โครงการ
การเรียนการสอนเพื่อเสริมประสบการณ์

ชื่อโครงการ Plasma-induced poly(acrylic acid) catalyst nanoparticles coated polyvinylidene fluoride hollow fiber membrane

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ภาควิชา Environmental Science

ปีการศึกษา 2020

คณะวิทยาศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย

การเหนี่ยวนำโพลีไวนิลลิดีนฟลูออไรด์เมมเบรนแบบเส้นใยกลวงด้วยพลาสมาร่วมกับอนุภาคนาโนคะตะลิสต์

นางสาวณัฐตยา สนศิริ

Plasma-induced poly(acrylic acid) catalyst nanoparticles coated polyvinylidene fluoride

hollow fiber membrane

Nattaya Sonsiri

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 2020

Title	Plasma-induced poly(acrylic acid) catalyst nanoparticles coated polyvinylidene fluoride hollow fiber membrane
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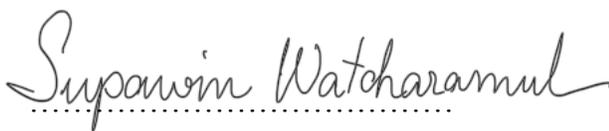
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ภาควิชา	วิทยาศาสตร์สิ่งแวดล้อม
ปีการศึกษา	2563

บทคัดย่อ

ความชอบน้ำของโพลีไวนิลลิดีนฟลูออไรด์เมมเบรนแบบเส้นใยกลวงถูกพัฒนาขึ้นโดยการกระตุ้นด้วยพลาสม่าและกรดอะคริลิก ตามด้วยการเคลือบอนุภาคนาโนไททาเนียมไดออกไซด์และซิงค์ไดออกไซด์ ส่งผลให้ลักษณะสัณฐานวิทยา องค์ประกอบทางเคมี และความชอบน้ำเปลี่ยนไป โดยสามารถวิเคราะห์ได้จากผลของกล้องจุลทรรศน์อิเล็กตรอนชนิดส่องกราด เทคนิคการวิเคราะห์ด้วยธาตุและค่ามุมสัมผัสน้ำของเมมเบรน พบว่า อนุภาคนาโนไททาเนียมไดออกไซด์และซิงค์ออกไซด์ถูกเคลือบบนผิวเมมเบรนได้สำเร็จ แต่อนุภาคนาโนซิงค์ออกไซด์ถูกเคลือบน้อยมาก ทำให้ส่งผลถึงค่ามุมสัมน้ำของเมมเบรนที่มีอนุภาคนาโนไททาเนียมไดออกไซด์เคลือบอยู่มีค่าน้อยกว่าเมมเบรนที่ถูกเคลือบด้วยอนุภาคนาโนซิงค์ออกไซด์และสารละลายผสมของอนุภาคนาโนไททาเนียมไดออกไซด์และซิงค์ออกไซด์ซึ่งลดลงจากเมมเบรนดั้งเดิม 77.9° ถึง 74.1° อีกทั้งเมื่อนำมาตรวจสอบค่าการซึมผ่านน้ำ พบว่า เมมเบรนที่ถูกเคลือบด้วยสารละลายผสมของอนุภาคนาโนไททาเนียมไดออกไซด์และซิงค์ออกไซด์ มีค่าการซึมผ่านน้ำมากที่สุด คือ 23.18 ลิตรต่อตารางเมตรต่อนาที และเมื่อนำมาบำบัดน้ำเสียย้อมรีแอคทีฟเรด 239 ที่ความเข้มข้น 100 มิลลิกรัมต่อลิตร และทำการเปรียบเทียบกับค่าความเป็นกรดด่าง 3 ค่า คือ 2, 4 และ 6 พบว่า เมมเบรนที่ถูกเคลือบด้วยอนุภาคนาโนไททาเนียมไดออกไซด์ ซิงค์ออกไซด์ และสารละลายผสมของอนุภาคไททาเนียมไดออกไซด์และซิงค์ออกไซด์ ไม่มีการเปลี่ยนแปลงในการลดความเข้มข้นของน้ำเสียสีย้อม

คำสำคัญ: โพลีไวนิลลิดีนฟลูออไรด์เมมเบรนแบบเส้นใยกลวง, ความชอบน้ำ, การซึมผ่านน้ำ, อนุภาคนาโนไททาเนียมไดออกไซด์, อนุภาคนาโนซิงค์ออกไซด์

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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 nanoparticle (TiO_2-NPs) and zinc oxide nanoparticles (ZnO-NPs) coated. The morphology, chemical composition and hydrophilicity of modified membranes were characterizaed by SEM, EDS, and water contact angle. The analysis of SEM and EDS were found. The TiO_2-NPs and the mix solution of TiO_2-NPs and ZnO-NPs were successfully coated on membrane surface, but ZnO-NPs were rarely coated. As a result, the water contact angle of the membrane was coated with TiO_2-NPs was less than that of the membrane was coated with ZnO-NPs. The mixed solutions of TiO_2-NPs and ZnO-NPs, which were reduced from the original membrane was 77.9° to 74.1°. Also, when testing the water permeability, the membrane was coated with TiO_2-NPs and ZnO-NPs. The highest water permeability was 23.18 $L/m^2 \cdot min$. The treated wastewater with Reactive Red 239 at a concentration of 100 mg/L and compared with the three pH values; 2, 4 and 6. The results found that the membrane was coated with TiO_2-NPs, ZnO-NPs, and the mix solution of TiO_2-NPs and ZnO-NPs did not found significantly changed.

Acknowledgements

Completing this senior project, I feel deeply indebted to a great many people who have greatly inspired and supported me during my bachelor study at Chulalongkorn University and the writing of this senior project.

In particular, I would like to express my special thanks of gratitude to my project advisor, Assistant Professor Sermpong Sairiam, Ph.D., for their able guidance and support in completing my project. He has taught me the methodology to carry out the research and to present the research works as clearly as possible. It was a great privilege and honor to work and study under his guidance. I am extremely grateful for what he has offered me.

Moreover, I am thankful to my chairman committee, Supawin Watcharamul, Ph.D., and Associate Professor Roongkan Nuisin, Ph.D., for suggestion all the time.

I would like to say thanks to my project colleagues, Miss Vanatchaporn Sayanwisuttikam and my friends for their teamwork and constant encouragement.

I am extending my thanks to the Physics Department teacher, Faculty of Pharmacy teacher, and Chula Unisearch teacher for Information Technology for their support during my research work. I also thank all the staff of Research section of Chulalongkorn University, for their kindness.

I thank the Department of Environmental Science, Faculty Science, Chulalongkorn University for their support to do this work and support to complete this project successfully.

Finally, my thanks go to all the people who have supported me to complete the research work directly or indirectly.

Thank you.

Nattaya Sonsiri

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Chapter I

Introduction

Almost 90% of dyes used in the textile industry are synthetic dyes and around polyvinylidene fluoride (PVDF) membrane has been extensively used in ultrafiltration (UF) for the produced water treatment, due to its excellent mechanical properties, thermal stability, and chemical resistance (Qin *et al*., 2015). However, PVDF membrane may be the problems of low water permeability and easy fouling, because the organic and colloidal matters existing in produced water are prone to deposition and absorption onto the membrane surface. To improve the membrane hydrophilicity and antifouling ability, the externalization of nanoparticles such as silica dioxide (SiO_2-NPs), zinc oxide (ZnO-NPs) and titanium dioxide nanoparticles (TiO_2-NPs) have gained special focus since their characteristics, especially super hydrophilicity, chemical stability, self-cleaning ability, and low cost (Li *et al*., 2017).

Semiconductor photocatalytic oxidation is as one of the less polluting, resource efficient, and sustainable photocatalytic techniques. In the photocatalytic redox process, photocatalysts lead to generate the actively free radicles such as hydroxide radical (•OH), superoxide radical (•O_2^-), and perhydroxyl radical (•OH_2) degrading organic contaminants into H_2O and CO_2. Photocatalytic particles are playing a major role in the treatment of industrial effluent and water, gas purification and antibacterial activity thus constituting an important pillar in the environment remediation. Recently, there are various nanosized photocatalyst and their composites were synthesized such as TiO_2, ZnO, silver, copper oxide and tungsten oxide. Photocatalytic degradation technology has entered for wastewater treatment due to its high efficiency, stability, low energy consumption and less secondary pollution (Pandiyaraj *et al*., 2020).

Photocatalyst can be activated by the photonic activation. Separating and recycling of catalysts from treated water have been considered as an obstacle to the application of the photocatalytic process in aqueous media. The photocatalytic membrane can degrade the foulant and prevent the membrane from the fouling. When UV or visible light acts as a catalyst motivator strikes the catalyst surface, some reactions occur to result in the production of •OH can convert the attached organic foulant into harmless inorganic substances. Recently, the fabrication of high-performance photocatalytic-membranes with remarkable self-cleaning, hydrophilicity and antibacterial properties .

TiO_2-NPs is one of the most auspicious and traditional semiconductor photocatalysts that has been widely investigated in effluent treatments and the elimination of contamination (Bensouici *et al.*, 2017; Yang *et al.*, 2018; Byrne *et al.*, 2019). The supremacy of TiO_2 over other photocatalysts stems from its unique properties including high stability, easy availability, environmental friendliness, chemical, and biological inertness, and economical viability. TiO_2-NPs is incorporated for the membrane to be more hydrophilicity and antifouling ability, that could be developed by various modification techniques (Liu *et al.*, 2021).

ZnO-NPs have been applied as a replacement for TiO_2-NPs because they have been similar properties. Hence, ZnO-NPs have attracted an increasing amount of interest in membrane modification to improve the performances of PVDF membranes. Nevertheless, ZnO-NPs for PVDF membrane modification was limited to blending ZnO-NPs into the casting solution and effected because the ZnO-NPs accumulated in the casting solution, causing them to be entirely enfolded by the polymer matrix. The challenge of this approach is how to stably immobilize ZnO-NPs on the membrane surface, since ZnO-NPs cannot self-assemble onto PVDF membrane surface without bonding with suitable functional groups (Chen *et al.*, 2019).

To achieve the stable attachment of semiconductor on the membrane surface, the bondings with key functional groups are needed. The polymer nature of PVDF membrane is not conducive to TiO_2-NPs and ZnO-NPs self-assembly (You *et al.*, 2012). Plasma-induced graft polymerization is a promising technique to provide chemical initiators or other components (Reis *et al.*, 2015). Poly(acrylic acid) (PAA) is a polymeric from of AA with multiple carboxylic functional groups (-COOH) that act as chelating centers for loading of nanoparticles loading and also contribute to increase the hydrophilicity of the PVDF membrane (Ju *et al.*, 2015). Alternatively, reduction by radio-frequency (RF) plasma discharge is considered as a more effective, safe, rapid reduction technique as well as an environmentally-friendly method, compared to other chemical and thermal techniques. The RF plasma can be generated using a RF electric field of 13.56 MHz. with introducing the sample into the plasma reactor, various physical and chemical reactions have been obtained between the material surface and active plasma species and radiations, which leading to modify the material surface properties. Therefore, RF plasma surface treatment has been used to improve the mechanical, electrical, and optical properties of different materials (El-Hossary *et al.*, 2021). Chen *et al.* (2019) reported that the water contact angle of membrane surface was decreased from 83.5° to 9.1° under 120 W, 300 sccm Ar flow rate, 400 sccm O_2 flow rate, 70°C AA temperature, 60% (v/v) AA concentration and 1% (m/v) nano-TiO_2 concentration. Also, the contact angles of the monomer triethylene glycol dimethyl ether were reduced from 32.0° of untreated to 7.0° by the condition of 1 W with 13.56 MHz of radio frequency and the monomer was heated to 80-90 °C (Zou *et al.*, 2011). In addition, Qian *et al.* (2016) also found that the TiO_2 modification dramatically reduced the water contact angle of polytetrafluoroethylene (PTFE) from 115.8° to 35° in 5-day operation with N_2 flow under a discharge power of 60 W with the mixture of 20 wt% AA monomer and the ethylene glycol (EG) by molar ratio of 1:6.5. As the results, the modified membrane with

high hydrophicity can be applied for dye wastewater due to high permeability and increase membrane performance. Pulse inductively couple 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. Moreover, 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). It is therefore of our interest to test the reduction of dye concentration by plasma-induced PAA-TiO$_2$/ZnO coated PVDF membrane via PICP method.

1.2 Objective

To decolorized Reactive Red 239 wastewater by plasma-induced PAA-TiO$_2$/ZnO coated PVDF membrane via PICP method.

Chapter II

Literature reviews

2.1 Azo dyes

The textile wastewater contains different chemical compounds and 15%-20% consumed dyes of the dying process. 60%-70% of total dyes in the textile industry are azo dyes. Among different types of azo dyes, the production of direct azo dyes is growing due to their increased consumption for textile printing. About 72 toxic chemicals have been identified in textile effluents, and it is estimated that approximately 200 billion liters of effluents are produce annually worldwide by textile industry. Many negative effects have been identified due to the hundreds of contaminants diluted in aquatic systems, affecting dissolved oxygen, turbidity, color, temperature and, consequently, aquatic organism. This has led to the study of other methods for decolorizing textile dye waste streams, including adsorption, chemical coagulation, chlorination, and ozonation (Kartal O.E. 2019).

2.1.1 Properties of Reactive Red 239

Reactive Red 239 (RR 239) is a well-known mono-azo dye. The properties of Reactive Red 239 can be seen that Table 2.1, that has been intensively used to dye fabric in various textile industries (Liu and Chiou, 2005). However, toxic information on RR 239 has not been widely reported, especially its toxicity on aquatic organisms such as fish embryos (Waraporn et al., 2014).

Table 2.1 Properties of Reactive Red 239

Molecular Structure	
Chemical Formula	$C_{31}H_{24}ClN_7O_{19}S_6$
Molecular Weight (g/mol)	1026.4
Maximum Wavelength (nm)	542
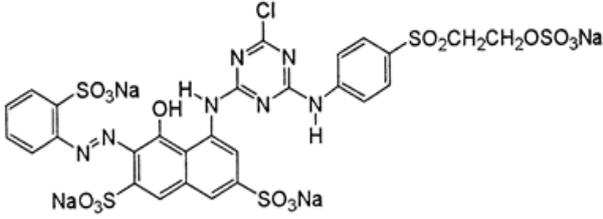
2.2 Membrane Technology

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. In general, microfiltration membrane (MF) and ultrafiltration membrane (UF) have been used for the reclamation of surface water. Moreover, the nanofiltration membrane (NF) with molecule weight cut-offs (MWCO) of around 150-3350 Da are proper for wastewater treatment and environmental remediation because of high inorganic ion removal applications. In pressure-driven membrane process, a pressure gradient between influent and permeate sides is employed as the driving force to separate the particles and solutes based on size, shape and charge. 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 (Riaz, S.-J. Park 2020).

Polyvinylidene fluoride (PVDF) is one of the most widely used membrane materials with the repeated unit of -$(CH_2CF_2)_n$- and polymers in membrane formulations due to its remarkable properties such as wide chemical compatibility, excellent mechanical properties, relatively easy processing and high temperature resistance. Li *et al*. (2021) used the PVDF membranes for 2-cp-containing wastewater treatment. Silva *et al*. (2020) developed PVDF membranes by a novel microwave-based method for water treatment, and Lu *et al*. (2021) prepared NH_2-MIL-53 on modified PVDF membranes by solvothermal method for dyes separations. It's outstanding properties such as high thermal and hydrolytic stability as well as good chemical resistance properties. 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 dissolved in varied solvents, making possible the versatile synthesis of flat-sheet, hollow-fiber, and nanofiber membrane. However, in water treatment, the main problem of PVDF membrane is fouling caused by its low surface energy and high hydrophobicity (Chen *et al*., 2019).

Membrane fouling generally occurs in form of foulant adhesion/deposition due to deposition of suspended or dissolved substances onto its external surface. Fouling is often the main limitation to successful membrane application of food and biotech industries. 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 reduction in the rate of fouling and concentration polarization (CP) are, therefore, important factors in the design and operation of membrane systems. Fouling can be related to different modes such as adsorption, chemical interactions, cake formation, and pore blocking by particles (Pan *et al*., 2019).

The water flux 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 fouling and the permeate flow may be as low as 20% of that of pure water. Polymeric membrane fouling is commensurate with the hydrophobicity of these materials. The more hydrophilic membranes are less susceptible to foul due to the reduced interaction between the membrane surface and organic matter and the absence of hydrogen bonding between water molecules and the membrane interface. So far, different methods have been studied to reduce fouling and increase the hydrophilicity of the polymeric in the membranes (Abdi *et al*., 2021).

2.3 Hydrophilic membrane modification

Ultrafiltration (UF) membrane is employed when high separation efficiency is required. Such filtration membranes as water treatment devices are susceptible to low fouling resistance. Membrane fouling affects productivity, and generates additional operating costs, and the need for regular chemical cleaning procedures that shorten the membrane lifetime. Membrane surface hydrophilicity is generally accepted as the main factor affecting resistance compared to hydrophobic membranes. To help solve these problems, materials scientists and chemical engineers are working to develop inexpensive, scalable, and sustainable methods to produce hydrophilic membranes for water purification (Qian *et al*., 2016). It is a problem for the efficiency and energy consumption of membranes designed for water purification. Several studies describe the modification of PVDF membranes with hydrophilic additives such as polymers and copolymers to improve their hydrophilicity. Hydrophilicity is an important factor in pressure driven filtration as a wetable surface would consume less energy and it would also reduce the membrane fouling due to the presence of the hydrated top surface (Lou *et al*., 2020). These methods include distributing of various types of hydrophilic particles and

nanoparticles on the membrane surface, incorporating these into the membrane matrix and creating a physical bond with the membrane surface. Wang *et al*. (2020) investigated the effect of UV irradiation on the surfaces coated TiO_2 nanoparticles and through surface reactions, they could change these surfaces from hydrophobic to hydrophilic, which the mechanism and process can be seen in Figure 2.1. By using this irradiation and photo-induced surface reaction, TiO_2 and other metal oxides were demonstrated to have the ability to create super- hydrophilic surfaces. Post-fabrication treatment via chemical treatment example plasma grafting of polar groups, are some of the techniques used to confer hydrophilicity to PVDF membranes. Due to the nature of PVDF hydrophobicity which makes it easily fouled during filtration process, the plenty of works have been devoted to developing an anti-fouling membrane utilizing hydrophilic/hydrophobic interactions or electrostatic repulsing between membrane surfaces and foulants (Guo *et al*., 2020). 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 e*t al*., 2017).
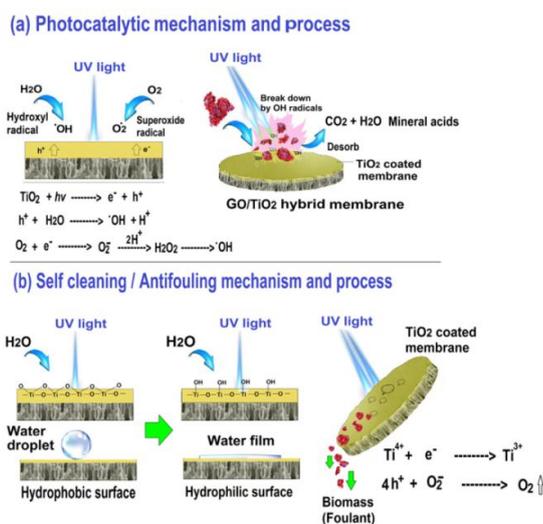
Figure 2.1 The mechanism and process a) the mechanism of photocatalysis process b) the mechanism of anti-fouling of treated membrane

2.3.1 Plasma-induced grafting technique

Plasma-induced graft polymerization is a promising technique to provide chemical initiators or other components. 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. Therefore, the activation of PVDF membrane is needed. 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) by introducing reactive groups onto the surface (Pasini *et al*., 2019).

The polymer nature of PVDF membrane is not conducive initiators or other components to TiO_2-NPs self-assembly. Plasma-induced graft polymerization is a promising technique to provide chemical initiators or other components. Thin and even polymer coating can thus be formed in the membranes surface without compromising the bulk structure under specific control. Therefore, poly(acrylic acid) (PAA) was grafted on PVDF membranes surface through plasma-induced polymerization to introduce functional group for TiO_2-NPs self-assembly. The fractional factorial design was applied to investigate the effects of experimental factors and their interactions on membrane modification (Pandiyaraj *et al*., 2020).

A novel membrane surface modification approach was proposed to obtain a PVDF-PAA-ZnO membrane which was modified from PVDF membrane through cold plasma-induced poly(acrylic acid) (PAA) graft-polymerization followed by simple nano-ZnO self-assembly. The technique of cold plasma treatment was applied to induce PAA polymerization by introducing chemical initiators on PVDF membrane surface (Pascariu *et al*., 2021). 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 surface treatment by PICP does not require lengthy treatment period to achieve desired effect.

2.3.2 Water contact angle

The hydrophilic properties are related to water absorption, which can be calculated as in Equation 1 (Azman Mohammad Taib and Julkaplt, 2019). 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. Contact angles are extremely sensitive to contamination; values reproducible to better than a few degrees are generally only obtained under laboratory conditions with purified liquids and very clean solid surfaces. If the liquid molecules are strongly attracted to the solid molecules then the liquid drop will completely spread out on the solid surface, corresponding to a contact angle of 0°. This is often the case for water on bare metallic or ceramic surfaces, although the presence of an oxide layer or contaminants on the solid surface can significantly increase the contact angle. Generally, if the water contact angle is smaller than 90°, the solid surface is considered hydrophilic and if the water contact angle is larger than 90°, the solid surface is considered hydrophobic. Many polymers exhibit hydrophobic surfaces. Highly hydrophobic surfaces made of low surface energy (e.g. fluorinated) materials may have water contact angles as high as 120°. Some materials with highly rough surfaces may have a water contact angle even greater than 150°, due to the presence of air pockets under the liquid drop. These are called superhydrophobic surfaces (Zou *et al*., 2011).

$$\text{Water Absorption (\%)} = (W_2\text{-}W_1/W_2) \times 100 \qquad \text{(Equation 1)}$$

Where W_1 and W_2 are the pervious immersed weight and the immersed weight afterward, respectively.

2.4 Photocatalytic degradation

Photocatalysis is one of the advanced oxidation processes (AOPs) based on the generation of very reactive hydroxyl radicals ($^{\bullet}OH$) which enhance the oxidation of organic compounds in water very quickly and non-selectively. In the meanwhile, due to their low absorption and abuse, it is untoward to degrade after being discharged in large quantities in the environment, thus which becomes the main factor of the new type water pollution. Hence, how to degrade antibiotics into H_2O_2 and CO_2 without secondary pollution is one of the main research directions devoted to environmental workers. Among the numerous wastewater treatment methods, photocatalytic degradation technology has entered the field of scientific researcher due to its high efficiency, stability, low energy consumption and less secondary pollution, and has turned into a promising wastewater purification technology. Thus, improving the yield of photocatalytic semiconductor electron-hole pairs and accelerating carrier separation are the research focuses of this technology. Titanium dioxide (TiO_2) has always been one of the photocatalytic semiconductor due to its light stability, suitable conduction energy level and environmental protection. It possesses a wide band gap (3.2 eV) and strong oxidation ability, but it only responds to the strong ultraviolet region, resulting in low utilization of visible light. Furthermore, the electron-hole pairs produced after absorbing energy are easily recombined quickly under the action of Coulomb force, which lonits the application and developmental element doping, coupling with visible light active semiconductor, and so on. Among the metallic oxide catalysts, TiO_2, SnO_2 and ZnO have

been considered as one of the most efficient photocatalysts. Nowadays there have been many studies on the photodegradation of TiO_2 and ZnO, the great preponderance and the prefect absence of secondary pollution as a result of photodegradation. The novel approach of solar photocatalysis presented here relies on ultraviolet (UV) radiation that triggers the semiconductor characteristics of titanium dioxide (Lou *et al.*, 2021). The activation of semiconductor is shown in Reactions 1-8; Excitation of UV with semiconductor (Reaction 1), hole (h^+) from valence band reacts oxidation with organic substances or ions in water (Reaction 2-3), oxidation reaction with dye solution (Reaction 4-5), e_{cb}^- in conduction band reacts reduction with O_2 (Reaction 6-7), and Reduction reaction with dye solution (Reaction 8).

$$TiO_2 + h_v \rightarrow e_{cb}^- + h_{vb}^+ \qquad \text{Reaction 1}$$

$$O_2 + e_{cb}^- \rightarrow O_2^- \qquad \text{Reaction 2}$$

$$h_{vb}^+ + H_2O \rightarrow {}^\bullet OH + H^+ \qquad \text{Reaction 3}$$

$$h_{vb}^+ + dye \rightarrow products \qquad \text{Reaction 4}$$

$${}^\bullet OH + dye \rightarrow products \qquad \text{Reaction 5}$$

$$e_{cb}^- + O_2 \rightarrow O_2^{\bullet -} \qquad \text{Reaction 6}$$

$$e_{cb}^- + O_2 + H_2O \rightarrow HO_2 + OH^- \qquad \text{Reaction 7}$$

$$O_2^- + dye \rightarrow products \qquad \text{Reaction 8}$$

2.5 Influence of operating parameters on photocatalytic process for wastewater treatment

In photocatalytic degradation of pollutants in wastewaters, the followings are operating parameters which affect the process: pH of the solution to be degraded, and catalyst loading.

2.5.1 Influence of pH on photocatalytic degradation

The interpretation of pH effects on the efficiency of dye photodegradation process is a very difficult task because of its multiple. The positive holes are considered as the major oxidation species at low pH, whereas hydroxyl radicles are considered as the predominant species at neutral or high pH levels. The photocatalyzed degradation of acidic azo dye and triazine containing azo dyes, although it should be noted that in alkaline solution, there is a coulombic repulsion between the negative charged surface of photocatalyst and the hydroxide anions. The most photocatalyst particles like TiO_2 particles tend to agglomerate under acidic condition and the surface area available for dye adsorption and photon absorption would be reduced. The effects of pH on photocatalytic degradation of organic pollution, two things must be borne in mind; firstly, industrial effluents may not be neutral, and secondly; pH of the reaction mixture influences the surface-charge-properties of the photocatalyst (Riaz, S.-J. Park 2020).

2.5.2 Catalyst loading effects on photocatalytic degradation

The effects of catalyst loading on photocatalytic degradation of dyes in wastewaters have been studied. The increase in the amount of catalyst increase the number of active sites on the photocatalyst surface, which in turn increase the number of hydroxyl and superoxide radicles. In addition, when the concentration above the optimum value, the degradation rate

decrease due to the interception of the light by the suspension. The excess catalyst prevent the illumination, $^\bullet$OH, a primary oxidant in the photocatalytic system decreased and the efficiency of the degradation reduced accordingly (Riaz, S.-J. Park 2020).

2.6 Photocatalytic membrane

Photocatalytic membranes (PMs), coupling of membrane filtration and photocatalysis in a single unit, have exhibited a great potential for use in energy-efficient water purification and wastewater treatment. The photocatalytic membranes have presented a trend developed from UV-responsive photocatalytic membranes (UV-PMs) (e.g., TiO_2-based and ZnO-based PMs) into visible light-responsive photocatalytic membranes (Vis-PMs) (e.g., modified TiO_2/ZnO -based, β-FeOOH-based, and g–C_3N_4–based PMs) (Shi *et al*., 2019).

2.6.1 Effect of photocatalyst loading on membrane fouling

This process can be an alternative to the decontaminant of water without the use of chemical reagents to avoid extra sludge. Lee *et al*. reported the application of a photocatalytic-membrane reactor for humic acid (HA) removal from water. In fact, the physicochemical properties of organic foulants were changed by the production of $^\bullet$OH and $O_2 \cdot$ active radicals. Many researchers have studied the effects of different photocatalysts on membrane fouling mitigation. Normalized flux was introduced as an index for the compression of different systems, which is calculated according to Equation 2;

$$\text{Normal flux} = \frac{J}{J_0} \quad \text{(Equation 2)}$$

Where J and J_0 are the solution flux and the pure water flux, respectively.

2.6.2 The effect of hydrophilicity

The hydrophobicity of membrane is one of the main factors in membrane fouling. Most of hydrophobic membranes adsorb a hydrophobic foulant, resulting in reduced membrane performance. Deposition of more photocatalysts with oxygenated functional groups on the surface has been reported to increase hydrophilicity and fouling mitigation. Many researchers that modified membranes were able to degrade the foulant reagent after time of UV or Vis irradiation. Agana *et al*. (2019) opt-out a 5nm TiO_2-ceramic UF (TC-UF) membrane and optimize the performance of membrane for the production of beverage wastewater. The authors prefer the TiO_2-ceramic UF membrane over the polymeric membranes and demonstrated that owing to the chemical stability of the ceramic membrane; it is more suitable than the polymeric membrane. Moreover, the ceramic membrane was modified with the antifouling TiO_2-NPs, well suited for the degradation of organic pollutants such as beverage production wastewater. Teli *et al*. (2019) prepared polysulfone (PSf)-polyaniline (PANI)/TiO_2 nanocomposite antifouling ultrafiltration (UF) membrane by adopting PIM. The TiO_2 nanoparticles were modified with PANI to reduce the agglomeration of particles. Thereafter these modified nanoparticles were introduced to the PSf matrix to obtain the UF membrane via PIM. Bovine serum, albumin and humic acid were used as foulant and the prepared nanocomposite UF membrane photocatalyst exhibit excellent hydrophilicity, water permeability and better antifouling properties.

Chapter III

Methodology

3.1 Chemicals and materials

1. Polyvinylidene fluoride (PVDF) hollow fiber membrane (Altrateck, China).

2. Acrylic acid (AA) (Loba Chemie, India).

3. Titanium dioxide nanoparticles (TiO_2-NPs) (Prime Nanotechnology, Thailand).

4. Zinc oxide nanoparticles (ZnO-NPs) (Prime Nanotechnology, Thailand).

5. Nitrogen gas and oxygen gas with industrial grade (Linde, Thailand)

6. Sulfuric acid (Qrec, Thailand)

7. Sodium hydroxide (Merck, Thailand)

3.2 Experimental procedures

3.2.1 Plasma activation

PVDF hollow fiber membrane used in this study was purchased from Altrateck, China and the specification was described in Table 3.1. The 25 cm length of PVDF membrane was placed in the chamber of the gas plasma treatment system. Oxygen gas was injected into the chamber. The initial store energy of the system is 9-9.5 kV and the pressure in the chamber was fixed at 0.3 mbar. Oxygen gas plasma produced in double shot pulses 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 for 1 hr. The AA solution was saturated by nitrogen gas for 1 hr with 20 bubbles/min. After that, the

membranes were dried in incubator (ULM 700, Memmert, Germany) at 60°C for 1 hr for the

polymerization of AA to poly(acrylic acid) (PAA).

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

3.2.2 Membrane coating with TiO_2-NPs, ZnO-NPs and TiO_2/ZnO-NPs

TiO_2-NPs and ZnO-NPs were supplied from Prime Nanotechnology, Thailand and the

properties were reported in Table 3.2. NPs were prepared by dissolving in 500 mL of DI

water supply from and specification from Table 3.2. The solutions were sonicated for 30 min

by an ultrasonic sonicator bath (DT510H, SONOREX, Germany) at 40 °C. The PAA-grafted

membranes obtained from section 3.2.1 were dipped in TiO_2 and ZnO-NPs solution for self-

assembly 24 hr. In this study, the membranes were coated for 24 hr with 3 different

conditions as described in Table 3.3 which were the individual TiO_2-NPs and ZnO-NPs, and

the mixture of TiO_2-NPs and ZnO-NPs solution. After that, the membranes were incubated in

oven (ULM 700, Memmert, Germany) at 60 °C for 60 min then dried in ambient for 15 min.

Finally, the membranes were contained in the zip bag.

Table 3.2 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		
Primary particle size (nm)	21	20-40
Tamped density (g/L)	130	-
Specific surface area (m/g)	50	-
Assay (%)	>99.5	>99
Loss on dry (%)	-	<0.5
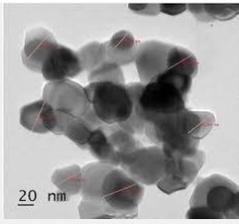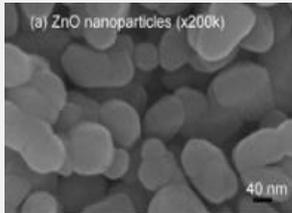
Table 3.3 The coated membranes by TiO$_2$-NPs and ZnO-NPs

Coated membrane	TiO$_2$ –NPs (mg/L)	ZnO-NPs (mg/L)
TiO$_2$	10	-
ZnO	-	10
TiO$_2$/ZnO	10	10

3.2.3 Membrane characterizations

After coating of TiO$_2$-NPs and ZnO-NPs on PVDF membranes, the coated membranes were analyzed the membrane morphology using Scanning Electron Microscopy (SEM) equipped with Energy Dispersive X-ray spectrometer (EDS) to quantify the concentration of

elements. All samples were coated with gold nanoparticles. The hydrophilicity was evaluated by water contact angle (WCA), which was measured using a Tensiometer (DCAT 11, Dataphysics, Germany) at ambient temperature.

3.2.4 Permeability of membrane

Ten fibers of membranes were plotted in the glass module with epoxy. After, a beaker was measured by the analytical balance and used to collect the water at the end of the module. The DI water was fed from a beaker to the glass module by peristaltic pump (Masterflex easy-load II Model 77201-60) and adjusted the pressure for 1 bar by a ball valve. DI water was fed into the membrane and finally, the retentate was recycled to the back of the system, which the system of permeability of membrane can be seen in Figure 3.1. At the end of the module was fed and drip was collected by the beaker. And the beaker was weighed again.

The flux of permeate was calculated by using the follow Equation 3:

$$J_w = \frac{V}{A\Delta t} \qquad \text{(Equation 3)}$$

Where; V is the permeate volume (L) (water density $= 0.997$ g/cm^3)

A is the membrane area (m^2)

Δt is the permeate time (min)
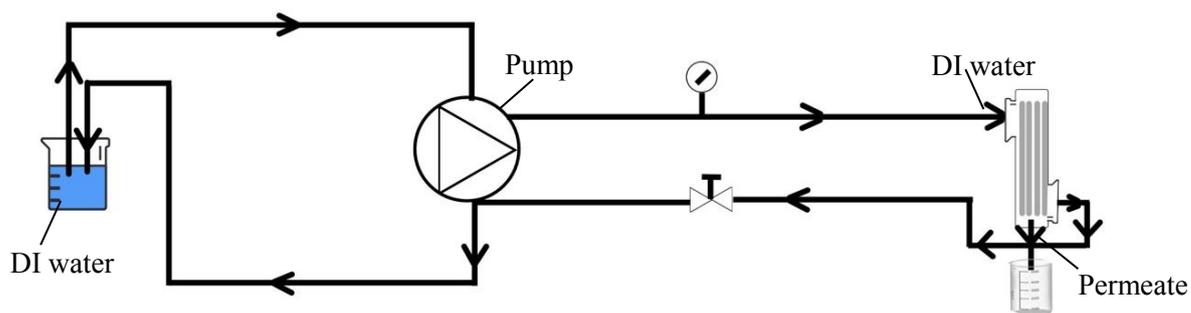
Figure 3.1 The system of permeability of membrane

3.2.5 Dye wastewater treatment by photocatalytic membrane

The coated membrane with TiO$_2$-NPs and ZnO-NPs were tested the membrane performance in photocatalytic membrane. Seven fibers were plotted in the glass module. In this work, the photocatalytic performance of TiO$_2$ and ZnO coatings was evaluated by the decolorization of Reactive Red 239, under UV-C. UV-C irradiation was provided with an input light power of 10 W each. The distance between the membrane glass module and the UV-C was 10 cm. The UV-C was placed on around the glass module. Firstly, the both ends of module were glued with epoxy. The dye wastewater was fed from a beaker with the dye solution to the glass module by peristaltic pump (Masterflex easy-load II Model 77201-60) and adjusted the pressure for 1 bar by a ball valve. This system was shown in Figure 3.2. Afterwards, the dye wastewater was stirred by a magnetic stirrer and measured pH by a pH meter. Next, the dye solution was kept for measuring the dye concentration (blank). After, the dye wastewater was fed into the module for about 30 min and collected at the end of the module (0 min) in the dark mode. After that, four UV-C were irradiated at room temperature. Later on, the solution of Reactive Red 239 was collected at 1 min, 2 min, 5 min, 10 min, 20 min, 30 min, and 60 min. Finally, the dye solutions were measured the concentration by a vis spectrophotometer (Spectro SC, Thailand) at 542 nm. In this test, the operating conditions

were tested at light intensity at 40 W and RR 239 concentration of 100 ppm at varied pH at

pH 2-6. The pH of RR 239 solution was adjusted by sulfuric acid and sodium hydroxide.
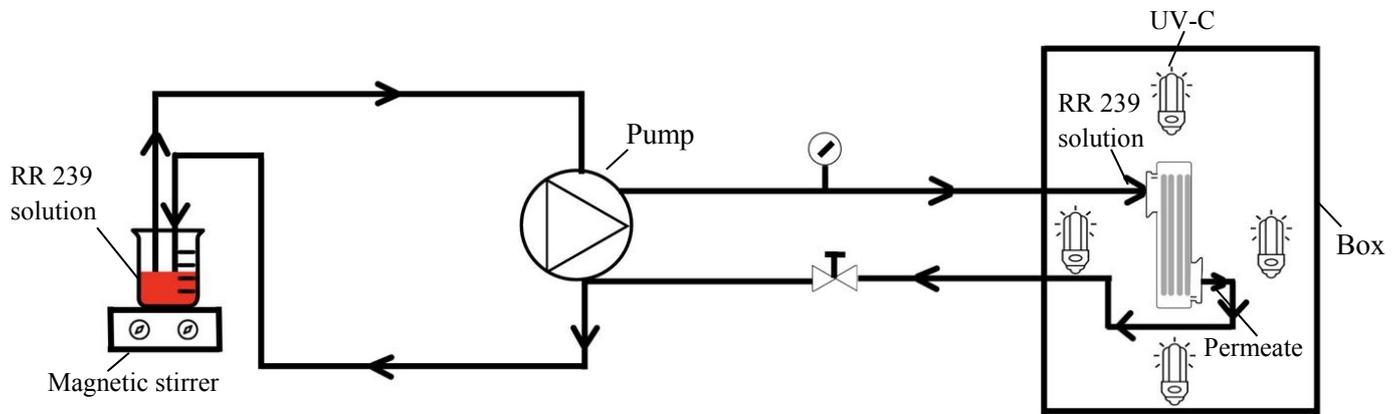
Figure 3.2 The system of dye wastewater treatment by photocatalytic membrane

Chapter IV

Results and Discussion

4.1 Membrane modification

Effect of semiconductor coatings

The PVDF membrane was immersed in various particles solution and activated by plasma-inducing. The different membrane coated was physically analyzed by Scanning Electron Microscopy (SEM). The coated membranes were characterized with 20,000 magnification. To affirm the change on membrane surface, the results can be seen in Figure 4.1, which shows the coated membranes with TiO_2-NPs and TiO_2/ZnO-NPs were found the particles on membrane surface as in Figure 4.1 (b) and (d). In contrast, there is nothing change on coated with ZnO-NPs as illustrate in Figure 4.1 (c). Additionally, the percentage of atomic concentration of the element composition on membrane surface investigating by EDS as shown in Table 4.1 with was proved the successful membrane modification by plasma-inducing and coating with TiO_2-NPs and ZnO-NPs. The percentage of O atomic concentration was increased comparing to the original membrane; the membrane was coated with TiO_2-NPs and TiO_2/ZnO-NPs increased from $4.26 \pm 0.06\%$ to $22.93 \pm 0.16\%$ and $9.72 \pm 0.09\%$, respectively. The percentage of Ti atomic concentration was found, which shows a successful coating, there found Ti at $8.06 \pm 0.06\%$ of the membrane was coated with TiO_2 and $8.04 \pm 0.10\%$ of the membrane was coated with TiO_2/ZnO. Also, the percentage of Zn atomic concentration was successful coated at $2.61 \pm 0.21\%$ of the membrane was coated with TiO_2/ZnO.

(a)

(b)

(c)

(d)
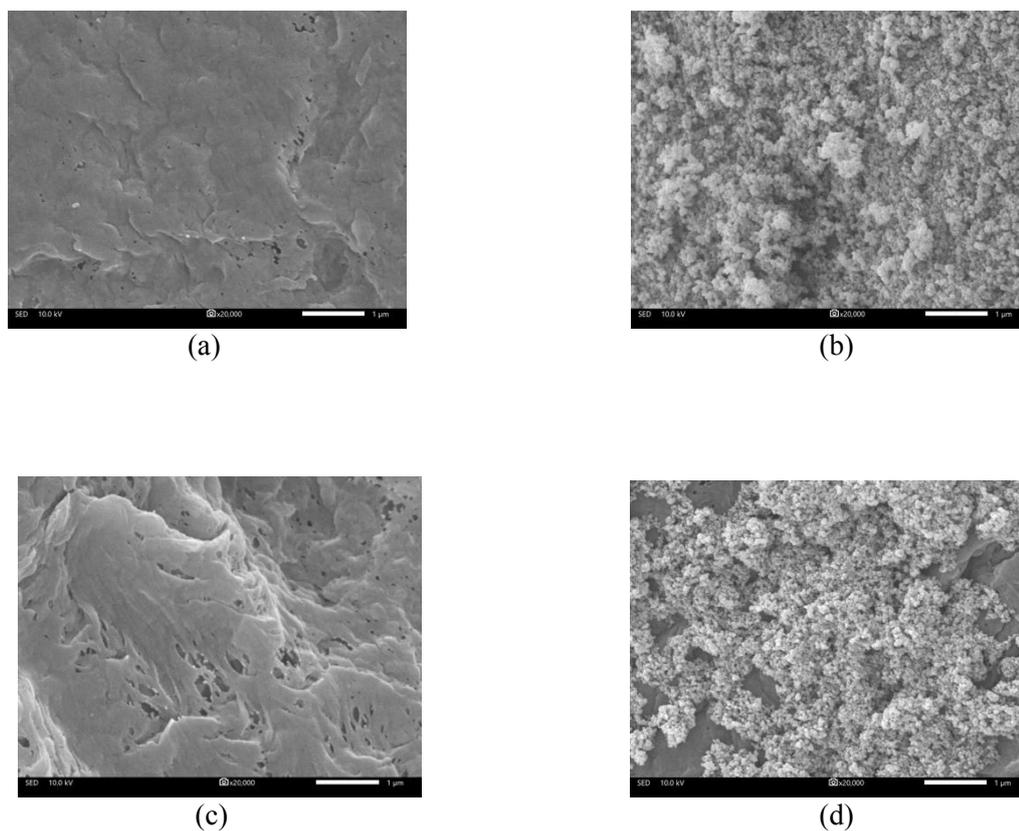
Figure 4.1 SEM images of membrane surface for 20,000x (a) original membrane; (b) TiO_2-NPs coated; (c) ZnO-NPs coated; (d) TiO_2/ZnO-NPs coated

Table 4.1 The element composition of membranes

Atomic concentration (%)					
Membrane sample	C	F	O	Ti	Zn
Original	67.40 ± 0.10	28.34 ± 0.10	4.26 ± 0.06	-	-
TiO_2	37.85 ± 0.11	31.15 ± 0.18	22.93 ± 0.16	8.06 ± 0.06	-
TiO_2/ZnO	37.35 ± 0.09	42.28 ± 0.18	9.72 ± 0.09	8.04 ± 0.10	2.61 ± 0.21

4.2 Hydrophilicity

The water contact angle of membrane was coated with TiO_2-NPs, ZnO-NPs, and TiO_2/ZnO-NPs compared with the original membrane as shown in Figure 4.2. The result of water contact angle of original membrane was $77.9°$. When O_2 plasma-treated membrane, the interaction between the plasma and the membrane surface, due to the interactions between oxygen atoms and oxygen metastable molecules and polymer molecules on the surface, this reduction is an indication of the improvement of the membrane surface hydrophilicity and size of titanium dioxide nanoparticles were small, that were helped improvement in hydrophilicity (Bahamonde Soria *et al*., 2020). Therefore, the water contact angle of modification membrane with TiO_2-NPs decline from $77.9°$ to $74.1°$ when to compared with the original membrane, but the membrane which coated with ZnO-NPs and TiO_2/ZnO-NPs increased from $77.9°$ to $86.3°$ and $80.1°$, respectively. This was because incorporation of fewer PAA molecules near the surface and most of ZnO-NPs was dissolved in the acid solution with low pH value (Chen *et al*., 2019)**.** Therefore, the distribution of ZnO-NPs is minimal, resulting in an increased water contact angle of ZnO-NPs and TiO_2/ZnO coated membrane.
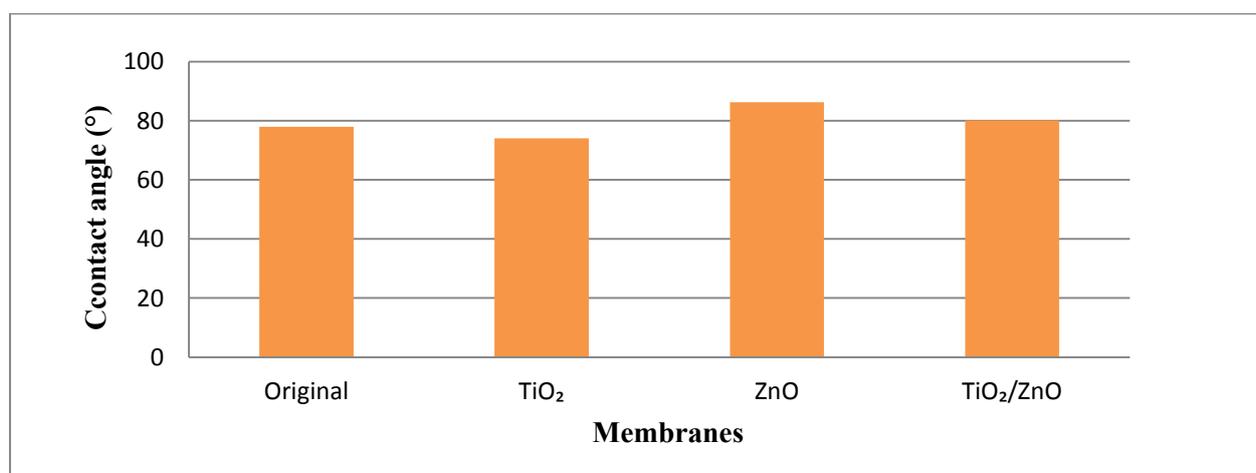
Figure 4.2 Relationship between the contact angle and the different coated membrane.

4.3 Water permeability

As fundamental and essential properties of a membrane, the water permeation of the optimized PVDF membrane was evaluated through water permeability measurement. As shown in Table 4.2, the coated membrane with different semiconductors coated showed extremely high permeation flux of DI water, reaching up to 23.18 $L/m^2 \cdot min$, which coated with TiO_2/ZnO. The flux of membrane was coated with TiO_2/ZnO was about 70,000 times higher than that the original membrane. While the membrane was coated with TiO_2, the permeated flux was slightly increased compared to the original membrane from 0.00033 to 1.73 $L/m^2 \cdot min$ and the lowest permeate flux was coated with ZnO with 0.0052 $L/m^2 \cdot min$. These results verified the fact that self-assembled TiO_2/ZnO-NPs through the grafted PAA on PVDF membrane surface remarkably improved the membrane hydrophilicity without blocking of membrane pores (Chen *et al*., 2019). The flux of the different coated membrane was compared to water contact angle, which found amount of TiO_2-NPs more the 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, resulting in better dispersion of TiO_2-NPs better than ZnO-NPs also, the few amount of ZnO-NPs was attached to the PVDF membrane. Therefore, the permeability flux was minimal and the water contact angle at a higher value than other coated membrane.

Table 4.2 Flux of different coated membrane

Membrane	Flux ($L/m^2 \cdot min$)
Original	0.00033
TiO_2	1.73
ZnO	0.0052
TiO_2/ZnO	23.18

4.4 Decolorization of Reactive Red 239

The effect of the concentration of RR 239 was studied at different pH; varying pH 2, 4, and 6. The results are shown in Figure 4.3. The experiments were conducted of 100 ppm. The pH was adjusted by adding an appropriate amount of H_2SO_4 and NaOH. The membrane coated with ZnO-NPs, the concentration of RR 239 was reduced more than the membrane was coated with TiO_2-NPs and TiO_2/ZnO-NPs at pH 2 because ZnO-NPs was dissolved in the acid solution with low pH value (Chen *et al*., 2019)**,** which helps react to light and dyes. Thus, causing the concentration of RR 239 to decrease. At pH 4, the membrane was different coated had hardly different concentration of RR 239. However, the membrane was coated TiO_2/ZnO-NPs was the greatest decreased in concentration from 0.98 to 0.92. As for pH 6, the concentration of RR 239 is higher than other pH because the water flux and organic rejection are decreased with increasing the pH for membrane, that under alkaline conditions the existence of OH ion generally decreases the water flux via the membrane pores producing a reduction in the operative membrane permeability (Isawi *et al*., 2018). Though, the membrane was coated with ZnO-NPs that reduced the concentration of RR 239 more than the membrane was coated with TiO_2-NPs and TiO_2/ZnO-NPs from 1.0 to 0.9. While, the membrane was coated with TiO_2-NPs and TiO_2/ZnO-NPs, that hardly reduced the concentration of RR 239, from 1.0 remains intact. Figure 4.4 shows the concentration of RR 239 in varied pH. The result showed at pH 2, there was a better reduction than pH 4 and 6. Due to the acidity makes the semiconductors more soluble and at pH 2, the surface of TiO_2-NPs and ZnO-NPs have negative ion because they absorb OH^- at the surface and make •OH that is more conductive to molecular breakdown. Therefore, able to react well in a decrease in the concentration of RR 239.
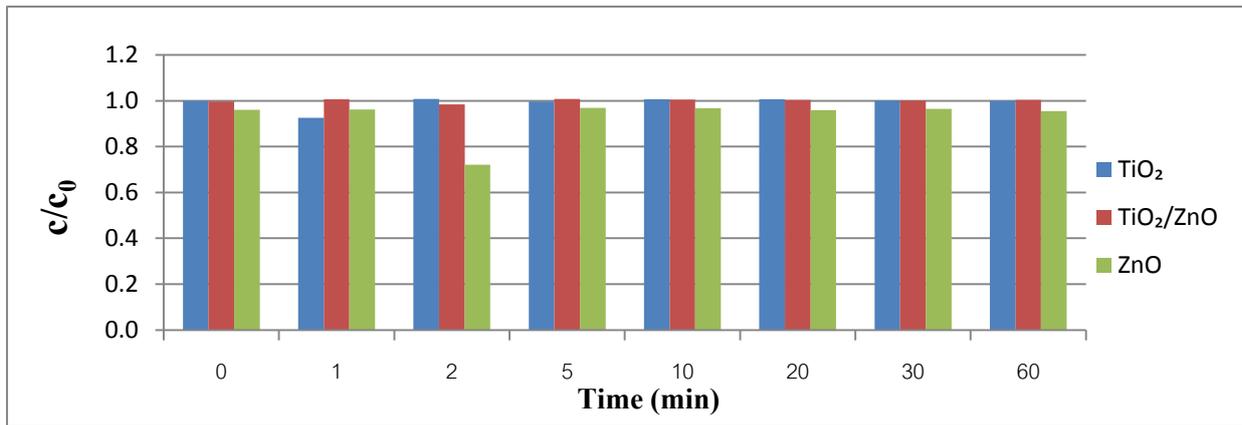
(a)
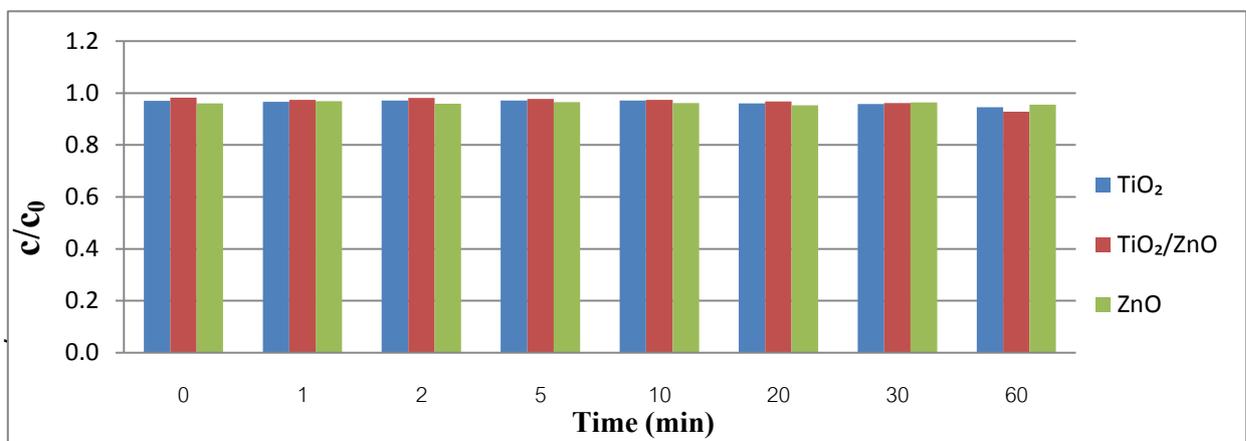
(b)
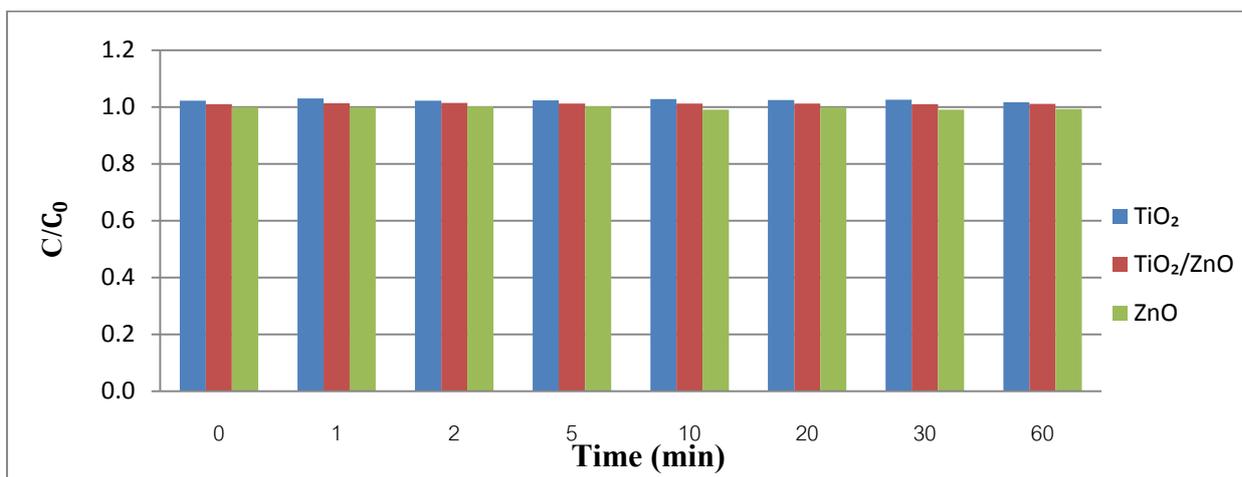
(c)

Figure 4.3 Relationship between the concentration of Reactive Red 239 and time at different pH; (a) pH 2, (b) pH 4, (c) pH 6, light intensity at 40 W, RR 239 concentration of 100 ppm, The energy of the system is 9-9.5 kV and the pressure in the chamber at 0.3 mbar.
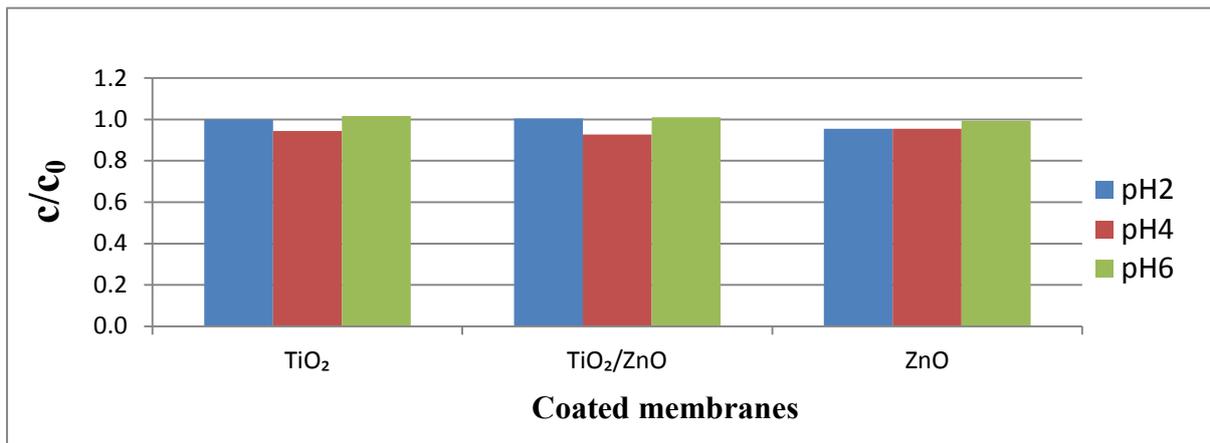
Figure 4.4 Relationship between the concentration of Reactive Red 239 and coated membrane at varied pH at light intensity at 40 W, RR 239 concentration of 100 ppm, The energy of the system is 9-9.5 kV and the pressure in the chamber at 0.3 mbar.

Chapter V

Conclusion

5.1 Conclusion

In this work, PVDF hollow fiber membrane was modified to enhance hydrophilicity property by plasma-induced PAA-TiO$_2$/ZnO coated PVDF membrane via PICP method for decolorization of Reactive Red 239. The morphologies and chemical compositions of TiO$_2$/ZnO-NPs coated on the membrane surface were characterized by SEM and EDS. TiO$_2$-NPs and ZnO-NPs were increased. The element compositions were changed, affected from plasma-induced technique and coating nanoparticles. Furthermore, the water contact angles of the membrane was coated with TiO$_2$-NPs has the reduction compared to the membrane was coated with ZnO-NPs and TiO$_2$/ZnO-NPs from 77.9° to 74.1°. The water contact angles effect the water flux, the membrane with TiO$_2$ as an element in coated have high water flux, which is apparently at the membrane was coated TiO$_2$/ZnO-NPs was flux 23.18 L/m^2·min. Overall, reducing the concentration of RR 239. These did not significantly changed, and to compared with different pH these also did not change.

5.2 Suggestions

- Take more time to treatment Reactive Red 239 for 2 hr onwards.
- Use more UV-C for treatment, light intensity of 40 W onwards.
- Use the glass quart for UV-C to shine through the membrane because the glass module that is too thick, and can not let the UV-C pass through.
- Test more concentration of nanoparticles.

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