดี **รหัสประจำตัวนิสิต** 593 33337 23

อาจารย์ที่ปรึกษา อาจารย์ ดร.เสริมพงศ์ สายเรี่ยม

คณะ วิทยาศาสตร์ **ภาควิชา** วิทยาศาสตร์สิ่งแวดล้อม

ปีการศึกษา 2562

บทคัดย่อ

การศึกษาการเพิ่มความชอบน้ำของเมมเบรนเส้นใยกลวงโพลิไวนิลไอดีนฟลูออไรด์โดยผ่านการกระตุ้นด้วยพลาสมา pulse inductively coupled plasma (PICP) และเคลือบด้วยอนุภาคนาโนแกรฟีน ผลจากการวิเคราะห์กล้องจุลทรรศน์แบบส่องกราด (SEM) พบว่าเมมเบรนที่ผ่านการกระตุ้นด้วยพลาสมาและเคลือบด้วยอนุภาคนาโนแกรฟีนมีพื้นผิวที่เรียบกว่าเมมเบรนปกติ การกระตุ้นด้วยพลาสมาและการเคลือบเมมเบรนด้วยกรดอะคริลิคทำให้เมมเบรนมีความชอบน้ำเพิ่มขึ้น สังเกตได้จากค่ามุมสัมผัสของน้ำ (WCA) เมมเบรนที่ลดลงจาก 73.6° ± 1.5°เป็น 63.86 ± 6.3° และเมื่อนำเมมเบรนที่เคลือบด้วยกรดอะคริลิคไปเกาะติดสารละลายอนุภาคนาโนแกรฟีนออกไซด์ที่เตรียมไว้ เมื่อเปรียบเทียบเวลาในเกาะติดเมมเบรนในนาโนแกรฟีนออกไซด์ที่ 1, 2, 4, และ 24 ชั่วโมงพบว่า ที่เวลา 24 ชั่วโมงค่ามุมสัมผัสของน้ำของเมมเบรนทุกความเข้มข้น (10, 20, 40 ppm) ลดลงมากที่สุด และเมมเบรนที่ผ่านกระตุ้นด้วยพลาสมาที่เกาะติดความเข้มข้นนาโนแกนฟีนออกไซด์ 10 ppm เป็นเวลา 24 ชั่วโมงมีค่ามุมสัมผัสของน้ำน้อยที่สุด (42.29 ± 6.2°) จากผลค่ามุมสัมผัสของน้ำแสดงให้เห็นว่าการกระตุ้นเมมบรนโดยพลาสมาและการเคลือบนาโนแกรฟีนออกไซด์ทำให้เกิดการเปลี่ยนแปลงของคุณสมบัติความชอบน้ำของเมมเบรนเส้นใยกลวงเพื่อที่จะสามารถนำเมมเบรนนี้ไปประยุกต์ใช้ในการบำบัดน้ำเสียด้วยเมมเบรนได้

คำสำคัญ: เมมเบรนโพลิไวนิลไอดีนฟลูออไรด์, ความชอบน้ำ, อนุภาคนาโนแกรฟีนออกไซด์, การกระตุ้นด้วยพลาสมา

Project Title Hydrophilic hollow fiber polyvinylidene fluoride (PVDF) membrane enhancement by graphene oxide nanoparticles via plasma-induced grafted polymerization

Name Miss Pitsinee Laohapakdee **Student ID** 593 33337 23

Project adviser Sermpong Sairiam, Ph.D.

Faculty Science **Department** Environmental Science

Academic year 2019

ABSTRACT

Hydrophilic enhancement was studied by modified hollow fiber polyvinylidene fluoride (PVDF) membrane via pulse inductively coupled plasma (PICP) induced and coated with graphene oxide nanoparticles (GO). The modified PVDF membranes were characterized by using a scanning electron microscopy (SEM) and the water contact angle. SEM analyzed morphology of modified PVDF membrane surface grafted with acrylic acid polymerization (PAA) was smoother than compare with surface of pristine membrane. Water contact angle (WCA) reported PICP method and grafted with PAA were supported modified PVDF membrane to increase hydrophilicity. WCA of modified PVDF membrane with grafted PAA was decreased from $73.6^{\circ} \pm 1.5^{\circ}$ to $63.86 \pm 6.3^{\circ}$. In comparison, WCA of modified PVDF membrane with grafted PAA and coated GO was lower than pristine membrane. Moreover, the WCA of modified PVDF membrane with grafted PAA and coated GO concentration of 10 ppm at 24 hours was lowest ($42.29 \pm 6.2^{\circ}$). Although, from the WCAs reported the modified PVDF membrane via PICP plasma-induced methods and coating GO exhibited hydrophilic hollow fiber PVDF membrane. There are suggested for wastewater treatment.

Keywords: Polyvinylidene fluoride **(**PVDF) membrane, Hydrophilicity, graphene oxide nanoparticles, plasma-induced graft polymerization

ACKNOWLEDGEMENTS

This senior project would not be successful if do not have the assistance of many people and the organizations. I would like to express my sincere thanks to all of them

First, I would like to thank my advisor, Sermpong Sairiam, Ph.D., for your support and suggest information in project. Without his kind direction and proper guidance this project would have been a little success. And I am thankful to my chairman committee, Supawin Watcharamul, Ph.D., and Assistant Professor Roongkan Nuisin, Ph.D., for design project suggestions and comments to complete the project.

I would like to thank Miss Hanh Le thi my, graduated school student for support measurement process and suggestion about results experiment.

In addition, I thanks Ms.Ketsara Songsod and Miss Pansuree Jariyawichit, Laboratory staff at Department of Environmental Science, Faculty of Science, Chulalongkorn University for all your help when I was doing laboratory.

My thanks also go to the Department of Environmental Science, Faculty of Science, Chulalongkorn University for budgets, material and instrument support my project.

My senior project would be difficult done if without my colleague, Miss Kankanok Saithai for their teamwork and assistance in measurement process my project. I'm really thankful for everything that she helps me.

Besides, I am also thankful to all my friends especially Miss Ganisa Prasertsri, Miss Kornwipa Sahin, Miss Paranee Wattanarojruang, Miss Phapasorn Panudomluck and Miss Suchana Amnuaychaichana for friendship and encouragement.

Finally, I would like to thank my family; my parents, grandfather for supporting me spiritually throughout my life.

Thank you

Pitsinee Laohapakdee

CONTENTS

Page

CONTENTS (continue)

Page

LIST OF TABLES

Page

LIST OF FIGURES

Page

CHAPTER I

INTRODUCTION

Membrane technology is one of technique for wastewater treatment. Polyvinylidene fluoride (PVDF) membrane is polymeric membrane material that widely used in filtration process to separate contaminants from wastewater industries because it is high mechanical strength, thermal stability and chemical resistance (Kang and Cao, 2014). In fact, the PVDF membrane is hydrophobicity in nature cause of the major problem of membrane filtration (Laohaprapanon *et al.*, 2017). PVDF hollow fiber membranes have substantial area per unit module volume more than flat sheet, higher packing density and higher a configuration for industrial scale (Dastbaz *et al.*, 2017) but the poor wettability of the PVDF hollow fiber membrane was limited their application in aqueous media. The problem is tendency fouling that accumulation of foulants on membrane surface, leading to reduce permeation and high cost to operation system. Also, biofouling begins with bacteria in wastewater attached on the membranes surface and develop biofilms comprising the polysaccharide, complex microbial cell. Organic fouling cause to pore blocking and pore narrowing for filtration process (Lee *et al.*, 2013). Coating or chemical grafting is to be more effective way to increase hydrophilicity and chemical properties of PVDF membrane.

Recently, the inorganic compounds such as titanium dioxide (TiO_2), zinc oxide (ZnO), graphene oxide (GO) were successfully coated for hydrophilic membrane modification and antifouling. They displayed achieve high permeability and obstruct biofouling due to low interfacial energy between a surface and water. GO nanoparticle is good one material for the coating on membrane to enhance hydrophilicity which high permeation. The coated membrane was increased oxygen containing functional such as carboxyl, epoxy, and hydroxyl by GO coating (Wang *et al.*, 2012). Moreover, functional group of inorganic compounds also reduce biofouling and accumulation on membrane surface (Lee *et al.*, 2013).

Although, coating is limited due to the distribution of particles is unequal on membrane surface and take a long time. It usually causes the increase permeation resistance, use high pressure and avoiding of membrane pore. Therefore, plasma treatment was used to activate PVDF membrane perior to

surface coating by GO nanoparticles. Pulse inductively couples plasma (PICP) is one of plasma treatment that high energy to active molecule onto surface and did not take long time to realize the result. PICP was studied effect of the physical properties on gelatin film and the results found that nitrogen plasma improved the hydrophilicity of the crosslinked gelatin surface (Prasertsung *et al.*, 2010). Nowadays, no study reported the plasma surface activation on PVDF membrane by PICP. Moreover, acrylic acid (AA) was plasma grafted on PVDF membrane to facilitate hydrophilicity instead of crosslinked process. Polyacrylic acid (PAA) is the most common polymer used for the synthesis of hydrophilic membrane surface (Kang and Cao, 2014). PAA is hydrophilicity in nature and functional groups could strongly bind nanoparticles via ion coordination or hydrogen bonding (You *et al.*, 2012). PVDF membranes with PICP induced-grafted with PAA reduced fouling and pressure on membrane surface and enhance attachment between nanoparticles and membrane surface.

The aim of the study is to modify PVDF hollow fiber membranes with graphene oxide nanoparticles and PAA to increase hydrophilicity property. The modified PVDF membranes were characterized the morphology and water contact angle.

Objective

To enhance hydrophilic hollow fiber PVDF membrane by coating GO and PAA via plasma-induced grafted polymerization using PICP

CHAPTER II

LITERATURE REVIEWS

2.1 Membrane process

The membrane filtration process is one of the technologies of water treatment, gas separation, food manufacturing, pharmaceutical industry and environmental filtration without chemicals. The general membrane filtration process was filtered using a membrane to separate liquids with many components. The filtration direction is cross flow filtration using pressure to allow the feed to move parallel to the surface of the membrane and liquid through the hole of the filter membrane. The membrane materials are inorganic and organic polymers, i.g. organic polymers are polysulfone (PSF), poly (ether sulfone) (PES), polyacrylonitrile (PAN), polyimide (PI), poly (vinylidene fluoride) (PVDF) and polytetrafluoroethylene (PTFE) (Liu *et al.*, 2011).

PVDF is a structure polymer -$(CH_2CF_2)_n$- that high mechanical strength, resistant to constantly changing temperatures and resistant to chemical changes (Kang and Cao, 2014). There is an important asset in the use of membrane for separation process. PVDF membrane can be divided into three characteristics: flat sheet, hollow fiber and tubular membrane. From previous studies, PVDF membrane was used in microfiltration filtration (MF), ultrafiltration (UF), membrane bioreactor (MBR), gas separation and water pollution disposal (Ayyavoo *et al.*, 2016). In nature, hydrophobic membrane has low surface energy, therefore, there is difficulty to adsorb and isolate liquids. Then, the membrane surface was adapted to more the water permeation.

2.2 Hydrophilic membrane modification

The hydrophilicity of membrane was improved for mitigate biofouling on membrane surface by surface modification. Surface hydrophilic modification can be classified in to two categories followed interaction with modifier and membrane; physical and chemical modification. For physical modification, membrane surface was interacted but not change composition of membrane. There are two ways to achieve the physical modification by coating modifying agent directly and immersion of membrane in active monomer solution and monomer immobilized onto membrane surface by crosslinking or polymerization (Kang and Cao, 2014). For chemical modification, membrane

surface was modified though covalent bonding interaction. Polymer of membrane was activated by high-energy radiation followed by grafting modifier. Covalent attachment on surface membrane offer a long-term and stability compare with physical modification. There are several studies the surface modification to hydrophilic nature (Liang *et al.*, 2013; Rahimpour *et al.*, 2008; Wang *et al.*, 2017; GaneshIsloor and Ismail, 2013). The membrane surface was improved by combination of plasma treatment that chemical modification and coating with inorganic nanoparticles for the increase hydrophilicity. The fabrication PVDF membrane grafted with poly(methacrylic acid) (PMAA) by plasma induced copolymerization and blending of silica nanoparticles (Liang *et al.*, 2013). The functionalized membrane was improved the wettability and converted membrane surface from hydrophobicity to superhydrophilicity. The hydrophilicity was reported by water contact angle (WCA). The membrane surface is hydrophobic when WCA is more than 90˚ and is hydrophilic when WCA lower than 90˚. Li *et al.* (2017) reported the WCA compare with pristine membrane (95.2˚). after modification with TiO_2, WCA was declined 40.3% (≈55˚). In contrast, the WCA of modification PVDF membrane with TiO_2:ZnO 1:3 was dramatically decreased 82.6% (≈13˚), indicating the photo-induced superhydrophilicity was realized.

2.3 Plasma-induced grafted polymerization

Plasma-induced grafted polymerization is surface modification methods to improve the properties of membrane. In addition, the surface modification can reduce the blockage of fouling on membranes. Plasma treatments include plasma sputtering, etching, implantation and spraying. During the process, insert gases are activated to form the plasma and exchange of ion and atoms on membrane (Ayyavoo *et al.*, 2016). The resulting mechanism is that gas plasma stimulates free radicals, charges or ions on the surface of the membrane (You *et al.*, 2012). Inducing free radicals up on the surface of membrane from protons, carbon bonding breakdown and collision of charges to changes the composition of the membrane and changes the physical and chemical properties of the membrane. Choosing a type of gas plasma treatment depends on whether it wants to induce elements on the membrane surface such as the use of O_2 plasma causing among functions with oxygen such as • OH, OH-, -OH, -CO on the surface of membrane (Liang *et al.*, 2014) as shown in Figure 2.1. The activated membrane surface is highly sensible to reactions and act as a primary

substance in the polymerization process. In addition, Khaledian *et al.* (2019) there is the use of Argon plasma activate the structural change of titanium oxide.

Free radicals or the functionals group were caused stimulating the surface of membrane with plasma-induced, the active site of the function group provides more opportunities to react or build bonds with other substances on the membrane surface. This causes chemical reactions between the skin of membrane and monomer and synthesized into long line polymers (Ayyavoo *et al.*, 2016). The effectiveness of membrane modifications depends on the type of plasma. The energy and pressure provided to membranes, which are also indicative of the stretching and end of the polymer. According the study of Laohaprapanon *et al.* (2017) found that monomer use of acrylic acid (AA monomer) to achieve self-polymerization reactions on membranes after plasma-treated stimulation, which polyacrylic acid formed with high hydrophilic properties, improves the filtration of water through membranes. Plasma induced vapor graft of acrylic acid was increased binding fastness of silver nanoparticle (AgNP) on the cotton fabrics (Wang *et al.*, 2017). Plasma induced copolymerization of poly(methacrylic acid) (PMAA) on PVDF by silica nanoparticles (NPs) improve hydrophilic and generate carboxyl groups to binding NPs on membranes surface (Liang *et al.*, 2013).

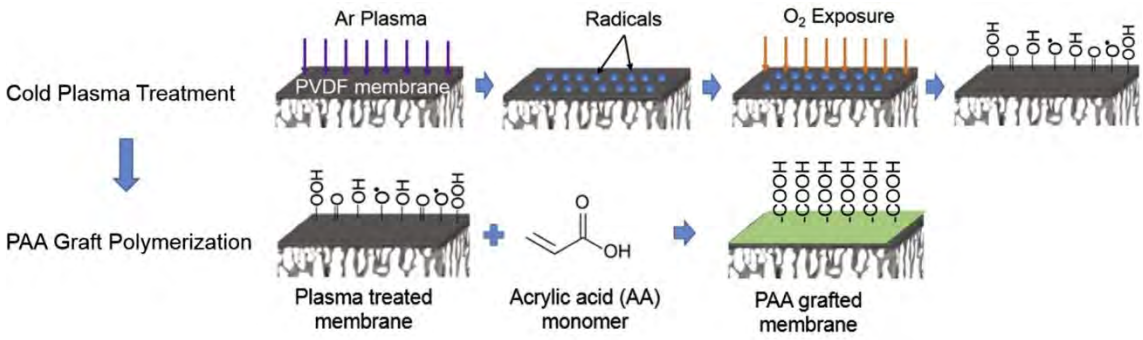


Figure 2.1 Schematic illustration of the PVDF-PAA membrane preparation. (Chen *et al.*, 2019)

Pulse inductively coupled plasma (PICP) is one of high energy plasma systems which can modify surface of polymer. The surface treatment by PICP does not require lengthy treatment time to achieve desire effect. The PICP system is flexibility in reducing and rising electron temperature of the plasma though variation of electrical energy stored and operating gas pressure

(Prasertsung *et al.*, 2010). In addition, inductively coupled plasma produced in a closed environment provides clean environment for treatment of biomaterials.

2.4 Coating

There are several methods to increase hydrophilicity such as physical blending. Catalyst and matrix membrane was mixed together before was fabricated membrane (You *et al.*, 2012). However, blending often lead of the reduction of membrane stability and performance because of the agglomeration of particle that limits free space for movement of polymer chains (Laohaprapanon *et al.*, 2017). Surface coating is candidate the physical surface modification. The thin layer was deposited on top layer of membrane (Ayyavoo *et al.*, 2016). The hydrophilic functional materials are physically deposited on membrane by three different mechanisms :

1. Adhesion/adsorption with binding energy improved by manifold interactions between functional group in macromolecular layer and on the hard surface.
2. Interpenetration by combining the functional material and base polymer in an interphase.
3. Macroscopic entanglement of functional group and pore structure of membrane.

Nanoparticles are often candidate coating material which increase hydrophilicity and antimicrobial activity. Nanoparticles are used to create suitable surface with physical and chemical characteristics (Chouirfa *et al.*, 2019). Nanoparticles were coated on top layer of membrane to be more effective than blending method (Laohaprapanon *et al.*, 2017). Nor *et al.* (2016), the result demonstrated that TiO_2 was dipped coating on alkaline treated PES membrane. Photocatalytic activity of TiO_2 was motivated by coating and enhance hydrophilicity.

2.5 Inorganic nanoparticles

Inorganic nanoparticles were served the aqueous properties of the membrane, improve physical and chemical membrane properties, eliminate pollution, and increase suitable for the membrane. The effective inorganic nanoparticles for PVDF membrane include aluminum oxide (Al_3O_4), silica dioxide (SiO_2), TiO_2, Zn, GO etc. (Li *et al.*, 2018),(Ayyaru and Ahn, 2018). In the previous research, the membrane was prepared by blending with nanoparticles that mixed nanoparticle solution and membrane together or coating that immersion membrane in the solution of inorganic nanoparticles and using ultrasonic frequency to increase dissolve solution. Ultrasonic wave can make the solution uniform and non-condensing that nanoparticles was more dispersed in the membrane surface (AyyaruDinh and Ahn, 2020).

Graphene oxide (GO) is a catalyst that can synthesize a layer of graphite with several hydroxyl and carbonyl groups (Lee *et al.*, 2013). GO is increase oxygen containing functional groups. Different hydrophilic functional groups of GO easily water take up or adsorption on membrane surface. GO is high aspect ratio, low density, and high strength material (AyyaruDinh and Ahn, 2020). Moreover, GO can induce negative charge and increase mechanical strength of host polymer (GaneshIsloor and Ismail, 2013). It is benefit in water treatment for permeability and antifouling. In previous study, GaneshIsloor and Ismail (2013) reported that GO was dispersed to PSF mixed matrix membrane. GO membrane surface was rather permeation water and expand salt rejection from measuring pure water flux. The study of Zhang *et al.* (2013) has modified PVDF membrane by oxidized low dimensional GO and the results found that there are many comprised oxygen functional groups to increases permeation flux compared with pristine and prospect for anti-irreversible fouling performance in multi-cycle bovine serum albumin (BSA) treatment. Goh *et al.* (2015) have reported the use of GO nanosheets on surface of polyamide hollow fiber membrane. The results found that a strong hydrophilicity was improved, and the antimicrobial property was conferred given a direct contact between bacterial cells and GO.

CHAPTER III

METHODOLOGY

3.1 Chemicals and materials

PVDF hollow fiber membrane was purchased from Altrateck (China). The specification of the PVDF membrane was reported by the manufacturer as shown in Table 3.1. Acrylic acid was purchased from Loba Chemie (India). The specification of acrylic acid (AA) was presented in Table 3.2. Graphene oxide nanoparticles (GO) were supplied from Prime Nanotechnology (Thailand). The properties of GO reported from manufacturer were summarized in Table 3.3. Deionize water (DI) was used to preparation solution. All chemicals used were analytical grade.

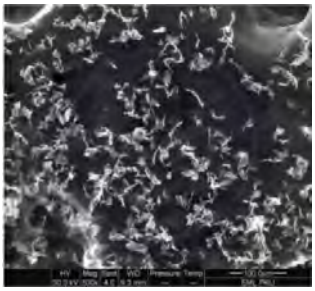
Table 3.1 The specification of the PVDF hollow fiber membrane.

Fiber outer diameter (mm)	1.13
Fiber inner diameter (mm)	0.8
Pore size (μm)	0.16
Membrane porosity (%)	70%

Table 3.2 The specification of acrylic acid.

Molecular Formula	$C_3H_4O_2$
Molecular Weight (g)	72.06
Purity (%)	98%
Density (d20˚C/4˚C) (g/cm^3)	1.048-1.052
Refractive index (20˚C; 589 nm)	1.4200-1.4224
pH	1-2

Table 3.3 The properties of graphene oxide nanoparticles (GO)

Appearance	Black powder/flakes
Flake sizes (Microns)	1-10
Characterization: SEM	
Single layer ratio	>99%

3.2 Methods

3.2.1 Plasma-induced graft polymerization with acrylic acid (AA)

A pulse inductively couple plasma (PICP) was set up followed Prasertsung *et al.* (2010). The commercial PVDF hollow fiber membrane was cut into 30 cm in length and were enclosed with cylindrical quart tube and placed in the plasma vacuum chamber. PICP was driven by discharging when charging potential to 10 kV. O_2 gas to generate O-containing functional groups that can be incorporated into membrane surface. O_2 gas was selected and filled at low pressure after a pre-evacuation of the quartz tube by system of diffusion and rotary pump. When operating, the current was discharged though a single turn steel coil around the quartz tube producing O_2 plasma inside though electromagnetic induction process. O_2 gas plasma produced in two shots pulse. Then, the plasma treated membranes were immersed into 70 wt% acrylic acid monomers (AA) solution which nitrogen purged to induce self-polymerization on the membrane surface for 1 hour. The unreacted monomer and PAA polymer were washed out using DI water. Then, functionalized membranes were activated in oven (ULM 700, Memmert, Germany) 60˚C for 1 hour before dip-coating GO at ambient conditions (Laohaprapanon *et al.*, 2017).

3.2.2 GO hydrophilic modification

The activated membranes by O_2 plasma using PICP followed by coating with PAA were coated with GO by dip-coating method. To functionalize PVDF membrane with GO, graphene oxide powders were dissolved in 500 ml in DI water. Before suspension functionalization PVDF membranes into GO solution, the suspended GO solution was sonicated by using ultrasonic sonicator bath (DT510H, SONOREX, Germany) to homogeneous suspension and prevent agglomerate of particle for 1 hour. After that, the activated PVDF membranes with PAA were dipped into varied GO concentration (10, 20, 40 ppm) and different coating time (1, 2, 4 and 24 hours) as presented in Table 3.4. Then, the removal weak boundary GO particles with DI water were done and the coated membranes were incubated in oven (ULM 700, Memmert, Germany) 60˚C for 1 hour. The membrane samples were air dried for 20 min. Finally, functionalization PVDF membranes were stored subsequent membrane in zip lock for characterization.

Table 3.4 The concentration of GO and coating time of membranes grafting without PAA

Membranes	Concentration of GO (ppm)	Coating time (hours)
C1	10	1
C2	10	2
C3	10	4
C4	10	24
C5	20	1
C6	20	2
C7	20	4
C8	20	24
C9	40	1
C10	40	2
C11	40	4
C12	40	24

Table 3.5 The concentration of GO and coating time of membranes grafting with PAA

Membranes	Concentration of GO (ppm)	Coating time (hours)
P0	0	0
P1	10	1
P2	10	2
P3	10	4
P4	10	24
P5	20	1
P6	20	2
P7	20	4
P8	20	24
P9	40	1
P10	40	2
P11	40	4
P12	40	24

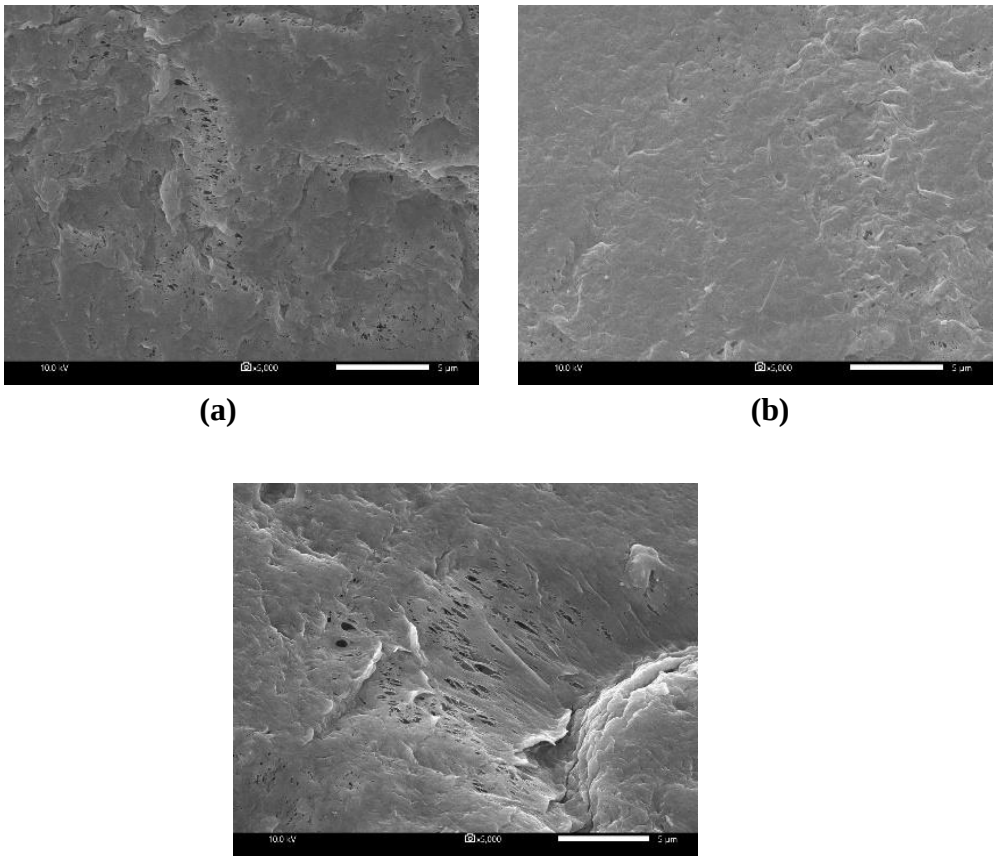
3.2.3 Membrane characterizations

A scanning electron microscopy (SEM) were used to analyze morphologies both the surface of unmodified and modified membranes (Shen *et al.*, 2017). Hydrophilicity were analyzed the water contact angle (WCA) by tensiometer (DCAT 11, Dataphysics, Germany) which recording diameter, surface tension and height of liquid in tube (Extrand and Moon, 2014).

CHAPTER IV
RESULTS AND DISCUSSION

4.1 Morphology of membrane

Membrane surface morphology was analyzed by SEM at different conditions as shown in Figure 4.1. The morphologies of pristine, PVDF plasma-induced, PVDF plasma-induced grafted PAA and GO at 40 ppm 4 hours were compared. The results found that the coating surface membrane by plasma grafted with PAA (P0) and P11 was smoother than the pristine. From SEM results, this was confirmed plasma method by PICP and grafting PAA were successful modification. Chen *et al.* (2019) found that the achievement using plasma method and grafting PAA was successful modification that plasma slowly reacted with PVDF membrane surface, resulting in more peroxide being formed and PAA grafting was higher oxygen-containing functional groups on membrane, leading to the low WCA. Structure of PVDF membrane was more improved the characteristics of high physical and chemical activities. This was because 70% aqueous of acrylic acid at 60˚C to graft on PVDF membrane with activated by PICP plasma, resulting to amount of carboxylic acid groups that can actively serve as binding site for nanoparticles coating with chemical bond (You *et al.*, 2012) and increase of Van Der Waals force in molecules interaction (Yu *et al.*, 2019). The surface of modified PVDF membrane by plasma-induced grafted PAA and coated with GO did not different compare to pristine membrane as shown in Figure 4.1. GO cannot be found on membrane surface and difficult to observe characteristic of GO on membrane surface as presented in Figure 4.1c). This result was similar with You *et al.* (2012) that morphology of modified PVDF membrane surface which grafted PAA PVDF membrane was no difference with surface of pristine.



(a) **(b)**

(c)

Figure 4.1 SEM images: (a) Pristine membrane, (b) PICP plasma-induced membrane (P0), (c) PICP plasma-induced grafted with PAA and coated GO 40 ppm 4 hours (P11)

4.2 Hydrophilicity

Polymer solution and GO nanoparticles were used to more hydrophilic nature that they were modified functional group by chemical reaction on PVDF membrane surface. Hydrophilicity of hollow fiber PVDF membrane can be measured by tensiometer in term of water contact angle values (WCA).

4.2.1 Effect of coating time

As shown in Figure 4.2, WCA of plasma-induced membrane and coated with GO at concentration of 10 ppm was decreased from 69.2˚ ± 7.1˚ to 49.3˚± 4.5˚ when the coating time was increased from 1 hour (C1) to 24 hours (C4). However, WCAs were slightly decreased when coating time was increased for 20, 40 ppm (C5 to C12). It could be demonstrated that hydrophilic properties of membrane was because of the increase of GO concentration (Lee *et al.*, 2013). The PVDF membrane is enhanced by the oxygen containing functional groups of the GO nanoparticle (Goh *et al.*, 2015).

The modified PVDF membrane grafted with PAA followed by coating GO was increased hydrophilicity as shown in Figure 4.3. For GO concentration of 10 ppm, WCAs of modified membrane grafted with PAA and coated GO from 1 hour (P1) to 24 hours (P4) were decreased from 57.8˚ ± 3.9˚ to 42.3˚± 6.2˚. For GO concentration of 20 ppm, WCA were declined from 69.1˚ ± 3.0˚ to 44.2˚± 5.8˚ when the coating time increase from 1 hour (P5) to 24 hours (P8). This was because the functional group of hydroxyl was attached on membrane surface (You *et al.*, 2012). For GO concentration of 40 ppm, WCA was increased from 57.8˚ ± 6.6˚ to 61.8˚ ± 2.9˚ when increase the coating time from 4 hours (P11) to 24 hours (P12). The WCA of P11 was lower than P12 because GO nanoparticles of modified membrane might be agglomerated on membrane surface which exhibited wetting and reduce hydrophilicity of membrane. According to the results, this was confirmed that the more positive effect of PAA-GO compare GO on PVDF membrane when longer time coating toward the hydrophilic improvement. WCA was slightly decreased with the coated PVDF membrane long period (You *et al.*, 2012). Coating GO for 24 hours was the lowest WCA to modified membrane.

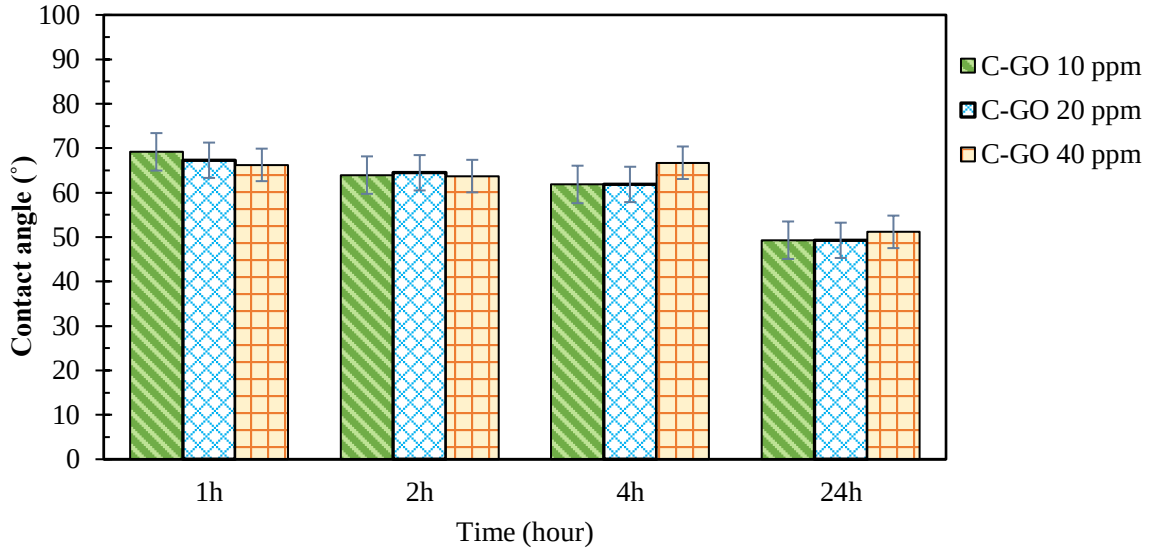


Figure 4.2 Contact angle of modified membrane coated with GO without PAA at different coating time

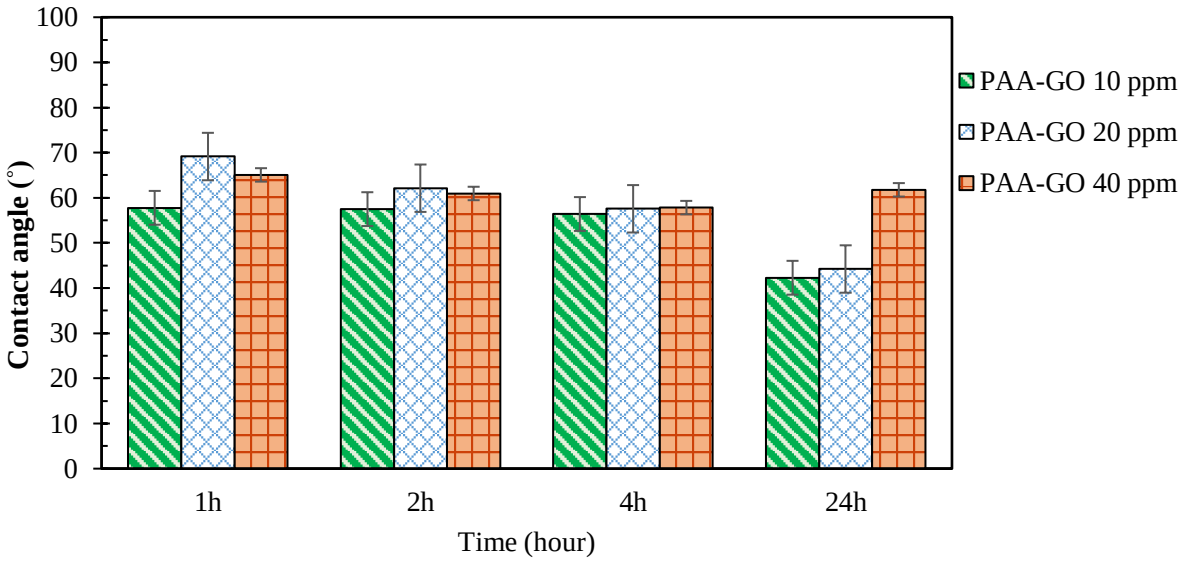


Figure 4.3 Contact angle of modified membrane with PAA and GO at different coating time

.

4.2.2 Effect of different GO concentrations

WCA of modified membrane with GO at different concentration for 24 hours was presented in Figure 4.4. The WCA of modified membrane via PICP plasma-induced grafted with PAA (P12) was decreased compare with pristine (P0) from 73.6˚ ± 1.5˚ to 63.9˚ ± 6.3˚. This was because the pristine (P0) was high characteristic of fluorine and weak affinity of PVDF toward water. After membrane induced by PICP plasma, the hydroxyl group was formed and then attributed to PAA (Laohaprapanon *et al.*, 2017). When increasing the concentration of GO from 10 ppm (C4) to 40 ppm (C12) at 24 hours coating time, WCAs of modified membrane without PAA grafting were increased from 49.3˚ ± 4.5˚ to 51.2˚ ± 5.8˚. While the WCA of modified membrane grafted with PAA when increase GO concentration from 10 ppm (P4) to 40 ppm (P12) were increased from 42.3˚± 6.2˚ to 61.8 ± 2.9˚ at 24 hours coating time. In comparison with WCA of PICP plasma-induced membrane with and without PAA grafting, the WCA of PICP plasma-induced grafted with PAA membrane (P12) was lower than that of without PAA grafting in concentration of GO 10 (C4) and 20 ppm (C8). This was because the modified PVDF membrane with GO nanoparticles have more hydrophilic although no grafted PAA on membrane leading to increase water permeate of membrane (AyyaruDinh and Ahn, 2020). The previous study of Goh *et al.* (2015) that the characteristic of hydrophilic PVDF membrane was enhanced by oxygen containing functional groups of GO nanoparticles on membrane surface. The modified membranes at high concentration (40ppm) were not low WCA because GO nanoparticles were agglomerated, resulting in water permeation was useless similar as a study of You *et al.* (2012) that the high concentration of ZnO was resulted higher WCA due to pore blocking of the ZnO assemble on surface membrane.

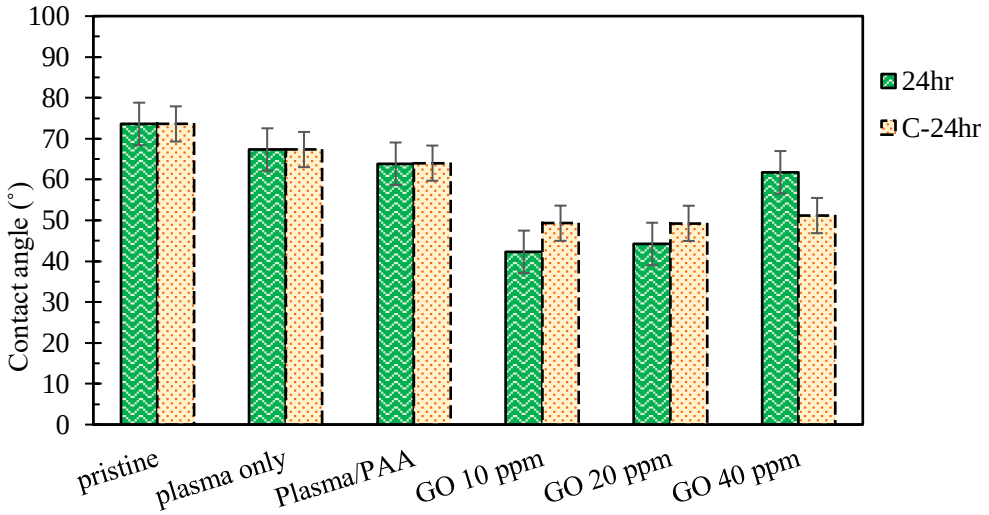


Figure 4.4 Contact angle of pristine and modified membrane control with PAA and GO at 24 hours

CHAPTER V

CONCLUSIONS

5.1 Conclusions

The PVDF hollow fiber membranes modified by PICP plasma-induced grafted PAA and coated with graphene oxide nanoparticle to increase hydrophilicity property. The modified PVDF membranes were characterized by using SEM and the water contact angle.

The morphologies were measured by SEM and characteristic of chemical composition were analyzed by WCA. The SEM results shown pristine PVDF membrane was roughness. When activated PVDF membrane with PICP plasma method and grafted with PAA, the PVDF membrane surface was smoother. However, morphology of modified PVDF membrane surface grafted with PAA was no significantly different compare with surface of pristine membrane. WCA reported PICP plasma method and polymerization of PAA were successfully coated onto PVDF membrane surface to enhance hydrophilic membrane. WCAs of modified PVDF membrane 40 ppm were decreased from pristine membrane 73.6˚ ± 1.5˚ to 42.3˚± 6.2˚ when the coating time increased 1 hour to 24 hours. When increasing concentration of GO nanoparticles from 10 to 40 ppm at 24 hours, WCAs of modified membrane that without PAA grafting and grafted with PAA were increased from 49.3˚ ± 4.5˚ to 51.2˚ ± 5.8˚ and 42.3˚ ± 6.1˚ to 61.8˚ ± 2.9˚,respectively. Although, GO nanoparticles were WCA of modified PVDF membrane decreased. PICP plasma method and grafted polymerization with PAA was supported modified PVDF membrane to superhydrophilicity.

5.2 Suggestions

The modified PVDF membranes should indicate water permeation flux and filtration for confirm hydrophilicity and antifouling potential. This study could apply in membrane technology for wastewater treatment. Membrane modifications reduced reactors of treatment process. GO nanoparticles were used at low concentration to modify membrane surface that it reduced the amount of GO residue in the environment.

REFERENCE

Ayyaru, S. and Ahn, Y.-H. (2018) Fabrication and separation performance of polyethersulfone/sulfonated TiO_2 (PES–$STiO_2$) ultrafiltration membranes for fouling mitigation, *Journal of Industrial and Engineering Chemistry*, 67, pp. 199-209.

Ayyaru, S., Dinh, T. T. L. and Ahn, Y.-H. (2020) Enhanced antifouling performance of PVDF ultrafiltration membrane by blending zinc oxide with support of graphene oxide nanoparticle, *Chemosphere*, 241, pp. 125068.

Ayyavoo, J., Nguyen, T. P. N., Jun, B.-M., Kim, I.-C. and Kwon, Y.-N. (2016) Protection of polymeric membranes with antifouling surfacing via surface modifications, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 506, pp. 190-201.

Chen, X., Huang, G., An, C., Feng, R., Yao, Y., Zhao, S., Huang, C. and Wu, Y. (2019) Plasma-induced poly (acrylic acid)-TiO_2 coated polyvinylidene fluoride membrane for produced water treatment: Synchrotron X-Ray, optimization, and insight studies, *Journal of Cleaner Production*, 227, pp. 772-783.

Chouirfa, H., Bouloussa, H., Migonney, V. and Falentin-Daudré, C. (2019) Review of titanium surface modification techniques and coatings for antibacterial applications, *Acta Biomaterialia*, 83, pp. 37-54.

Dastbaz, A., Karimi Sabet, J., Ahadi, H. and Amini, Y. (2017) Preparation and characterization of novel modified PVDF-HFP/GO/ODS composite hollow fiber membrane for Caspian Sea water desalination, *Desalination*, 424, pp. 62-73.

Extrand, C. and Moon, S. I. (2014) Measuring contact angles inside of capillary tubes with a tensiometer, *Journal of colloid and interface science*, 431, pp. 200-203.

Ganesh, B., Isloor, A. M. and Ismail, A. F. (2013) Enhanced hydrophilicity and salt rejection study of graphene oxide-polysulfone mixed matrix membrane, *Desalination*, 313, pp. 199-207.

Goh, K., Setiawan, L., Wei, L., Si, R., Fane, A. G., Wang, R. and Chen, Y. (2015) Graphene oxide as effective selective barriers on a hollow fiber membrane for water treatment process, *Journal of Membrane Science,* 474, pp. 244-253.

Kang, G. d. and Cao, Y. m. (2014) Application and modification of poly (vinylidene fluoride)(PVDF) membranes–a review, *Journal of Membrane Science,* 463, pp. 145-165.

Khaledian, H. R., Zolfaghari, P., Elhami, V., Aghbolaghy, M., Khorram, S., Karimi, A. and Khataee, A. (2019) Modification of immobilized titanium dioxide nanostructures by argon plasma for photocatalytic removal of organic dyes, *Molecules,* 24(3), pp. 383.

Laohaprapanon, S., Vanderlipe, A. D., Doma Jr, B. T. and You, S. (2017) Self-cleaning and antifouling properties of plasma-grafted poly (vinylidene fluoride) membrane coated with ZnO for water treatment, *Journal of the Taiwan Institute of Chemical Engineers,* 70, pp. 15-22.

Lee, J., Chae, H., Won, Y. J., Lee, K., Lee, C., Lee, H. H., Kim, I. and Lee, J. (2013) Graphene oxide nanoplatelets composite membrane with hydrophilic and antifouling properties for wastewater treatment, *Journal of Membrane Science,* 448, pp. 223-230.

Li, N., Tian, Y., Zhang, J., Sun, Z., Zhao, J., Zhang, J. and Zuo, W. (2017) Precisely-controlled modification of PVDF membranes with 3D TiO2/ZnO nanolayer: enhanced anti-fouling performance by changing hydrophilicity and photocatalysis under visible light irradiation, *Journal of Membrane Science,* 528, pp. 359-368.

Li, N., Tian, Y., Zhao, J., Kong, L., Zhang, J., Zuo, W., Cui, H. and Lin, Q. (2018) Anti-irreversible fouling of precisely-designed PVDF-ZnO membrane: Effects of ion strength and co-existing cations, *Applied Surface Science,* 459, pp. 397-405.

Liang, S., Kang, Y., Tiraferri, A., Giannelis, E. P., Huang, X. and Elimelech, M. (2013) Highly hydrophilic polyvinylidene fluoride (PVDF) ultrafiltration membranes via postfabrication grafting of surface-tailored silica nanoparticles, *ACS Applied Materials & Interfaces,* 5(14), pp. 6694-6703.

Liang, S., Qi, G., Xiao, K., Sun, J., Giannelis, E. P., Huang, X. and Elimelech, M. (2014) Organic fouling behavior of superhydrophilic polyvinylidene fluoride (PVDF) ultrafiltration membranes functionalized with surface-tailored nanoparticles: Implications for organic fouling in membrane bioreactors, *Journal of Membrane Science,* 463, pp. 94-101.

Liu, F., Hashim, N. A., Liu, Y., Abed, M. M. and Li, K. (2011) Progress in the production and modification of PVDF membranes, *Journal of membrane science,* 375(1-2), pp. 1-27.

Nor, N., Jaafar, J., Ismail, A., Mohamed, M. A., Rahman, M., Othman, M., Lau, W. and Yusof, N. (2016) Preparation and performance of PVDF-based nanocomposite membrane consisting of TiO2 nanofibers for organic pollutant decomposition in wastewater under UV irradiation, *Desalination,* 391, pp. 89-97.

Prasertsung, I., Mongkolnavin, R., Kanokpanont, S. and Damrongsakkul, S. (2010) The effects of pulsed inductively coupled plasma (PICP) on physical properties and biocompatibility of crosslinked gelatin films, *International journal of biological macromolecules,* 46(1), pp. 72-78.

Rahimpour, A., Madaeni, S., Taheri, A. and Mansourpanah, Y. (2008) Coupling TiO2 nanoparticles with UV irradiation for modification of polyethersulfone ultrafiltration membranes, *Journal of Membrane Science,* 313(1-2), pp. 158-169.

Shen, L., Feng, S., Li, J., Chen, J., Li, F., Lin, H. and Yu, G. (2017) Surface modification of polyvinylidene fluoride (PVDF) membrane via radiation grafting: novel mechanisms underlying the interesting enhanced membrane performance, *Scientific Reports,* 7(1), pp. 2721.

Wang, C., Ren, Y., Lv, J., Zhou, Q., Ma, Z., Qi, Z., Chen, J., Liu, G., Gao, D. and Lu, Z. (2017) In situ synthesis of silver nanoparticles on the cotton fabrics modified by plasma induced vapor phase graft polymerization of acrylic acid for durable multifunction, *Applied Surface Science,* 396, pp. 1840-1848.

Wang, Z., Yu, H., Xia, J., Zhang, F., Li, F., Xia, Y. and Li, Y. (2012) Novel GO-blended PVDF ultrafiltration membranes, *Desalination,* 299, pp. 50-54.

You, S., Semblante, G. U., Lu, S., Damodar, R. A. and Wei, T. (2012) Evaluation of the antifouling and photocatalytic properties of poly (vinylidene fluoride) plasma-grafted poly (acrylic acid) membrane with self-assembled TiO_2, *Journal of Hazardous Materials*, 237, pp. 10-19.

Yu, Z.-R., Li, S.-N., Zang, J., Zhang, M., Gong, L.-X., Song, P., Zhao, L., Zhang, G.-D. and Tang, L.-C. (2019) Enhanced mechanical property and flame resistance of graphene oxide nanocomposite paper modified with functionalized silica nanoparticles, *Composites Part B: Engineering*, 177, pp. 107347.

Zhang, J., Xu, Z., Mai, W., Min, C., Zhou, B., Shan, M., Li, Y., Yang, C., Wang, Z. and Qian, X. (2013) Improved hydrophilicity, permeability, antifouling and mechanical performance of PVDF composite ultrafiltration membranes tailored by oxidized low-dimensional carbon nanomaterials, *Journal of Materials Chemistry A*, 1(9), pp. 3101-3111.

BIOGRAPHY

Name: Miss Pitsinee Laohapakdee

Education: Department of Environmental Science, Faculty of Science, Chulalongkorn University

Academic year: 2019

Postal address: 222 village No.6, Thasae sub-district, Thasae district, Chumphon 86140

E-mail address: peace39655@gmail.com

Mobile (Personal): (+66)93 574 1698