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ชื่อโครงการ   Plasma-induced poly(acrylic acid)- TiO_2/ZnO nanoparticles coated

polyvinylidene fluoride membrane to enhance hydrophilicity

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คณะวิทยาศาสตร์   จุฬาลงกรณ์มหาวิทยาลัย

การเคลือบไททาเนียมออกไซด์/ซิงค์ออกไซด์บนโพลีไวนิลลิดีนฟลูออไรด์เมมเบรนโดยการกระตุ้นด้วย

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Plasma-induced poly(acrylic acid)- TiO_2/ZnO nanoparticles coated polyvinylidene

fluoride membrane to enhance hydrophilicity

Kankanok   Saithai

Title   Plasma-induced poly(acrylic acid)- TiO_2/ZnO nanoparticles coated

       polyvinylidene fluoride membrane to enhance hydrophilicity

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ปีการศึกษา	2562		

บทคัดย่อ

ความชอบน้ำของโพลีไวนิลลิดีนฟลูออไรด์เมมเบรนแบบเส้นใยกลวงถูกพัฒนาขึ้นโดยการกระตุ้นด้วยพลาสม่าและกรดอะคริลิก ตามด้วยการเคลือบอนุภาคนาโนไททาเนียมไดออกไซด์และซิงค์ออกไซด์ ส่งผลให้ลักษณะสัณฐานวิทยา องค์ประกอบทางเคมี และความชอบน้ำเปลี่ยนไป โดยสามารถวิเคราะห์ได้จากผลของกล้องจุลทรรศน์อิเล็กตรอนชนิดส่องกราด เทคนิคการวิเคราะห์ด้วยธาตุและค่ามุมสัมผัสน้ำของเมมเบรน พบว่า อนุภาคนาโนไททาเนียมไดออกไซด์และซิงค์ออกไซด์ถูกเคลือบบนผิวเมมเบรนได้สำเร็จและเพิ่มขึ้นตามเวลาที่ใช้ในการเคลือบ นอกจากนี้ค่ามุมสัมผัสน้ำลดลงเมื่อเมมเบรนถูกกระตุ้นด้วยพลาสม่า กรดอะคริลิกและการเคลือบด้วยสารละลายผสมของอนุภาคนาโนไททาเนียมไดออกไซด์ที่มีความเข้มข้น 10 มิลลิกรัมต่อลิตร และอนุภาคนาโนซิงค์ออกไซด์ที่มีความเข้มข้น 10 มิลลิกรัมต่อลิตร เวลาเคลือบ 24 ชั่วโมง จากเมมเบรนดั้งเดิม 73.5° ถึง 51.5° แสดงให้เห็นว่าเมมเบรนนั้นมีความชอบน้ำมากขึ้น แต่อย่างไรก็ตาม การเคลือบเมมเบรนด้วยอนุภาคนาโนไททาเนียมไดออกไซด์ที่มีความเข้มข้น 10 มิลลิกรัมต่อลิตร เวลาการเคลือบ 24 ชั่วโมง ทำให้เมมเบรนมีความชอบน้ำมากที่สุด โดยมีค่ามุมสัมผัสน้ำลดลง 34.9° เกิดจากการรวมตัวกันของอนุภาคนาโนไททาเนียมไดออกไซด์และซิงค์ออกไซด์บนผิวเมมเบรน อย่างไรก็ตาม เมมเบรนที่ถูกกระตุ้นด้วยพลาสม่า กรดอะคริลิกและเคลือบด้วยอนุภาคนาโนไททาเนียมไดออกไซด์และซิงค์ออกไซด์นั้นสามารถนำไปประยุกต์ใช้ในการบำบัดน้ำเสียได้

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Project Title   Plasma-induced poly(acrylic acid)- TiO$_2$/ZnO nanoparticles coated polyvinylidene fluoride membrane to enhance hydrophilicity

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Department   Environmental Science

Academic year   2019

Abstract

Hydrophilic of polyvinylidene fluoride (PVDF) hollow fiber membrane was enhanced through pulse inductively couple plasma (PICP) induced poly(acrylic acid) (PAA) polymerization followed by titanium dioxide nanoparticles (TiO$_2$ NPs) and zinc oxide nanoparticles (ZnO NPs) coated. The morphology, chemical composition and hydrophilicity of modified membranes were characterized by SEM, EDX and water contact angle. The result of SEM and EDX analyses found that TiO$_2$ NPs and ZnO NPs were successfully coated on membrane surface and increased belong to immersion time. In addition, the water contact angle was declined when membrane was modified via PICP induced PAA- 10 ppm TiO$_2$/ZnO NPs coated at 24 hr from original 73.5° to 51.5°, indicating the modified membrane was enhanced hydrophilicity. Nonetheless, 10 ppm TiO$_2$ NPs of 24 hr coating time gave the highest hydrophilicity in term of contact angle (34.9°) because of the mixing solution between TiO$_2$ NPs and ZnO NPs cause agglomeration on membrane surface. However, the modified membrane by PICP induced PAA-TiO$_2$/ZnO NPS coated has potential in the application for wastewater treatment.

Keywords: PVDF hollow fiber membrane, Hydrophilicity, Plasma-induced grafted polymerization, Titanium dioxide nanoparticles (TiO$_2$ NPs), Zinc oxide nanoparticles (ZnO NPs)

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Chapter I

Introduction

1.1 Rational

Large volumes of produced water from industries are generated and released to the environment everyday (Gopakumar *et al.*, 2019). The wastewater required to treat before release to natural water resources. Recently, membrane as one of most promising technologies is widely used for municipal and industrial wastewater treatment owing to its advantages in small space occupation, high quality of treated water and easy operation (Wu *et al.*, 2020). Especially, polyvinylidene fluoride (PVDF) membrane has been extensively used in microfiltration and ultrafiltration processes for industrial application because of its excellent mechanical properties, thermal stability and chemical resistance (Qin *et al.*, 2015). However, the nature of PVDF membrane being hydrophobicity may result in the problems of low water permeability and easy fouling (Chen *et al.*, 2019b).

There are three groups of major factors including pore blocking, solute aggregation that leads to cake formation or gel layer on the membrane surface or adsorption through the membrane that influence membrane fouling which are the properties of the feed solution including the composition, concentration, pH, and ionic condition (Li and Chen, 2010). Liang *et al.* (2014) studied the antifouling performance of membrane with realistic feed water, containing synthetic foulants (natural organic matters in wastewater) and $CaCl_2$/$MgCl_2$ (water hardness). NaCl was added to adjust ionic strength and solution pH was buffered with $NaHCO_3$ in actual membrane bioreactor plant supernatant and the results found that the water flux of original PVDF membrane was decreased and the percentage of flux recovery substantially deceased (Liang *et al.*, 2014). As the result, the membrane lifetime was shorten and the operational cost was increased.

In the past decades, there were witnessed a considerable growth of research promoting better understanding of membrane fouling mechanisms. Generally, consensus has been reached that membrane surface hydrophilicity significantly affects organic

fouling development, and that a greater surface hydrophilicity favors the amelioration of membrane fouling (Liang *et al.,* 2014). There are many ways to increase hydrophilicity of membrane such as membrane modification by coating and blending with the hydrophilicity materials.

The semiconductor catalyst has the characteristics of superhydropilicity as well as membrane foulant removal, leading to the beneficial effect to the filtration process and antifouling performance such as nanoparticles of silica dioxide (SiO_2), aluminum oxide (Al_2O_3), zinc oxide (ZnO) and titanium dioxide (TiO_2) (Li *et al.,* 2017). The permeation flux of the modification of PVDF membrane by plasma-induced $PAA-TiO_2$ was increased compared to the pristine membrane for four times and the oil rejection rate of modified membrane was higher than that of pristine membrane (92%) (Chen *et al.,* 2019b). In addition, the result of hydrophilicity test of functionalized PVDF membrane via plasma-induced PAA-ZnO was tremendously enhanced by the self-assembly of ZnO and the highest water flux was found at 0.5 wt% ZnO. The membranes were then severely fouled on filtration of alginate (1 wt%) and the ZnO-coated membranes were able to fully recover their original fluxes upon UV irradiation for 30 min (Laohaprapanon *et al.,* 2017).

According to the previous researches, titanium dioxide (TiO_2) has been extensively studied in antifouling performance of membrane because of its photocatalytic and superhydrophilic properties. However, the activity of TiO_2 was limited owing to its wide band gap, which electrons are promoted from the valence to the conduction bands (Li *et al.,* 2017). ZnO is the second most studied semiconductor after TiO_2 that was similar with TiO_2 in terms of band gap energy and relative position of the band edge. Two combination is conductive to the migration of photo-generated electron-hole pairs and then the lifetime of charge carriers was enhanced, presenting an ideal combination pattern (Li *et al.,* 2017). Nevertheless, the coating nanoparticles are limited due to the poor dispersibility and entirely enfolded by polymer matrix (Müller *et al.,* 2017). The surface of the modified PVDF membrane with 3D TiO_2/ZnO nanolayer displayed excellent photocatalytic activity and stable reusability during methylene blue (MB) degradation.

Fouling potential evaluation of humic acid (HA) revealed that the composite modified membrane possessed excellent antifouling property due to the superior hydrophilicity and photocatalysis under visible light irradiation (Li *et al.*, 2017). The self-assembly or a chemical bonding process has been proven to be an effective strategy (Qin *et al.*, 2015). The challenge in the self-assembly method is the need to have key functional groups on the surface of the membrane that can stably hold TiO_2/ZnO (You *et al.*, 2012).

Plasma-induced graft polymerization is an alternative technique that eliminates the need for chemical initiators or other components. Pulse inductively coupled plasma (PICP) is one of the high energy plasma systems which could be used to modify surface of polymer (Prasertsung *et al.*, 2010). The activated species of low energy plasma can trigger polymerization reaction on or near the surface of a wide variety of materials even with short bursts of plasma exposure. PAA is hydrophilic in nature, and its functional groups could strongly bind nanoparticles via ion coordination or hydrogen bonding (You *et al.*, 2012). Under specific conditions, plasma can result to thin and even polymer coatings without compromising the bulk structure. Therefore, in this study, PAA was plasma-grafted on PVDF to facilitate the self-assembly of TiO_2/ZnO nanoparticles.

This study is aim for the plasma-induced PAA-TiO_2/ZnO coated PVDF membrane to increase attachment of membrane and increase hydrophilicity. The modified membrane was investigated. The physical and chemical changes of modified PVDF membrane were analyzed.

1.2 Objectives

To modify PVDF hollow fiber membrane by plasma-induced poly(acrylic acid)-TiO_2/ZnO to increase hydrophilicity using PICP.

Chapter II

Literature reviews

2.1 Membrane Technology

Due to population growth and industry development, there is ever increasing amounts of uncontrolled wastewater discharge causing serious environmental problems. Over the past few decades, various technologies have been explored for treatment of organic wastewater. Membrane technology has been considered as one of the most promising methods for water decontamination owing to its advantages of high separation selectivity, low energy consumption, no requirements for additional chemicals, easy scale up and continuous operation (Pan *et al.*, 2019). Synthetic membrane processes perform versatile functions with the membrane acting as a barrier interface between feed and product (Singh, 2015) as shown in Figure 2.1.
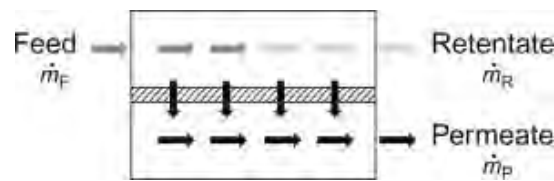
Figure 2.1 Membrane separation process (Cui, Jiang and Field, 2010)

Membranes might be described as conventional filters but with much finer mesh or much smaller pores to enable the separation of tiny particles, even molecules (Cui, Jiang and Field, 2010). The selective permeation of membranes with different structures or physicochemical properties can be attributed to different mechanisms associated to sieving, steric hindrances, membrane/solvent/solute(s) interactions, solution/diffusion characteristics, and electrical migration. The external action of pressure, electrical, and concentration driving forces together with different transport mechanisms leads to the membrane separation processes (de Pinho and Minhalma, 2019). There are four major pressure-driven membrane processes that can be divided by the pore sizes of membranes and the required transmembrane pressure (TMP): microfiltration (MF) (0.1–5 μm),

ultrafiltration (UF) (1–100 nm), nanofiltration (NF) (0.5–10 nm), and reverse osmosis (RO) (<0.5 nm). Figure 2.2 presents a classification on the applicability of different membrane separation processes based on particle or molecular sizes. RO process is often used for desalination and pure water production, but it is the UF and MF that are widely used in food and bioprocessing.
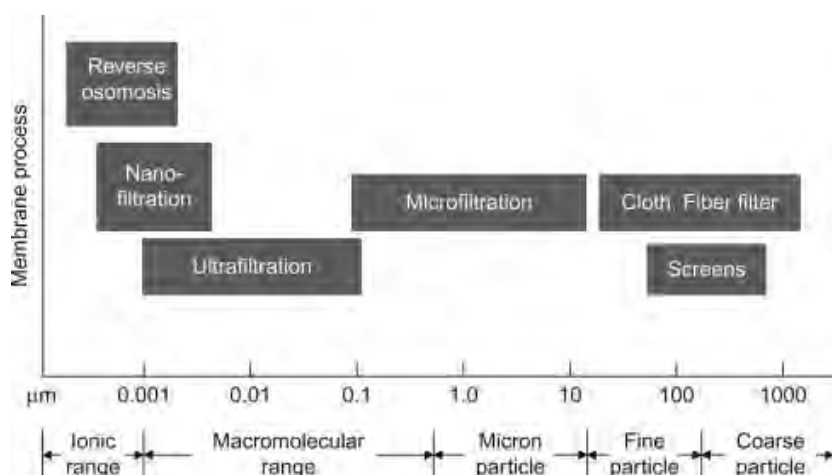
Figure 2.2 Ranges of different separation processes based on sizes (Cui, Jiang and Field, 2010).

While MF membranes target on the microorganism removal, and hence are given the absolute rating, namely, the diameter of the largest pore on the membrane surface, UF/NF membranes are characterized by the nominal rating due to their early applications of purifying biological solutions (Cui, Jiang and Field, 2010).

In membrane separation processes, the membrane module is the system where the membranes are inserted. The modules should accommodate membranes with a very high packing degree and the pumping system for solutions distribution should present a reasonable cost. There are several modules capable of satisfying the above requisites and they should be carefully chosen considering the physicochemical characteristics of the feed to be processed (de Pinho and Minhalma, 2019). The membrane modules are designed and developed by industry manufacturers in order to achieve different characteristics on the hydrodynamic conditions, filtration areas, energy consumptions, etc

(Cui, Jiang and Field, 2010). There are four configurations i.g. the shares among tubular, capillary/hollow fiber, spiral wound and flat/plate as shown in Figure 2.3.

(a)   (b)

(c)   (d)
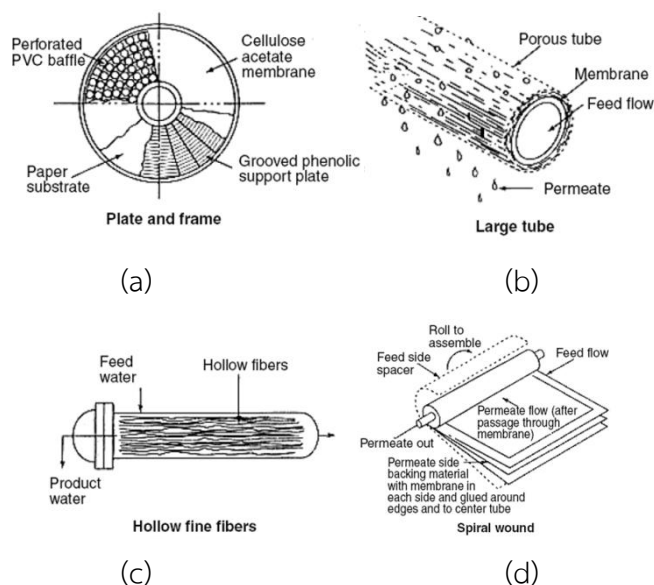
Figure 2.3 Configuration of membrane (Sr and Sincero, 2002)

The performance of membrane technology directly associated with parameters such as pore size, type and properties of the membrane material and composition of effluents to be treated, as well as operating parameters such as retention time, pH, temperature (Kamali *et al.*, 2019). For a membrane process to be effective, the membrane must combine high permeability with high selectivity. For liquid separations, the membrane should preferably have both hydrophilic and hydrophobic characteristics depending on kinds of membrane material.

2.2 PVDF hollow fiber membrane

Synthetic membranes can be made from a large number of materials. The material is selected based on processing requirements, thermal and chemical stability and fouling tendency. The most common material is polymeric with an asymmetric (anisotropic) or symmetric (microporous) structure (Singh, 2015). In terms of materials, membranes can be classified into polymeric or organic membranes and ceramic or

inorganic membranes. Organic membranes are usually made up of various polymers, polyvinylidene fluoride (PVDF) is ones of the typical. Polymeric membranes are relatively cheap, easy to manufacture, available in a wide range of pore sizes, and they have been widely used in various industries. Nevertheless, most of the polymeric membranes have limitations on one or more operating conditions (pH, or temperature, or pressure, or chlorine tolerance, etc.), which hinder their wider applications. Membranes used for removal of dissolved volatile species from water usually are hydrophobic in nature so as to provide less mass transfer resistances. Polypropylene (PP) and polytetrafluoroethylene (PTFE) membranes are the ideal candidates because of their good hydrophobicity. However, the commercial PP and PTFE membranes are limited to their symmetric structures, restricted pore size range and porosity. Alternatively, polyvinylidene fluoride (PVDF) has become a new membrane material in recent years due to its both good hydrophobicity and feasibility to form asymmetric membranes via phase inversion methods (Tan *et al.*, 2006).

PVDF is a semi-crystalline polymer mainly consisting of 59.4 wt.% fluorine and 3 wt.% hydrogen, and produced by free radical polymerization leading to the formation of the $-CH_2-CF_2-$ repeating units. The arrangements of the CH_2 and CF_2 bonds within the molecular chains result in the formation of a specific crystal structure leading to the formation of a polymer with unique properties. The PVDF chains can crystallize into three distinct phases (α, β, γ) depending on the fabrication technique. Due to the high electrical dipole moment of these crystalline phases, PVDF dissolves in varied solvents, making possible the versatile synthesis of flat-sheet, hollow-fiber, and nanofiber membranes (Nthunya *et al.*, 2019). Thus, PVDF membranes are extensively used due to its outstanding mechanical properties, thermal stability, and chemical resistance (Chen *et al.*, 2019a).

However, the pristine PVDF membrane is hydrophobic which makes it easily fouled during filtration process. Thus, the plenty of works have been devoted to developing an

anti-fouling membrane utilizing hydrophilic/hydrophobic interactions or electrostatic repulsion between membrane surfaces and foulants (Guo *et al.*, 2020).

The hollow fibers membrane module, showing in Figure 2.4, is composed by several polymeric capillary fibers that are introduced inside an outer shell. The feed solution may flow on the inside of the fibers and the permeate is collected in the space between the fibers and the outer shell. In this situation, the membrane active layer is inside the fibers. One other situation is when the feed solution flows on the outside of the fibers, the active layer is on the outer fiber face and the permeate is collected inside the fibers. The choice between these two situations depends mainly on the application purpose and on the feed solution characteristics (de Pinho and Minhalma, 2019).
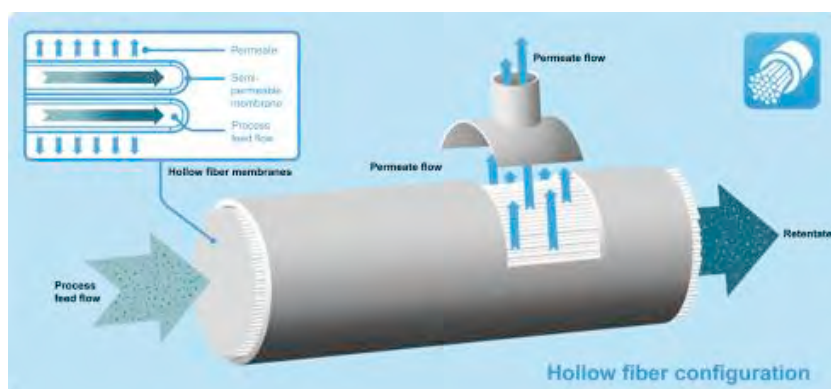
Figure 2.4 Representation of a hollow fiber module (de Pinho and Minhalma, 2019)

2.3 Membrane fouling

Fouling is generally defined as a process resulting in a loss of performance of a membrane due to deposition of suspended or dissolved substances onto its external surface. Fouling is often the main limitation to the successful membrane application of food and biotech industries (Cui, Jiang and Field, 2010). Fouling causes a loss in water flux and quality, reduced operating efficiency, lost service time, premature membrane replacement and higher operating costs. In addition, anticipated lower throughput warrants more membrane surface area resulting in higher capital costs. Prevention and/or reduction in the rate of fouling and concentration polarization (CP) are, therefore,

important factors in the design and operation of membrane systems (Singh, 2015). Fouling can be related to different modes such as adsorption, chemical interactions, cake formation, and pore blocking by particles. These modes can lead to blockage or partial blockage of the active membrane area or to deposition of a layer onto the membrane surface (Pan *et al.*, 2019). Generally, four fouling mechanisms for porous membranes can be observed, as shown in Figure 2.5
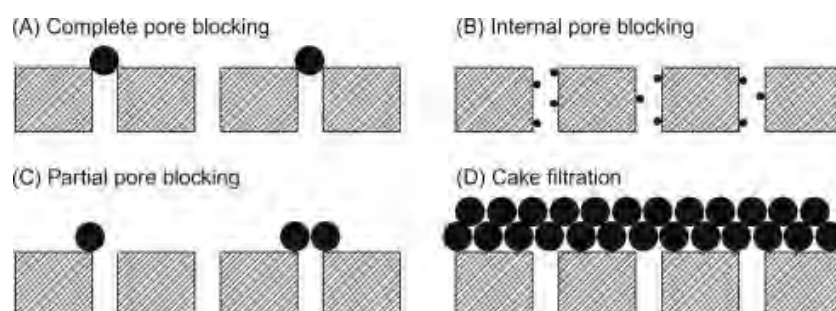
Figure 2.5 Fouling mechanisms of porous membranes (Cui, Jiang and Field, 2010)

The flux of a solvent through a membrane is roughly proportional to the applied pressure but for liquids other than pure water this proportionality does not exist due to CP and/or fouling and the permeate flow may be as low as 20% of that of pure water. The permeate flux stabilises after an initial rapid decline. The steady-state flux value is a function of the nature of the feed (e.g., viscosity, solute concentration and diffusivity, pH, ionic strength) and operating conditions such as fluid shear rate at the membrane surface and trans-membrane pressure drop (Singh, 2015). The water flux and fouling potential of membranes were evaluated as J/J_0 (J and J_0 represent the membrane flux at a single moment and the initial flux, respectively). The original PVDF membrane experienced a drastic flux decline during HA filtration but the flux of the TiO_2/ZnO modified membranes slower speed decline (Li *et al.*, 2017).

2.4 Hydrophilic membrane modification

The hydrophilic properties are related to water absorption, which can be calculated as in Eq. (1.1) which W_2 is the immersed weight afterward and W1 is the previous immersed weight (Azman Mohammad Taib and Julkapli, 2019).

$$\text{Water Absorption (\%)} = (W_2\text{-}W_1 / W_2) \times 100 \qquad\qquad (1.1)$$

A higher percentage of water content results from higher hydrophilic properties and a lower percentage of water absorption is proportional to high hydrophobic properties. The contact angle test is commonly used to determine the hydrophilicity and hydrophobicity on the surface of a material. This test could be performed by using different liquids, the most common of which is a water droplet. The degree of the angle on the surface of materials is calculated, as explained in Fig. 2.6 (Azman Mohammad Taib and Julkapli, 2019).

Figure 2.6 Different properties of contact angle test (Azman Mohammad Taib and Julkapli, 2019)

Hydrophilic membranes are less susceptible to fouling than hydrophobic membranes. The influence of the membrane material on the fouling of membranes shows that the flux of hydrophilic membranes is only marginally reduced, whereas the flux reduction of hydrophobic membranes is significant. In general, hydrophilic polymers have restricted
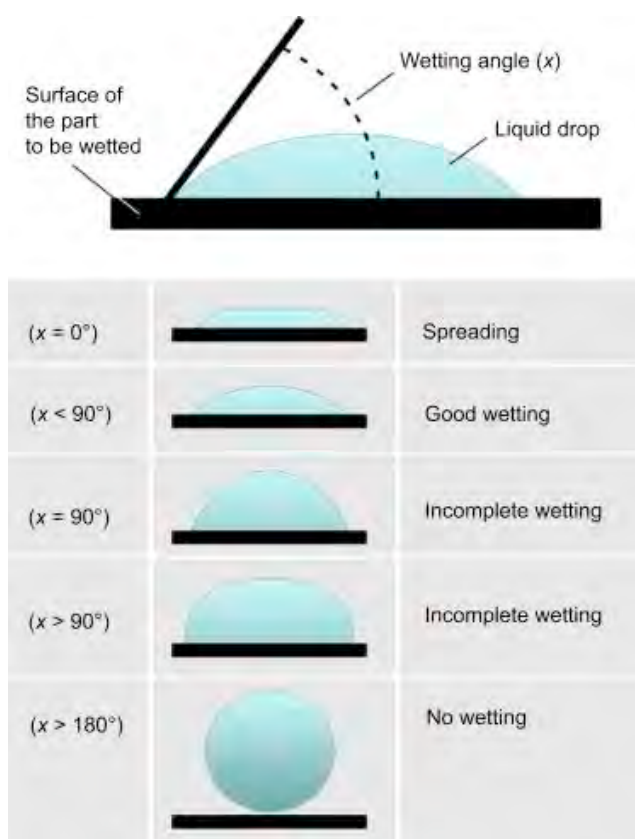
chemical and thermal stability (de Pinho and Minhalma, 2019). The hydrophilic or photocatalytic modification could change the surface morphology and chemical property of membranes, resulting in anti-fouling performance, which has drawn much attention from scholars worldwide. Although the common methods of membrane modification including surface coating, chemical grafting, and blending modification, enhanced the anti-fouling property to a certain extent, these methods had various defects in some aspects (Li *et al.*, 2017).

2.5 Plasma induced grafting technique

The improvement in membrane hydrophilicity and fouling resistance was limited through such blending, since nanoparticles were poorly dispersed and entirely enfolded by the polymer matrix, which significantly decreased the modification efficiency. Attaching nanoparticles on the membrane surface through self-assembly or chemical bonding processes has been proven to be more effective in membrane performance improvement compared with the blending method. Under this condition, most loaded nanoparticles can be exposed to the reaction environment rather than being entrapped in the membrane matrix, and nanoparticles uniformly disperse on the membrane surface. The challenge in the self-assembly method is the achievement stable attachment of nanoparticles on the membrane surface via bonding with key functional groups. PVDF membrane is not conducive to nanoparticles self-assembly (Chen *et al.*, 2019b) therefore, the activation of PVDF membrane is needed. Plasma-induced graft polymerization is a promising technique to provide chemical initiators or other components. The species activated by low energy plasma can trigger polymerization reactions of a wide variety of materials on or near the membrane surface. Plasma treatment has various kinds for example; cold plasma such as radio frequency (RF) generated plasma has been reported to modify the surface of poly (lactide-co-glycolide) (PLGA) by introducing reactive groups onto the surface (Kan *et al.*, 1998). Pulse inductively coupled plasma (PICP) is one of the high energy plasma systems which could be used to modify surface of polymer due to the fact that the surface treatment by PICP does not require lengthy treatment period to

achieve desired effects. The pulse treatment is more practical where the design of PICP is much simpler than typical inductively coupled RF reactor plasma. In addition, inductively coupled plasma produced in a closed environment provides clean environment for treatment of biomaterials. Single pulse plasma minimizes the thermal load of the sample, more, the purposed PICP system has flexibility in reducing and rising electron temperature of the plasma through variation of electrical energy stored and operating gas pressure. Prasertsung *et al.* (2010) studied about the effects of pulsed inductively coupled plasma (PICP) on physical properties and biocompatibility of crosslinked gelatin films. The result found that PICP did not significantly affect the thermal behavior and the degree of crosslinking of crosslinked gelatin film and the contact angle by both water and ethylene glycol of crosslinked gelatin films treated with nitrogen plasma was decreased in comparison with untreated film (Prasertsung *et al.,* 2010).

Serveral researches which studied membrane modification through plasma induced grafting technique found that the functionalized membrane has highly hydrophilicity. Comparison of the pristine and modified PVDF membrane by plasma induced graft copolymerization and dip coating with silica nanoparticles, the water permeability sharply increase after modification (Liang *et al.,* 2013). The modified membrane surface significantly improved the wettability of the membrane and converted the membrane surface from hydrophobic to superhydrophilic. Besides, the modification dramatically enhanced the monopolar functionality of the membrane, which potentially endowed the membrane surface with a tightly bound hydration layer that acted as a repulsive barrier to foulants (Liang *et al.,* 2014). Chen *et al.* (2019) modified PVDF membrane via plasma-induced poly(acrylic acid) (PAA) graft-polymerization followed by ZnO nanoparticles self-assembly. ZnO nanoparticles were immobilized onto membrane surface through the adsorption of PAA layer to form a PAA-ZnO coating without valence change. The carboxyl groups of PAA layer provided complexing ligands to coordinate with Zn^{2+} and form bidentate species on the ZnO nanoparticles surface that converted hydrophobic membrane surface to hydrophilic membrane, leading to the dramatically

improvement of membrane performance in water permeation flux (Chen *et al.*, 2019a). Liang *et al.* (2014) investigated the modification PVDF membrane via plasma-induced poly(methacrylic acid) (PMAA) graft- copolymerization, providing sufficient carboxyl groups as anchor sites for the binding of silica nanoparticles. The result revealed that the modification doubled surface energy of the functionalized membrane significantly improved the wettability of the membrane and converted the membrane surface from hydrophobicity to highly hydrophilicity (Liang *et al.*, 2013). The modified membrane has reliability and durability of the antifouling property of the superhydrophilic membrane When the modification membrane was applied in filtration the synthetic foulant-mixture solution (sodium alginate, Suwannee River natural organic matter and bovine serum albumin) (Liang *et al.*, 2014). You *et al.* (2012) functionalized PVDF membrane by plasma-grafted poly(acrylic acid) followed by TiO_2 nanoparticles self-assembly and the membrane with TiO_2 loading maintained the highest pure water flux and the best protein antifouling property. The fabricated membranes were demonstrated huge potential for use in membrane reactors with high hydrophilicity and fouling mitigation (You *et al.*, 2012). Thin and even polymer coatings can thus be formed in the membrane surface without compromising the bulk structure under specific control (Chen *et al.*, 2019b).

2.6 TiO_2/ZnO nanoparticles

The hydrophilic modified organic nanoparticles could only hinder the adsorption of foulants onto the membrane surface while the membrane foulants would not be degraded fundamentally. Specifically, the membrane with photocatalytic modification would have a great potential in oxidative degradation of membrane foulants, and thus solved the problem of membrane fouling effectively. A number of advanced PVDF membranes have been developed by various modification techniques with the incorporation of nanoparticles (NPs) to improve the membrane hydrophilicity and antifouling ability. Many types of semiconductor catalyst nanoparticles, having the characteristics of super-hydrophilicity as well as membrane foulants removal, leading to beneficial effect to the filtration behavior and anti-fouling potential of membranes (Li *et*

al., 2017), have been utilized in membrane modification, such as iron (Fe^0, Fe$_2$O$_3$, Fe$_3$O$_4$), SiO$_2$, Al$_2$O$_3$, TiO$_2$, ZrO$_2$, carbon nanotubes, graphene oxide, etc.

TiO$_2$ NPs have gained special focus due to their features, such as super hydrophilicity, chemical stability, self-cleaning ability, and low cost (Yemmireddy and Hung, 2017). TiO$_2$, being a common photocatalyst, has been extensively studied in the removal of organic contaminants due to its wide source and abundant content, light stability in solution, and high photocatalysis under UV irradiation (Li *et al.*, 2017). When TiO$_2$ is irradiated with UV light (10–400 nm) and absorbs equal or greater energy than its band gap, electrons are promoted from the valence band to the conduction band. The electron–hole pairs are generated and reacted with nearby oxygen or water molecules to form radicals, which can oxidize a variety of substances. The anatase phase of TiO$_2$ was proved to be the best choice for photocatalytic processes in the presence of the UV light because the rutile phase has narrower band gap causing its lower photocatalytic performance. Thus, the membrane/TiO$_2$ composite can kill bacteria, destroy organic contaminants, and self-clean upon exposure to UV light (You *et al.*, 2012). However, the activity of TiO$_2$ in the visible region was restricted owing to its wide band gap. ZnO as another plentiful semiconductor with high electron mobility could enlarge the dynamic range of light response. ZnO was similar with TiO$_2$ in terms of band-gap energy and relative position of the band edge. Both nanoparticles (TiO$_2$/ZnO NPs) in combination is conductive to the migration of photo-generated electron-hole pairs, and then the lifetime of charge carriers could be enhanced, presenting an ideal combination pattern. Li *et al*. (2017) modified PVDF membrane by using atomic layer deposition (ALD) coat three-dimensional (3D) TiO$_2$/ZnO photocatalyst on membrane surface and pore walls. The photo-induced superhydropilicity was realized with a decline of 82.6% of water contact angle and an increase of 33.5% for the pure water flux (Li *et al.*, 2017).

Chapter III

Methodology

3.1 Chemicals and material

Poly(vinylidene fluoride) hollow fiber membrane was supplied by Altrateck (China). The specification of the membrane was reported by the manufacturer as presented in Table 3.1. Acrylic acid (AA) was purchased from Loba Chemie (India). The specification of acrylic acid was presented in Table 3.2. A commercial titanium dioxide nanoparticles (TiO_2 NPs) and zinc oxide nanoparticles (ZnO NPs) were supplied from Prime Nanotechnology (Thailand). The properties of ZnO NPs and TiO_2 NPs were summarized in Table 3.3. Deionized water (DI) was used for solution preparation. All chemical used were analytical grade.
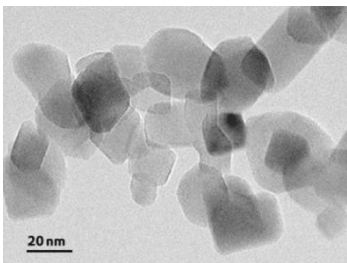
Table 3.1 Specification of the PVDF hollow fiber membrane

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	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 TiO$_2$ NPs and ZnO NPs

Properties	TiO$_2$ NPs	ZnO NPs
Appearance	White powder	White powder
Forms	80% Anatase, 20% Rutile	-
Morphology	20 nm	-
Primary particle size (nm)	21	20-40
Tamped density (g/L)	130	-
Specific surface area(m^2/g)	50	-
Assay (%)	>99.5	>99
Loss on dry (%)	-	<0.5

3.2 Experimental procedures

3.2.1 Plasma activation

The 30 cm of PVDF membranes were mounted to the cylindrical quartz tube plasma system. A pulse inductively couple plasma (PICP) is driven by discharging of current from capacitor bank. The initial store energy of the system is 2.4 kJ when the charging potential is 10 kV. Oxygen gas is filled at low pressure after a pre-evacuation of the quartz tube by a system of diffusion and rotary pump. When operating, the current is discharged through a single turn steel coil around the quartz tube producing O$_2$ plasma inside through electromagnetic induction process. O$_2$ gas plasma produced in double shot pulse and generated free radicals on the membrane surface. The plasma-treated membranes were immersed in 70% nitrogen-purged aqueous acrylic acid (AA) solution for graft polymerization. Following, the membranes were dried in incubator (ULM 700, Memmert, Germany) at 90°C for 30 min for the polymerization of AA to poly(acrylic acid)

(PAA). After the AA reaction, the membranes were rinsed three times with DI water to remove unreacted AA monomers and PAA homopolymers.

3.2.2 Membrane coating with TiO_2 NPs and ZnO NPs

The TiO_2 NPs and ZnO NPs solution were prepared by dissolving with DI water and stirred for 15 min using magnetic stirrer. Following, the solutions were sonicated for 30 min by an ultrasonic sonicator bath (DT510H, SONOREX, Germany) at 40°C. The PAA-grafted membranes were dipped in TiO_2/ZnO NPs solution for TiO_2/ZnO self-assembly. The compositions of TiO_2 NPs and ZnO NPs are listed in Table 1. After that, the membranes were rinsed three times with DI water. Finally, the modified membranes were incubated in oven (ULM 700, Memmert, Germany) at 60°C for 60 min and then dried in ambient for 15 min.

Table 3.4 The compositions of TiO_2 NPs and ZnO NPs and immersion time of coated plasma-induced hollow fiber PVDF membrane

Membrane	TiO_2 NPs (ppm)	ZnO NPs (ppm)	Immersion Time (hr)
C1	0	0	0
C2	10	0	2
C3	10	0	4
C4	10	0	24
C5	0	10	2
C6	0	10	4
C7	0	10	24
C8	10	10	2
C9	10	10	4
C10	10	10	24

Table 3.5 The compositions of TiO$_2$ NPs and ZnO NPs and immersion time of PAA- grafted hollow fiber PVDF membrane

Membrane	TiO$_2$ NPs (ppm)	ZnO NPs (ppm)	Immersion Time (hr)
P1	10	0	2
P2	10	0	4
P3	10	0	24
P4	0	10	2
P5	0	10	4
P6	0	10	24
P7	10	10	2
P8	10	10	4
P9	10	10	24

3.3 Membrane characterizations

The surface morphology of PVDF hollow fiber membrane was examined by scanning electron microscope (SEM). Energy dispersive spectroscopy (EDS) was applied to determine of components and concentration of different elements. The hydrophilicity of each membrane was evaluated through their contact angle. The dynamic contact angle of PVDF hollow fiber membrane at 28 °C was measured by Tensiometer (DCAT 11, Dataphysics, Germany). This tensiometric method determines the advancing contact angle by measuring the force when a sample of fiber is brought into vertical contact with deionized water. As the forces of interaction and geometry of the solid was measured with a known surface tension of water, the dynamic contact angle was calculated. The advantages of this method are that the actual measurement is simple to perform and that wetting characteristics of a single fiber can be easily obtained (Yu Wang, Chung and Gryta, 2008).

Chapter IV

Results and Discussion

4. 1 Morphological study

4.1.1 Effect of coating TiO_2 NPs and ZnO NPs

The PVDF membrane was immersed in the various particles solution. To affirm the change on membrane surface can be seen from Figure 4.1, which shows the coating layer on membrane surface. There is no TiO_2 and ZnO NPs on surface of original PVDF membrane (C1) while there are TiO_2, ZnO or TiO_2/ZnO NPs, being intensive distributed and superimposed on modified membrane surface (C3, C6, C9). The strong and dense collectives of nanoparticles denote the aggregation (Ashraf *et al.*, 2018). The result showing in Figure 4.1 showed the agglomeration of TiO_2/ZnO NPs is stronger than TiO_2 or ZnO, it was obviously observed two different particle forms tend to adhesion. The loosely joint particles show the agglomeration which may be broken by mechanical stress. The agglomeration of nanoparticles reduces the potential enhancement of mechanical properties in nanocomposites, due to the restriction of interfacial area (Ashraf *et al.*, 2018). Due to the agglomeration, the result of Laohaprapanon *et al.* (2017) reported that the flux may decrease because nanoparticles aggregation attributed on surface and inside pores of the membrane matrix (Laohaprapanon *et al.*, 2017). In addition, amount of TiO_2 NPs more than ZnO NPs in TiO_2/ZnO layer that indicating TiO_2 NPs has capability of coating better than ZnO NPs because particles size of TiO_2 NPs was smaller than ZnO NPs.
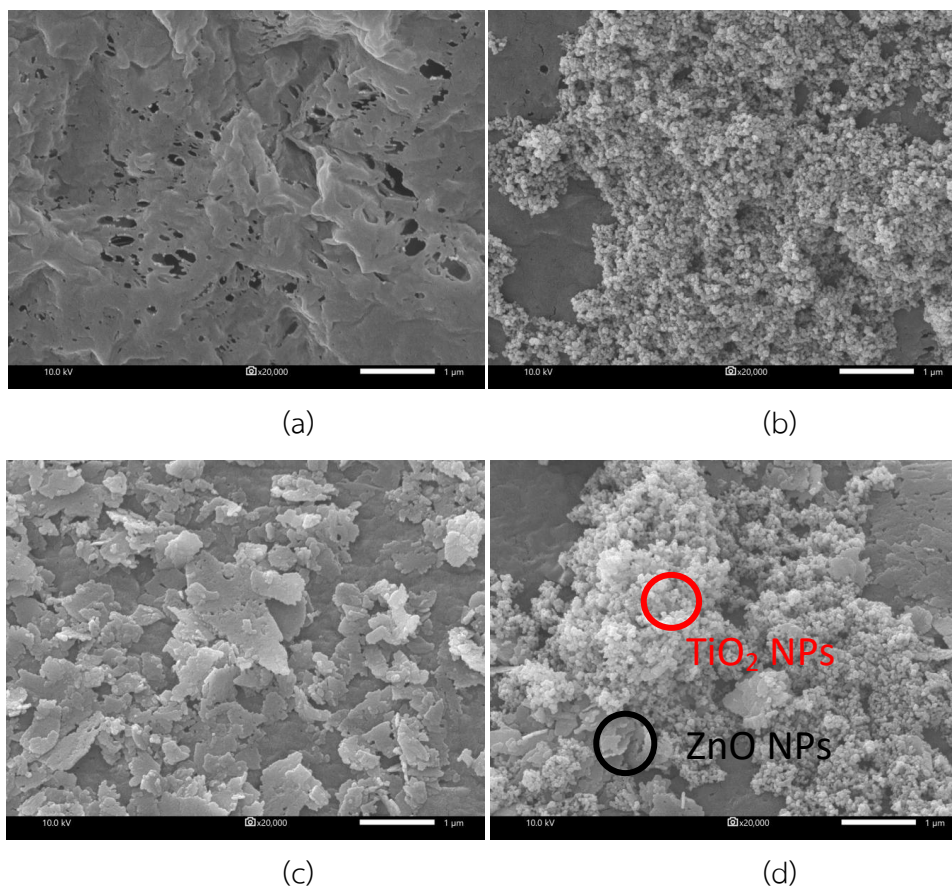
Figure 4.1 SEM images of membrane surface (a) C1; (b) C3; (c) C6; (d) C9

Additionally, the percentage of atomic concentration of the element composition on membrane surface investigating by EDX as shown in Table 4.1 prove the successful membrane modification by plasma-inducing and coating with TiO_2 NPs and ZnO NPs. When membrane was coated with TiO_2 NPs (C3), ZnO NPs (C6) and TiO_2/ZnO NPs (C9), the percentage of Ti and Zn atomic concentration was found and O atomic concentration was increased comparing to the pristine membrane 4.26±0.06% to 13.15±0.23%, 7.35±0.06% and 10.51±0.07%, respectively. The surface [O]/[F] ratio, as calculated from the percent atomic concentration of O and F found that the modified membranes with oxide nanoparticles resulted in a higher [O]/[F] ratio due to the defluorination caused by O_2 plasma and the oxidation reaction on the plasma-treated membrane surface during the air exposure stage might also slightly contribute to the increase of [O] (Liang *et al.,* 2013). Additionally, the oxide nanoparticles conduce to greatly increase of [O]. The increase of [O] was used as a an additive to improve membrane porosity and hydrophilicity (Liang *et al.,* 2013).

Table 4.1 The element composition of membranes

Membrane Sample	Atomic concentration (%)				
	C	F	O	Ti	Zn
C1	67.40±0.10	28.34±0.10	4.26±0.06	-	-
C3	60.24±0.09	20.51±0.25	13.15±0.23	6.10±0.07	-
C6	62.86±0.09	25.16±0.84	7.35±0.06	-	3.84±0.07
C9	60.32±0.07	23.39±0.15	10.51±0.07	3.61±0.10	2.14±0.05

4.1.2 Effect of coating time

The PVDF membrane was immersed in solution of 10 ppm TiO_2 NPs and 10 ppm ZnO NPs at varied time to study the effect of coating time on the membrane. When increased immersion coating time from 2 hr to 4 hr, the amount of TiO_2 NPs and ZnO NPs was sharply found and the particles have good distribution as shown in Figure 4.2. The particles overlapped and adhered together when rising time because nanoparticles had high surface energy, tending to agglomerate to reach more stable state (Gebru and Das, 2017).
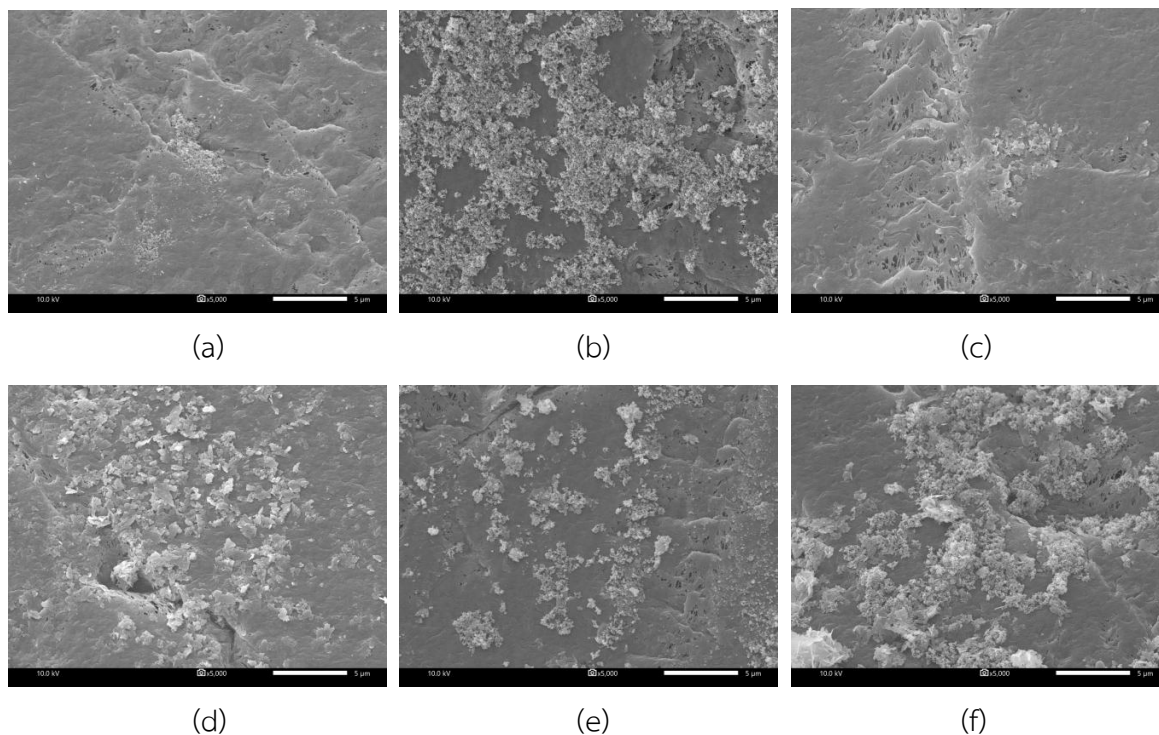

(a)　　　　　　　　(b)　　　　　　　　(c)

(d)　　　　　　　　(e)　　　　　　　　(f)

Figure 4.2 Membrane surfaces of (a) C2 (2 hr); (b) C3 (4 hr); (c) C5 (2hr); (d) C6 (4 hr); (e) C8 (2 hr) and (f) C9 (4 hr)

4.2 Hydrophilicity

The water contact angle value (WCA) can represent the hydrophilicity of membrane. Membrane hydrophilicity is one of properties that prove the membrane able to antifouling (Liu *et al.*, 2011). If the contact angle value is lower than 90°, indicating the membrane is hydrophilicity (Azman Mohammad Taib and Julkapli, 2019).

The WCAs of membrane modification by plasma-induced coated with TiO_2, ZnO and TiO_2/ZnO NPs without PAA in different dipping time were presented in Figure 4.3. When increasing dipping time from 2 hr to 4 hr or 24 hr, WCAs did not decrease because coating with ZnO and TiO_2/ZnO NPs have agglomeration which differ from coating with TiO_2. TiO_2 NPs is smaller size than ZnO NPs, therefore, they did not agglomerate causing WCA of modification membrane with TiO_2 the most decline from 53.1° to 34.9° when increased immersion time form 2hr to 24 hr. This was similar with Qin *et al* (2015) that increasing dipping time of TiO_2 cause WCA greatly decrease (Qin *et al.*, 2015). Additionally, the WCAs of modification membrane by plasma-induced PAA- TiO_2 NPs, PAA-ZnO NPs and PAA-TiO_2/ZnO NPs coated in different dipping time was found that the WCAs trend to decrease when increased dipping time because of PAA affect to progressive distribution so the nanoparticles had slightly agglomeration.
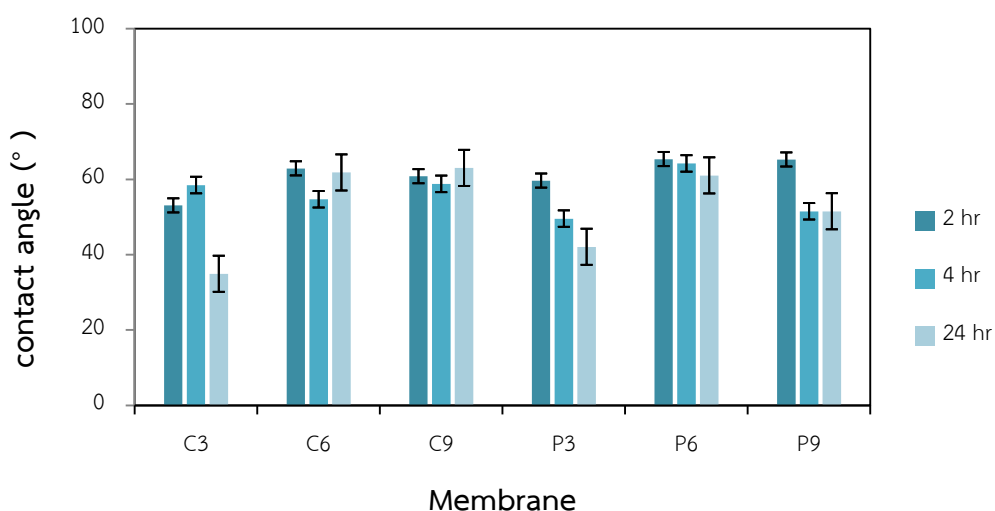

Figure 4.3 Contact angle of modified membrane which different coated: TiO_2/ZnO, ZnO, and TiO_2 NPs with and without PAA

The result of WCAs of original and modification membrane for 24 hr as shown in Figure 4.4, WCA of pristine membrane was 73.5°. When O_2 plasma-treated membrane, the WCA slightly declined because O_2 plasma increase [O] which [O] assist to improve membrane porosity and hydrophilicity (Liang *et al.*, 2013). Furthermore, the species activated by low energy plasma can trigger polymerization reactions of a wide variety of materials on or near the membrane surface (Chen *et al.*, 2019b), which AA monomer or the oxide nanoparticles increasingly able to polymerize or coat on membrane surface. After functionalized by plasma, membranes were coated with TiO_2, ZnO and TiO_2/ZnO with and without PAA for 24 hr. The results found that the contact angle of plasma-induced PAA-ZnO coated was 61.0°. The ratio of TiO_2/ZnO (1:1) found that the WCA decreased to 51.5°, indicating TiO_2 contribute to decline the WCA which the result similar with Li *et al* (2017)'s study. Li et al (2017) studied modification of PVDF membrane with 3D TiO_2/ZnO by atomic layer deposition (ALD), the result found that the combination of TiO_2 and ZnO in 1:1 ratio cause WCA decrease to 25.0° from 53.9°, having only TiO_2 (Li *et al.*, 2017). The mixture solution of TiO_2 and ZnO could assist to enhance hydrophilicity of membrane. However, even though polymerization of PAA causes carboxyl groups on membrane surface which the oxide nanoparticles bond to, less agglomeration than coated without PAA so, the WCA of plasma-induced coated with TiO_2 was the lowest.
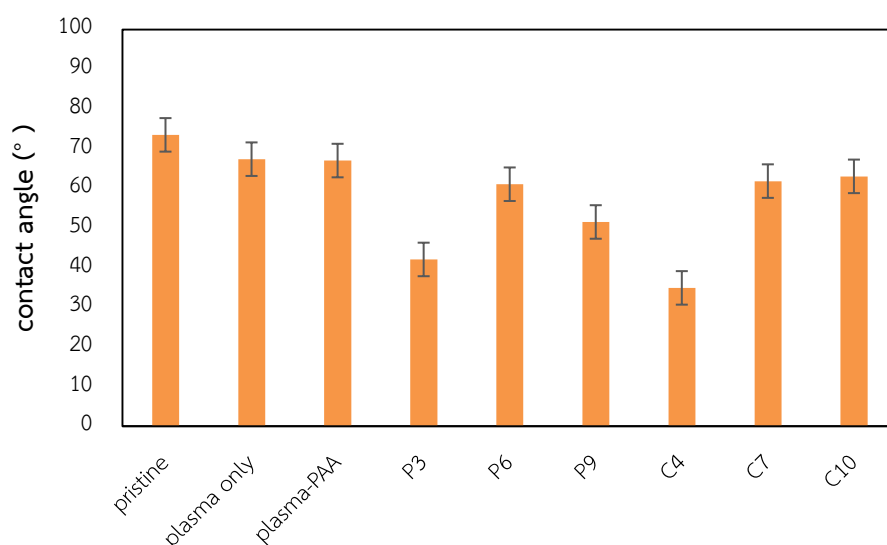

Figure 4.4 Contact angle of the pristine and modified membrane for 24 hr

Chapter V

Conclusion

5.1 Conclusion

In this work, PVDF hollow fiber membrane was modified to enhance hydrophilicity property by plasma-induced poly(acrylic acid)- TiO_2/ZnO nanoparticles coated. The physical and chemical changes were analyzed.

The morphologies and chemical compositions of TiO_2/ZnO NPs coated on membrane surface were characterized by SEM and EDX. The result showed that TiO_2/ZnO NPs were successfully coated on the membrane surface. TiO_2 NPs and ZnO NPs were increased when rise the coating time, however, they greatly adhere causing the nanoparticles agglomeration. The element compositions were changed, affected from plasma-induced technique and coating nanoparticles. Furthermore, the water contact angles were decreased from original 73.5° to 67.3° when the membrane was modified via PICP and decreased to 63.0° when coated with the mixed solution between 10 ppm TiO_2 NPs and 10 ppm ZnO NPs for 24 hr without PAA. Nonetheless, the WCA of plasma-induced PAA-TiO_2/ZnO NPs was decreased to 51.5°. The WCAs of modified membrane with TiO_2 NPs and ZnO NPs were decreased when the immersion time was increased. When membrane was plasma induced and coated by 10 ppm TiO_2 NPs, the WCA was declined to 34.9° which presented high hydrophilicity.

5.2 Suggestion

This study should analyze water flux of modified membrane for confirm hydrophilicity of membrane and verify antifouling property of modified membrane by synthetic foulant solution filtration under realistic conditions. The results could indicate that modified membranes have potential to apply in membrane technology for wastewater treatment.

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