Doctoral Dissertation

Enhanced photocatalytic and antibacterial properties by $AgTiO_2$ coating for water treatment

($AgTiO_2$ 被覆材による水処理用途での光触媒能と抗菌性の向上)

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SUMMARY

Access to clean water has been crucial global problem, especially with climate change, increasing population, and industrial activities. As one of Malaysia's leading economic activities, the Oil and Gas Industry generates a massive amount of wastewater called Produced Water (PW). Dissolved organics in produced water, such as organic acids and phenolic compounds, are concerning due to the possibility that they can be toxic, non-biodegradable, and have bioaccumulation properties. Conventional treatments such as adsorption, incineration, and biological treatment seem to have difficulties treating these dilute but toxic components in an economical and environmentally friendly manner. Regulations on wastewater management has also been stricter around the globe. Therefore, there is a need on a new water treatment method to treat the diluted organics in a large volume of wastewater.

Membrane technology has been of interest in the water treatment technologies' industrial and research scenes. It offers simpler configuration and maintenance. However, the application is limited by the reduction of performance over time due to fouling phenomena. Photocatalyst offer an effective method to decompose organics in an environmentally friendly manner. This study researched on photocatalytic removal of diluted organic in water and potential of biofouling reduction by deposition of $AgTiO_2$ coating on membrane surface.

In Chapter 1: Introduction, the research background and purpose of this research were discussed. At the end of this chapter, the thesis framework was shown.

In Chapter 2: Preparation and characterization of TiO_2 and $AgTiO_2$ coatings; the method to prepare $AgTiO_2$ coatings on membrane support were explained. The prepared membranes were characterized with XPS, SEM, TEM, and ICP analysis to understand the prepared coatings. Results shows that the concentration of silver deposited on the membrane can be control by the concentration of silver in the precursor (silver acetate solution) used during the photochemical deposition step. Via XPS, it was found that the state of silver prepared through this method is oxide state.

In Chapter 3: Removal of dissolved organic pollutants in water by photooxidation, the photocatalytic performance of prepared membranes was studied. Decomposition of diluted formic acid was performed under UV-light, and the concentration was evaluated using UV-spectrophotometer. $AgTiO_2$ membranes show better photocatalytic activity then TiO_2 membrane. The concentration of silver on the membrane was found to influence its photocatalytic performance. In relation to PW application which commonly contain high salts,

influence of salt types; NaCl, $MgSO_4$, $MgCl_2$ and K_2SO_4 and concentration were studied. All salts were found to inhibit the membranes' photocatalytic performance.

In Chapter 4: Antibacterial activity of $AgTiO_2$ membranes, the antibacterial activity towards E. coli by prepared $AgTiO_2$ membranes were investigated. Silver dissolution from membrane was found to be significantly increased in the presence of NaCl as compared to only water. Comparing membrane with lower Ag deposition, and around 20 times higher deposition, the silver dissolution from these membranes reached almost the same value after some time. However, as the amount of silver deposited on the membrane was higher, the antibacterial performance show around four times higher than the lower silver membrane. Based on other tests performed, it was concluded that there are potential of contribution from the silver oxide deposited on the membrane surface on the antibacterial activity of the $AgTiO_2$ membranes

In Chapter 5: Antibacterial activity in filtration system, prepared $AgTiO_2$ membrane was used to filter E. coli suspension in water. E. coli growth was found to be inhibited by short contact with silver on the coated membrane.

Finally, Chapter 6: Conclusion, the thesis was summarized, and future works were proposed.

TABLE OF CONTENTS

CHAPTER 1

Introduction

1.1 Produced water from Oil & Gas Industry

Oil and Gas is one of the important economic sectors (under Mining & Quarrying) in Malaysia. In 2021, Petronas, Malaysia's national oil company, made RM 248 billions in revenue and was placed at 216th place in Fortune Global 500 (Star, 2022). Based on the report by U.S Energy Information Administration 2021; Malaysia is the second largest oil producer in the Southeast Asia (EIA, 2021). Figure 1.1 shows the total annual crude oil production in Malaysia until 2019 based on data from (EIA, 2021) where it shows the production was around 700 thousand barrels per day for this 10 years.

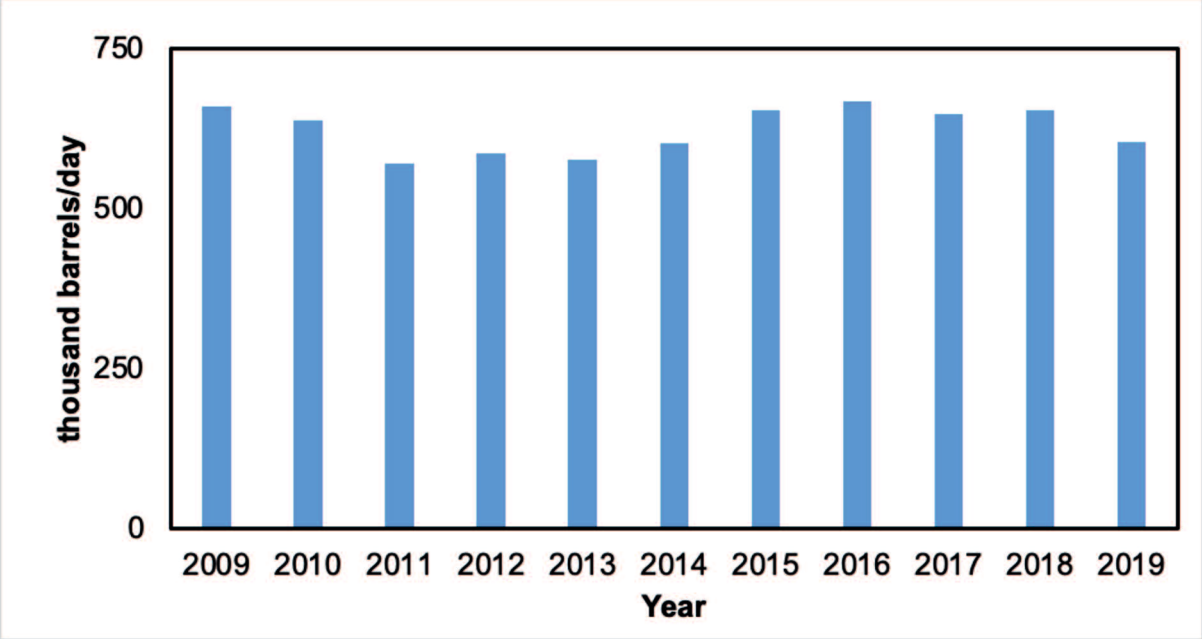

Figure 1.1 Malaysia crude oil production 2009-2019

Compared to other countries such as United Stated of America, Malaysia's oilfields are all located offshores, meaning that the oilfields are located under the sea. Malaysia's oil and gas landscapes can be seen in Figure 1.2 (Bhattacharya and Hutchinshon, 2022) where the fields shown are all located at South China Sea in between East Malaysia and West Malaysia.

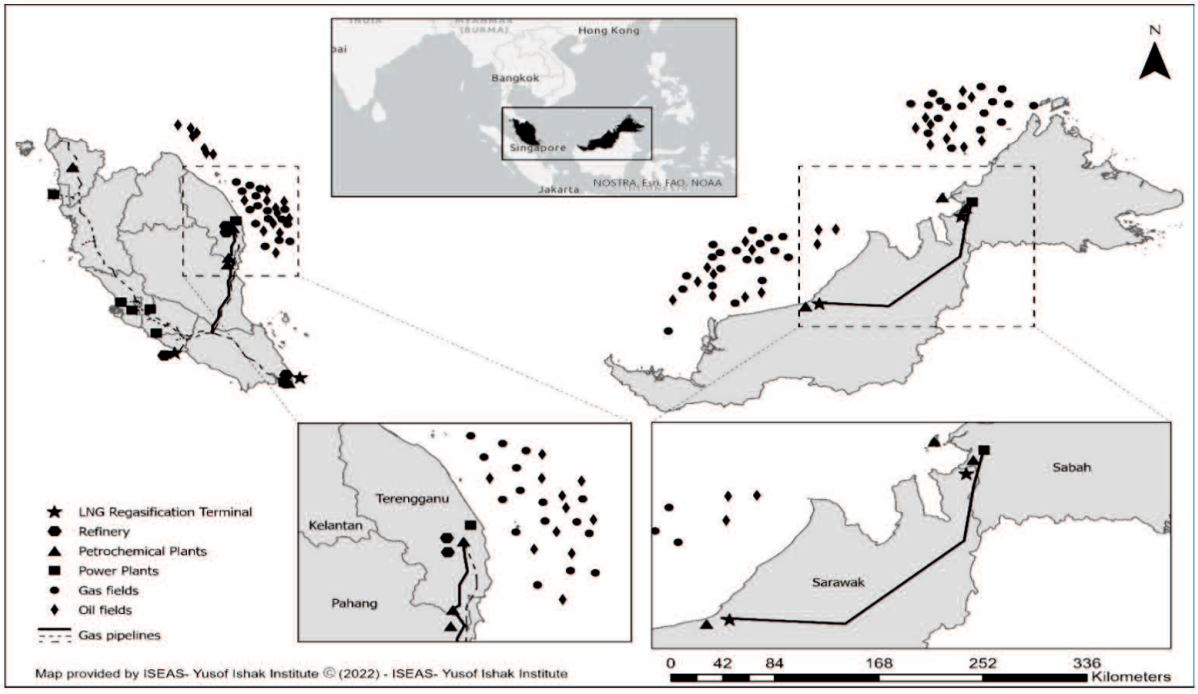

Figure 1.2 Malaysia's Oil and Gas Landscape

Industrial wastewater produced during oil and gas extraction process was called Produced Water (PW). The amount of PW generated by one oilfield can be varied throughout the lifetime of the reservoir, as can be seen in Figure 1.3 based on production profile for Murchison field, North Sea. The volume can also be increasing as the reservoir mature. Processes during the operation, such as water flooding, can also increase the volume of this wastewater further (Veil et al., 2004). As shown in Figure 1.4, generated water-to-oil (WOR) ratio over the years by UK North Sea oil can reach up to 3.5. Thus, as far as petroleum remain as one of the main fuel sources worldwide, wastewater generated from this activity can be concerning.

Malaysia especially, is in a great need of improved water service industry continuously as it is still a developing country. In Malaysia, there are still limitation in the good practice of managing waste from Oil and Gas Industry (Lodungi et al., 2016). As a developing country, the need for better wastewater management including reusage is of interest (Zaini et al., 2008). Previously, towards 'Vision 2020', the vision stated that 'In Support of Vision 2020 (towards achieving developed-nation status), Malaysia will conserve and manage its water resources to ensure adequate and safe water for all (including the environment)'.

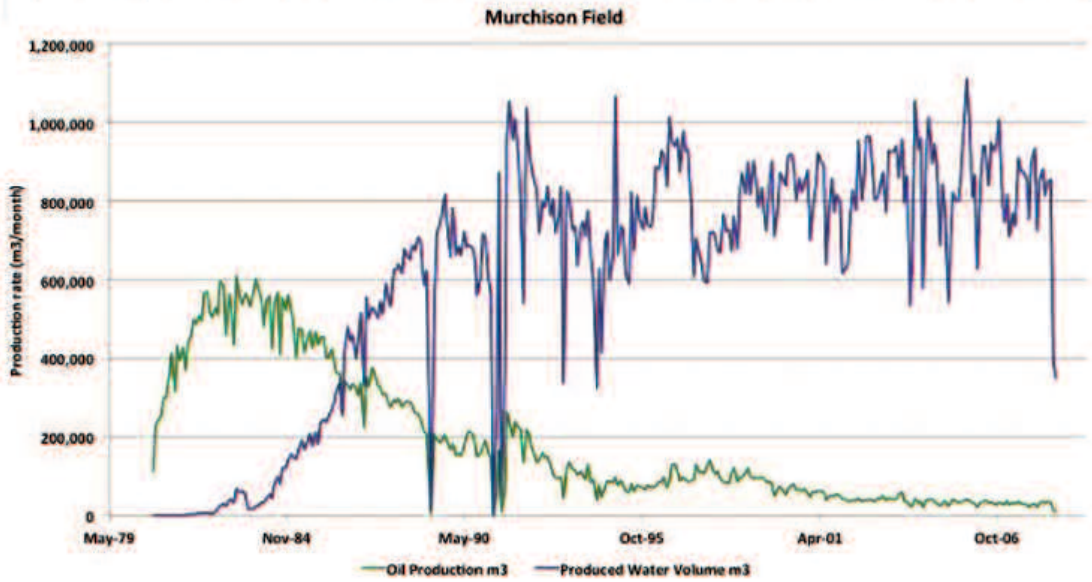

Figure 1.3 Oil and water production profile for the Murchison field, North Sea (Gluyas et al., 2019)

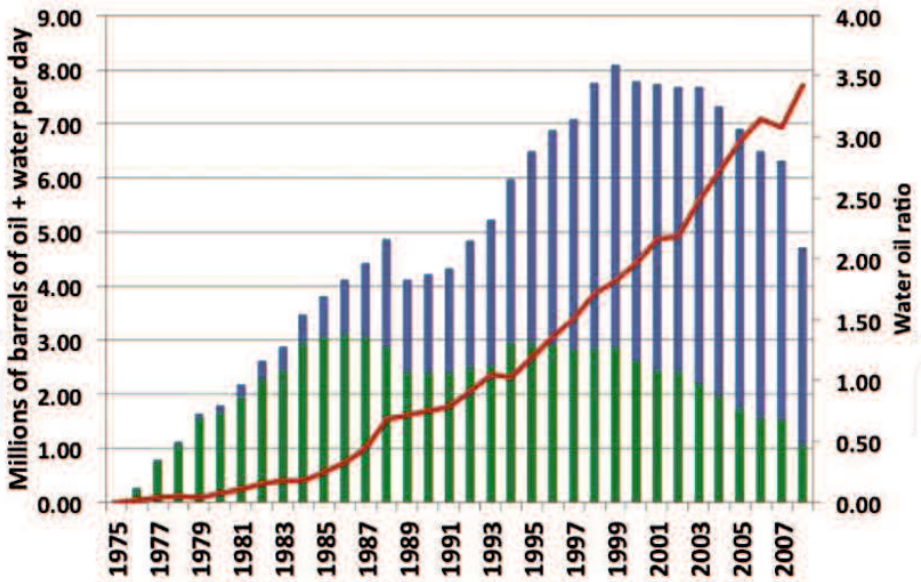

Figure 1.4 UK North Sea oil production (green) and produced water generation (blue) with WOR trend in red (Gluyas et al., 2019)

1.1.1 Characteristics of PW

The generated PW can be varied in composition containing organics and inorganics substances that can come from the underground reservoirs. Additional chemicals added during the operation such as biocides and corrosion inhibitors can also be found in the wastewater

(Jimenez et al., 2018). PW pH can be in a wide range; typically, 4.3-10 (Jimenez et al., 2018). Table 1.1 shows important parameters of produced water.

Table 1.1 Summary of PW parameters (Tibbetts et al., 1992)

Characteristics/Components	Values
Density (kg/m^3)	1014-1140
Chemical oxygen demand (COD; mg/L)	1220
Total suspended solids (TSS; mg/L)	1.2-1000
Total Organic carbon (TOC; mg/L)	0-1,500
Total Oil (IR; mg/L)	2-565
Chloride (mg/L)	80-200,000
Bicarbonate (mg/L)	77-3990
Sulfate (mg/L)	<2-1650

Salinity is expected to be crucial composition in PW from Malaysia's reserved; as all Malaysia's oilfields are offshore fields shown previously. The concentration of chloride ions can be from 80 to 200,000 mg/L as can be seen in Table 1.1.

Improving the management of PW will be reflected to a more sustainable oil and gas industry (Chen et al., 2022).

1.1.2 Regulations on PW discharge

In the USA, under the United States Federal Effluent Limitation Guideline (ELG) of 40 CFR Part 435; under Subpart C: Onshore and Subpart E: Agricultural and Wildlife Water Use, 'no discharge of waste pollutants into navigable waters' from Oil & Gas Activities were permitted (Colorado, 2012). The regulations also mentioned that PW discharge 'shall not exceed Effluent limit for Oil & Grease of 35 mg/L'. Whole effluent toxicity (WET) test is carried out to evaluate the wastewater (Colorado, 2012).

For another top petroleum producer, Norway, under the EU Water Framework Directive (200/60/EC), the involved parties are committed to 'zero environmental harmful discharge' which has been proposed in the Storting's white paper No.58 (1996-1997) towards a more sustainable development of oil and gas industry (St.Report.58, (1996-1997)). Environmental impact factor (EIF) was developed to achieve this policy where it is used to evaluate the quality in term of composition and amount of PW (Roe Utvik et al., 2004).

Malaysia's regulations regarding the discharge of wastewater falls under The Malaysian Department of Environment which imposed a stringent limitation on discharge effluent. Environmental Quality Act (1974) and Industrial Effluent (Regulations) 2009 covers physical, chemical and biological parameters (Razali et al., 2020). Other regulations involving this wastewater will be Petroleum Regulation 1974 and Petroleum Development Act 1974. Recently, in October 2021, Malaysian government took a more serious role in wastewater discharge, where they announced the Water Services Industry (Prohibited Effluent) Regulations 2021, which prohibited the discharge of containing of pollutants including oil and grease. The activity of oil and gas extraction near to human area can be more critical, in case of the waste water or spill from this activity can interfere the source of fresh water for the living things around the area (Jong et al., 2021).

With responsible bodies announcing a more stringent regulations regarding industrial wastewater discharge, work on improving and refining the PW treatment will be of interest.

1.2 Produced water treatments and challenges

Due to the stringent regulations of its final disposal discussed above, there is a need of effective treatments on produced water. The regulations like 'Zero Discharge' will mean that any contaminant in PW need to be completely removed.

1.2.1 PW treatments in practice

Over the years, PW treatments have been renewed and improved to meet the required standards. Factors such as the area regulations, technical ability of the operator, cost and availability of equipment can affect the design of PW management system in that oilfield (Onyems Igwe and Al Saadi, 2013).

PW management aimed to handle this wastewater via minimizing the amount, recycling for enhanced oil recovery (EOR) or other applications such as agricultural and industrial use, and finally to safely disposed the wastewater through methods such as discharge to water bodies, underground injection, or transported for offsite disposal (Arthur et al., 2011, Onyems Igwe and Al Saadi, 2013, Jimenez et al., 2018).

Initial treatment of PW aims to eliminates solid particles mainly through physical separation such as gravity separator, hydrocyclones, and other technologies such as flocculation, coagulation and induce flotation. One of Malaysia's oilfields, Pul-A field, Malaysia, previously used corrugated plate interceptor (cpi) a kind of gravitational separator

in their PW treatment management. Report on 2011, shows improved treatment using a new equipment consist of vertical separator, combined with induced gas and cyclonic fluid motion and improved the treated water (Rosli et al., 2011). Some conventional treatments that were common practice previously has now been discouraged due to the toxicity effect such as application of polymeric flocculants (Mallevialle et al., 1984). Alternatively, recent studies were working on biodegradable coagulants such as bentonite and chitosan (Marey, 2019). After the primary separation, the wastewater will undergo further water treatment processes such as biological treatments.

Biological treatment offers degradation of pollutants and works by converting contaminants in PW to simpler substances through the addition of microorganisms such as bacteria and algae. Organic contaminants in wastewater acted as the feed for these microorganisms, generating additional biomass that usually need further separation through sedimentation. Activated sludge treatment was reported to be able to remove up to 99% of the Total Petroleum Hydrocarbon (TPH) (Jimenez et al., 2018). There are four categories of PW treatment via biological methods (Abujayyab et al., 2022) i.e.: 'fixed film (biofilm), membrane bioreactor, suspended growth such as ponds and activated sludge, and bio electrochemical treatments'. Many of reported study on biological treatment of PW use the real wastewater due to the composition of wastewater that can contribute to the microorganism's growth (Freedman et al., 2017, Shrestha et al., 2018).

Organic composition in PW can contribute largely to the total impact factor (EIF) and should be a concern in treating PW (Faksness et al., 2004). This includes the organics in dispersed and dissolved forms, including BTEX (Benzene, Toluene, Ethylbenzene, Xylene), NPD (naphthalenes, phenanthrenes, and dibenzothiophenes), PAH (polycyclic aromatic hydrocarbons), organic acids, and alkylated phenols (Roe Utvik and Hasle, 2002).

1.2.2 Challenge in PW treatment

Table 1.2 shows the organic compositions of PW from main sources in the Norwegian sector of the North Sea. Roe Utvik reported that Phenols found in the PW can be alkylated up to C7 (Roe Utvik and Hasle, 2002), while another reported that Phenol can also be presence at up to C9 (Faksness et al., 2004). Organic acids found in PW are mainly in the C1-C6 forms (Roe Utvik and Hasle, 2002). Even though organic acids did not influenced the EIF directly, it is still an important parameter and as its toxicity is considered in the WET (Whole Effluent Toxicity) test which were carried out on PW discharge analysis (Vries and Jak, 2018).

Even at relatively low-concentration, organics In PW can be highly toxic pollutants towards surrounding environment such as aquatic life which can finally be transferred to human via consumption (Fakhru'l-Razi et al., 2009, Hadiyanto et al., 2018, Jimenez et al., 2018).

Table 1.2 Chemical composition of PW from main sources of the North Sea (Roe Utvik and Hasle, 2002).

Component	Concentration (mg/L)
Dispersed oil	10-40
BTEX	1-40
NPD	0.9-10
PAH	0.01-0.13
Organic acids	55-760
Phenol	0.1-6
C1-C4 alkylated phenols	0.17-11.3
C4-C7 alkylated phenols	0.1-0.8

PAHs and higher alkylated phenols (C6-C9) were considered as to be related to the dispersed oil, while lower alkylated (C0-C3) phenols and BTEXs were dissolved in the PW (Faksness et al., 2004). Reduction of EIF value around 65% is possible if the dispersed oil concentration can be reduced from 40 mg/L to 5 mg/L. This condition removed 69% of higher alkylated phenols (C6-C9) but no removal of C0-C3 phenols (Faksness et al., 2004). CTour, a hybrid technology that was studied with real PW treatment, has been reported to be highly efficient to remove dispersed oil and PAH components. It also shows removal of higher alkylated phenols but negligible removal of lighter phenols, C0-C3 (Knudsen et al., 2003, Voldum et al., 2008). Another patented technology, Mare's Tail, applied coalescer to improve hydrocyclone efficiency in removing dispersed oil. While the removal of naphthalene, PAHs, and C6 to C9 phenols were significantly improved, it shows negligible effect on removal of C0-C5 phenols (Denney, 2004). Phenols is considered as a critical pollutant from Oil and Gas Industry. For example, under Environmental Quality Act 1974 of Malaysia, the Phenol discharge limit is 0.001-1 ppm depending on the distance with a river (water bodies) (DOE, 1974).

Conventional treatments such as biological treatment can be limited to treat the organics due to the toxicity towards living microorganisms (Tungler et al., 2015). The biological treatment also shows low efficiency in the removal of highly toxic recalcitrant compounds such as BTEX and phenols (Jimenez et al., 2019). High salinity condition of wastewater can also affect the microbial population in biological treatment of PW (Kose Mutlu et al., 2019). Other

than that, the treatment usually requires large space to be feasible, thus can be a limiting choice for the PW treatment especially in offshore locations.

The limitation by conventional methods to effectively remove these diluted organics encourage the works on a more efficient systems for their removal (Levec and Pintar, 2007, Nageeb, 2013, Coha et al., 2021).

Currently, there are various methods applied for the removal of dissolved organics in water. Adsorption and membrane technologies separate the organics from water while decomposition processes like wet air oxidation, incineration, and advanced oxidation process such as UV, hydrogen peroxide, ozone, Fenton, and photocatalyst convert the organics to simpler compounds such as carbon dioxide.

1.3 Treatment technologies for dissolved organics

1.3.1 Adsorption

In adsorption process, the wastewater with absorbable contaminants (solute) will be in contact with solid (adsorbent) that has porous surface. When in contact, solute from the solution will be deposited on the adsorbent surface due to intermolecular forces developed (Nageeb, 2013). It has been widely used in wastewater treatment since it offers advantages of low cost, efficient, and applicable in many conditions (Cheng et al., 2021)

The economically low cost, and efficiency in binding pollutants make adsorbents gain interest among researchers. There are many potential adsorbents that has its own characteristics such as activated carbons (Zhou et al., 2017, Rahman et al., 2019, Al-Kaabi et al., 2019), biochars (Cheng et al., 2021) resins (Liu et al., 2019) and zeolite (Ba Mohammed et al., 2021).

Liu and his team studied the adsorption performance of novel ethylenediamine rosin-based resin (EDAR) for removal of 4-nitrophenol (4-NP) from water (Liu et al., 2019). It shows high efficiency on 4-NP but less effective on other phenols such as 4 – methyl phenol (4-MP). It shows the importance of nitro group in the adsorption performance of the material. Another research synthesized novel zeolite (NaY) and Nickel modified NaY zeolites (Ni-NaY) to remove phenol from aqueous solution (Ba Mohammed et al., 2021). Ni-NaY shows higher adsorption capacity compared to NaY (almost 10% difference). They also reported that Ni-NaY still had 90% removal efficiency even after 5 cycles of treatment which shows a good performance by modified zeolite as an adsorbent.

Unfortunately, a common problem in adsorbent application is that suspended particles can plug the adsorbents thus require regeneration that will cost more. This becomes a limitation to this application (da Silva et al., 2015). Collection of the pollutants by the adsorbents also means that the pollutants still need to be transferred and treated further which requires another treatment process.

1.3.2 Membrane Technology

Membrane technologies includes microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis. Membrane technologies offer advantages such as smaller footprint, little to none chemicals required, easily can be combine with other treatment processes, and low energy consumption and potential of continuous operation (Zolghadr et al., 2021).

Total suspended solids (TSS), oil and grease (O&G) and sulfate from PW was reported to be efficiently removed through membrane treatments (Al-Ghouti et al., 2019). Reverse osmosis (RO) process is commonly used as one of the stages in produced water treatment to separate dissolved organics. Compared to microfiltration and ultrafiltration, RO operates at higher pressure which differentiate the membrane's selectivity (Hadiyanto et al., 2018).

A recent study works on emergency disk tube-reverse osmosis (DTRO) treatment system and successfully removed refractory organic matter (OM) such as humic and fuvic like substances. It additionally removed more than 80% of dissolved OM (Wu and Li, 2021). Sun and his team successfully remove 78-100% of three low molecular weight compounds in PW by coupling ultrafiltration with reverse osmosis (Sun et al., 2021). In another study of PW treatment, the researchers pointed out that RO process successfully decreased total dissolved solid (TDS) and chemical oxygen demand (COD) but as the scale build up on RO membrane, the performance deteriorate significantly (Guo et al., 2018). Other type of membrane has also been studied in hybrid forms. (Mahbouba et al., 2021) evaluated the performance of polyether sulfone ultrafiltration membrane (UFM) in combination with conventional treatment to treat PW from Al-Ahdab oil field, Iraq. The study found that without pretreatment, the application was limited due to membrane fouling and concluded the need on multiple technologies to meet the required standards. (Kusworo et al., 2018) proposed another hybrid treatment of membrane filtration with adsorption by carbon-bentonite adsorbent. It shows positive result on reduction of Total Dissolved Solid (TDS) and suggested that the adsorption pretreatment before membrane reduced fouling of the membrane.

The efficiency of conventional membrane technology application commonly will be reduced over time due to membrane fouling cases. To manage these problems, operators usually include membrane cleaning or periodic replacement after some time. Chemical cleaning for the membrane fouling will incur more cost as it become a new source of waste to be manage eventually (Fakhru'l-Razi et al., 2010). From previous reports, it seems that the application of membrane in need of a pre-treatment and post-treatment steps before the treated water meets the regulations standards.

1.3.3 Incineration

Incineration has been a common practice for wastewater treatment. In current industrial practice, incineration is normally chosen as a last resort due to limitation by other technologies (Tungler et al., 2015). Recently, Chen and his research team has coupled incineration of landfill leachate to membrane bioreactor and found that the removal of phenolic compounds, polyphenols and polycyclic aromatics to be enhanced compared to without incineration (Chen et al., 2020b).

Incineration technology consumed fuel while generating toxic byproducts such as dioxin, furan and sulfur dioxide (Tungler et al., 2015). Apart from that, heating the fluid cause oil loss in vapors thus resulting the condensates to require some more treatments (Onyems Igwe and Al Saadi, 2013).

1.3.4 Wet air oxidation (WAO)

WAO usually applied in wastewater treatments by oxidizing pollutants with oxygen at elevated temperature. The treatment was usually applied under the condition where incineration and biological treatment are not feasible (Tungler et al., 2015). Application of catalyst with WAO, (CWAO) offer milder operation conditions thus reduce the process cost and risks. The catalyst application is the driving force in formation of free radicals to perform oxidation in the wastewater. CWAO can be used as a pretreatment before biological treatment, since it usually are able to reduce the organics to a more degradable components (Levec and Pintar, 2007). It has shown potential to degrade organic compounds from textile industrial wastewater (Rodríguez et al., 2008), refractory pollutants (Sushma et al., 2018) and phenols (Lai et al., 2019, Geng et al., 2020).

Massive works on development of new catalysts in recent years resulted in more environmentally friendly oxidation processes (Levec and Pintar, 2007). Combination of

membrane application with CWAO also shows promising results (Iojoiu et al., 2007, Kumakiri et al., 2011b, Bao et al., 2021).

For some examples, Bao and his research team applied catalyst, Molybdenum (Mo)-based nanocrystal deposited on ceramic membrane to perform CWAO on organics, among them is humic acid, and found that higher than 90% performance was achieved under ambient condition (Bao et al., 2021). Application of Cerium-incorporated Manganese dioxide, (MnCeOx) catalysts for degradation of phenol is developed by a redox-precipitation preparation method in another study and shows excellent activity and stability (Geng et al., 2020). Higher temperature (70 °C) shows a better result compared to 50°C. (Parvas et al., 2019) used non-noble metal Nickel (Ni) with different loadings and coated on precipitated support (CeO_2–ZrO_2) for degradation of phenol and obtained a positive result at 160 °C. Increasing catalyst loading also increase the degradation performance.

In CWAO, the process the require contact of pollutant solutes with catalyst and oxygen simultaneously. It was discussed before that the major limitation of CWAO is the oxygen transfer and solubility in the reaction solution (Iojoiu et al., 2007, Monteros et al., 2015). To improve the oxygen delivery, (Kumakiri et al., 2011b) reported on a Platina membrane contactor where they successfully removed 97% of C2-phenol. However, the catalyst was deactivated after the treatment process and was able to be regenerated by heat treatment.

1.3.5 Advanced Oxidation Processes

Advanced oxidation process (AOP) are promising treatments to remove organic contaminants in water through the generation of hydroxyl radicals (·OH) (Wang et al., 2019a) which can react with solute through fast reaction kinetics (Coha et al., 2021). Compared to adsorption and membrane technology discussed above, AOP process enables the pollutants to be completely oxidized into carbon dioxide and water, or at least other less harmless compound, thus making it a more favorable choice to treat the organics in PW treatment (Coha et al., 2021).

1.3.5.1 Ozone

Ozone is highly oxidative chemicals compared to oxygen and air; however, it is considered as expensive oxidant. The chemical also has low solubility which will limit its application in wastewater. Salinity in PW can cause lower solubility of ozone into the wastewater, thus reduce its treatment efficiency (Jimenez et al., 2018). At low concentration, removal of pollutants will

require higher ozone application; thus will cost more (Amin et al., 2010). Combined treatment may be appropriate for ozone application to reduce the amount of chemicals used.

Recently, Gorito et al. (Gorito et al., 2021) successfully removed some low concentration organic micropollutants in water that are critical under EU regulations using ozone-based water treatment (O_3, O_3/UV, and O_3/H_2O_2) from river reservoir for drinking water purpose. In another study, zeolite with ozone was found to be effective to remove phenol and COD as compared to without ozone. By acting as adsorbent, zeolite was found to provide the needed surface for contact between ozone and pollutants (Amin et al., 2010).

1.3.5.2 Fenton

Fenton reaction is one of the AOP that has been actively studied in recent years. It involves catalytic decomposition of hydrogen peroxide (H_2O_2) by Iron (Fe^{2+}) to produce hydroxyl radicals. The generated hydroxyl radicals will then oxidize targeted contaminant. While the main mechanism of degradation looks simple, the process and involves multiple other reactions (Gar Alalm et al., 2015, Bello et al., 2019).

Unfortunately, oxidation through Fenton have limitations such as acidic pH requirement, potential toxic byproduct generation (Iskander et al., 2020), iron sludge production and also risky bulk chemicals usage (Yang et al., 2019). To overcome these, some approaches such as heterogeneous Fenton, fluidized bed Fenton, application of chelating agent and in-situ generation of Fenton's reagent have been researched (Bello et al., 2019, Liu et al., 2021). Combining it with other methods and reagents such as ultraviolet light increase the treatment performance (Jimenez et al., 2018).

1.3.5.3 UV-light

Ultraviolet (UV) light technology is another method in advanced oxidation process. But it usually is combined with another AOP for a better performance. Application of UV light to aid Fenton mechanism usually resulted in higher performance. With UV lamp assisted, Jimenez and her team able to increase the removal of oil and grease and phenol (>15% improvement) by Fenton process from a synthetic PW prepared with same salinity as the seawater (Jimenez et al., 2017). In another study, removal of micropollutants including humic acid in real wastewater successfully increased by combining UV with chlorination (up to 64.2% higher than without chlorination) (Wang et al., 2019a).

1.3.5.4 Photocatalyst

Photocatalysis involves application of catalysts that are activated under light induction. Without addition of liquid chemicals in water treatment, heterogenous photocatalyst involved two phases, solid (photocatalyst) which usually are semiconductors such as titanium dioxide (TiO_2), zinc oxide (ZnO), tungsten (VI) oxide (WO_3) and others, and the wastewater (liquid). The process offer advantage with application at ambient temperature and pressure and efficient removal of diluted but non-biodegradable organic contaminants in water (Trojanowicz et al., 2018, Yaqoob et al., 2020). The reaction mechanism is further described in section 1.5.1.

1.4 TiO_2 based photocatalysts

1.4.1 Introduction to photocatalysis by TiO_2

From previous studies, application of heterogenous photocatalysts seems to be a high potential candidate for removal of PW organics in a simple and environmentally safe manner.

Titanium dioxide semiconductor was largely used for photocatalytic reaction with advantages such as high catalytic activity, low cost, stability, and non-toxicity (Fujishima et al., 2000). Additionally, photocatalytic oxidation by TiO_2 does not require pH adjustment (Coha et al., 2021) and has a wide range of applications (Zheng et al., 2017, Horovitz et al., 2020, Ju, 2019).

In the photocatalytic reaction, semiconductors are illuminated with greater light energy than their band gaps, exciting electrons from valence band to the conduction band, leaving empty positive holes in valance band. There are two ways the system helps organic degradation; indirectly; the electron and holes can induce hydroxyl and superoxide radicals' generation which will oxidize organic pollutants, or directly where organic solute is adsorbed on catalyst surface and oxidized by positive holes (Fujishima et al., 2000, Jimenez et al., 2019, Rostam and Taghizadeh, 2020). Equations 1.1 to 1.6 shows the reactions that occur in this situation when supplied with light (hv) (Abdullah et al., 2019). Figure 1.5 illustrate the photocatalytic mechanism.

$$TiO_2 + hv \rightarrow (e_{cb}^- + h_{vb}^+) \quad \text{.....(1.1)}$$

$$hv_{vb}^+ + H_2O \rightarrow \cdot OH + H^+ \quad \text{..... (1.2)}$$

$$e_{cb}^- + O_2 \rightarrow \cdot O_2^- \quad \text{..... (1.3)}$$

$$2H_2O + 2 \cdot O_2^- \rightarrow H_2O_2 + 2HO \cdot + O_2 \quad \text{... (1.4)}$$

$$H_2O_2 + e_{cb}^- \rightarrow 2HO\cdot \quad \text{..... (1.5)}$$

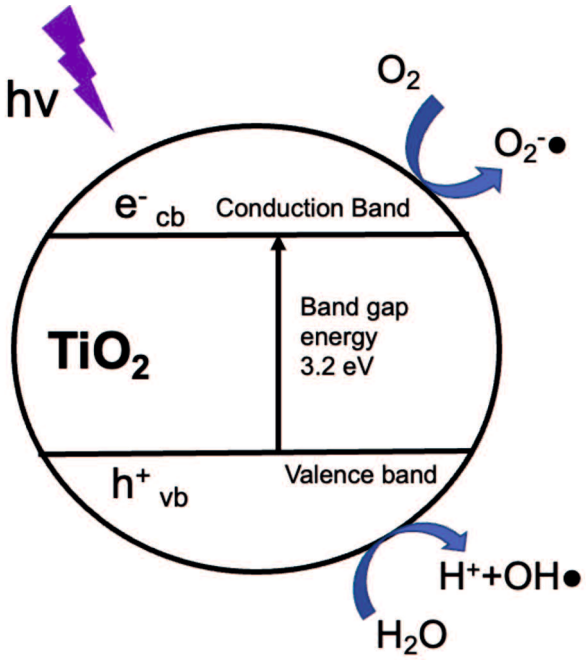

Figure 1.5 Photocatalytic mechanism

One of the main limitations in TiO_2 application for organics degradation is the wide band gap (3.24 eV) that need to be overcome by the excited electron to initiate further reactions. This will limit the formation of radicals for the oxidation of organics (Chen et al., 2020a). Another limitation will be the fast recombination rate of separated charges (Wang et al., 2019b). Works on modification of TiO_2 to enhance its application are actively studied.

1.4.2 Modification of TiO_2

Currently, various methods are studied on modification of TiO_2 to improve its catalytic activity including doping, sensitizing, and modification. Since the organic decomposition depends on the generated electron-hole pairs, photocatalytic activity can be improved by lowering the band gap that the irradiation needs to overcome to excite electrons, or slowing down the recombination of excited electron to its holes (Mezbour and Fouzi Ghorab, 2019). Doping TiO_2 with metal and transitional metal (Ag, Au, Cu, Co, Cr, Fe, Mn, Mo, Nb, Ni, Pt, Ru,V) or non-metal (B, C, F, N, I, P, S) shows enhanced photocatalytic activity (Fujishima et al., 2000, Zaleska, 2008, Monteros et al., 2015, Durgam et al., 2020)

It was reported that metal deposition on TiO_2 act as electron traps and prevent the recombination of electron and holes (Subrahmanyam et al., 2012). Noble metal doping on TiO_2 will give significant benefit to the process, especially when the dopant is easily obtained and

economically feasible (Sescu et al., 2020). Compared to non-metal dopant, metal dopant shows higher stability, milder conditions and simpler process during preparation (Kanakaraju et al., 2022).

Table 1.3 shows some recent studies on modified TiO_2 nanoparticles for photocatalytic decomposition of organics in wastewater.

Table 1.3 Modified TiO_2 for treatment of organics in wastewater

Dopant	Target contaminant	Light source	Results	Reference
Noble Metal				
Ag	Methylene blue (MB)	UV-light	Degradation of MB increase with increased silver amount. 10 % Ag-TiO_2 shows 97% degradation after 35 minutes. Band gap was reduced to the range of 3.22 eV to 2.67 eV proposed to be the reason of increased performance.	(Abbad et al., 2020)
Au, Paladium (Pd)	2,4 dinitrophenol and Rhodamine 6G (R6G)	UV-A	TiO_2-Pd shows higher removal rate than TiO_2-Au. 96% of R6G was successfully degraded by TiO_2-Pd in 120 minutes	(Sescu et al., 2020)
Ag	2-chlorophenol	UV-light	Enhanced 2CP (2-chlorophenol) degradation at low 2CP concentration. Alkaline pH shows the best condition for the degradation.	(Onkani et al., 2020)
Transitional metal				
Aluminium (Al), Copper (Cu), Manganese (Mo), Tungsten (W)	Rhodamine B	Visible light	Highest rate constant (k) obtained (0.0351 min^{-1}) by W/TiO_2 photocatalyst proposed to be due to decreased band gap.	(Khlyustova et al., 2020)
Iron, Fe (III)	Methyl Orange (MO) and 4-CP	Visible light	0.1 mol% Fe doped TiO_2 shows highest photocatalytic activity while increasing the dopant higher, reduced the performance.	(Ismael, 2020)
Co-doped				
Copper (Cu^{2+})/ZnO	Benzene series in oilfield PW	UV-light	Optimal degradation rate at catalyst dosage of 2.0 g/L and ambient pH and temperature (25°C)	(Ji et al., 2023)

1.4.3 Silver-deposited TiO_2 photocatalyst

Noble metal, silver (Ag) stands out for industrial applications due to its low cost and the doping mechanism on TiO_2 can be simple but produce remarkable photocatalytic efficiency (Wodka et al., 2010). When deposited on TiO_2 and supplied with appropriate light, the metal-doped photocatalyst shows a promising results in decomposition of organic pollutants such as dyes (Seery et al., 2007, Nainani et al., 2012, Abbad et al., 2020, Durgam et al., 2020) Phenols (Mezbour and Fouzi Ghorab, 2019) and organic acids (Pipelzadeh et al., 2012, Wodka et al., 2010). $AgTiO_2$ can be prepared through various methods. Table 1.4 below explained on different method to prepare $AgTiO_2$ particles.

Table 1.4 Preparation method for $AgTiO_2$

Preparation method	Precursor/Binder/Chemicals	Condition	References
Sol-gel Method	Titanium precursor such as Titanium tetraisopropoxide (TTIP) Organic solvents such as ethanol Silver precursor such as silver nitrate ($AgNO_3$)	Involves preparation of gel before calcination (500° C) to remove solvents.	(Onkani et al., 2020) (Abbad et al., 2020) (Zhao and Chen, 2011)
Photoreduction	TiO_2 nanoparticles Silver precursor such as $AgNO_3$ and CH_3COOAg	Under UV-light at ambient temperature	(Nainani et al., 2012) (Wodka et al., 2010) (Gao et al., 2018) (Liang et al., 2017)
Wet impregnation/ Chemical reduction method	TiO_2 nanoparticles Silver precursor such as $AgNO_3$ Reducing agents such as sodium borohydride or other organic solvents	Mixing followed by calcination (400°C-500°C) to remove solvents	(Zhou et al., 2014) (Mezbour and Fouzi Ghorab, 2019) (Freire et al., 2020)
Hydrothermal method	Titanium precursor such as Titanium tetraisopropoxide (TTIP) Silver precursor such as $AgNO_3$	Performed in autoclave for the pressurized conditions and temperature of 180°C. Followed by drying and calcination (500°C)	(Avciata et al., 2016) (Hariharan et al., 2020)

In comparison to other methods, photoreduction was reported to produce high purity nanoparticles because of its simplicity, less chemicals used, and better performance in contaminants decomposition (Gao et al., 2018) while being cheaper than some other dopants and fast preparation at ambient temperature (Wodka et al., 2010).

Wodka reported facile deposition of Ag on TiO_2 by photoreduction treatment method (PRT) using silver salt, silver acetate (CH_3COOAg) while most of reported studies used silver nitrate ($AgNO_3$) as the silver precursor for photoreduction of silver onto TiO_2 (Seery et al., 2007, Sclafani et al., 1991, Mezbour and Fouzi Ghorab, 2019). It was proposed that utilization of CH_3COOAg allows formation of metallic silver without additional chemicals and produced pure composite. Prepared nanocomposite was studied under UV and artificial sunlight. Results shows the photocatalysts performed better under UV-light compared to sunlight and able to remove up to 99% oxalic acid. Furthermore, it shows a potential to remove large size organic such us humic acid up to 62.7% under UV light (Wodka et al., 2010). No changes of band gap energy were reported after deposition of silver on TiO_2 in this study.

On more recent studies, the photocatalytic activity of TiO_2 and Ag-TiO_2 was investigated by Abbad and team by doping silver on TiO_2 through sol-gel method. Ag-TiO_2 shows better decomposition of MB under UV irradiation as compared TiO_2 only. The team explain that this positive result was due to the reduction of recombination rate of electron-holes and can be related to the band gap changes. Depending on the silver concentration, band-gap energy of prepared Ag-TiO_2 can be reduced to 2.67 eV (Abbad et al., 2020).

Ag doped TiO_2-PC500 through wet chemical reduction shows improved photocatalytic performance under both UV and visible light as compared to without Ag in another study to treat dye (congo red, CR and crystal violet, CV). Addition of H_2O_2 improved decomposition of CV significantly in both catalysts (with and without Ag) while COD removal shows average reduction in this study (Mezbour and Fouzi Ghorab, 2019).

In photocatalytic reaction with $AgTiO_2$, the electron generated from TiO_2 when irradiated will be transferred to silver particles due to its ability to attract electrons (Sclafani and Herrmann, 1998) thus making silver as an electron sinks (Liang et al., 2017). Since it moves further from its hole, the recombination will be inhibited or slowed down thus increase the photocatalytic activity.

Silver also shows better localized surface plasmon resonance compared to other metal such as gold (Au) which form Schottky barrier on TiO_2 surface. This contributed to the

improved charge separation and quantum efficiency (Gao et al., 2018). Another study, on the other hand proposed no formation of Schottky barrier on TiO_2 surface with deposition of silver due to closeness of Fermi level of Ag and TiO_2. The silver strong photocatalytic improvement was proposed due to the ability of silver to also capture a hole under this condition and thus, increased the charge separation (Wodka et al., 2010).

To further research into $AgTiO_2$, factors such as doping amount and reaction with other wastewater particles were worth looking into. Some studies found that lower Ag loading on TiO_2 gave better photocatalytic performance compared to higher loading for certain contaminants such as oxalic acid (Wodka et al., 2010), 2 CP (Onkani et al., 2020) and dye, such as rhodamine B (Liang et al., 2017). However, some study reported that the highest silver amount they studied shows the better performance where the grain size of prepared particles seems to slightly decreased with higher silver concentration (Abbad et al., 2020).

Presence of other materials in the wastewater can potentially interfere the photocatalytic activity. Salt ions, in wastewater especially produced water that came from seawater can influence photocatalytic activity. There is much available research on TiO_2 mechanism studies in water, but its activation in sea water has not been fully explored (Porcar-Santos et al., 2020). The discussion on effect of salinity on photocatalytic activity is still not fully understood. For example some study shows negative influence of chloride ions (Cl^-) towards decomposition of organic such as dichloroethane (Chen et al., 1997), and dye but at higher concentration of the ion (Chakkunny et al., 2021), while some shows positive influence by cations on decomposition rate of dye (Makita and Harata, 2008). Other study shows that the severity of salt anions effect on photocatalytic activity can depend on the target contaminant (Tavakoli Joorabi et al., 2022).

1.5 Photocatalytic membranes for water treatment

Another important limitation of TiO_2 nanoparticles application in suspended reactor is that it will be harder to recover and regenerate TiO_2 nanoparticles, aggregation of the particles, and scattering conditions in the suspended reactor (Chen et al., 2022). The scattering of nanoparticles can then limit light delivery to the nanoparticles (Dong et al., 2015, Horovitz et al., 2020).

All the listed problems here can be overcome by the deposition of nanoparticles on membrane/lattice support. This system will integrate the oxidation and separation of effluent from catalyst at one time and avoid secondary pollution and catalysts lost (Vospernik et al.,

2006, Kumakiri et al., 2022). Therefore, it will be economically more feasible in term of the ability to reuse and regenerate the catalyst easily. Apart of that, membrane technology also gives a possibility of low operational cost and small footprint which will be favorable in PW treatment since offshore locations have limited space (Onyems Igwe and Al Saadi, 2013).

Some recent preparation of TiO2 membranes is TiO2/PAN (polyacrylonitrile) nanofibrous membrane prepared via electrospinning for toluene degradation (Su et al., 2017). TiO_2 nanoparticles was highly dispersed on the nanofibers surface. 97.9% toluene conversion was achieved at the highest ratio of TiO_2/PAN studied, 4/1.

In another recent report, Polyvinylidene Fluoride (PVDF)-TiO_2 hollow fiber photocatalytic membrane was studied for separation and degradation of surfactants laden in PW (Rawindran et al., 2019). Increasing the amount of TiO_2 nanoparticles resulted in increased surface hydrophilicity, porosity, and tensile strength of the membrane. However, excessive amount tof TiO_2 (>2%) resulted in reduced membrane performance.

(Vereb et al., 2020) studied ultrafiltration with TiO_2/CNT (carbon nanotube) of real PW with pre-ozonation. The results show that TiO_2-CNT application removed >98% oil with pre-ozonation contributed to reducing the filtration resistance.

1.5.1 Polymeric vs Inorganic photocatalytic membrane

There are various studies reporting on photocatalytic membranes prepared via different methods. The photocatalyst can be prepared together before membrane is form (in-situ) or coated as a separate layer on the membrane's surface (ex-situ). Polymeric membranes offer advantages in term of cost, and flexibility of the desired membrane, however, in photocatalytic application, there are risk of polymer degradation by light and generated oxidative radicals (Choo, 2018, Labuto et al., 2021). Thus, the application in real wastewater system is questionable.

Apart from that, polymeric coatings were also proposed to be used when preparing coated membrane. This binder applied to deposit photocatalyst can limit the delivery of light and also the contact of pollutants to our photocatalyst (Kumakiri et al., 2011a).

Inorganic membranes are a batter choice especially when advanced oxidation involves due to the membrane durability (Phan et al., 2018, Horovitz et al., 2020). There are also more sustainable towards harsh cleaning chemicals used in practice to remove foulants (Fakhru'l-Razi et al., 2009). PW can also be present in extreme conditions due to the uncertainties of the wastewater conditions, thus a more resistance membrane can be an optimal choice.

1.5.2 Photocatalytic membrane reactors configuration

Although photocatalysis technology had been studied for a long time, the application in real wastewater at large scale is almost non-existence. As photocatalyst in wastewater treatment involves solid and liquid phase, the mass transfer of reactant in liquid to the solid catalyst is a critical parameter (Choo, 2018). There are different configurations for photocatalytic membranes reactor (PMR) that had been reported. However, for fixed photocatalyst in membrane proposed, we discussed here three configurations; submerged photocatalytic membrane, membrane contactor, and photocatalytic membrane filtration.

1) Submerged photocatalytic membrane

This configuration is the standard fixed catalyst on membrane configuration as an alternative to a conventional suspended membrane reactor. Fixed-bed photocatalytic membrane reactor (FPMR) was prepared by covering ceramic membrane with photocatalyst, pyrogenic titania shown in Figure 1.6 (Phan et al., 2018). The reactor shows steady performance with high photocatalytic activity on oxalic acid degradation. As discussed above, advantage of this configuration as compared to suspended photocatalyst is that photocatalysts are not easily agglomerated, and since the photocatalyst is fixed to the support, it will not cause secondary pollution, and the regeneration of photocatalyst will be easier (Wang, 2018).

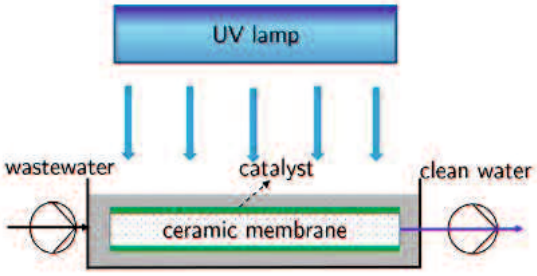

Figure 1.6 Fixed-bed photocatalytic membrane reactor (FPMR) (Phan et al., 2018)

2) Photocatalytic membrane filtration

Immobilizing photocatalyst on membrane can also be applied for filtration system. Here, the configuration combined photocatalyst with the separation function of the membrane. Therefore, the treated water by photocatalyst on membrane surface will be passed through the membrane that can have additional feature: removal of other pollutants during the separation through membrane (Wang, 2018).

TiO_2 immobilized on polypropylene membrane surface via surface modification of grafting polymerization offers a strong deposition of TiO_2 on the membrane surface. This membrane was used to degrade Phenol (200 mL at 10 mg/L) under UV-irradiation in PMR. Results show that reaction rate constant k= 0.0672 h^{-1} was achieved with highest grafting degree in the study (12.9% wt). The experimental set-up was shown in Figure 1.7 below.

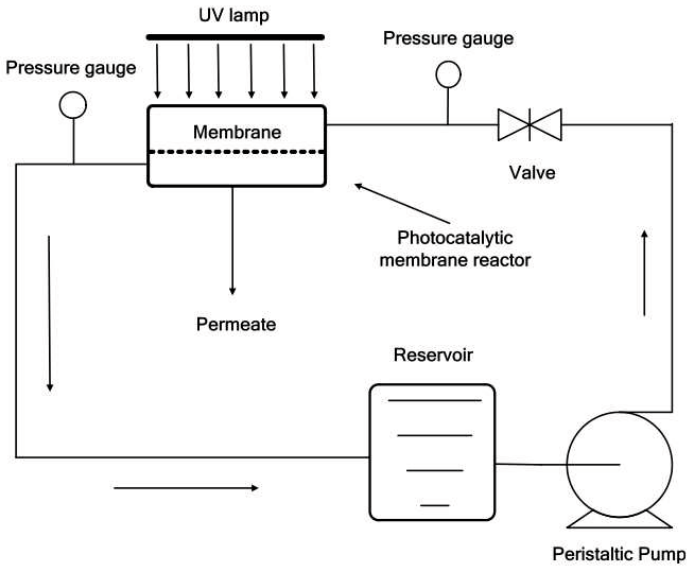

Figure 1.7 PMR configuration (Yang et al., 2011)

3) Photocatalytic membrane contactor

Membrane contactor offers advantages in photocatalytic oxidation due to ability to deliver oxygen in a better manner to the catalyst surface. In membrane contactor system, the liquid and gas flow were kept separated by controlling the gas pressure in the gas-side. With this configuration, the gas pressure can be controlled to optimize the contact between the gas, liquid and solid photocatalyst layer (Kumakiri et al., 2011a). Figure 1.8 shows the photocatalytic membrane contactor set up.

This study reported an comparable performance of membrane contactor with Pt-TiO_2 (photocatalytic) compared to Platinum Contactor only, but with lower amount of deposited Pt. Deposition of Pt on TiO_2 also increased the lifetime of Platinum on the membrane (Kumakiri et al., 2011a).

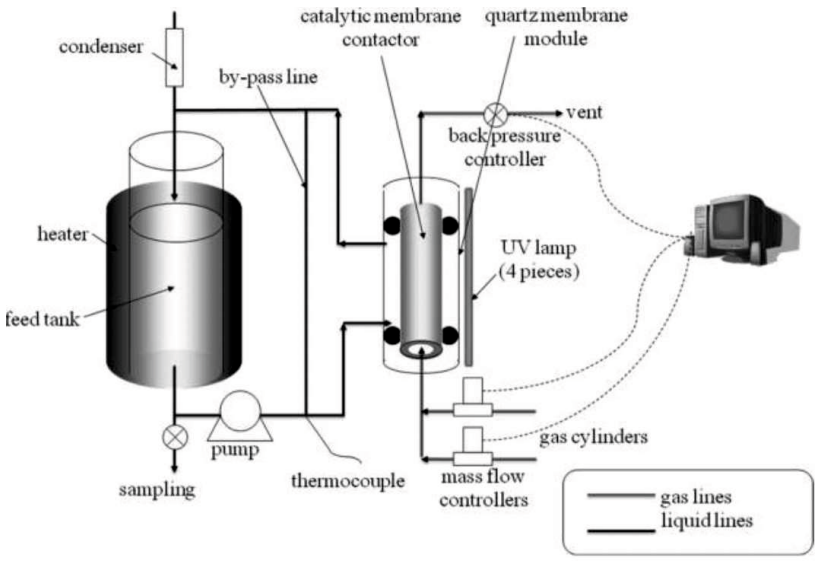

Figure 1.8 Photocatalytic membrane contactor (Kumakiri et al., 2011a)

1.5.3 Membrane Fouling

In section 1.3.2 on the introduction to Membrane technology, the membrane applications usually are limited by the fouling phenomenon. As the membrane is always in contact with wastewater, chemical and biological deposition will occur over time. These will cause membrane fouling. Fouling can occur due to different foulants such as biological and organic foulants. Over time, this will resulted in reduction of membrane efficiency and eventually reduce its lifetime (Jepsen et al., 2018). Common practice to mitigate fouling of a membrane includes backwash and crossflow set up. However, even with these steps; the flux of a membrane can reduced up to 80% due to the fouling cases (Ashaghi et al., 2007).

Application of membrane for PW treatment in previous studies suggested that fouling is a problem that requires attention (Jepsen et al., 2018). For offshore platforms, additional units to manage this fouling issues can lead to undesirable cost with membrane application (Fakhru'l-Razi et al., 2009).

Another way to mitigate membrane fouling is by coupling it with photocatalyst. The photocatalyst ability to degrade foulants, improved membrane hydrophilicity and potential of antibacterial properties had been the reasons of this possibility (Nasrollahi et al., 2021).

Fouling can also be caused by biological matters build up on membrane surface. This is called as biofouling and was said to cause 45% of membrane fouling (Nguyen et al., 2012). Management of membrane biofouling in practice involves application of cleaning chemicals

and biocide. Disinfectant chemicals commonly used in water treatment such as chlorine react with components in water and produce harmful, carcinogenic disinfection byproducts (DBPs) (Prasse et al., 2020).

1.5.4 Ag-based membranes with antibacterial properties

Modification of membrane to make an antibacterial membrane can be an alternative to reduce biofouling cases (Samree et al., 2020). Nanoparticles such as silver, in the form of its ions or other silver-based materials, have been widely known to have good antibacterial properties. It has been used and studied for the application in coatings (Orti-Lucas and Munoz-Miguel, 2017), medical applications (Xu et al., 2020) and water treatments (Tan et al., 2022). Incorporating silver nanoparticles into membranes can reduce biofouling by inhibiting bacterial growth (Aryanti et al., 2017).The application of silver in membranes for antibacterial and anti-biofouling purposes has been studied for some times.

Nanoparticles of silver (10-100nm) have high antimicrobial potential without harming human (Zhu and Lua, 2021). The mechanism of inhibitory action of silver on microorganisms is partially known and is still being discuss (Hou et al., 2015). Silver ions (Ag^+) oxidized from AgNPs are the most discussed in silver antibacterial activity studies, and it is accepted as at least a part of their antibacterial properties (Marambio-Jones and Hoek, 2010). Naturally, silver can be oxidized in the presence of oxygen and generate silver ions (Ag^+) which can be released around the membrane in water and leach into the solution. Silver ions are proposed to have the ability to attack bacteria's cell walls (Prabhu and Prabhu, 2012, Yin et al., 2013, Ng et al., 2013), which induces dysfunctionality and eventually death. Other routes suggested Ag^+ attacking enzymes, nucleic acid, and DNA (Pan et al., 2018, Mannix-Fisher and McLean, 2021).

Apart from that, during the contact with AgNPs or Ag^+, the generation of reactive oxidative species (ROS) can induce oxidative stress and contribute to bacterial inhibition (Fan et al., 2019, Jeon and Lee, 2020). For example, Hou et al. (Hou et al., 2015) implanted Ag ion in TiO_2 thin films. They concluded that the higher the silver ion released from the thin film, the higher its antibacterial activity. However, they also proposed that the silver ion can generate ROS, which is the actual route that the bacteria was damaged. Another route will be the role of silver nanoparticles (AgNPs) themselves, which can directly damage the cell membranes when in contact with the particles (Marambio-Jones and Hoek, 2010, Goei and Lim, 2014,

Peng et al., 2020). Smaller sized AgNPs can also penetrate into the cell and disturb the cell's function (Yin et al., 2013).

For application in industrial scale and release of wastewater into natural water sources, uncontrol silver release, however, can cause other challenges such as silver accumulation in water resources that can then be toxic to other aquatic animals. The uncontrolled silver release over time will also cause a reduction of the membrane lifespan (Uz et al., 2020). Many factors can influence the silver dissolution activity. These include surface coating and functionalization, temperature, pH, dissolved oxygen, presence of other materials such as organic matter and other ions (Sotiriou et al., 2012).This factors can determine the silver ion release into solution and possible reaction to microorganisms by the ions can be discussed.

With antibacterial property, deposition of silver on membrane resulted in an antibacterial membrane which potentially able to reduce biofouling phenomena (Samree et al., 2020). Table 1.5 shows some studies on Ag-based membranes with antibacterial activity. Most of these membrane preparations involve polymeric materials whether as the membrane itself or as the coating material. As discussed in membrane preparation before, (Section 1.5.1), polymeric membrane has some limitation for application in wastewater treatment due to its lower durability. The incompatibility of antibacterial nanocomposite with polymeric material can also cause limitation in the application as it resulted in the detachment of materials from the membrane (Aryanti et al., 2017).

The reported studies here also mostly proposed the silver ions released from membrane as the main reason for antibacterial criteria of the membrane. Sizes of AgNPs reported in these studies were less than 100 nm, or doped nanoparticles such as $AgTiO_2$ were less than 200 nm in size (Li et al., 2015). In most of the studies, silver states were reported and assumed to be in metallic state based on the preparation method, even though some studies did not perform analysis to confirm the state of silver. In a silver-based antimicrobial membrane, factors such as the position, size and concentration of the silver can play important role in its antibacterial activity (Aryanti et al., 2017). Silver conditions and state can also influenced its antibacterial performance (Lalueza et al., 2011).

Table 1.5 Silver based membranes with antibacterial activities

Membr.	Preparation method	Silver condition	Antibacterial performance	Proposed mechanism	Ref.
Ag/TiO_2/PVDF	1) TiO_2-PVDF prepared via blending 2)Photoreduction of silver	Ag/TiO_2 nanoparticles: 40 nm – 200 nm Ag in Ag^+ and Ag^0 state	High efficiency on E. coli compared to pristine membrane observed using disk diffusion method under visible light	Destruction of cell wall by reactive species (•OH) under light	(Li et al., 2015)
TFC-S-AgNPs	1) TFC membrane was prepared through interfacial polymerization 2) AgNPs was attached to Polyamide (PA) thin film composite via covalent bonding	AgNPs size: 14.8 nm	Clear surface (LB media + E. coli) observed under TFC-S-AgNPs membrane compared to other membranes.	1) Ag^+ attack by enhancing ROS generation 2) AgNPs attached to the cell membrane and disturb the cell function	(Yin et al., 2013)
Nanocomposite membrane with embedded AgNPs	Wet phase inversion technique to embed AgNPs in polysulfone membrane	Highest AgNPs size= 100 nm but uniformly distributed	Bacterial growth inhibition over 98% Bacterial detachment from membrane increase to 75% (compared to 18% for pristine membrane)	AgNPs as antibacterial and antiadhesive agent	(Liu et al., 2013)
Ag-TFN membrane	In-situ hybridization	AgNP size = ~35 nm	100% inhibition of E. coli, 91% inhibition of P. Aeruginosa as compared to bare TFC (19% for E. coli and 22% for Aeruginosa)	1)Direct contact with AgNPs 2)ROS generation 3)Ag^+ released	(Jeon and Lee, 2020)

Ag-MAF-PA	Ag-MAF prepared via metal and ligand dispersion method Ag-MAF-PA prepared via dispersion in MPD solution	Ag state: Ag3d peak at 366 eV and 372 eV.	75% E. coli inhibition	Ag^{+}	(Dadashi Firouzjaei et al., 2022)
AgNPs antibacterial PES membrane	Interfacial polymerization	Ag size: 10-100 nm	Killed 100% E. coli	Ag^{+}	(Zhu and Lua, 2021)
TiO_2-Ag-PVDF membrane	Dip coating	Ag average size = 5-20 nm	94 % antibacterial performance 65% biofouling reduction	Ag^{+}	(Samree et al., 2020)
PVDF/ Ag@TiO_2	Chemical reduction of $AgNO_3$ by ascorbic acid Embedment of prepared Ag@TiO_2 to PVDF membrane using APtes as crosslinker	Ag size = 20-35 nm	Higher flux achieved compared to non-modified membrane Significant inhibition efficiency for example 74% reduction with highest concentration of E. coli studied.	Not discussed	(Mishra et al., 2021)

Ion exchange membrane	Ion exchange method using $AgNO_3$ Reduction of silver under UV-light (photoreduction)	Ag state= metallic	Stable E. coli inhibition zone over few cycles	Not discussed	(Jiang et al., 2022)
AgNPs @PA membrane	Ag-based nanorods incoprated into PA active layer through interfacial polymerization	Ag size= ~5 nm Ag state= metallic silver	Low adhesion of bacteria on membrane surface	Direct killing proposed by the right size (small) and morphology (non-agglomerated AgNPS)	(Istirokhatun et al., 2022)
Ag-CNT	Chemical deposition using AgNO3	Ag size= 9.2 ± 3.0 nm	Significant hollow area around Ag-CNT, with high foulinf resistance	Ag^+ released react components in E. coli protein Direct contact to AgNPs ROS attacks	(Fan et al., 2019)
PI-Ag/CM	Half encapsulated AgNPs by polymide (PI), covalently grafted on ceramic membrane	Ag size= 50-80 nm Ag state= metal Ag and Ag-O		Ag^+	(Peng et al., 2020)
Ag-decorated TiO_2 membrane	Ag-TiO_2 deposited by sol-gel method on microporous alumina support. Photoreduction of Ag	Ag size = 20-30 nm	Highest Ag deposition shows highest antibacterial performance	Ag^+ Direct interaction with AgNps	(Goei and Lim, 2014)

Ag Nanosheet @ TiO_2 ultrafiltration membrane	2D silver nanosheets introduced into a sol to prepare the membrane	Ag size= 15 nm Ag state = based on peaks shown is Ag oxides	Clear inhibition zone with presence of silver	Ag^+	(Li et al., 2020)
AgNPs-TFC	In-situ prepation through formation of $AgNO_3$ active layer, then reaction with sodium borohydride ($NABH_4$) to form AgNPs.	AgNP size = less than 15 nm	Number of: E. coli reduced 78%, P. aeruginosa 91% and S. aureus 96% after 5 hours incubation.	Toxicity of AgNPs	(Ben-Sasson et al., 2014)
AgO-MF	AgO coating deposited via magnetron sputtering (MS-PVD) on microfiltration polyamide membrane	AgO nanoparticles size 25 nm	100% reduction of E,coli viability	AgO as strong bactericidical agent	(Kacprzynska-Golacka et al., 2020)

AgNPs: Silver nanoparticles, PVDF: Polyvinylidene fluoride, PA: Polyamide, PI: PolyimideCNT: Carbon Nanotube, TFC: Thin-film composite, TFN: Thin-film nanocomposite, MAF: Metal azolate framework, MF: Microfiltration, CM: ceramic membrane, MF: Microfiltration, AgO: Silver oxide.

1.6 Aim of the thesis

Oil and Gas Industry produced high amount of wastewater called produced water during the extraction process. Complete removal of dissolved organics in PW was reported to be challenging to treat and removed from the wastewater. Stricter regulations imposed by responsible bodies on Oil and Gas activities resulted in the need of new water treatment method. At just ambient temperature and pressure, photocatalysts offers a promising method to treat this diluted but non-biodegradable organic pollutants in water without the need of other functional chemicals.

Depositing potential photocatalyst on membrane removed the need of catalyst separation from wastewater which can caused secondary pollution. Apart from that, fixing photocatalyst can also help the delivery of light to the photocatalyst. Many photocatalytic membrane preparations reported involves polymeric membrane or polymeric binders. The

material can be degraded under light and due to the radicals generated in photocatalytic environment. Inorganic membrane offers better sustainability as it can sustain higher temperature and pressure. However, application of membrane is limited by membrane fouling phenomena where it reduces photocatalyst performance and eventually membrane lifetime.

Therefore, the thesis aims to evaluate the potential of $AgTiO_2$ coated on inorganic support for photocatalytic removal of dilute organics and the coating perspective to reduce membrane biofouling.

1.6.1 Research Objectives

1. Characterize $AgTiO_2$ powder and coating prepared by photodeposition of silver on TiO_2 using silver acetate (CH_3COOAg) solution.
2. Investigate the performance of $AgTiO_2$ coated membrane prepared under different silver concentration and examine the influence of salinity on its performance.
3. Study antibacterial property of the membrane
4. Study antibacterial property of $AgTiO_2$ membrane in a filtration system

1.6.2 Thesis Outline

As the overall objective is to investigates and study enhanced photocatalytic and antibacterial property of $AgTiO_2$ coatings. this thesis covers several chapters as can be seen in the thesis overview, Figure 1.9.

This dissertation consists of six chapters. This thesis begins with introduction of the study and literature review in **Chapter 1**. **Chapter 2** discussed the preparation and characterization of prepared AgTiO2 membrane via ICP analysis, SEM, TEM, and XPS analysis. The photocatalytic activity of prepared membranes was reported in **Chapter 3** and the influence of salinity was also discussed. **Chapter 4** focuses on the antibacterial property of prepared material, in various evaluation methods and proposed antibacterial mechanism that is most probable by these prepared membranes. **Chapter 5** evaluated the antibacterial performance of prepared membrane in a filtration system. While **Chapter 6** summarized main result and propose future work.

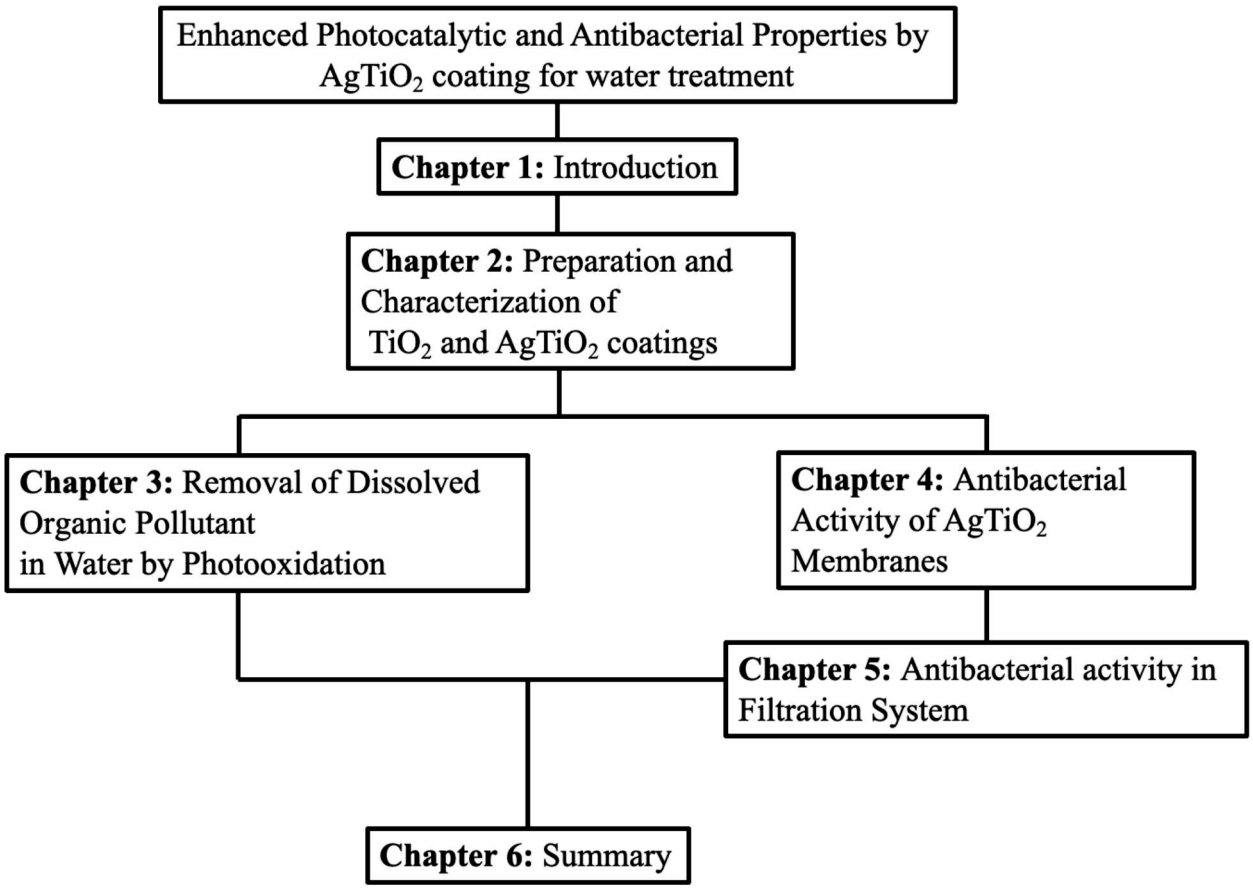

Figure 1.9 Thesis Overview

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CHAPTER 2

Preparation and Characterization of TiO_2 and $AgTiO_2$ Coatings

2.1 Introduction

Since the potential has been discovered by Dr. Fujishima (Fujishima et al., 2000), TiO_2 has been the semiconductor of choices in various studies for the application in advanced oxidation process due to its high photocatalytic efficiency, non-toxicity and cheaper price. Deposition of photocatalyst nanoparticles on membrane surface ease the separation step after the process and reduce the light scattering effect that can limit the light delivery.

TiO_2 application is limited by the high band gap especially to be use under visible light range. The rate of charge recombination is also quite fast, thus reducing the photocatalytic activity. Modification of TiO_2 improves its photocatalytic performance. Doping with Nobel metal has shown promising potential in decomposing diluted organics in water (Gao et al., 2018). Silver has been a favorable candidate for application in wastewater treatment due to its enhancement of photocatalytic activity, antibacterial, and non-toxicity (Chakhtouna et al., 2021). Photocatalytic potential of $AgTiO_2$ can depend on factors such as oxidation state of silver presence, size of the particles, amount of loaded silver (Chakhtouna et al., 2021).

Application of photocatalytic membrane offer advantages in real industrial wastewater treatment, where the organic pollutants can be decomposed and the photocatalyst can then be reused without having to have another separation process. There are many methods to deposit photocatalyst on membrane for this purpose and the characteristics of photocatalyst can be influenced by the preparation method. For example, application of polymeric binder to immobilized photocatalyst on membrane surface can possibly limit the light delivery to the photocatalyst itself.

This chapter reported the preparation of $AgTiO_2$ membrane and powder, then characterize them through different analysis to evaluate the size, distribution, state, and other conditions of the coating.

2.2 Material and Method

2.2.1 Membrane supports

Porous flat disks with a diameter of 47 mm were prepared and provided by Universitat Jaume I., Spain. They prepared the disks by using kaolin (ER, Calabar S.A. Spain), alumina (AR12B5, Aluminium Pechiney, France), and potato starch (Sigma Aldrich Inc. USA), with polyvinyl alcohol (PVA, Mowiol 4-88, Sigma Aldrich Inc. USA) as ligand and sintered at 1673 K for four hours. Resulting disks have an open porosity of 56.5 %, and the mean pore diameter is around 0.50 μm, measured by mercury intrusion at UJI. Figure 2.1 shows the XRD of the disks measured at UJI. Porous flat supports were composed of mullite and corundum, with a small proportion of cristobalite. Another type of support, glass fibre membrane was a commercial membrane and used as it is.

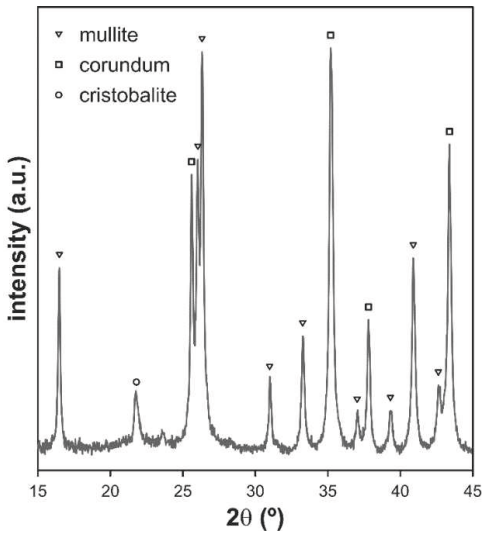

Figure 2.1 Fraction of the diffractogram of the support.

2.2.2 TiO_2 immobilization via mechanical deposition

For ceramic porous flat support, mechanical deposition of TiO_2 were performed. TiO_2 (Aeroxide P25, Evonik Industries, Germany) immobilization on flat and tubular support was performed via mechanical deposition on support surface. Then, the support was calcined in air at 400ºC for 3 hours with temperature rising rate of 5 ºC/min. This method used to fixed TiO_2 on porous support did not require any solvent or binder, making it a facile and a more environmentally friendly process (Kumakiri et al., 2011) . Under heat treatment, catalyst was sintered to the substrate by forming physical bonding and harden the catalyst on the substrate

surface. Prepared flat membrane were characterize by scanning electron microscopy (FE-SEM, JSM-633F, JSM-7600FG, JEOL Ltd. Japan).

2.2.3 Preparation of TiO_2 coatings via chemical deposition

TiO_2 was also deposited on glass fiber membrane by another method that does not require calcination (Kumakiri et al., 2022). 2.5g TiO_2 P25 was mixed with 43g IPA (Isopropyl Alcohol, FUJIFILM Wako Pure Chemical Corporation, Japan, purity 99.7%) solution and ultrasonicated for 10 minutes. TTIP (Titanium Tetraisopropoxide, Wako Pure Chemical Industries, Ltd., Japan, purity 95 %) solution was added and sonicated again for another minute. After that, glass fiber membrane was soaked in solution for 30 seconds and took out from solution. After drying for two days to remove IPA solution, the membrane was heated at 120ºC for 2 hours. The membrane was then washed and dried before usage. This membrane was also characterize using FE-SEM.

2.2.4 Silver photodeposition on TiO_2 membranes

Following TiO_2 immobilization on supports, deposition of silver on TiO_2 was performed through photoreduction treatment method (PRT) as reported in previous study (Wodka et al., 2010). For flat membrane and glass fiber membrane, one piece of membrane was used with surface area of 17.35 cm^2. Prepared TiO_2 membrane was placed into 30g of different (1 x 10^{-5} mol/L to 1 x 10^{-3} mol/L) silver acetate (CH_3COOAg, FUJIFILM Wako Pure Chemical Corporation, Japan with purity >97%). and irradiated under UV-light (black lamps) at light intensity of 3.3 mW/cm^2 for 1 hour. Three pieces of black lamps (TOSHIBA, maximum light emission at 352 nm) were used for this purpose. The light strength was measured by a photometer (C10427H102428, Hamamatsu Photonics, Tsukuba, Japan). Inductive Coupled Plasma (ICP) emission spectroscopic analyzer (SSI Nanotechnology Co.Ltd. SPS3500) was used to analyze silver amount. The difference between Ag amount detected was considered as deposited silver on TiO_2 membrane; as shown by equation (2.1) below.

$$\text{Loaded Ag (mg)} = \left(\Delta\text{Ag concentration before and after PRT, } \frac{\text{mg}}{\text{L}}\right) \times PRT\ vo. \quad \ldots (2.1)$$

Deposition percentage was also calculated based on equation (2.2) below.

$$\text{Deposition \%} = \frac{\Delta\text{Ag concentration before and after PRT, } \frac{\text{mg}}{\text{L}}}{\text{Initial concentration of Ag, } \frac{\text{mg}}{\text{L}}} \quad \ldots\ldots (2.2)$$

For further observation, $AgTiO_2$ was also prepared as particles (powder). Since the amount of silver was very low, it is harder to observe the particle on membrane surface. With

the same silver solution and amount as above, 150 mg of P25-TiO_2 powder was used. After photodeposition, the suspension was centrifuged and washed with distilled water. The size and distribution of $AgTiO_2$ prepared via photoreduction was carried out on powder form by TEM (JSM-7600F JEOL Ltd, Tokyo, Japan). Powder was dispersed in ethanol and sonicated before loaded on TEM grid. The state of silver on membrane and in powder form were analyzed by Thermoscientific K-Alpha X-Ray Photoelectron Spectroscopy (XPS) using AlKα radiation of 1486.6 eV. The C1s peak for XPS was calibrated at 284.8 eV.

2.3 Results and Discussion

2.3.1 TiO_2 immobilization

2.3.1.1 Mechanical deposition on flat support

The weight of flat porous membrane increased in average around 0.06 g after TiO_2-mechanical deposition. Figure 2.2 a) shows SEM surface image of bare porous support while Figure 2.2 b) is the surface of TiO_2 flat membranes. TiO_2 layer can be observed on support surface and through the EDS mapping, TiO_2 particles were covering the support surface. In the

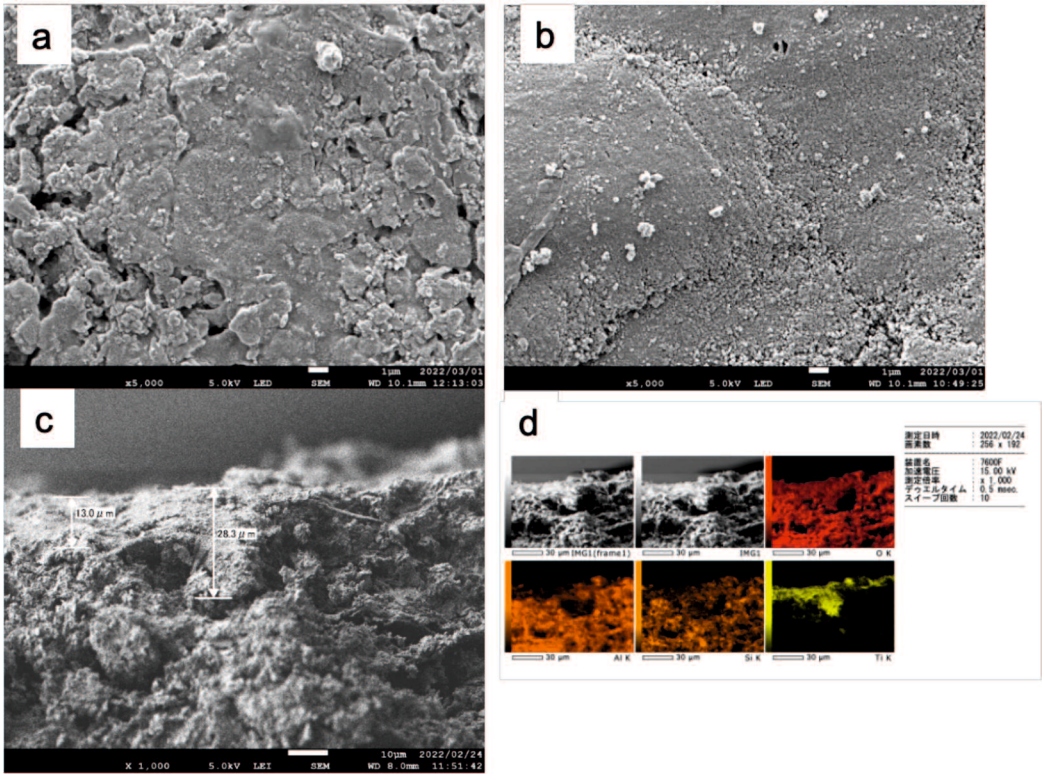

Figure 2.2 SEM images of a) Surface of flat support, b) Surface of TiO_2 coated flat support, c) Cross section of TiO_2 coated flat support, and d) EDS-SEM of c) (Che Abdul Rahim et al., 2022).

cross-section image (Figure 2.2 c), thickness of TiO_2 layer can be estimated around 13.0 µm, while some thicker deposition can reach up to 28.3 µm. The thicker part can be due to the porosity of the support. This is supported by the EDS mapping of membrane cross section, where TiO_2 element layer can be seen clearly on the support surface.

2.3.1.2 Chemical coatings on glass fiber membrane

Deposition of TiO_2 via chemical coatings were performed to glass fiber membrane. Membrane weight change was found to be 0.02 to 0.07 g. As the binder and solvent were removed via heating and drying, this can be regards as the weight of TiO_2 deposited on membrane surface. Figure 2.3 show the SEM image of glass fiber membrane before and after coated with TiO_2. From the 2.3 (b), we can see that the coating material covered and modified the fiber of the membrane.

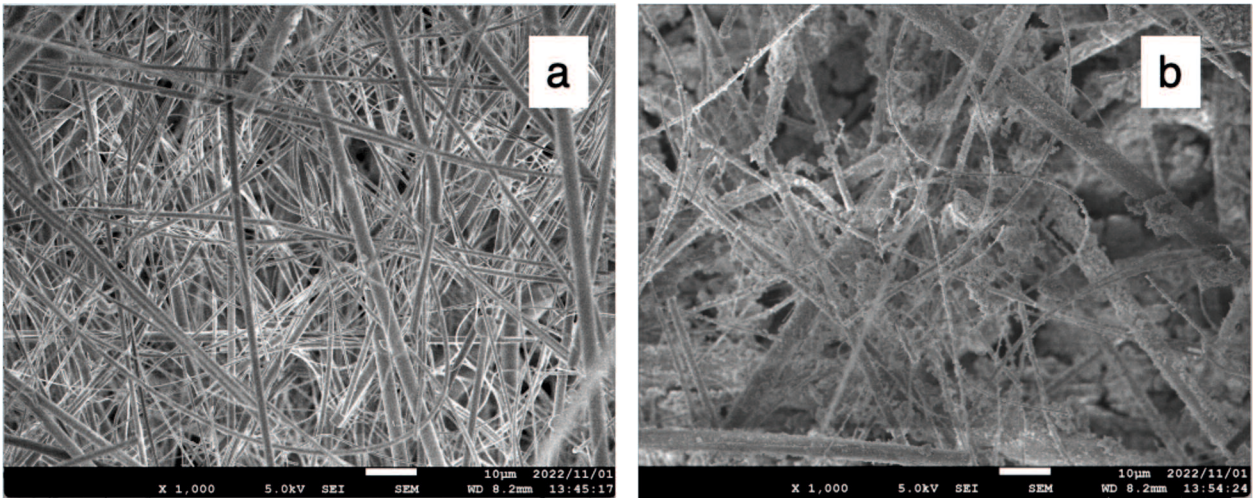

Figure 2.3 SEM images of a) Pristine glass fiber membrane, and b) TiO_2 coated glass fiber membrane

2.3.2 Influence of different silver concentration

In all conditions, the color of the TiO_2 powder/membrane changes from white to brownish with deposition of silver. The higher the amount of deposited silver, the darker the color changed.

Photochemical reduction of silver on TiO_2 under same condition has previously been reported to be higher than 85% silver deposition from silver salt precursor, CH_3COOAg (Che Abdul Rahim et al., 2023). In most of the cases, we can achieve higher than 90% deposition as can be seen in Figure 2.4. As shown in the figure, as the initial concentration of silver precursor,

CH_3COOAg increase, the amount of silver deposited also increased. Table 2.1 summarized the average silver amount (mg) deposited on TiO_2-membrane and TiO_2-powder based on equation 1. The results shows that photodeposition method deposited silver at the average of high percentage on the TiO_2 powder and on the membrane.

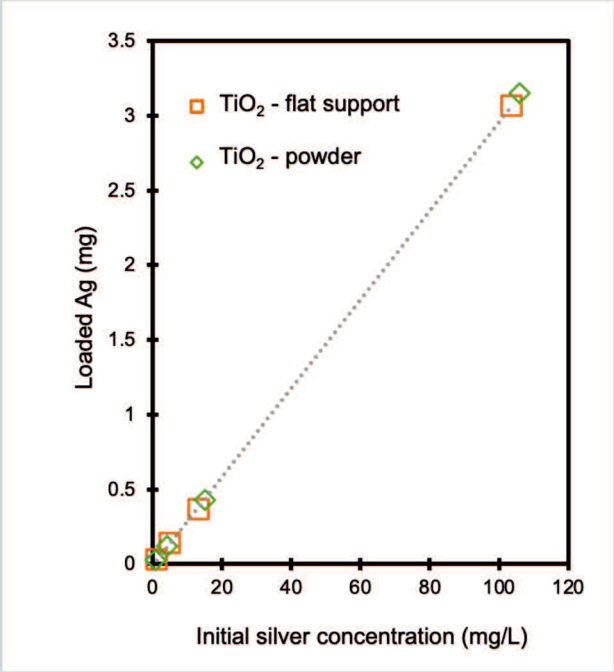

Figure 2.4 Initial silver concentration (mg/L) vs amount of silver deposited (mg).

Table 2.1 Comparison of different silver amount on membrane and powder

Sample	Initial silver concentration (mg/L)	Deposited silver	Deposition %
Powder preparation (mg/g-TiO_2)			
P-AgT1	0.936	0.167	90.26
P-AgT2	4.148	0.819	98.68
P-AgT3	15.249	2.814	93.70
P-AgT4	106.007	20.191	98.72
Flat membrane (mg/cm^2)			
F-AgT1	1.155	0.002	90.30
F-AgT2	4.945	0.008	97.48
F-AgT3	13.156	0.021	93.67
F-AgT4	103.531	0.177	98.75

2.3.3 TEM-EDS on prepared powder

TEM analysis was carried on $AgTiO_2$ powder to observe the size and distribution of particles. Figure 2.5 shows TEM images of the $AgTiO_2$ powder prepared by photoreduction method. For lower silver concentration (Figure 2.5 a) and b), no silver particles can be detected in these images. In contrary, Figure 2.5 c) and d), shows spherical silvers highly distributed and can be seen overlapping between particles. However, not all images were able to be used to evaluate the silver spherical size due to low amount or intensity that caused overlapping. Figure 2.6 then shows TEM image of each concentration that allowed observation of the silver spherical clearer. The size of spherical silver seems to increase from Figure 2.6 a) to Figure 2.6 d) as the concentration of silver increased. Figure 2.7 shows the histogram of silver sizes from AgT1, AgT3 and AgT4 images in Figure 2.6. AgT2 TEM image (Figure 2.6 b)) shows limited number of silvers to perform the size evaluation. Based on the evaluation in Figure 2.7, the sizes of silver in lowest concentration shown in Figure 2.6 a) (AgT1) were mostly 1-2 nm, while for AgT3 (Figure 2.6 b)), the size of silver increased to average of 2-6 nm. Highest silver concentration (AgT4) in Figure 2.6 c) shows bigger sizes of silver in the range of 2-10 nm. However due to overlapping of particles, the sizes here can only be estimated.

Figure 2.8 then shows the EDS mapping of elements, Ti and Ag of the particles at different silver concentration. This figure supported that that both the size and the size distribution of silver particles increased with higher silver precursor concentration. For lower concentrations (AgT1 and AgT2), due to the low concentration of silver, it is harder to scan silver element clearly in the sample, however, we can conclude that there is no silver agglorometion found in the samples.

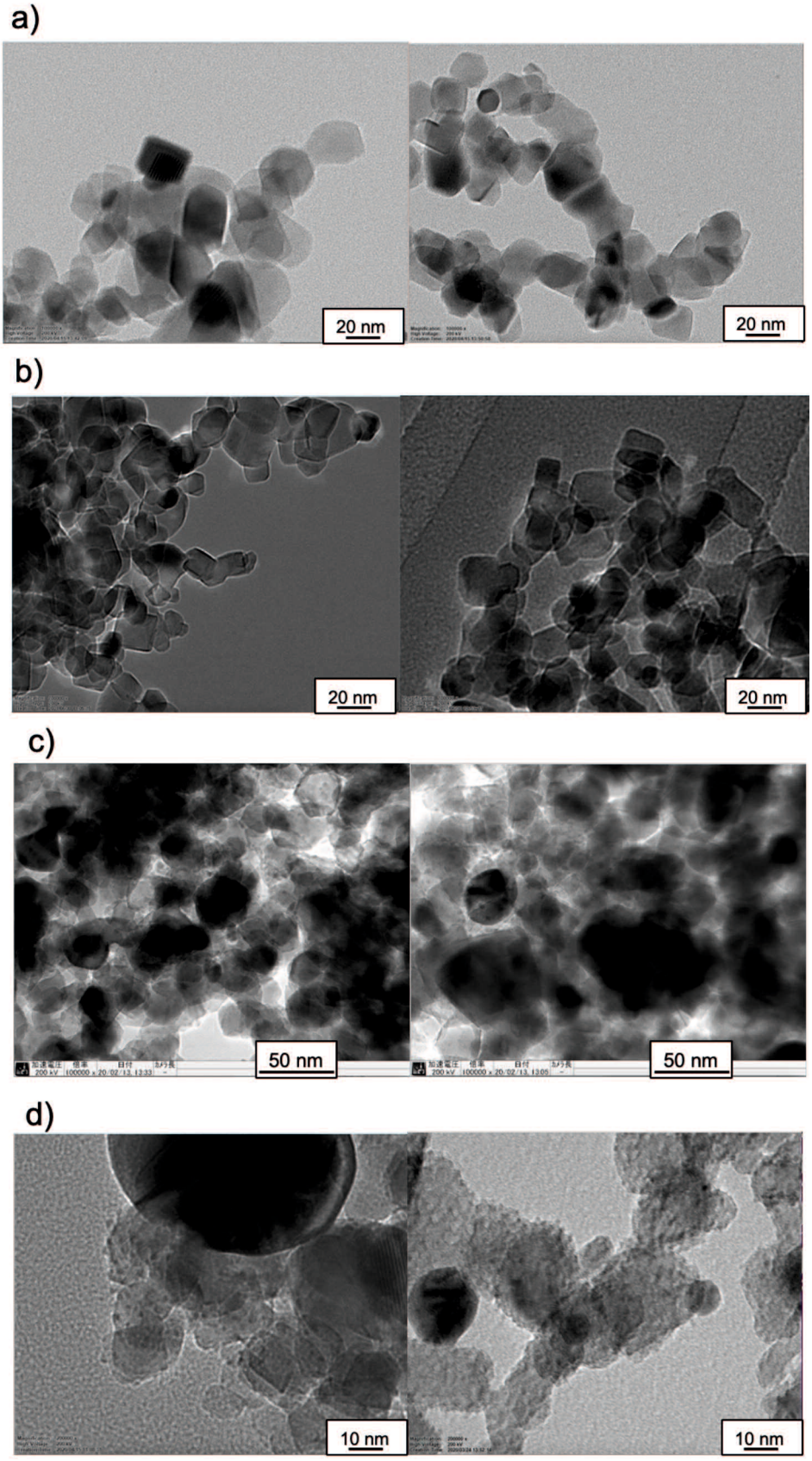

Figure 2.5 TEM images for $AgTiO_2$ powder with different silver concentration, a) AgT1, b) AgT2, c) AgT3 and d) AgT4

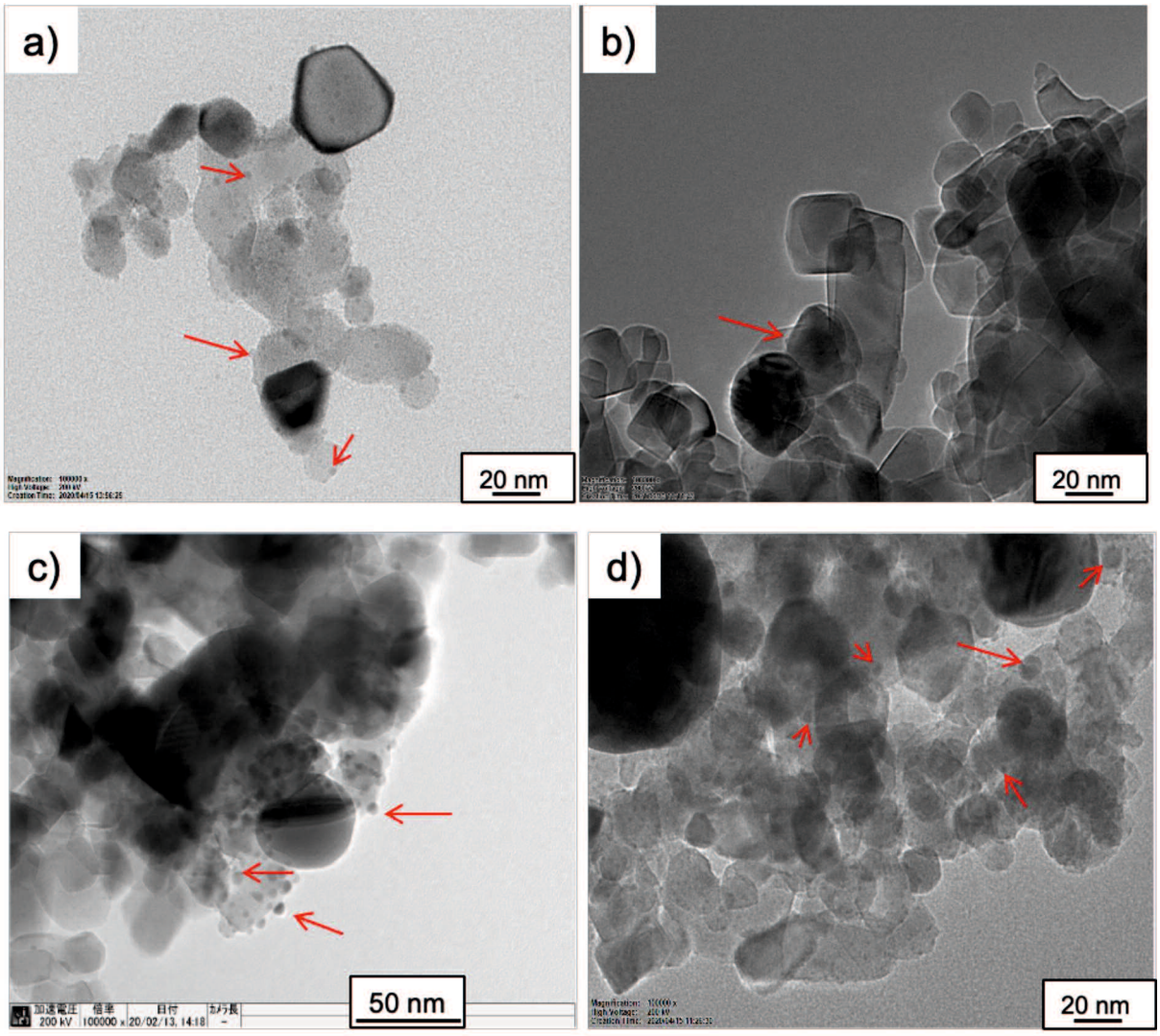

Figure 2.6 100k x Magnification TEM image on $AgTiO_2$ powder at different initial silver concentration a) AgT1, b) AgT2, c) AgT3, and d) AgT4.

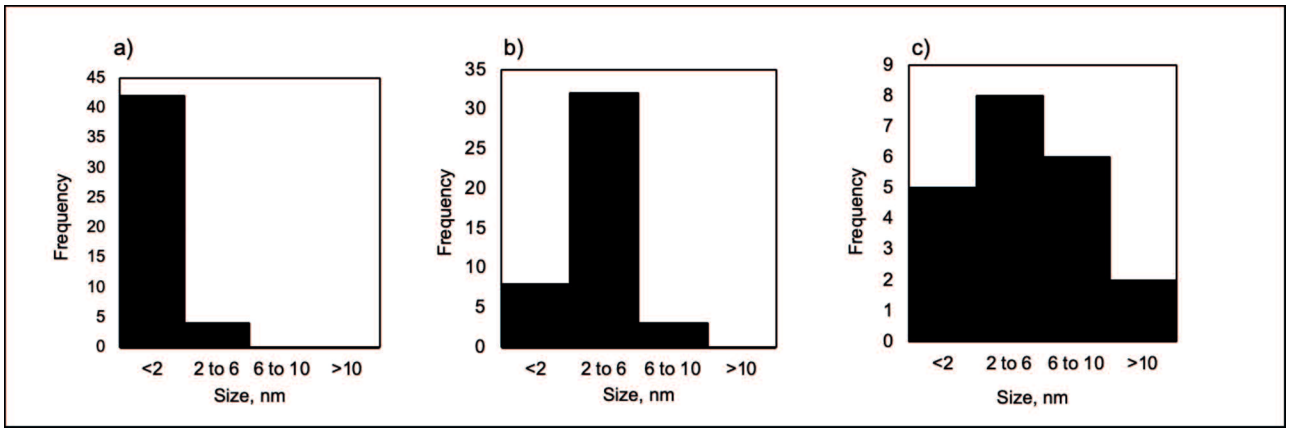

Figure 2.7 Histogram of silver size distribution for based on image in Figure 2.6 (a, c, and d).

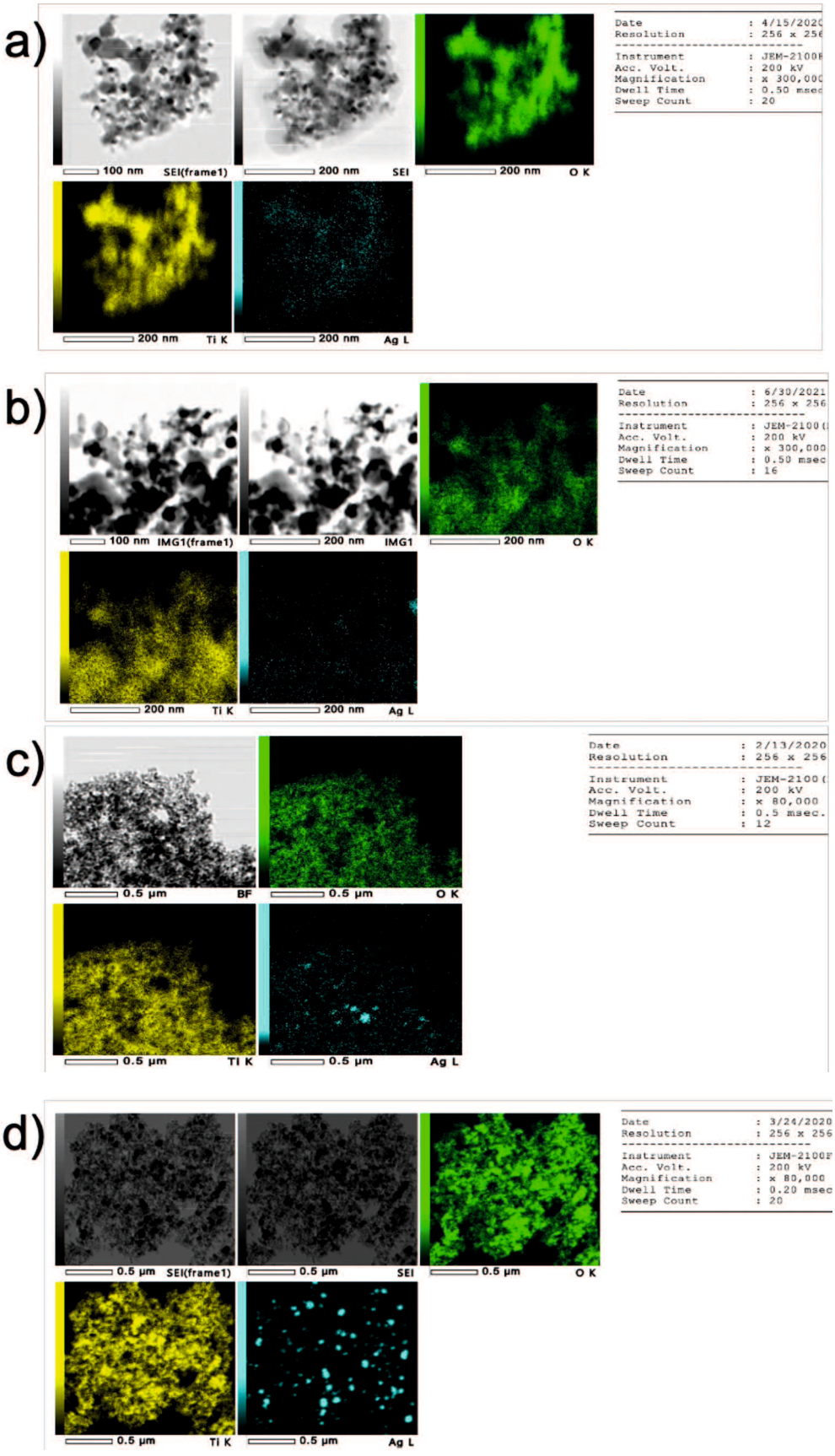

Figure 2.8 EDS mapping of elements of $AgTiO_2$ powder; a) AgT1, b) AgT2, c) AgT3, and d) AgT4. Figure 2.6 b) and d) were published in (Che Abdul Rahim et al., 2023).

2.3.4 XPS analysis on prepared powder

Figure 2.9 shows XPS results of $AgTiO_2$ powders prepared with solutions of two different Ag concentrations. Figure 2.9 a) shows the survey scan. The existence of silver was more apparent in the AgT4 sample, because the significantly higher amount of silver on AgT4 powder sample (Table 2.1). Figure 2.9 b) shows O1s core-level spectrum with the main peak at 529.6 eV showing lattice O^{2-} present in many metal oxides (Le et al., 2018), which is related to TiO_2 lattice and silver oxides. Fitting the peak with a nonlinear least-squares fit program using the Gauss-Lorentzian equation, shows appearance of a smaller peak at around 530 – 531 eV which represents hydroxyl groups related with adsorbed H_2O on the sample's surface (Mohanty et al., 2012). Figure 2.9 c) shows the Ti2p main peak located at 458. 4 eV ($Ti2p_{3/2}$) and another peak at 464.1 ($Ti2p_{1/2}$), which correspond to Ti^{4+} from TiO_2 (Le et al., 2018). Peak separation of 5.7 eV for Ti2p doublet, as shown in Figure 2.9 c), supported that Ti is in the Ti^{4+} state (Goei and Lim, 2014). Silver photo deposition did not affect the TiO_2 peak as reported earlier (Wodka et al., 2010).

Figure 2.9 d) shows Ag3d scan. Peak fitting performed on AgT4 suggested the existence of silver in three different states, Ag^0, Ag^+ and Ag^{2+}. The bonding energy for these 3 states reported by a study based on Ag-foil are 368.2 eV (Ag0), 367.8 eV (Ag_2O), and 367.4 eV (AgO). In Figure 2.9 d) we can see that the main state of our Ag was silver oxide, Ag_2O, observed at $Ag3d_{5/2}$, at 367.31 eV (AgT4) (Naumkin et al., 2012, Moulder et al., 1992). Silver metal (Ag^0) at 368.16 eV and a more oxidized silver state AgO (Ag^{2+}) at 366.74 eV were also found. Wodka et al. reported the formation of Ag^0 (Wodka et al., 2010) as the main Ag state from photoreduction of CH_3COOAg on TiO_2 nanoparticles. They used a strong xenon arc lamp of 250W. On the contrary, Li et al. (Li et al., 2015) reported a formation of Ag_2O. They used $AgNO_3$ as a precursor of silver and performed photoreduction under 20 W UV-light at a 10 cm distance for 10 minutes.

In our study, photoreduction was performed using three 8 W UVA blacklights from a 5.5 cm distance, which resulted in 3.3 mW/cm^2 light intensity. Weaker UV irradiation may cause the deposition of silver oxide instead of silver metal. Oxidation of metallic silver in the air (Viet et al., 2018) can be another possibility of the Ag_2O formation.

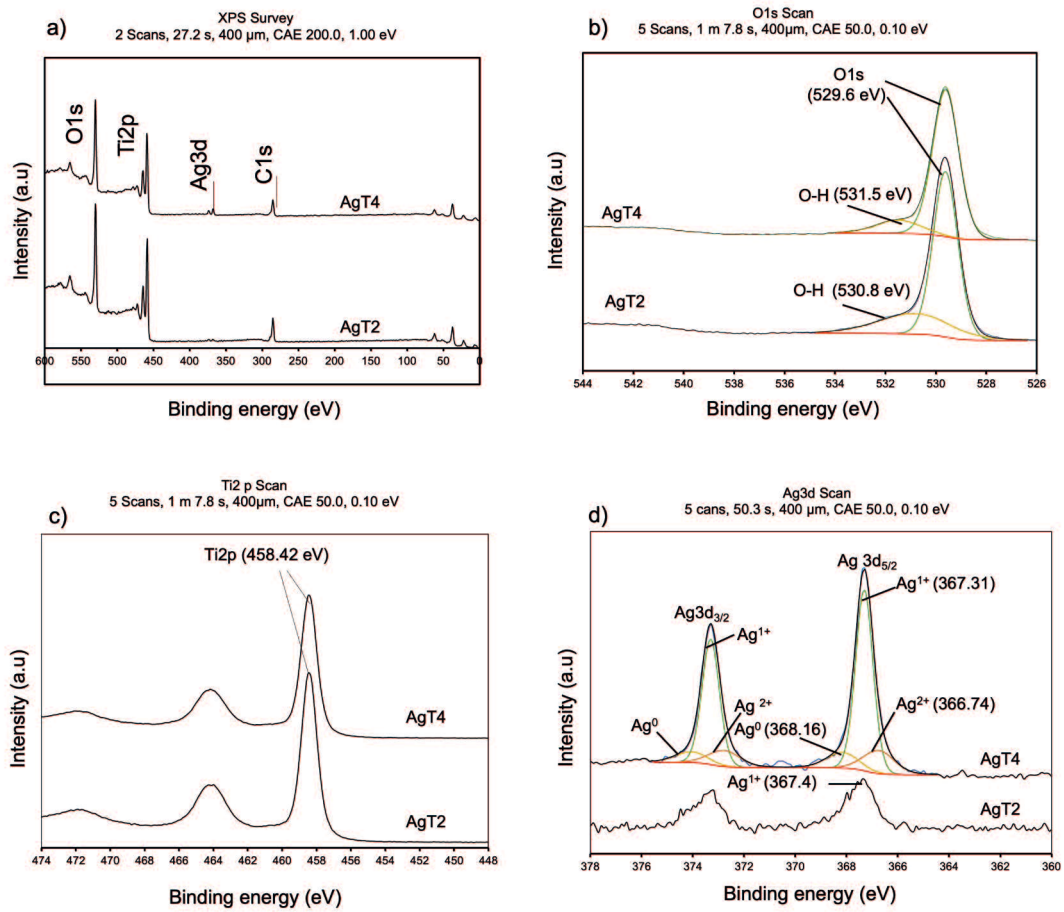

Figure 2.9 XPS analysis of $AgTiO_2$ powder at two concentrations (AgT2 and AgT4) a) Wide scan b) O1s peak, c) Ti2p peak, and d) Ag3d peaks with doublet fitting (Che Abdul Rahim et al., 2023).

2.3.5 XPS analysis on prepared membranes (flat support)

XPS analysis was also performed on TiO_2 and $AgTiO_2$ membrane at AgT4 concentration. Figure 2.10 shows the result of XPS scan where in Figure 2.10 a) of TiO_2 membrane, there are no appearance of Ag3d peak. While in Figure 2.10 b), the Ag3d peak can be seen. Double fitting of Ag3d peak shows that the state of silver is almost the same as in powder form; as shown previously in Figure 2.9 d).

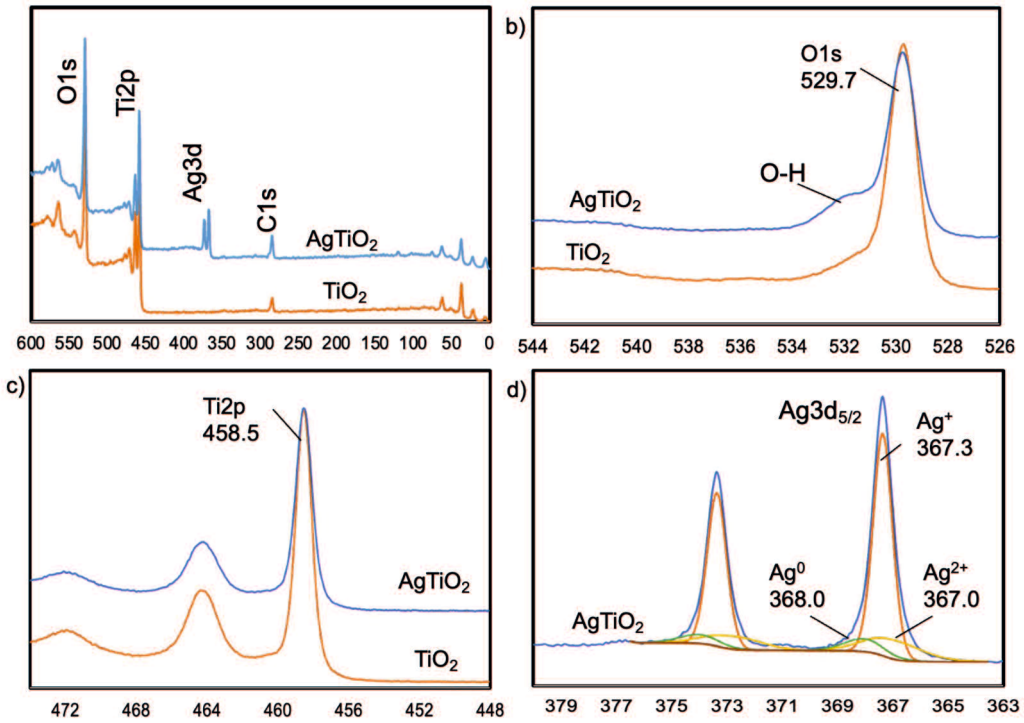

Figure 2.10 XPS analysis on TiO_2 and $AgTiO_2$ membrane a) Wide scan, b) O1s, c) Ti2p and d) Double fitting of Ag3d peak on $AgTiO_2$ membrane (Che Abdul Rahim et al., 2022).

2.3.6 Zeta Potential

Surface charge on TiO_2 photocatalyst can be affected by pH of the solution. Figure 2.11 shows the zeta potential of TiO_2 (P25) particles and $AgTiO_2$ particles measured by Zetasizer Ultra (Malvern Instruments Ltd.). HNO_3 and NaOH were used to adjust the pH of the solution. (Che Abdul Rahim et al., 2022). The silver deposition of $AgTiO_2$ here were 0.89 and 8.9 mg-Ag/g-TiO_2, respectively.

From our preparation data, with around 0.06 g of TiO_2 loading on flat support, F-AgT2 membrane will have silver amount around 2.5 mg Ag/g of TiO_2. From Figure 2.11, the isoelectric point (IEP) of TiO_2 was about 6.5, which value is similar to what has been reported

(Lee et al., 2003). The IEP value became smaller with silver deposition on TiO_2. Increasing the silver concentration seems to not affect the isoelectric point of the particles.

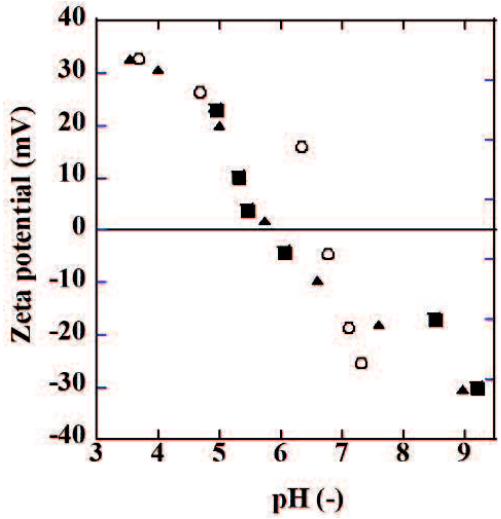

Figure 2.11 Zeta potential as a function of pH (○: TiO_2 (P25), ■: Ag-TiO_2 (0.89 mg-Ag/g-TiO_2), ▲: Ag-TiO_2 (8.9 mg-Ag/ g-TiO_2))(Che Abdul Rahim et al., 2022).

2.4 Summary

Photodeposition of silver salt, CH_3COOAg on TiO_2 membranes shows that regardless of the type of support and method of TiO_2 deposition on membrane support, high amount (>85%) of silver from the precursor were successfully transferred to the membrane as shown by ICP results. The higher concentration of silver precursor (CH_3COOAg) used during silver deposition stage (PRT); the bigger silver agglomeration can be found. Silver state observed via XPS was found to be mainly in oxide state in both conditions, particles, and membranes. Zeta-potential result shows that the IEP value of $AgTiO_2$ particles slightly lowered as compared to TiO_2.

***Note:**

Disk ceramic supports were prepared and characterized by XRD and other methods by Dr. S. Mestre. XPS analyses was performed by Mr. T. Tonosaki. Materials used for the zeta potential measurements were prepared and characterized using ICP by Mr. S. Yamada. The zeta potential measurements were performed by Dr. I. Kumakiri.

2.5 References

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CHAPTER 3

Removal of Dissolved Organic Pollutant in Water by Photooxidation

3.1 Introduction

Optimization of silver deposited on TiO_2 in photocatalytic decomposition of organics can depends on silver conditions, such as its size, oxidation state, and concentration (Abbad et al., 2020, Chakhtouna et al., 2021). Diluted organics will be of interest since it has been reported to be difficult to be removed through conventional methods (Faksness et al., 2004, Jimenez et al., 2018).

While various photocatalytic materials and membrane configurations have been studied, limited discussion on the photocatalyst activity under saline condition were found. Most discussion on salinity involves NaCl and the influence of salts are not fully understood. For a real wastewater application, especially since PW involves seawater, salinity can influence any treatment technologies used (Chakkunny et al., 2021).

In this chapter, the performance of prepared TiO_2 and $AgTiO_2$ membranes were observed through the photooxidation of formic acid. Formic acid is a simple organic, available in wastewater such as PW. Its decomposition is simpler and easier to follow for the purpose of discussion on the reaction. Influence of silver concentration on the prepared membrane towards the photooxidation of formic acid was discussed. Considering the PW treatment applications, sodium chloride (NaCl) and magnesium sulfate ($MgSO_4$), were used as salts. Magnesium chloride ($MgCl_2$) and potassium sulfate (K_2SO_4) were also used as comparisons. Since chloride ions enhanced silver ions released (Levard et al., 2013) from silver-materials, the silver dissolution from prepared membrane was also examined.

3.2 Material and Method

3.2.1 Photocatalytic decomposition of formic acid in water

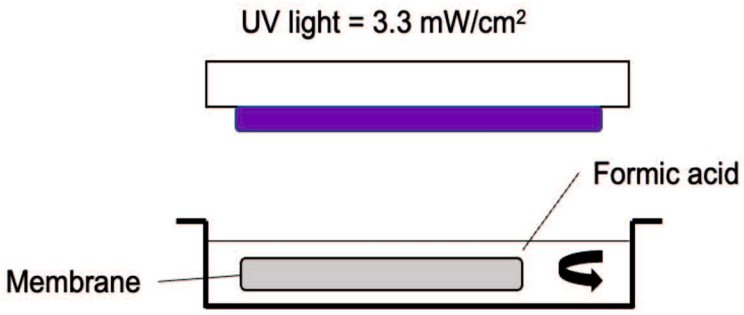

Figure 3.1 Experimental set-up

Figure 3.1 shows the experimental set up. Photocatalytic activity of prepared flat membranes and powder were evaluated by the decomposition of 0.02 weight % (0.2 mg/g) formic acid, (HCOOH, Fujifilm Wako Pure Chemical Corporation, Japan) diluted in water to make 40 g solution. Previous studies on diluted organics had been reported to use formic acid concentration around 200 mg/L (Kumakiri et al., 2011). Thus, we used the same concentration of formic acid (200 mg/L) in this study.

The membrane surface area was 17.35 cm^2 per membrane piece. Experiments were carried out at room temperature. A piece of membrane was soaked in the solution and kept under dark for 20 minutes before applying UV-light with the same intensity used in the silver photoreduction. Visible light study for photocatalytic activity has been of interest lately. This study used the intensity of black lamps that simulate the UV-A part of the sunlight.

Concentration of HCOOH was measured by UV-Vis Spectrophotometer UV-1800 (Shimadzu) at 205.6 nm wavelength. Standard curve for HCOOH was prepared in the UV-Vis photometric program. Photocatalytic decomposition of formic acid was carried out under UV light irradiation of 3.3 mW/cm^2 and 450 rpm agitation. Sample was taken over time and returned after UV-vis reading to continue the decomposition experiment.

3.2.2 Influence of salts towards photocatalytic activity

To understand the effect of salt ions to our photocatalytic membrane, different inorganic salts: NaCl, $MgSO_4$, $MgCl_2$, and K_2SO_4 (Fujifilm Wako Pure Chemical Corporation, Japan) were dissolved in 200 mg/L of HCOOH. Final concentrations of salts in 40 g HCOOH solution were: 60 mmol/L for NaCl, $MgSO_4$ and K_2SO_4. While for $MgCl_2$ was 30 mmol/L.

In study of different salt concentration, 0.6 mmol/L to 60 mmol/L NaCl and $MgSO_4$ were studied in the same manner as previous experiments. Performance of $AgTiO_2$ (AgT2) and

bare TiO_2 membrane were compared. Separate HCOOH UV-vis standard curves were prepared for each salt and concentration. Decomposition experiment was carried out with 450 rpm agitation to supply oxygen. The membrane was carefully washed after each experiment to remove salts residue.

3.2.3 Silver dissolution under experimental condition

To observe the dissolution activity under experimental condition as the photocatalytic study, prepared flat $AgTiO_2$ membrane were immersed in 40 g aqueous solution (in Formic acid and with salt presence) at room temperature. Experiments were carried out in dark and under UV-light and magnetically stirred at 450 pm for 1 hour. The concentration of silver remained in the solution was measured by ICP.

3.3 Result and Discussion

3.3.1 Decomposition of formic acid by prepared flat membranes

3.3.1.1 Influence of UV-light

Here the effect of UV-light on the decomposition activity was observed. Based on result shown in Figure 3.2, both TiO_2 and $AgTiO_2$ membrane (AgT2) shows almost negligible performance under dark condition. Formic acid concentration did not show changes over time. Some evaporation may occur which cause the concertation to increase over original concentration.

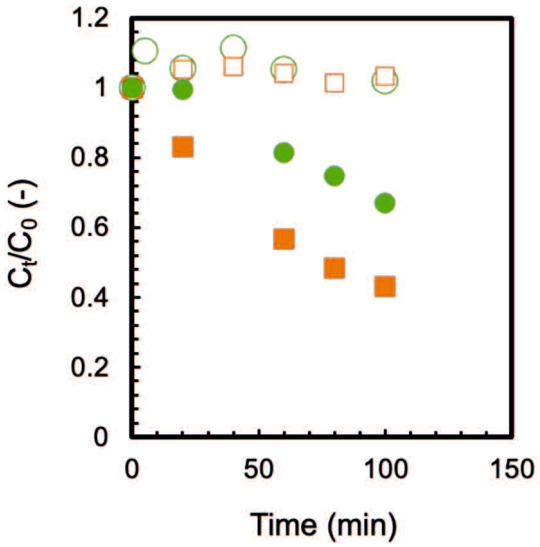

Figure 3.2 Decomposition of formic acid by ○ TiO_2 membrane and □ $AgTiO_2$ membrane prepared on flat porous support under Dark (open) and UV-light (close)

However, as UV-light were introduced, the concentration of formic acid reduced. This shows that the little influence of adsorption of formic acid to the membranes.

3.3.1.2 Influence of different silver concentration

Under UV-light irradiation, formic acid concentration reduced over time in the presence of prepared photocatalytic membranes. Figure 3.3 shows the results of photocatalytic decomposition of formic acid by different membranes. The concentration change was fitted with the first order equation to obtain the rate constant, k using the equation (3.1) below.

$$\text{Ln}\,(C_t/C_0) = -kt \ldots\ldots\ldots\ldots \quad (3.1)$$

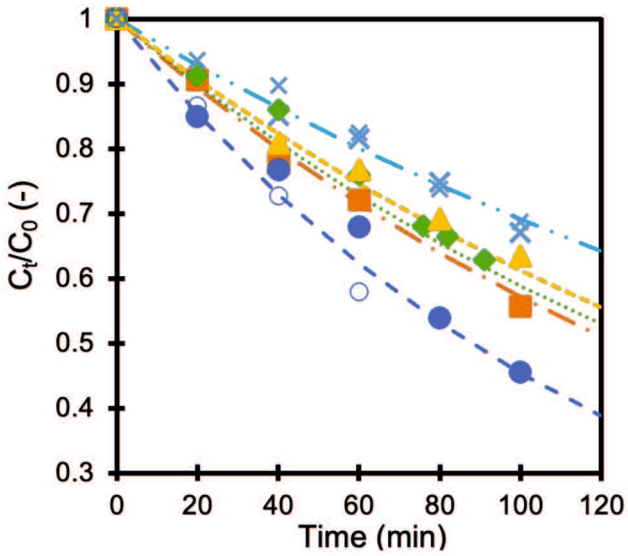

Figure 3.3. Normalized formic acid concentration as a function of time (x: TiO_2 membranes, ☐ AgT1 membrane, ○AgT2 membrane, ◇ AgT3 membrane, △ AgT4 membrane, smaller keys: repeated points with same membrane). All fitting line was obtained after repeating the experiment using same membrane (Che Abdul Rahim et al., 2022).

The experiments were performed at least twice by the same membrane to obtain the fitted line. Compared to without silver (TiO_2 membrane); silver deposition on the membrane improved its photocatalytic activity as can be seen in the summary of k-value (min^{-1}) in Table 3.1. However, as we can see from the results; addition of silver had an optimum value to the rate constant where excessive silver reduced the photocatalytic performance.

As we can see from results in chapter 2; deposition of higher amount of silver on TiO_2 membrane (AgT3 and AgT4) seems to result in higher agglomeration size of silver on TiO_2.

Deposition silver was reported to enhanced photocatalytic decomposition of formic acid by reducing the recombination rate of separated charges. (Pipelzadeh et al., 2011). However, at higher concentration, the agglomerated silver can then become the center of the charges recombination instead (Seery et al., 2007). Apart from that, the bigger size of silver on TiO_2 surface can possibly limit the delivery of light to TiO_2 surface to initiate the photocatalytic activity itself.

Table 3.1 Comparison of different silver amount on membrane

Flat Membrane	Mass of silver (mg/cm^2)	k x 10^2 (min^{-1})
TiO_2	0	0.39
AgT1	0.002	0.57
AgT2	0.008	0.78
AgT3	0.021	0.50
AgT4	0.177	0.48

3.3.1.3 Reproducibility of same preparation method (AgT2)

For the next experiments, AgT2 membranes which shows optimal performance were prepared with the same method to check its reproducibility. Result in Figure 3.4 shows that it is possible to obtain reproducible result with same preparation method. Moving forward, fresh AgT2 membrane used for next experiments are evaluated first to check the performance.

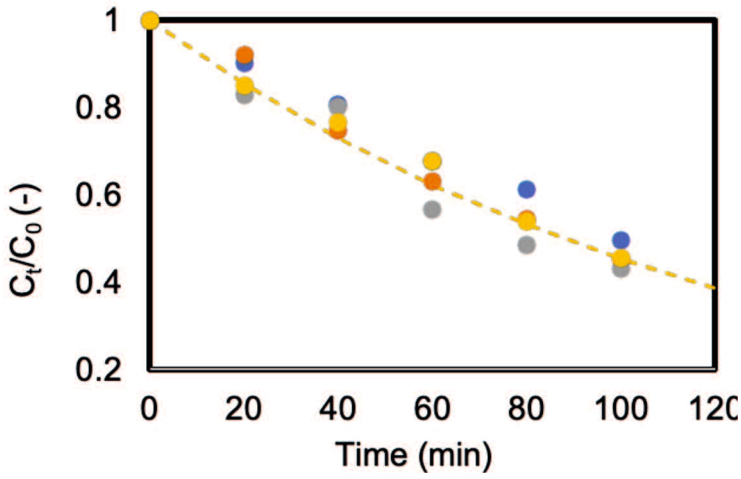

Figure 3.4 Evaluation on reproducibility of same preparation method on AgT2 membrane. Different color marker shows different membrane while yellow marker shows the membrane (AgT2) shown in Figure 3.3.

3.3.2 Influence of salinity

3.3.2.1 Influence of different salts

To study the influence of different salts towards the decomposition activity, TiO_2 and AgT2 (noted as $AgTiO_2$ membrane) membrane were used. Figures 3.5 a) and b) show the photocatalytic activity by TiO_2 and $AgTiO_2$ under the influence of different salts. Results show that addition of all different salts reduced the membrane performance.

Addition of 60 mmol/L NaCl into the solution reduced $AgTiO_2$ membrane to half (Figure 3.5 (b). It was also observed that the addition of NaCl (60 mmol/L) and $MgCl_2$ at same Cl^- concentration (30 mmol/L) shows almost same performance, while $MgSO_4$ and K_2SO_4 at same SO_4^{2-} concentration also shows comparable performance. These conditions suggest that the anions (Cl^- and SO_4^{2-}) plays role in the inhibition of formic acid decomposition both by TiO_2 and $AgTiO_2$ membranes. This changes on membrane activity were not permanent, where the photocatalytic performance return to the original performance under no salt conditions just after washing the membranes with water (open symbol in Figure 3.5).

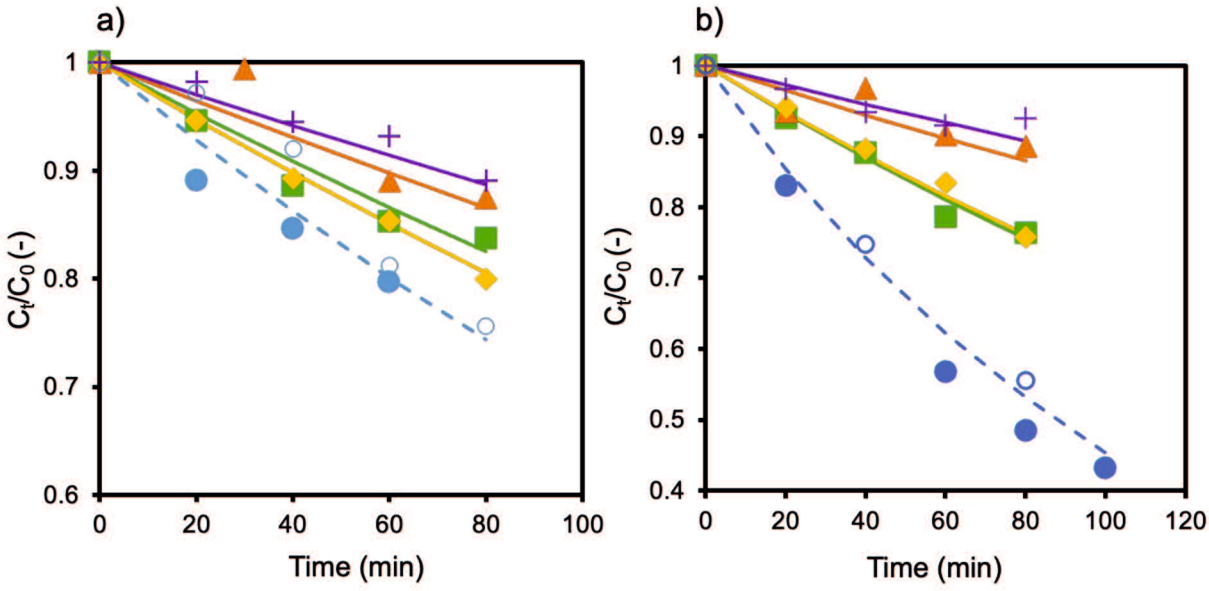

Figure 3.5 Influence of different salt towards formic acid decomposition; a) TiO_2 membrane, b) $AgTiO_2$ membrane; ○: No salt, □: with 60 mmol/L NaCl, ◇ with 30 mmol/L $MgCl_2$, △: with 60 mmol/L $MgSO_4$ and + with 0.06 mol/L K_2SO_4, Open ○: membrane performance after washing (no salt) (Che Abdul Rahim et al., 2022).

3.3.2.2 Influence of salt concentration

Figure 3.6 shows the influence of different NaCl and $MgSO_4$ concentrations on reaction constants of formic acid decomposition. The presence of $MgSO_4$ in the solution reduced the photocatalytic activity at all concentrations on both, TiO_2 and $AgTiO_2$ membranes. The inhibition effects were almost the same towards TiO_2 and $AgTiO_2$ membranes as can be seen in Figure 3.6 (a and b). Under the influence of NaCl, however, the effect was more severe on TiO_2 (Figure 3.6 a) as compared to $AgTiO_2$ (Figure 3.6 b))

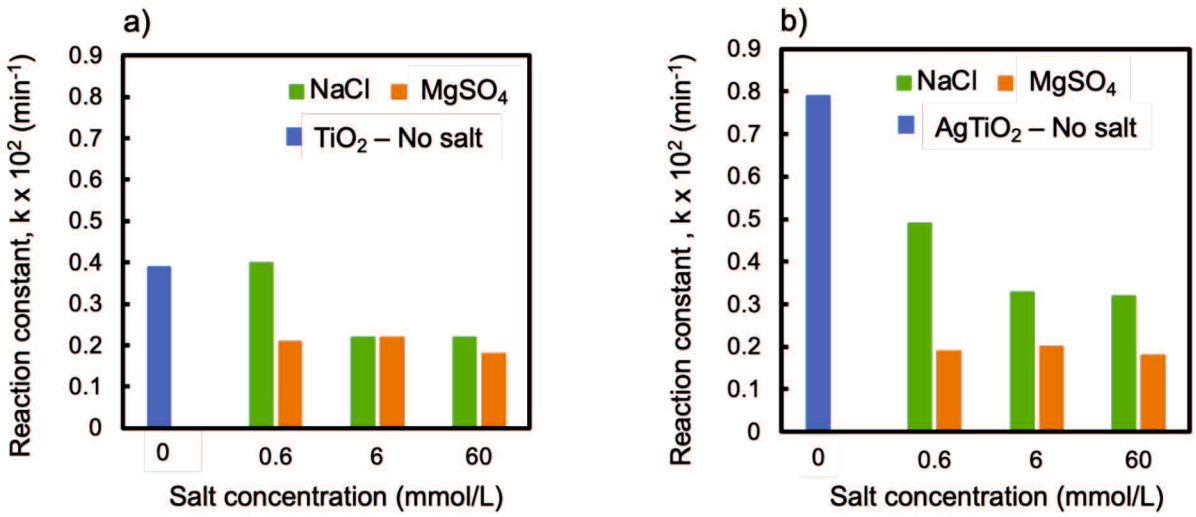

Figure 3.6 Influence of salt concentration on the rate constant a) TiO_2 and b) $AgTiO_2$ membrane (Che Abdul Rahim et al., 2022).

Formic acid pH in our experiment was 3.1 at the beginning concentration of HCOOH solution (0.2 mg/g) and then increase to 3.3 at half of the concentration of HCOOH solution (0.1 mg/g). With acidic pH during the experimental condition, the surface of both TiO_2 and $AgTiO_2$ would be positively charged during the experiments based on our zeta-potential result in Chapter 2.3.6. Thus, it can be proposed that the anions (SO_4^{2-} and Cl^-) presence in the solution can be adsorbed on the positively charged surface resulted in the alteration of the photocatalyst surface. Since the surface of photocatalyst is an important part in the photocatalytic reaction mechanism as shown in Figure 1.5 (Chapter 1), the adsorption of anions on the photocatalyst surface can limit the light delivery and also the generation of oxidative radicals.

3.3.3 Silver dissolution under experimental condition

Chloride ion was reported to enhanced silver dissolution in solutions (Levard et al., 2013, Uz et al., 2020). Figure 3.7 shows the influence of salinity and light towards silver dissolution into solution. Here it can be seen that higher silver amount can be detected under the presence of NaCl. Under UV-light, it seems that the silver detected were very low, suggesting that under UV-light, the silver ions released can be photoreduced again on TiO_2 surface. Figure 3.8 then shows that the higher concentration of NaCl, the higher silver amount released from the membrane. It has also been previously reported (Levard et al., 2013).

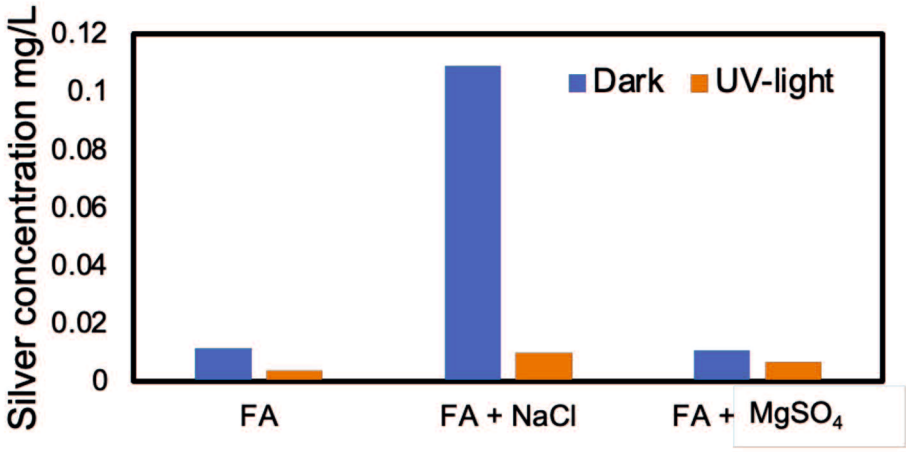

Figure 3.7 Silver dissolution from membrane in different conditions after one hour. (Salts concentration was at 60 mmol/L)(Che Abdul Rahim et al., 2022).

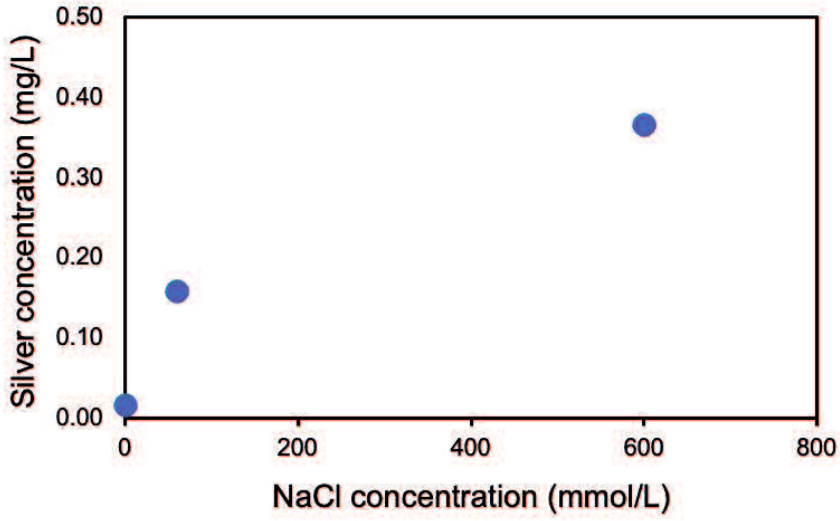

Figure 3.8 Influence of NaCl concentration towards silver dissolution from membrane after one hour

Silver is not environmentally stable where it can easily be oxidized into silver ions. Chloride ions are inorganic ligands that has strong attraction to silver and potentially form Ag-Cl complex (Levard et al., 2013). The solubility of these complex depends on the ratio of chloride to silver (Cl/Ag). We previously observed this condition by changing the silver concentration. In our current experimental condition, there are no white precipitate (Ag-Cl) can be seen but at higher silver concentration, the solution became cloudy (white precipitate formation). Therefore, it can be proposed that Cl^- ion in the solution attract the oxidation of silver to form Ag-Cl. However, since our silver concentration is low, the complex is very soluble (Levard et al., 2013), thus it dissociate back to silver and Cl^-.

Section 4.3.1 discussed the silver dissolution further for the conditions involved in antibacterial studies.

3.3.4 XPS analysis under experimental condition

For the purpose of observation on changes on $AgTiO_2$ nanoparticles under different conditions; XPS was performed on $AgTiO_2$ powder prepared using initial concentration of AgT4 (method explained in Chapter 2). Table 3.2 shows the main peak of sample under different conditions. Sample 1 and 2 were from same AgT4 powder sample, while Sample 3 and 4 were from another prepared AgT4 that was prepared two days earlier before applying UV/kept in dark. Sample 5 and 6 was separately prepared and placed in salts solution same as photocatalytic experimental conditions (Section 3.2.2) for 100 minutes (UV-light, stirring, room temperature). All samples were centrifuged, washed and recentrifuged before most of the supernatant was removed (except Sample 5 and 6 where they were not washed after salt experiments).

As can be seen, the state of elements shows no significant changes thus can be conclude that the characteristic of catalyst remained even after salt experiments. Table 3.3 shows $Ag3d_{5/2}$ peaks of different silver states and ratio of Ag/Ti for the samples. Result shows that under all condition, silver remained in oxide state as the main state (Ag_2O). However, the intensity of different silver states shows some variations under different conditions. Under no salinity conditions, metallic silver (Ag^0) was highest in the freshly prepared sample (Sample 1). This percentage reduced when the nanocomposite was kept over time as can be seen in sample 2. Comparing the same nanocomposites in dark (Sample 3) and under UV-light irradiation (Sample 4), it shows that under UV, higher percentage of metallic silver was present. UV-light might induce higher silver oxide to be reduced to metallic silver further. After salts experiments, sample with NaCl (Sample 5) shows almost same condition with sample 3, which

was saltless sample kept in dark. Peculiarly, behavior of sample after reaction with $MgSO_4$ shows higher metallic silver and lower silver oxide as compared to Sample 3 and 5. Sample under UV-light also shows the highest Ag/Ti ratio as compared to other samples similar to what has been reported (Wodka et al., 2010).

Table 3.2 Main peak of element under different conditions.

Sample	Condition	Ti2p	Ag3d3	Ag3d5	O1s
1	Freshly prepared	458.61	373.51	367.5	529.85
2	Kept in air in the lab> 7 days	458.47	373.45	367.46	529.65
3	Kept in dark > 4 hrs	458.42	373.3	367.3	529.62
4	Under UV-light > 4 hours	458.49	373.43	367.45	529.65
5	After NaCl experiment and kept in dark	458.57	373.13	367.38	529.8
6	After $MgSO_4$ experiment and kept in dark	458.73	373.53	367.52	529.96

Table 3.3 XPS analysis on $AgTiO_2$ powder: silver states %.

Sample	Ag_2O (A)		Ag^0 (B)		AgO (C)		Ag/Ti
	BE (eV)	%	BE (eV)	%	BE (eV)	%	
1	367.48	42.6	368.11	28.17	367.3	29.23	0.024
2	367.5	50	368.3	21.05	367.1	28.95	0.019
3	367.31	73.2	368.16	10.7	366.74	20.9	0.021
4	367.42	61.3	368	20.9	367.2	17.4	0.039
5	367.4	72.88	368.27	8.47	366.85	18.64	0.024
6	367.52	58.18	368.18	29.09	366.85	12.73	0.028

3.4 Summary

From this study, results show that the rate of photocatalytic decomposition of diluted formic acid decrease under the presence of salts. Zeta potential analysis in Section 2.3.6 previously shown that the photocatalyst (TiO_2 and $AgTiO_2$) surface is positively charged under acidic condition (formic acid solution). Thus, it was proposed that the negatively charged anions was adsorbed on positively charged surface thus hindering the photocatalytic activity.

However, the mechanism needs further study to understand the different influences of SO_4^{2-} and Cl^- on $AgTiO_2$ and TiO_2 membranes. XPS analysis shows that the silver state (Ag_2O) did not change in different conditions and after salt experiments. $AgTiO_2$ membrane shows improved photocatalytic performance compared to TiO_2 membrane. Even though the performance was affected by salinity, the results suggest a wider application potential of photocatalytic membranes. For a real PW application, the size of possible $AgTiO_2$ membrane was calculated. Based on a cost study report (Hackney and Wiesner, 1996), after primary treatments, 37.85 m^3/day amount of PW needed to be treated for its organics composition (the report used adsorption technology). With our membrane, we obtained k=0.0078 min^{-1} by 0.001735 m^2 membrane surface area in treating 40 g solution of organics. So, we proposed that with this information; 1641.74 m^2 membrane surface area is required to polish PW for the removal of dissolved organics.

3.5 References

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CHAPTER 4

Antibacterial Activity of $AgTiO_2$ Membranes

4.1 Introduction

Even though membranes application in water treatment offers advantages such as ease of operation and minimization of operating conditions, one of the limitations in the application will be the fouling phenomena. Prolong contact of membrane with wastewater will easily cause build-ups on membrane surface. This will cause the membrane fouling. Application of membrane filtration in PW treatment has reported that fouling cases can be a critical issue (Jepsen et al., 2018).

Biofouling is specifically referring to the microorganisms act as the foulant. Over time, microorganisms in contact with the membrane surface can attach to the surface, and form biofilm build up. Biofouling was said to cause 45% of membrane fouling (Nguyen et al., 2012). Biofouling can result in higher operating pressure on membrane application, poorer product quality, the need on frequent chemical cleaning and eventually shorten the lifetime of the membrane (Kang et al., 2004).

It was also reported that membranes affected with biofouling was found to be harder to clean due to the biofilm build up that protect the bacteria (Baker and Dudley, 1998). The biofilm layer can also make microorganisms resistance to biocide. Chemical cleaning using disinfectant such as chlorine is a common practice to control biofouling (Nguyen et al., 2012). However, chemicals application on a prolong period can damage the membrane especially polymeric membranes (Gohil and Suresh, 2017) and also it can be harmful to human and animal health by generating carcinogenic byproducts (Prasse et al., 2020).

Modification of membrane with antibacterial property is another way that can control biofouling cases. Silver, with a significant antibacterial property has been applied in various application to control bacterial growth such as medical (Xu et al., 2020), coatings (Orti-Lucas and Munoz-Miguel, 2017), and water treatments (Tan et al., 2022, Zhu and Lua, 2021) . However, the silver's role in the antibacterial activity is still not fully understood (Hou et al.,

2015). Ag^{+} is commonly accepted as the main mechanism in silver's antibacterial activity, while generation of reactive oxygen species and silver nanoparticles itself has also been reported to contribute to the activity.

For application in industrial scale and natural water source, uncontrol silver release from silver-based material can cause other challenges such as silver accumulation in water resources that can then be toxic to other aquatic animals. It can also eventually reduce the lifespan of the membrane (Uz et al., 2020). Many factors can influence the silver dissolution activity. This includes surface coating and functionalization, temperature, pH, dissolved oxygen, presence of other materials such as organic matter and other ions (Sotiriou et al., 2012).

This chapter study the antibacterial activity of prepared $AgTiO_2$ membrane. The silver dissolution under experimental condition was also investigated in order to see the effect of silver ions available in the solution. Other antibacterial tests were explored to propose potential $AgTiO_2$ membrane antibacterial activity.

4.2 Material and Method

4.2.1 Preparation of samples

For silver dissolution study, the fresh whole membrane prepared via method such as in Chapter 2 of flat membrane was used. Two concentrations of CH_3COOAg were studied where low Ag (5×10^{-5} mol/L) and high Ag (1×10^{-3} mol/L) concentration were compared. This is the same concentration as AgT2 and AgT4 as the previous section (Chapter 2). Membranes was washed and dried before usage. Apart from that, bare flat support was soaked in 5×10^{-5} mol/L CH_3COOAg for 1 hour in dark condition to make Support-Ag sample. This membrane was left to dry before dissolution test.

For antibacterial study, TiO_2 powder was mechanically deposited on membrane, then it was cut further before silver application. Same as whole membrane in dissolution study above, 30 g of two CH_3COOAg concentrations were used, low Ag (5×10^{-5} mol/L) and high Ag (1×10^{-3} mol/L) and PRT was performed on TiO_2 membranes. After the silver deposition, the membranes were cut further smaller and sonicated in water to remove residues from cutting. For the purpose of differentiating them over whole membrane, cut membrane were labelled (AB) used for antibacterial test. From ICP results, deposited silver was 3-4 times higher than the whole membrane. Support-Ag (AB) was also prepared by cutting and sonicating the bare membrane to smaller pieces, before soaking in 30 g 5×10^{-5} mol/L CH_3COOAg same as the

whole membrane. Based on ImageJ (National Institutes of Health (NIH), United States) analysis, surface area of cut membranes were 0.52 ± 20% cm^2. All these samples including bare support and TiO_2 membranes were autoclaved at 120°C for 20 minutes prior usage.

Moving on, another membrane, Treated $AgTiO_{2\text{-low Ag}}$ membrane was prepared by removing silver oxide layer from $AgTiO_{2\text{-low Ag}}$ in 0.09 M NaCl solution for more than 3000 minutes in the incubator (37°C) before Vacuum Dried at 120°C for 20 minutes to imitate the autoclave condition. Higher temperature fastens the dissolution of silver. For transportation, these membranes were transferred in Nitrogen gas, to avoid further oxidation of silver left.

4.2.2 Silver dissolution under experimental condition

Prepared flat membranes were immersed in different 40 g aqueous solution at room temperature. For the influence of salt, same concentration of NaCl with LB media was used (0.09 M). While for saltless influence, the solution was only water. All the experiments were carried out in dark and magnetically stirred at 450 pm. Membrane were soaked in the solutions for different periods with no particular order meaning. After a particular time of immersion, the membrane was removed from the solution, rinsed with water, and soaked in a fresh solution. The concentration of silver remained in the solution was measured by ICP. For reproducibility, same membrane was soaked at least twice for the same duration to discuss the effect of time duration towards silver dissolution. A few membranes were prepared under the same conditions and tested to confirm the results.

4.2.3 Antibacterial study

4.2.3.1 Microorganisms and Media

In most studies, *E. coli* bacteria were used to evaluate biofouling of membranes. This study used *E. coli* strain DH5α obtained from Hoshida Lab (Yamaguchi University) and was maintained on Luria-Bertani (LB) agar plate. The cells were then inoculated freshly (pre-culture) each time a day before usage in LB medium prepared using 0.5% yeast extract, 1% peptone (Kyukoto, Japan), 0.5% (0.09 M) NaCl (Sigma Aldrich Inc., USA) and incubated at 37ºC overnight with 150 rpm agitation.

4.2.3.2 Microbial inhibition by membranes

One milliliter of LB medium was put into each well (24-well plate such as Figure 4.1), and one membrane piece was placed in the well. Ten microliters of E. coli pre-culture (OD_{600} of pre-

cultures were 3-4) were inoculated. The growth of *E. coli* was analyzed by the optical density at 600 nm (OD_{600}) wavelength using a spectrophotometer (Genesys 10uv, ThermoFisher, Tokyo). After around 21 hours incubation at 37°C, the culture was diluted (10^1) and OD_{600} was measured. This study was all performed under dark. Further observation was carried out on some samples by spreading the used media on growth agar, and continuing the incubation for another night, after the removal of membrane pieces.

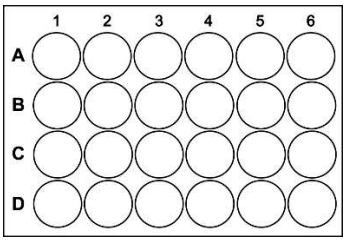

Figure 4.1 24-wells plat

4.2.3.3 Microbial Inhibition by acetate solutions

In order to observe the effect of bulk silver ions in solution towards E. coli growth, CH_3COOAg and Sodium acetate ($CH_3COONa \cdot 3H_2O$, FUJIFILM Wako Pure Chemical Corporation, Japan, purity 99%) solutions were added to LB medium at a final concentration of 0 to 5 x 10^{-5} mol/L. OD_{600} of the solutions after overnight (around 21 hours) growth was measured.

4.2.4 Other antibacterial tests

4.2.4.1 Effect of Vitamin C addition

Hou et al. (Hou et al., 2015) proposed the addition of Vitamin C in antibacterial study by Ag ion implanted TiO_2 to scavenge potential reactive oxygen species. In this study, L-ascorbic acid ($C_6H_8O_6$, FUJIFILM Wako Pure Chemical Corporation, Japan, purity 99.6 %) were added into the media to make 5 x 10^{-3} mol/L final Vitamin C concentration. The experiment was then carried out same as 4.2.2.3.

4.2.4.2 Direct observation of antibacterial activity

To check the effect of direct contact with $AgTiO_2$, microscopic observation was performed using $AgTiO_2$ nanoparticles (Che Abdul Rahim et al., 2023). An Axio Imager A1 fluorescence microscope (Carl Zeiss, Jena, Germany) equipped with the filter set 38HE and 43HE was used to observe green and red fluorescence.

4.2.4.3 Disk diffusion method

Disk diffusion method were commonly performed to observe the antibacterial potential of solid material. Diluted E. coli pre-culture were spread on LB growth agar. Membrane pieces were placed upside down and let grow overnight in incubator at 37°C under dark condition. Observation was made the next day.

4.3 Results and Discussion

4.3.1 Silver dissolution under experimental condition

Table 4.1 shows average amount of silver deposited on whole membranes for dissolution study.

Table 4.1 Amount of silver on membranes

Membrane	Sample	Silver amount (mg/cm^2)	Amount of deposition (mg/cm^2)
Support-Ag	1	0.002	0.004 ± 0.001
	2	0.005	
$AgTiO_2$-low Ag	1	0.010	0.010 ± 0.002
	2	0.008	
	3	0.011	
	4	0.008	
$AgTiO_2$-high Ag	1	0.177	0.163 ± 0.04
	2	0.140	
	3	0.203	
	4	0.123	

As silver ions (Ag^+) are accepted as silver forms that play important role in attacking bacteria, the behavior of silver dissolution from prepared $AgTiO_2$ membrane was studied. Figure 4.2 shows silver leaching over time from silver-based membranes prepared in this study, in water and in NaCl solution. As discussed in Chapter 3, since NaCl can increase the silver dissolution, in this part of the study, we performed the dissolution study under the same NaCl concentration as the bacterial growth media (0.09 M).

From Figure 4.2, we can see that, under saltless condition (x), the silver leaching is minimal and almost negligible at all times studied. The saltless condition was studied using $AgTiO_{2\text{-low Ag}}$ membrane and results shows less than 0.4% of silver was lost from the membrane after around 36 hours of total experiment time. This shows that our $AgTiO_2$ membrane is quite stable in water (Istirokhatun et al., 2022).

However, in the presence of salt, the results show higher released of silver into the solution. From $AgTiO_{2\text{-low Ag}}$ membrane, shorter times released lower amount of silver (until at 360 minutes) before a stabilized amount at 1.5 - 2.1 µmol/L. Performing the experiment again using the same membrane shows same trend. This condition can also be seen using the Support-Ag membrane (green marker).

With $AgTiO_{2\text{-high Ag}}$, the dissolution rate shows faster silver released in the shorter time, then again, reaching a plateau at 1.7 - 2.3 x 10 µmol/L. Again, preparing another membrane under same condition shows same trend with $AgTiO_{2\text{-high Ag}}$ membrane.

Previously when we make observation for silver dissolution under light and different salts condition, we found that $AgTiO_{2\text{-low Ag}}$ membrane will release negligible amount of silver after multiple usage of the membrane. We found this condition to happened after 70 hours (add up) of dissolution study under different conditions. Total silver leached was around 21% from the membrane. So, we proposed that the membrane will reach a saturation silver released at some point even though it still shows some colored surface (as compared to white TiO_2 membrane). This saturation phase has been also reported in many studies on Ag dissolution behavior from membranes (Peng et al., 2020, Aoki et al., 2018).

At this point, prepared $AgTiO_{2\text{-low Ag}}$ membrane can possibly remove most of its silver oxide layer as observed by XPS, and the appearance of metallic silver which has a lower dissolution rate (Goderecci et al., 2017). However, with $AgTiO_{2\text{-high Ag}}$ membrane, results still show steady released even after around over a week usage maybe due to the higher amount of AgO_x on the membrane surface. This amount of time only leached 4% of silver from $AgTiO_{2\text{-high Ag}}$ membrane.

4.3.2 Microbial inhibition by prepared membrane

Antibacterial study was performed on cut membranes. The color of cut membranes are comparable to the whole membrane, where $AgTiO_{2\text{-high Ag}}$ (AB) shows dark color and $AgTiO_{2\text{-low Ag}}$ (AB) shows very light brownish color. Similarly, Support-Ag (AB) shows white color as the whole membrane prepared the same way. Figure 4.3 shows the results of OD_{600} after an overnight incubation of E. coli with prepared membranes. The error bar represents the standard deviation of obtained results of at least 5 individual freshly prepared membranes. Here the results show that Blank, Bare support, and TiO_2 membrane showed negligible effect on the E. coli growth. $AgTiO_2$ coated membrane however shows antibacterial activity where 20% of growth was inhibited by $AgTiO_{2\text{-low Ag}}$ (AB) and 80% effect can be seen by $AgTiO_{2\text{-high Ag}}$ (AB).

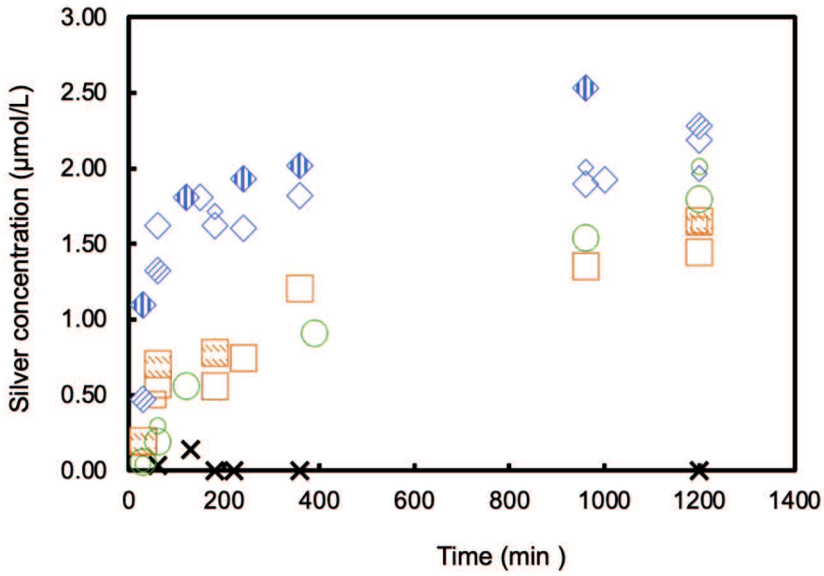

Figure 4.2 Silver dissolution study. (+ $AgTiO_{2\text{-low Ag}}$ (AB) $_{in}$ water, ◇ for $AgTiO_{2\text{-high Ag}}$, ■ for $AgTiO_{2\text{-low Ag}}$ and ○ for Support-Ag in 0.09 M NaCl. Different patterns show different set of membranes. Smaller markers show repeated results using the same membrane.)(Che Abdul Rahim et al., 2023)

With almost same trend of silver ions dissolution between Support-Ag and $AgTiO_{2\text{-low Ag}}$ membrane in section 4.3.1, we expected some antibacterial activity by the Support-Ag (AB) membrane. However, this membrane did not show any antibacterial activity towards E. coli growth. Comparing $AgTiO_{2\text{-low Ag}}$ (AB) $_{and}$ $AgTiO_{2\text{-high Ag}}$ (AB) membranes, even though both membranes show small difference in the silver concentration released over time, the $AgTiO_{2\text{-high Ag}}$ (AB) significantly show stronger antibacterial activity. With these results, the silver ions released from these membranes cannot be directly related to the inhibition activity as shown in Figure 4.3.

In some studies, AgOx is reported to have a strong bactericidal; where some report stronger (Rebelo et al., 2016) while other reports as good as the metallic silver (Kacprzynska-Golacka et al., 2020). To see the antibacterial activity without silver ions, fresh $AgTiO_{2\text{-low Ag}}$ (AB) was soaked in 0.09 M NaCl in the incubator (37ºC) to remove silver ion faster. After around 3000 minutes, about 26% of silver were removed from membrane measured via ICP. Based on previous results, we assumed that this membrane has removed high amount of silver

oxide on the membrane surface. This sample was labelled as 'Treated $AgTiO_{2\text{-low Ag}}$ (AB)' in Figure 4.3.

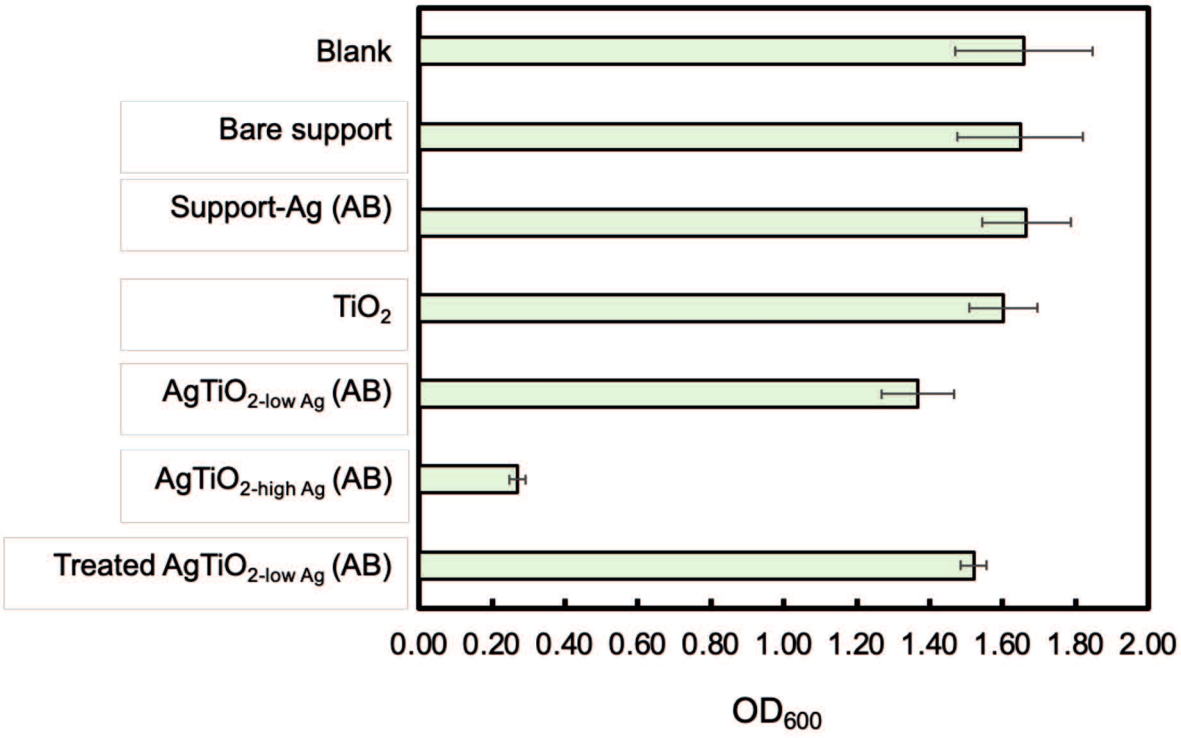

Figure 4.3 OD_{600} of *E. coli* by different membranes after overnight incubation (Che Abdul Rahim et al., 2023)

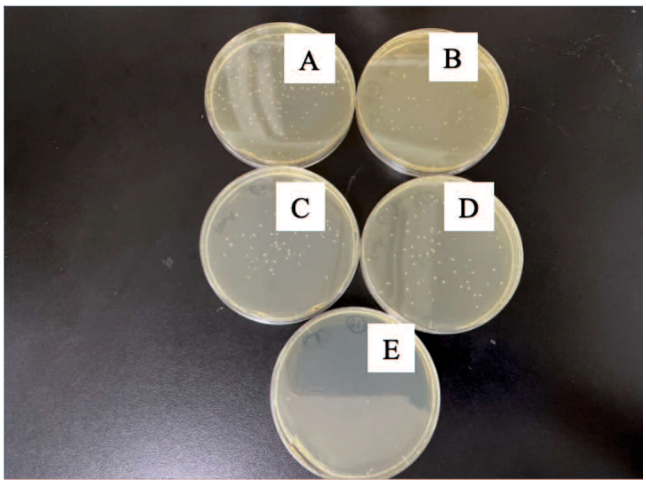

Figure 4.4 E. coli growth (100x dilution) observation after first day incubation with A) Blank, B) Bare-support, C) TiO_2 membrane, D) $AgTiO_{2\text{-low Ag}}$ (AB) and E) $AgTiO_{2\text{-high Ag}}$ (AB)

Proposing that the silver oxide on membrane play important role in the antibacterial activity, 'Treated $AgTiO_{2\text{-low Ag}}$ (AB) shows lower inhibition due to lower silver oxide amount

on the surface. Apart from that, diluted used media with E. coli after antibacterial experiment were spread on LB agar plate to observe the growth. Result in Figure 4.4 supports that very low E. Coli was left in the solution due to the primary inhibition, thus only small growth can be observed on the agar plate after a day incubation.

4.3.3 Microbial inhibition by acetate solutions

The influence of bulk silver on the *E. coli* growth was studied by adding CH_3COOAg solution to the media. In order to examine the role of silver ion, sodium acetate (CH_3COONa) solution was also used. The inhibition rate on the *E. coli* growth in Figure 4.5 was calculated using the equation 4.1 below.

$$Inhibition\ rate\ \% = (\ 1 - \frac{OD_{600}}{OD_{600blank}}) \ x\ 100 \ \ldots\ldots (4.1)$$

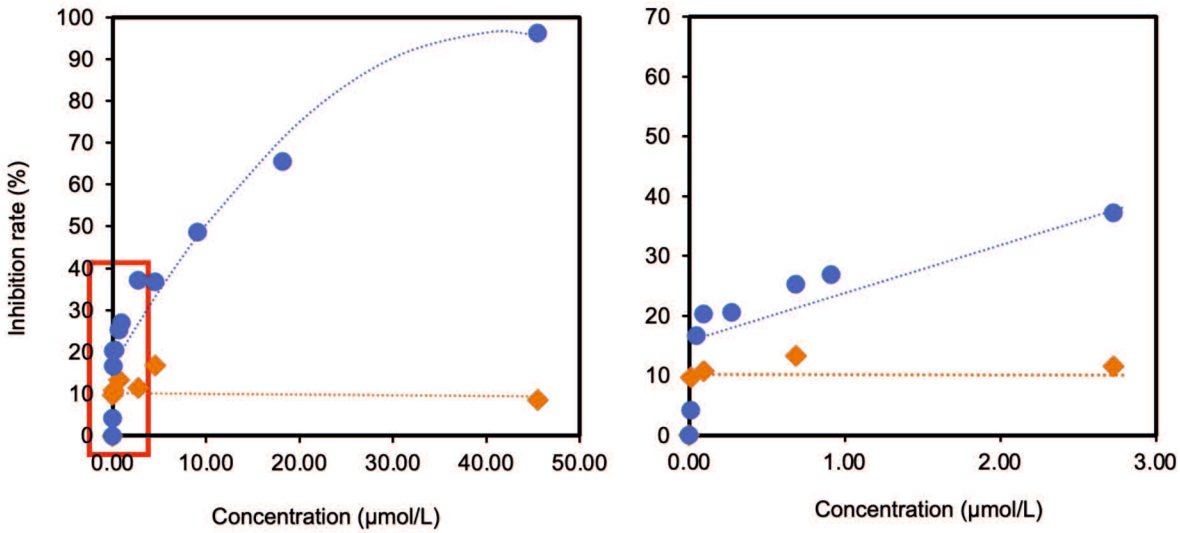

Figure 4.5 Effect of CH_3COOAg (○) and CH_3COONa (◊) concentrations on *E. coli* growth; a) whole result and b) Magnified for the red box area (Che Abdul Rahim et al., 2023)

Figure 4.5 shows that increasing the concentration of CH_3COOAg increased the antibacterial effect on E. coli. Addition of CH_3COONa did not increase the inhibition rate, showing that acetate ions are inert in terms of microbial activity (Mannix-Fisher and McLean, 2021). Almost 70% inhibition was observed with 20 µmol/L CH_3COOAg while increasing the concentration higher than 40 µmol/L inhibits the bacteria more than 90%. Previously, Peetsch et al., reported comparable value for minimal inhibition concentration (MIC) on *E. coli* by silver acetate (with 99% purity) in LB media (Peetsch et al., 2013).

Even the silver toxicity is proposed to be different in bulk materials as compared to nanoparticles due to its physiochemical properties (Wang et al., 2017, Choi and Chung, 2020), with these results, we can propose that the silver ions need to be in a higher concentration to cause the inhibition of E. coli as strong as the one showed by $AgTiO_{2\text{-high Ag}}$ (AB) in Figure 4.3.

4.3.4 Other antibacterial tests

4.3.4.1 Effect of Vitamin C addition

Influence of adding Vitamin C to the LB media was also studied. Figure 4.6 shows that addition of Vitamin C to normal E. coli in growth media inhibit the growth by 50% compared to without. The error bar shows standard deviation of at least two samples. In our study, the addition of Vitamin C also reduced the pH of media from 6.07 to 5.14. Here we can see that Vitamin C itself, an antioxidant, reduced the E. coli growth. This can be due to the pH changes. In a natural condition, Vitamin C has also been reported to have antimicrobial effect at certain concentration (Mathew et al., 2017).

Under the presence of $AgTiO_{2\text{-high Ag}}$ (AB) membrane, as discussed before, 80% of E. coli was inhibited. Based on these two results, it seems that both $AgTiO_2$ membrane and Vitamin C has strong effect to reduce E. coli growth. However, when combining Vitamin C and $AgTiO_{2\text{-high Ag}}$ (AB), the inhibition by $AgTiO_2$ membrane seems to be reduced. Explaining this condition will be the reduction of $AgTiO_2$ membrane effect can be due to the adsorption of Vitamin C ion onto the positively charged $AgTiO_2$ surface. Under this condition, the contact of E. coli with the Ag_2O on the surface can be limited. This can support the strong role of silver on membrane surface as the inhibition mechanism.

Another reported discussion will be due to the reactive oxygen species produced by the mitochondria of living cells naturally. Under oxidative stress that can be generated with contact with metal such as silver, excessive amount of ROS can be generated, thus can damage the cell itself (Guo et al., 2013). Vitamin C then, can act as ROS scavenger, where it will be adsorbed into the cells, and reduce the oxidative stress experienced by bacterial cell (Fujii et al., 2020). Hou et al., in his discussion on silver activity by Ag-ion implanted TiO_2-thin film proposed that, via addition of Vitamin C as antioxidant, we can propose the potential of inhibition mechanism since antioxidants potentially scavenge reactive oxygen species (ROS) (Hou et al., 2015). Potentially, under influence of silver, Vitamin C now play its role as antioxidant and scavenge the generated ROS that is caused by silver and reduced the antibacterial effect instead

of causing further inhibition (Hou et al., 2015). However, no tests had been carried out to confirm the contribution of ROS further in this study.

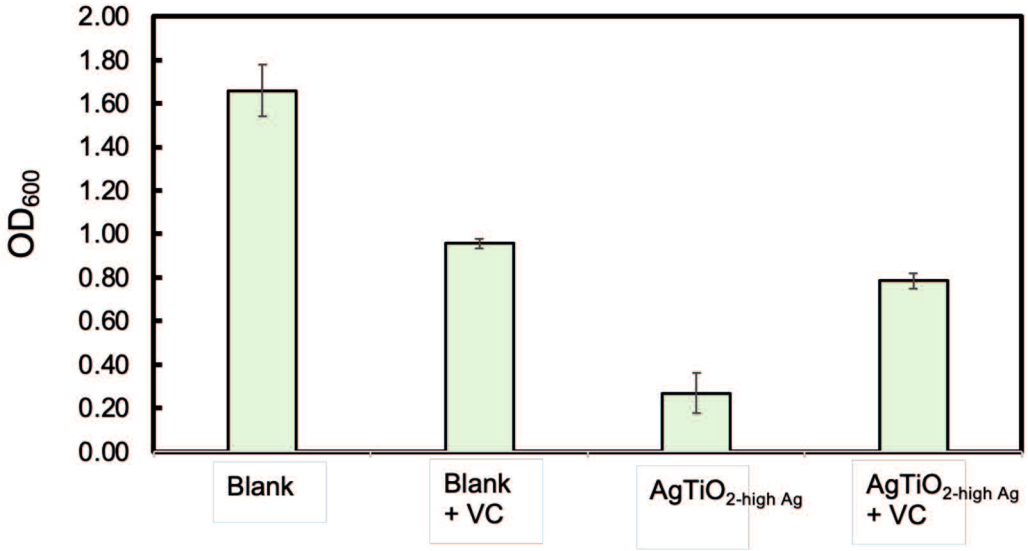

Figure 4.6 Effect of Vitamin C antioxidant addition to the antibacterial activity

4.3.4.2 Direct observation of antibacterial activity

As we cannot discussed the direct relationship of released silver ions and the inhibition of E. coli, here, direct observation of the antibacterial activity was studied. To observe the influence of prepared $AgTiO_2$ directly to the bacteria, the powder was deposited on glass plates. E. coli cells suspension in water were than applied on the powder. For comparison, the suspension was also applied on bare glass plates (Che Abdul Rahim et al., 2023).

Figure 4.7 shows example of observation made. Figure 4.7 a) shows the glass surface while 4.7 d) shows the glass surface covered with $AgTiO_2$ composite powder. Figure 4.7 b) and e) shows the stained red fluorescent protein indicating E. coli cells under blank (b) and $AgTiO_2$ influence (e). The dead cell was then expressed by green fluorescent of Sytox Green and can be seen in Figure 4.7 c) Blank, and 4.7 d) with $AgTiO_2$. The figure clearly shows that under the influence of $AgTiO_2$ (Figure 4.7 f)), the number of cells that can be observed is higher as a result of higher dead cells. Since this test was performed without salinity involves, the silver ions released was proposed to be negligible as have been discussed before. Therefore, this supports the possibility of silver deposited on TiO_2 direct contribution to the antibacterial activity. Table 4.2 shows the results from all the experiments.

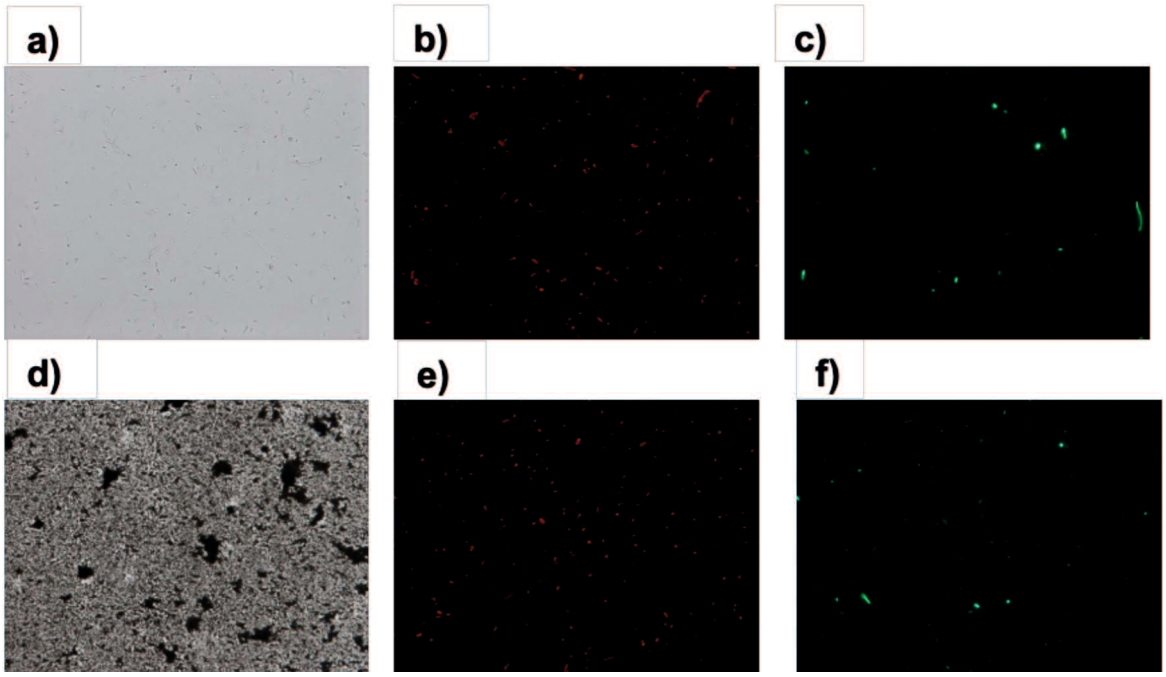

Figure 4.7 Direct antibacterial study on nanoparticles; a) bright field, b) E. coli cells (red); c) dead cells (green) without $AgTiO_2$, d) bright field, e) E. coli cells (red), f) dead cells (green) with $AgTiO_2$ (Che Abdul Rahim et al., 2023).

Table 4.2 Summary of the cell counts on a glass without (blank) and with $AgTiO_2$

Sample No.	Blank		$AgTiO_2$	
	Red	Green	Red	Green
1	170	37	231	187
2	220	51	196	160
3	225	27	196	121
4	173	25	172	132
5	193	25	246	164
6	224	33	-	-

4.3.4.3 Disk diffusion method

Disk diffusion tests were carried out to evaluate the antibacterial performance of the prepared membranes. These tests are commonly carried out to observe potential antibacterial activity of membranes (Yin et al., 2013, Goei and Lim, 2014). As can be seen in Figure 4.8, bare support and TiO_2 membrane pieces shows no antibacterial activity. However, compared to the antibacterial study by membrane in part 4.4 above, it seems that $AgTiO_{2\text{-low Ag}}$ membrane also shows no inhibition zone. In contrary, the inhibition zone for $AgTiO_{2\text{-high Ag}}$ membrane can be clearly seen as hollow area around the cut membranes. Disk diffusion test can show antibacterial property of a solid surface potentially by the diffusion of antibacterial material.

The result show significant antibacterial activity by $AgTiO_{2\text{-high Ag}}$ membrane and supported the result in part 4.3.2.

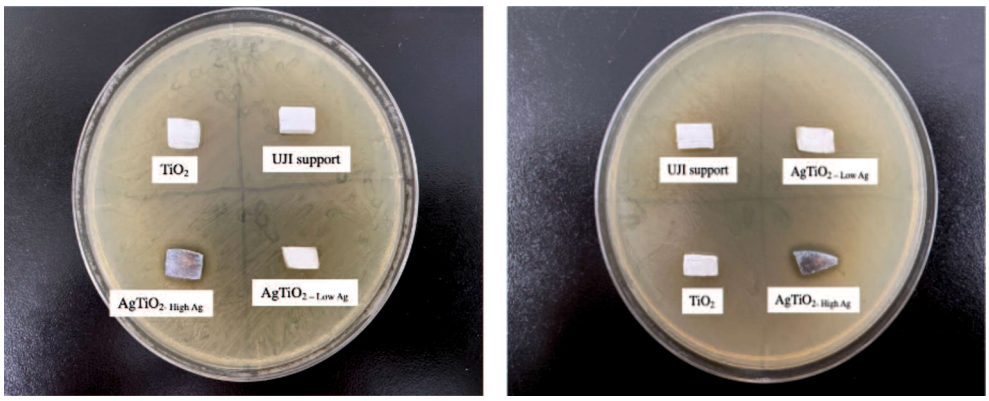

Figure 4.8 Inhibition of *E. coli* growth via disk diffusion method for two set of experiments

The mechanism of antibacterial activity by silver is still not fully understood. Silver ions released from silver nanoparticles are the most discussed cause of the antibacterial activity, where silver ions attack the bacteria's cell walls and then the enzymes, RNA or DNA (Pan et al., 2018, Mannix-Fisher and McLean, 2021) inducing dysfunctionality and result in an eventual death. Formation of reactive oxygen species by the reaction between Ti^{3+} and oxygen vacancy in $AgTiO_2$ is also proposed to be the cause of bacteria elimination in dark conditions (Viet et al., 2018).

However, our result shows low influence of silver ions to explain the inhibition difference between $AgTiO_{2\text{-high Ag}}$ (AB) and $AgTiO_{2\text{-low Ag}}$ (AB). We also did not observe Ti^{3+} peak on the XPS result of $AgTiO_2$ powder (Chapter 2). Under this condition, the significant difference between the membranes will be the amount of silver deposited on the membrane surface. Contact between silver nanoparticles and E. coli had been reported to cause damage to the bacteria cell wall (Marambio-Jones and Hoek, 2010). Rebelo et al (Rebelo et al., 2016) also proposed that silver oxide has stronger bactericidal effect than silver ion from their study. Therefore, the high amount of silver oxide on membrane surface of $AgTiO_{2\text{-high Ag}}$ (AB) can possibly contributed to the high inhibition of E. coli.

4.4 Summary

Prepared $AgTiO_2$ membrane shows potential of antibacterial activity which can potentially resulted in reduction of membrane biofouling cases. The higher silver deposited on membrane, the more significant its antibacterial activity. Different prepared silver-based membranes show almost same dissolution rate of silver however, in the antibacterial study, the $AgTiO_{2\text{-high Ag}}$

(AB) membrane shows significant antibacterial effect compared to the others. Therefore, silver ions cannot be directly related to the antibacterial performance. From our ICP results on cut membrane, the $AgTiO_{2\text{-high Ag}}$ (AB) contains >20 times higher silver (mainly silver oxide) compared to $AgTiO_{2\text{-low Ag}}$ (AB) on the membrane surface. Under the microscopic observation study performed, direct contact of $AgTiO_2$ with E. coli resulted in high amount of dead cell. Silver oxide nanoparticles had also been reported to have strong bactericidal ability. Therefore, the silver oxide deposited on the $AgTiO_2$ coating can potentially contributed largely to the antibacterial activity in this study.

***Note:**

Disk ceramic supports were prepared and characterized by XRD and other methods by Dr. S. Mestre. The TiO_2/glass samples for the direct observation by a microscope were prepared by Dr. I. Kumakiri. Microscope observations were performed by Dr. S. Hoshida.

4.5 References

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CHAPTER 5

Antibacterial Activity by Filtration System

5.1 Introduction

Membranes can be applied in variety of configurations depending on the wastewater and target treatments. In a filtration system, membrane act as the separator between the wastewater and clean water. Microfiltration membrane for example, has been used extensively for separation and concentration in various industries. Fouling phenomena such as biofouling cause by microorganisms is one of the main drawbacks of the membrane application. As biofouling events can cause severe effect to membrane performance, development of biofouling resistance membranes is highly of interest in recent years.

In all membrane reactor configurations, bio foulant build up on the membrane can potentially be control by the antibacterial membrane. This will maintain membrane performance and ensure a longer membrane lifetime (Kang et al., 2004).

Modification with silver can be a potential method to prepare antibacterial membrane. A study on microfiltration membrane modified with silver oxide has shown outstanding performance in inhibiting E. coli and B. subtilis growth (Kacprzynska-Golacka et al., 2020). In a recent study, silver nanowire glass fiber membrane was reported to be prepared for the first time for the point-of-use (POU) water disinfection (Bahcelioglu et al., 2020). The silver glass fiber membrane also shows great performance as antibacterial membrane.

In this chapter, the previous deposition method was used to deposit silver on TiO_2-glass fiber membrane. The flux of the membrane was compared to bare membrane, and the antibacterial performance via filtration system was observed.

5.2 Material and Method

5.2.1 Membrane and materials

Membrane used in this study due to our available rig and membrane was glass fiber membrane. TiO_2 membrane was prepared using glass fiber membrane as explain in Chapter 2 (Section 2.2.3). $AgTiO_2$ membrane was then prepared using Photoreduction method with 1 x 10^{-3} mol/L CH_3COOAg, the same way as reported in Chapter 2. Prepared membranes were washed and dried before application.

5.2.2 Water flux study

In the water flux evaluation, tubing connected to the filtration rig was arranged in different height. The water passed through filtration rig was taken every 10 seconds of filtration. Amount of this water was measured, and flow rate was calculated.

5.2.3 Antibacterial study

In the filtration study, 1% of E. coli suspension was prepared by mixing E. coli preculture (O.D of 3-4) in distilled water. Since the preculture was directly used into the suspension, NaCl will be presence in the solution at around 9 x 10^{-4} M of concentration. Before filtration, distilled water was filtered through and OD_{600} reading of the water before and after filtration was recorded. This is to ensure that the filter is clean, and no particles that might be deposited on membrane was filtered through. The E. coli suspension was then filtered through different membrane using a syringe manually, and around 10 ml sample was taken at different filtration amount points.

100 µL of the filtered sample were then diluted (10^4) and spread on agar LB media. The agar plate was then incubated overnight at 37ºC, and cell count was performed the next day. In the multiple filtration study, filtrates were refilter to see the effect. Figure 5.1 shows the method of refiltration experiment.

All chemicals and materials used in this study was prepared the same as antibacterial study in chapter 4 (LB media, E. coli preculture).

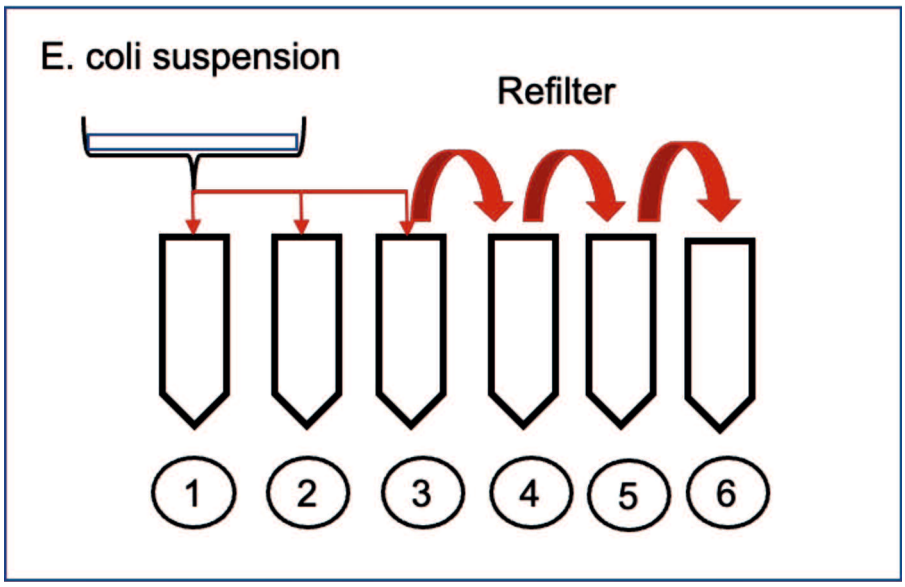

Figure 5.1 Experimental set-up for refiltration experiment. Sample 1-3 were primary filtrate at different volume, while sample 4-5 were refiltration of sample before them.

5.2.4 SEM observation on used filtration membrane

Used $AgTiO_2$ membrane after filtration was treated via graded ethanol series treatment: the used membrane was soaked 15 minutes each in 50% Ethanol, 70% Ethanol, 90% Ethanol, 99.5 % Ethanol, 99.8% Ethanol, 99.8% Ethanol, T-Butanol and again T-Butanol.

This membrane was maintained in frozen condition by placing in the ice bath, and then quickly transferred in the Vacuum Dryer. The membrane was freeze dried for 2-3 hours, then observe through scanning electron microscopy (FE-SEM, JSM-633F, JSM-7600FG, JEOL Ltd. Japan) after coated with Platina.

5.3 Result and Discussion

5.3.1 Water flux study

Two membranes for each condition were used in this study. Table 5.1 shows details of the membrane used in this study.

Table 5.1 Membranes used for water flux study

Membrane	TiO_2 amount (g)	Silver amount (mg)
Blank (1,2)	0	0
TiO_2-1	0.019	0
TiO_2-2	0.029	0
$AgTiO_2$-1	0.034	3.50
$AgTiO_2$-2	0.022	3.86

Figure 5.2 shows the flux versus different height in the water flux experiment. This experiment was manually carried out by placing the tubing at different height. Due to the manual gravitational filtration without pump (pressure), some limitation will be backflow pressure from membrane and bubble formation in the tubing developed from the pressure around the filtration rig. Water flow was also more difficult without other forces at point lower than 5 cm height. Considering the limitations, Table 5.2 shows all the results obtained. The results in Figure 5.2 show average of 3 readings per point. Results shows that the higher the position of tubing placed, the higher the flux of water passing through all the membrane. This condition is due to the higher pressure with higher height position of the tube.

From the result in Figure 5.2, we also can see that the coating affects the flow rate. Addition of coatings (TiO_2 and $AgTiO_2$) reduced the flow rate of water passing through the membrane. This is not reported in a study on silver nanowire decorated GFM (Bahcelioglu et al., 2020). This is because from SEM image shown in Chapter 2 (Figure 2.3) our coating seems to be positioned around the fibers, and also in between the spaces of the GFM. Compared to the silver nanowire GFM prepared via simple dip and dry method where it was shown to be deposited around the glass fibers only, which proposed to not affecting pore size or structure of the membrane (Bahcelioglu et al., 2020).

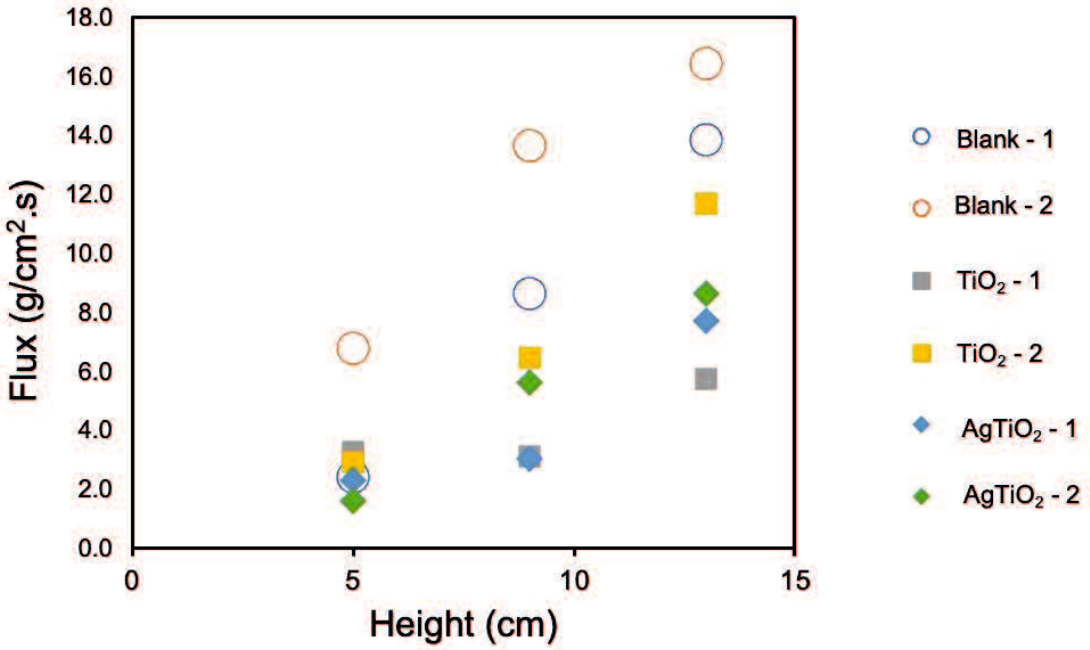

Figure 5.2 Flux vs height of tubing (cm) of different membranes

Table 5.2 Raw data from water flux (Figure 5.1)

			Reading 1		Reading 2		Reading 3	
Membrane	Assignation	Height (cm)	Time (s)	Weight (g)	Time (s)	Weight (g)	Time (s)	Weight (g)
Blank	1	5	9.96	3.64	10.46	4.496	10.3	4.211
		9	10.66	14.366	11.2	13.991	9.83	14.248
		13	10.46	29.277	10.36	13.987	10.41	25.85
	2	5	10.76	9.731	10.53	10.678	10.19	13.412
		9	9.92	17.666	10.46	27.05	10.35	24.493
		13	6.2	16.496	10.49	37.66	10.41	34.357
TiO_2	1	5	10.43	6.127	9.91	5.665	10.09	5.061
		9	10.48	5.162	10.43	4.756	10.47	5.627
		13	10.4	8.936	10.66	10.741	10.32	8.76
	2	5	10.08	4.232	10.39	4.737	10.85	5.626
		9	11.12	11.317	10.28	9.765	11.32	9.828
		13	9.94	25.822	10.65	16.482	10.23	17.22
$AgTiO_2$	1	5	10.34	4.102	10.41	3.629	10.35	3.915
		9	10.33	5.13	10.48	5.178	10.56	4.865
		13	10.57	12.948	10.96	15.449	8.75	10.766
	2	5	10.23	2.304	10.46	2.235	10.37	3.53
		9	10.39	8.286	10.29	7.953	10.42	12.02
		13	10.45	14.35	10.54	13.438	10.4	15.256

5.3.2 Antibacterial study

Membrane sets 1 from above studies were then used for antibacterial filtration study (Blank-1, TiO_2-1 and $AgTiO_2$-1). Another set here were membranes prepared and used earlier. TiO_2 and silver deposition amount for this membrane was shown in Table 5.3 below.

Table 5.3 Additional membranes for antibacterial filtration

Membrane	TiO_2 amount (g)	Silver amount (mg)
Blank- 3	0	0
TiO_2 -3	0.057	0
$AgTiO_2$-3	0.067	3.77

Based on primary study through pristine membrane, E. coli (which size reported to be 1-2 μm) can passed through the pristine membrane (the OD_{600} and cell count were almost the same for before and after filtration samples). Figure 5.3 shows the OD_{600} reading of the E. coli suspension by different membranes at different filtration amount. The figure shows that earlier

filtration point shows some reduction of OD_{600} reading compared to later. This can suggest that some E. coli was potentially trapped on the membrane.

Figure 5.4 shows the antibacterial study through different filtration membrane. Prior to the filtration, we cleaned the membrane by filtering water until the OD_{600} reading after filtration reached same or less than the reading before. The feed was introduced to the filtration membrane using syringe manually, and timed. The average flow rate was around 1.5 ml/s.

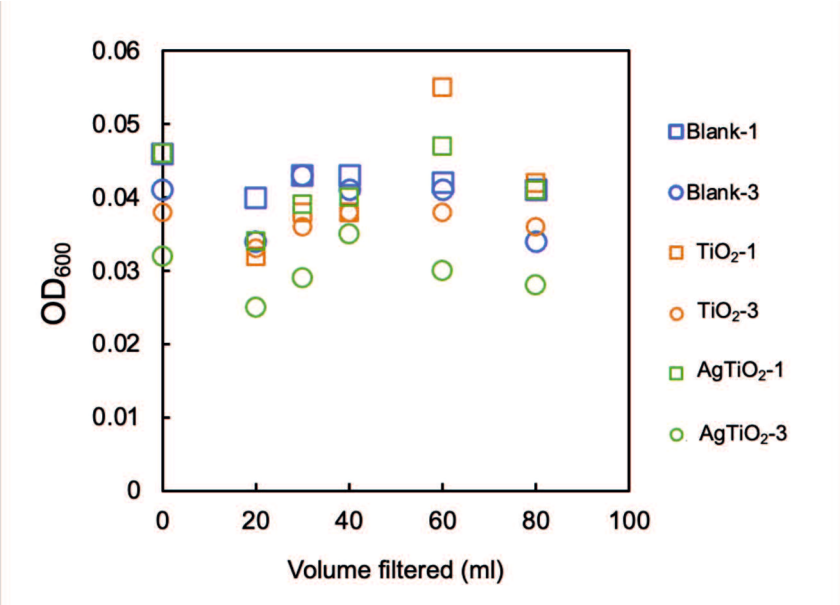

Figure 5.3 OD_{600} changes of different filtered amount by different membranes

In the Filtration study, the E. coli passed through membrane will then be inoculated onto agar media. E. coli growths were then evaluated through colonies count after a day of incubation. The results in Figure 5.4 shows that filtration product (permeate) via $AgTiO_2$ membrane significantly resulted in lower E. coli growth after a day of incubation as compared to pristine and TiO_2 membrane. In previous chapter (Chapter 4), the bacterial growth was evaluated by OD_{600} changes after overnight incubation with the membranes which resulted in long contact between E. coli and silver. Here even the contact with silver was a short time, the antibacterial effect can be observed clearly.

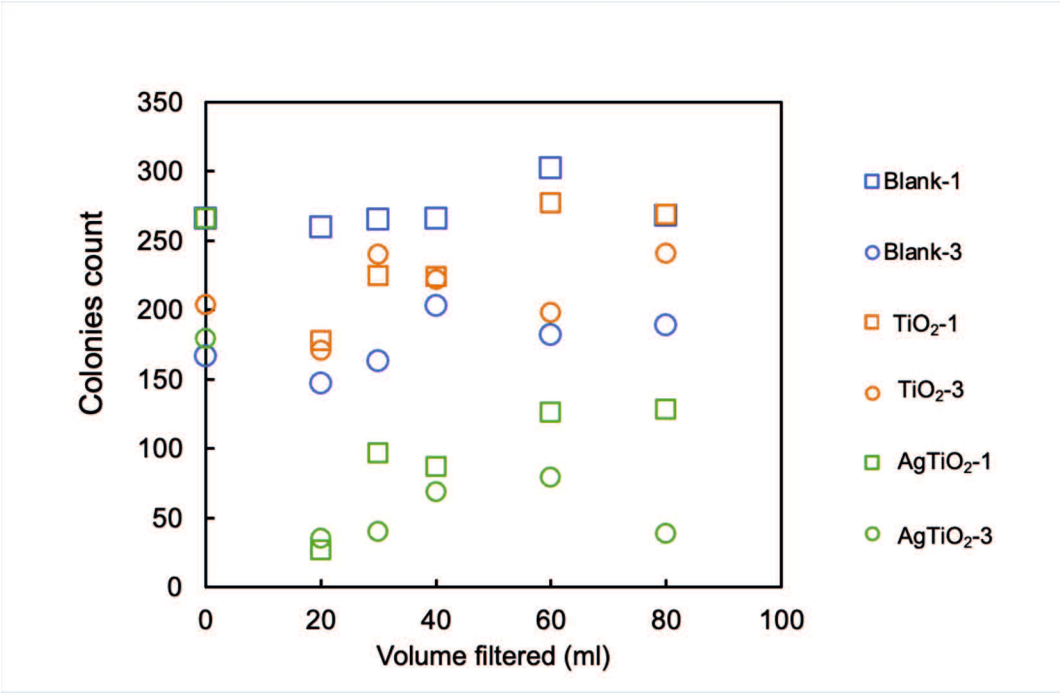

Figure 5.4 Colonies count from different filtered amount by different membranes

Figure 5.5 shows the result of multiple filtrations on the permeate. Sample 4 which was the refiltration of sample 3 shows further inhibition of E. coli. After that, refiltration did not improve the inhibition further. The result proposed increased inhibition by double filtration of the sample. Previous study on silver nanowire coated GFM shows doubled E.coli removal after two-stage serial filtration (Bahcelioglu et al., 2020).

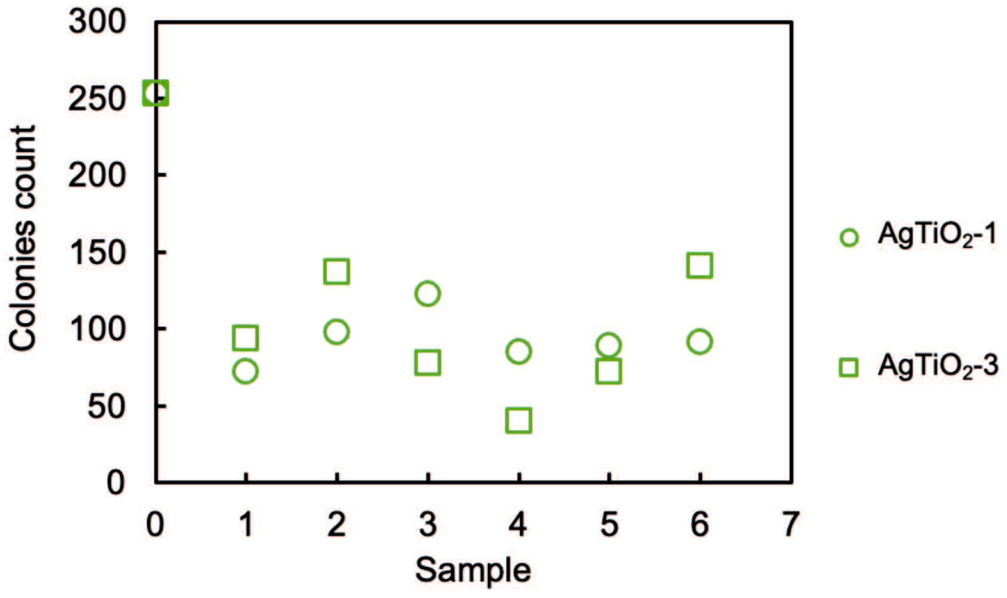

Figure 5.5 Effect of Refiltration

5.2.3 SEM observation on $AgTiO_2$ membrane after filtration

The size of E. coli was reported to be 1-2 µm. Here, we freeze dried the used $AgTiO_2$ membrane after filtration experiment using E. coli suspension. Figure 5.6 shows the SEM image at 10k Magnification.

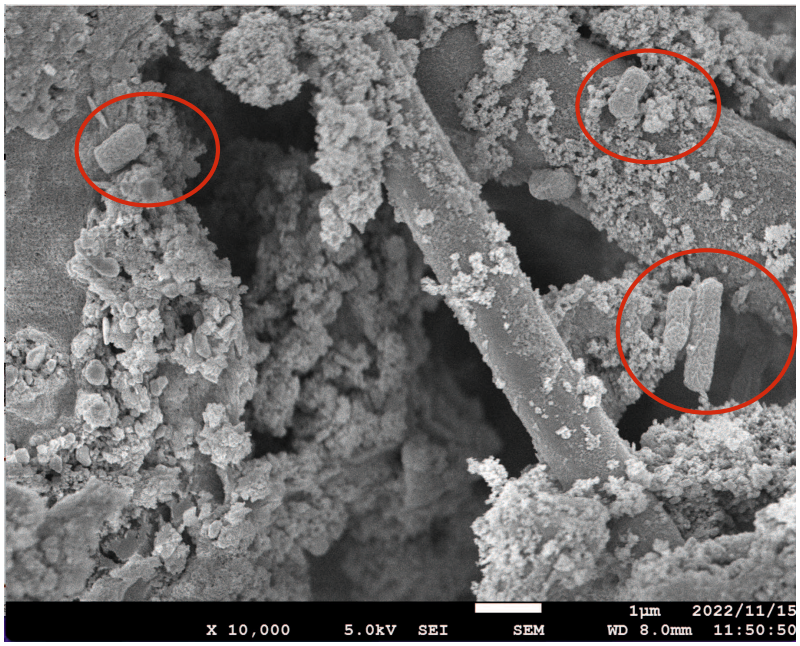

Figure 5.6 SEM image of freeze dried $AgTiO_2$ membrane after filtration experiment.

Figure 5.6 shows that there is some E. coli (red circles) trapped on the $AgTiO_2$ membrane. The results show potential of trapping small amount of E. coli on the membrane. This can contribute to the E. coli removal that was projected in Figure 5.3.

However, observation directly on OD reading suggested small different of OD changes between TiO_2 and $AgTiO_2$. This can possibly suggest TiO_2 coating also trapped the bacteria but did not show high E. coli removal in the antibacterial study. Therefore, the E. coli inhibition in our study cannot be because of trapped cells on the membrane only. Nanofiltration polysulfone membranes modified with silver nanoparticles by a previous study had also suggested the contribution of contact between bacterial cells and AgNPs on membrane surface to its antibacterial activity (Andrade et al., 2015, Bahcelioglu et al., 2020, Kacprzynska-Golacka et al., 2020).

Reported study on contact time with silver surface as far as we can find is for thin silver metallic covered on stainless steel plate. This study reported that shortest time evaluated (5 minutes) of contact between E.coli and silver film has shown antimicrobial effect (Codita et

al., 2010). Contact between bacterial cell wall and the metal surface is proposed to produced Van der Waals and electrostatic forces which can possibly produce other interaction that led to the bacterial destruction (Codita et al., 2010).

(Bahcelioglu et al., 2020) in the filtration study via silver nanowire (AgNW) glass fiber membrane reported 80% E. coli removal efficiency at 1ml/min of flowrate going through the membrane. Higher flow rate seems to reduce the E. coli removal efficiency. Compared to other studies proposing that the E. coli removal were due to being filtered out, with no changes of pore size after coating in the study by Bahcelioglu et al., they suggested the contribution of AgNW coated to the membrane itself to also contribute to the E. coli removal.

Potentially, as Chapter 4 shows strong antibacterial activity by the silver fixed on the membrane itself, the contact between E. coli and silver on the membrane during filtration can cause strong effect. However, the influence of contact time can be limiting in the filtration set up. A more thorough study on silver contact time will be able to discuss this question. Previously, a study using microfiltration membranes modified with silver oxide by plasma treatment also shows significant antibacterial effect on E. coli and Bacillus subtilis (B. subtilis). In their study, E. coli suspension was filtered through the prepared membrane, and complete bacterial inhibition was achieved after the filtration. The result was proposed to be due to the structure of its coating and the fact that silver oxide is a strong bactericidal agent. (Kacprzynska-Golacka et al., 2020). Silver nanoparticles could be attached to bacterial cell wall and penetrate or released ions into the cell and cause destructive behavior to the bacteria. In this study, the exact flow rate used during antibacterial study was not reported.

Other than that, contact with silver nanoparticles can also cause generation of ROS as discussed in Chapter 4, that can be damaging to the bacteria. Finally, release of ion from lower durability membrane can highly influence antibacterial activity (Woskowicz et al., 2020).

Since this condition is not studied further, we cannot conclude that the E. coli reduction was due to which condition, but with available result, we can suggest that there is contribution of deposited silver on the glass fiber membrane towards the antibacterial activity.

5.4 Summary

$AgTiO_2$ membrane as filtration membrane shows potential removal of E. coli from the feed suspension. Observation of growth from permeated solution after $AgTiO_2$ membrane shows significant E. coli removal as compared to other membranes. However, the OD changes are

almost the same with TiO_2 coated membrane suggesting that the trapped E. coli can also be at same amount.

Therefore, the result suggests the contribution of antibacterial activity by silver deposited on the membrane. It can be through the activity of silver particles or silver ion released from the membrane and picked up by E. coli cells or also due to the short contact between E. coli and silver on the membrane surface. However, the mechanism of silver attack in this system needs to be further study to be understood.

This study shows potential of $AgTiO_2$ coating to reduce E. coli in the filtration configuration. Therefore, the application of the coating can be wider.

5.5 References

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CHAPTER 6

Conclusion

6.1 Dissertation Conclusion

As one of the oil and gas producer in the world, Malaysia is dealing with the production of wastewater from the activity. Currently, the regulations on this wastewater discharge are not as strict as some other top producers' such as Norway. However, with a higher freshwater problem facing by the country, it can be expected that the regulations can be stricter. With recurrent problems of clean water supply, wastewater need to be managed better, to ensure a safe and constant supply of fresh water. In 2019, Prof. Dr. Zulkifli Yusop, a water expert from Centre for Environmental Sustainability and Water Security (IPASA), encourages that the water researchers in Malaysia to put more efforts to reduce water pollution since it is threatening the country's water resources.

Many conventional water treatment methods can remove main contaminants in the produced water; however, they seem to have problem to remove dissolved organics which can be toxic to the marine population and eventually human consumption. Advanced oxidation process, via photocatalytic oxidation offers a promising solution to this problem. Depositing the nanoparticles photocatalyst on membrane support open a wider application and remove the need for the nanoparticle's recovery letter on. However, with membrane application, they come the risk of membrane fouling which can reduce the membrane performance and lifetime. Many reported photocatalytic membranes were on polymeric membrane or involved polymeric coatings. But this material can be degraded by the light irradiation and radicals' generations during photocatalytic reaction.

Here, this dissertation covered the potential of photocatalytic $AgTiO_2$ coating on inorganic membrane supports for the application in water treatment. Since PW involves seawater with higher salts concentration, the performance of membrane was also studied under influence of different salts.

As application of membrane was reported to be limited by fouling phenomena, silver, with antibacterial property offer added value to the membrane and potentially can reduce the biofouling cases. Therefore, with AgTiO2 coated membrane, the antibacterial property of the membrane was also evaluated.

In chapter 3, we found that the optimal photocatalytic performance was obtained by depositing minimal silver concentration at 0.008 mg/cm^2 of membrane, where, increasing the amount further, reduce the performance due to the agglomeration of silver particles. Under salinity, anions Cl^- and SO_4^{2-} were found to cause inhibition of the performance, due to the adsorption of these ions on the positively charged TiO_2 surface. However, the membrane can be recovered by simply washing it with water to remove the salt ions. The silver state/release after salts experiment were evaluated with XPS and ICP and it was concluded that under the silver state did not change, while the silver release under UV-light used was negligible, thus proposing that the limitation was mainly by the adsorption of salt ion on the surface.

In chapter 4, the antibacterial property of prepared membranes was reported. Under experimental condition with NaCl at 0.09 M concentration, the silver ions release into the solution was comparable between different silver concentration on the membranes, and different preparation methods. However, the antibacterial activity is very significant by membrane with high silver concentration, thus leaving a question of how this antibacterial mechanism happened. Further tests found that the antibacterial activity can largely be contributed by the silver oxide on fixed on the prepared membranes.

In chapter 5, we evaluated the potential of $AgTiO_2$ membrane as a filtration membrane due to the potential of different photocatalytic membrane reactors. Results show that the permeate from $AgTiO_2$ membrane deposited on glass fiber membrane shows significant antibacterial effect towards E. coli.

With these results, the thesis found that, the prepared $AgTiO_2$ coatings on membrane support offer a potential for the application in photocatalytic water treatment, with a good photocatalytic performance in water, and potential antibacterial activity with the silver oxides fixed on membrane surface. With the knowledge of salinity effect towards the activity, the treatment system can include required measures before the application of the photocatalytic membrane. The potential of the membrane for PW treatment is still there due to the ability to remove diluted organics.

6.2 Future Work

With the potential shown by $AgTiO_2$ membranes, we proposed future works of:

1. Different photocatalytic set up such as photocatalytic membrane contactor, to see the effect of controlled oxygen supply towards the photocatalytic activity.

2. Treatment of different organics for example phenolic compounds to compare the differences.

3. Treatment of real wastewater from Oil and Gas Industry or with more complex simulated wastewater closer in composition with PW.

APPENDIX

A) Publications

1. Izumi Kumakiri, Kohei Murasaki, Shotaro Yamada, Azzah Nazihah Binti Che Abdul Rahim, Haruyuki Ishii. 2022. A Greener Procedure to Prepare TiO_2 Membranes for Photocatalytic Water Treatment Applications. Journal of Membrane Science & Research. 8(2).

2. A.N. Che Abdul Rahim, Shotaro Yamada, Haruki Bonkohara, Sergio Mestre, Tsuyoshi Imai, Yung-Tse Hung, Izumi Kumakiri. 2022. Influence of salts on the photocatalytic degradation of formic acid in wastewater. International Journal of Environmental Research and Public Health (IJERPH). 19. 15736.

3. A.N. Che Abdul Rahim, H.Hoshida, S. Mestre, I. Kumakiri. 2022. Antibacterial properties of photochemically prepared $AgTiO_2$ membranes. Water & Science Technology. 87(2): 381-392.

B) International conferences

1. [Online] Azzah Nazihah binti Che Abdul Rahim, Sergio Mestre, Izumi Kumakiri. Influence of inorganic ions towards $AgTiO_2$ membrane performance. 18th Young Scientist Seminar (YSS), Yamaguchi University, Japan. 27th -28th November 2021. (Poster presentation).

2. [Online] Azzah Nazihah binti Che Abdul Rahim, Sergio Mestre, Izumi Kumakiri. Photocatalytic Decomposition of Organics by Ag-TiO_2 membrane. 6th International Symposium on "Green and Smart Technologies for a Sustainable Society", Santander, Cantabria, Spain. 9th -10th December 2021. (Video presentation).

3. [Hybrid] Azzah Nazihah binti Che Abdul Rahim, Sergio Mestre, Izumi Kumakiri. Photocatalytic Oxidation of Diluted Organic by Silver Deposited TiO_2 membrane. 15th International Conference on Catalysis in Membrane Reactors. Waseda University, Japan. 31st July – 4th August 2022. (Oral presentation).

C) Domestic conferences

1. [Online] Che Abdul Rahim A.N., Mestre, Kumakiri, I. Salt Influence towards photocatalytic activity of silver doped TiO_2 membrane. The Society of Chemical Engineers, Japan (SCEJ) 52nd Autumn Meeting, Okayama University, Japan. 21st -24th September 2021. (Oral presentation).

2. [Online] Che Abdul Rahim, A.N., Mestre, S., Kumakiri, I. Influence of operation condition on the oxidation property of Ag-TiO_2 membranes. Chemical Engineering Society Convention, Kansai, Japan. 14th -15th December 2021. (Oral presentation).

3. [Hybrid] [Selected as Featured Presentation – Press Release Target] Che Abdul Rahim, A.N., Mestre, S., Kumakiri, I. Silver dissolution from Ag-TiO_2 membrane in saline condition. SCEJ 87th Annual Meeting, Kobe University, Japan. 16th -18th March 2022. (Oral presentation).

4. [Hybrid] Azzah Nazihah binti Che Abdul Rahim, Sergio Mestre, Izumi Kumakiri.Antibacterial Property of $AgTiO_2$ membrane. The Membrane Society Japan 44th Annual Meeting, Waseda University, Japan. 9th -10th June 2022. (Poster presentation).

D) Workshops

1. [Online] Azzah Nazihah, Izumi Kumakiri. Photocatalytic decomposition of organics by Ag-TiO_2 membrane and inhibition behavior of salt ions. International workshop on "Women Scientists Working on Membranes". 5th October 2021. (Oral presentation).

2. [Online] Azzah Nazihah binti Che Abdul Rahim, Sergio Mestre and Izumi Kumakiri. Oxidation of diluted organics by facile prepared $AgTiO_2$ membrane. International workshop on membrane technology.9th December 2021. (Oral presentation).