POLYVINYLIDENE FLUORIDE MEMBRANE COATED WITH TITANIUM DIOXIDE NANOFIBERS FOR PHOTOCATALYTIC MEMBRANE PROCESS

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Special dedicated to my beloved parents

(Mohamad Nor Bin Toyib and Khadijah Binti Mat),

and my dearest family members.

I dedicated this work in sincere gratitude for your love, support and patience.

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ABSTRACT

Photocatalytic oxidation nowadays has been pledging as the valuable process for air and water purification because of its capability to degrade organic pollutants. Photodegradation of organic pollutants by suspended photocatalyst have major drawbacks in terms of difficulty in post-recovery treatment. In this study, polyvinylidene fluoride (PVDF) nanocomposite membrane consisted of electrospun titanium dioxide (TiO_2) nanofibers (PVDF/e-TiO_2) was prepared by hot pressing the as-spun TiO_2 nanofibers onto PVDF flat sheet membrane. The TiO_2 nanofibers acted as a photocatalyst, while PVDF membrane acted as a support. The hot press technique was carried out by applying heat at 100 °C, 160 °C and 180 °C for 30 minutes. The nanocomposite membranes were characterized by field emission scanning electron microscopy (FESEM), energy dispersive x-ray spectrometry (EDX), differential scanning calorimetry and UV-vis-near-infrared spectroscopy. The FESEM images and EDX analysis showed good adhesion and dispersion of TiO_2 nanofibers in the PVDF membrane. Nanocomposite membrane prepared at hot pressing temperature of 100 °C (PVDF/e-TiO_2-100) exhibited appropriate morphological structure and physical properties. PVDF/e-TiO_2-100 exhibited the highest photocatalytic activity in the degradation of bisphenol A (BPA) under UV irradiation compared to the PVDF/e-TiO_2-160 and PVDF/e-TiO_2-180 with degradation rate of 84.53 %, 77.61 % and 62.54 %, respectively. Meanwhile, the pure water flux was reduced as the hot press temperature increased; 15.79 L/m^2.h (100 °C), 14.80 L/m^2.h (160 °C), 8.88 L/m^2.h (180 °C). However, the BPA rejection of the PVDF/e-TiO_2-100 was found to be the lowest among the prepared nanocomposite membranes. Based on the obtained results, it can be concluded that a fine-tuning on the optimization study of the membrane pore size by several approaches is required in order to ensure the developed PVDF/e-TiO_2 membranes can be efficiently functioned by means of photodegradation and filtration applications.

ABSTRAK

Pengoksidaan fotopemangkinan pada masa kini telah menjadi proses yang berharga untuk pembersihan air dan udara disebabkan oleh keupayaannya untuk mendegradasi pencemar organik. Fotodegradasi bahan pencemar organik oleh ampaian fotomangkin mempunyai kelemahan utama daripada segi kesukaran untuk merawatnya selepas digunakan. Dalam kajian ini, membran komposit nano polivinilidena florida (PVDF) yang terdiri daripada gentian nano pintalan elektro nanogentian titanium dioksida (TiO_2) (PVDF/e-TiO_2) telah disediakan melalui proses tekanan panas gentian nano TiO_2 di atas membran kepingan rata PVDF. Gentian nano TiO_2 bertindak sebagai fotomangkin, manakala membran PVDF bertindak sebagai sokongan. Teknik tekanan panas telah dijalankan pada suhu 100 °C, 160 °C dan 180 °C selama 30 minit. Membran komposit nano telah dianalisa dengan mikroskopi medan pengimbas elektron (FESEM), spektroskopi serakan tenaga sinar x (EDX), kalorimeter pengimbasan pembezaan, dan spektroskopi UV-vis inframerah terhampir. Imej FESEM dan analisis EDX menunjukkan lekatan dan taburan gentian nano TiO_2 yang baik dalam membran PVDF. Penyediaan membran komposit nano pada suhu 100 °C mempamerkan struktur morfologi dan ciri-ciri fizikal yang bersesuaian dengan aplikasi. PVDF/e-TiO_2-100 mempamerkan aktiviti fotopemangkinan tertinggi dalam degradasi bisfenol A (BPA) di bawah sinaran UV berbanding PVDF/e-TiO_2-160 dan PVDF/e-TiO_2-180. Peratusan degradasi masing-masing adalah 84.53 %, 77.61 % dan 62.54 %. Fluks air tulen telah berkurangan apabila suhu tekanan panas meningkat; 15.79 L/m^2.h (100 °C), 14.80 L/m^2.h (160 °C), 8.88 L/m^2.h (180 °C). Walau bagaimanapun, PVDF/e-TiO_2-100 didapati menyingkirkan BPA paling rendah di antara membran komposit nano PVDF/e-TiO_2 yang lain. Berdasarkan keputusan yang diperoleh, dapat disimpulkan bahawa kajian pengoptimuman terhadap saiz liang membran dan struktur membran komposit nano adalah penting bagi memastikan membran PVDF/e-TiO_2 berfungsi dengan cekap semasa aplikasi fotodegradasi serta aplikasi pemisahan.

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LIST OF ABBREVIATIONS

AOP	-	Advanced Oxidation process
BPA	-	Bisphenol A
BSA	-	Bovine Serum Albumin
EDC	-	Endocrine Disrupting Compound
DSC	-	Differential Scanning Calorimetry
FESEM	-	Field Electron Scanning Microscopy
FTIR	-	Fourier Transform Infrared
HPLC	-	High Performance Liquid Chromatography
MF	-	Microfiltration
NF	-	Nanofiltration
PAN	-	Polyacrylonitrile
PE	-	Polyethylene
PMR	-	Photocatalytic Membrane Reactor
PS	-	Polysulfone
PTFE	-	Polytetrafluoroethylene
PVDF	-	Polyvinylidene fluoride
PVP	-	Polyvinylpyrrolidone
PWF	-	Pure Water Flux
RO	-	Reverse Osmosis
TiO_2	-	Titanium Dioxide
TNF	-	Titanium Dioxide Nanofibers
TTIP	-	Titanium Tetraisopropoxide
UF	-	Ultrafiltration
UV	-	Ultraviolet
XRD	-	X-ray Diffraction

LIST OF SYMBOLS

A	-	Effective membrane area, m^2
C_0	-	Initial concentration of pollutants, ppm
C_t	-	Concentration of pollutants at time, ppm
c_f	-	Pollutants concentration in the feed, ppm
c_p	-	Pollutants concentration in the permeate, ppm
Eg	-	Band gap energy, eV
$h\nu$	-	Photon energy, eV
J	-	Pure water flux, L./m^2.h
l	-	Membrane thickness, m
Q	-	Permeate water volume over time, $m^3.s^{-1}$
r_m	-	Membrane mean pore size, nm
W_d	-	Weight of dry membrane, g
W_w	-	Weight of wet membrane, g
v	-	Permeate water volume , L
Δt	-	Time of the permeate collection, h
ΔP	-	Load pressure, Pa
ε	-	Membrane porosity, %
ρ	-	Density of water, 0.998 g/cm^3
η	-	Water viscosity, 8.9 x 10-4 Pa.s
λ	-	Wavelength, nm

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CHAPTER 1

INTRODUCTION

1.1 Research Background

Increasing demands and shortage of clean water sources due to the rapid development of industrialization, population growth, and long-term drought have become a serious issue worldwide. Due to this problem, various practical strategies and solutions have been adopted to yield more viable water resources. Wastewater is liquid waste discharged by domestic residences, commercial properties, industries, and agricultural activities, which often contain some contaminants resulting from the mixing of wastewater from different sources (Busca *et al.*, 2008). However, it is worth to realize that wastewater also consists of pure water, and therefore numerous processes have been implemented to clean up waste water depending on the type and extent of contamination (Teh and Mohamed, 2011). Disposal untreated waste water or minimal wastewater treatment of household and factories directly into drains and rivers has resulted in contaminated raw surface water (Musson and Townsend, 2009). Treated wastewater then can be reused as drinking water after it has been cleared from contaminants. The treatment of wastewater is not only important for health, but also to environment. Without proper treatment, many ecosystems would be severely damaged once the treated water is discharged into the environment.

Currently, there are several conventional wastewater treatments available in order to treat specific wastes such as sewage, industrial and agricultural wastes, and radioactive wastewater. There is no treatment technology that applies the same to all pollutants removal. Among those wastewater treatments, membrane technology is leading in providing promising and innovation approach in upgrading and expansion of wastewater treatment plant (Madaeni *et al.*, 2011). This technology can improve the purification of the wastewater, make it more attractive compared to the conventional methods (Singh *et al.,* 2008). Membrane technologies are looking forward to increase the effectiveness of treating pollutants in wastewater treatment, however it also possessed some limitations related to fouling that will consequently reduce the permeate flux and efficiencies of the separation process (Shon *et al.*, 2007). Photodegradation of pollutants in wastewater via the application of photocatalysis is compromising as the best technology in treating micro pollutants and to reduce membrane fouling problems.

Wastewater from pharmaceutical industries poses one of the biggest challenges to the industrial waste treatment system. A wide variety of products in the pharmaceutical manufacturing industries require large amount of chemical substances in the manufacturing process. Waste water streams generated from this pharmaceutical manufacturing have been heavily contaminated with different type of chemicals, toxins and organic contents. Along with very complex contaminants, it becomes challenging for the treatment of the wastewater as the regulations for waste discharged is very stringent. Endocrine-disrupting compound (EDC) is one of the pharmaceutical wastes that require a critical concern for its treatment. For years, EDC have been detected in wastewater effluents and raw drinking water sources around the world at very low concentrations (Yoon *et al.*, 2007). Since EDC have potential risk to humans and wildlife even at the minimal trace levels, removal of EDC becomes important in water industry in order to protect the environment and eliminate refractory organic.

Nowadays, photocatalytic process has shown a great potential as a low-cost, and sustainable treatment technology in wastewater industry. The ability of this advanced technology has been widely demonstrated to remove persistent organic compounds and microorganisms in water. Recently, the main technical barriers that impede its commercialization remained on the post-recovery of the catalyst particles after the water treatment. To date, the photocatalyst recovery can be achieved by the hybridization of the catalyst onto the support materials. Although the immobilization of the photocatalyst on the support materials will reduce the amount of catalyst active site, it can reduce the catalyst post-recovery step and at the same time can reduce the cost of the process.

Over the last decades, a great deal of interest has been focused on the photodegradation of organic compounds presence in water and wastewaters with the application of Titanium dioxide (TiO_2) as the photocatalyst. Generally, TiO_2 has been considered as one of the best semiconductor photocatalysts available for photocatalysis, due to its high photoactivity and photodurability owing to chemical and biological inertness, mechanical robustness, flexibility in its surface function, high mechanical stability, large surface area to volume ratio towards the light irradiation, and low cost (Doh *et al.*, 2008). The vast surface area of nanostructured TiO_2 photocatalyst allows high in excellent interaction between the pollutants and the catalyst, leading to better photocatalytic activity (Herrmann, 1999). Nanoparticles, nanotubes, nanowires, nanorods, and nanofibers are several forms of nanostructured photocatalysts that were produced for their higher purity, large surface area, and great size uniformity. These fascinating properties have an ability to reduce the toxicity of the pollutants to a safer level at reasonable cost (Colmenares *et al.*, 2009).

Photodegradation of organic pollutants by suspended photocatalyst has a major drawback in terms of difficulty to separate very small particles of the photocatalyst which requires another post-recovery treatment. To overcome this difficulty, the immobilizations of photocatalyst in/on a support/host have been introduced. Nowadays, membrane support has been widely used for photocatalyst in photocatalytic process. However, the incorporation of the photocatalyst in/onto the polymeric membrane support results in a loss of photoactivity, attributed by the reduced active surface accessible for components of the solution. It is believed that, the immobilization of the photocatalyst in/on the membrane support can be improved by introducing nanomaterials. In addition, the optimization study of the membrane microstructures and characteristics by several approaches is necessary to develop photocatalytic membranes with enhanced photocatalytic properties.

1.2 Problem Statement

Disposal untreated waste water or minimal wastewater treatment of household and factories directly to drains and rivers has resulted in contaminated raw surface water. With the deterioration in water quality, the use of clean water for daily use such as cooking, washing clothes, cleaning the dirt, to drink and so on is impaired. There are many contaminants or a pollutant that can caused disease that is depends on the type of pollutants that present in the wastewater itself. High pressure-driven membranes such as nanofiltration (NF) or reverse osmosis (RO) might be a powerful option to deal with such micro-pollutants (Kimura *et al.,* 2004). However, lack of information on their performance is apparent. Among various types of organic micro-pollutants with low molecular weight, endocrine disrupting compounds (EDCs) have been received a considerable attention recently. With rapid development of analytical techniques, it has been reported even at very low concentration, EDC effluents have become a major source of pollutant that polluted many aquatic environments. Pollution of drinking water sources with organic micro-pollutants is one of the great concerns in such situations. Their concentrations in the raw water were affected by the percentage of treated wastewater. One of EDCs that available abundantly in wastewater is bisphenol A (BPA). For instance, BPA is an important raw material in the production of polycarbonate plastics and epoxy resins, which high volume of this chemical waste produced daily could severely affect the aquatic ecosystem, as well as human.

To overcome this problem, the use of membrane filtration processes has been widely utilized over the past decade in order to remove the unwanted micro- and macro- particles. For example, unwanted particles that attached the outer layer of membrane thus forming a cake layer became the main obstacle in membrane filtration efficiency as it affected the productivity (Leong *et al.,* 2014). This phenomenon has practically and economically retarded membrane applications in water treatment development. The reduction in productivity caused by membrane fouling can be interpreted as the declined in flux with time of operation due to the increased of hydraulic resistance. It also can be defined that extra energy supply is needed by the membrane filtration system in order to maintain the system performance. Moreover, the cleaning processes have been introduced to the system to remove the cake layer from the outer layer of membrane so that it can produce the permeate volume as much as at earlier stages.

At the moment, photocatalytic oxidation has been pledging as the valuable process for air and water purification because of its capability to produce harmless products by degrading the organic pollutants without the involvement of chemicals (Huang *et al.*, 2007; Litter, 1999). This advanced oxidation process (AOPs) has a variety of reactions such as organic synthesis, water splitting, photo reduction, hydrogen transfer, gaseous pollutant removal, and others (Gaya and Abdullah, 2008; Herrmann, 1999). The photocatalytic process has a great deal of interest in photodegradation of organic compounds present in wastewater with incorporation of titanium dioxide (TiO_2) as a photocatalyst.

Over the past decades, nanomaterials show a wide ranging potential in various major areas including industrial, biomedical and electronic applications. It has attracted the attention of many people especially researcher to further research and to improve the characteristics of the nanomaterials. Nanomaterial such as nanoparticles (Fischer *et al.*, 2015), nanowires (Zhang *et al.*, 2015), nanofibers (Vahtrus *et al.*, 2015), and nanotubes (Arruda *et al.*, 2015) only have size ranging from 1-100 nm. Commonly, nanomaterial is used as a catalyst in order to improve the process efficiencies because of the small particles will lead to a greater surface area for the reaction between pollutants and catalyst (Shen *et al.*, 2014). Due to its high active surface area, nanomaterial can be used to reduce the toxicity of pollutants to safer level at very reasonable cost (Kriklavova and Lederer, 2011). Nanofibers membrane is one of the advanced technologies used because of its small pore size and large surface area to volume ratio. It also has a good flexibility of its surface function and high mechanical performance such as tensile strength (Huang *et al.*, 2003; Lev *et al.*, 2011). The excellent features of nanofibers lead to many important technology development applications.

There are several techniques have been used to produce nanofibers such as melt blowing, forcespinning, and electrospinning. For example, heated air blows were used to produce nanofibers in melt blown process while in forcespinning, the centrifugal forces has been used to turn the material into nanofibers (Ellison *et al.,* 2007; Padron *et al.,* 2013). Apart from that, electrospinning is the simplest available method used to produce fibers with diameters ranging between 10nm to 10 µm by accelerating a jet of charged precursor solution in an electric field (Nor *et al.,* 2013; Vonch *et al.,* 2007).

The suspended TiO_2 photocatalysts have higher photocatalytic efficiencies because the overall active surface of the TiO_2 particles are in contact with the organic pollutants in water/air and directly absorbed more UV light. However, this kind of process requires another post-treatment in order to separate the catalyst which are the discharge of the catalyst with effluent might be harmful to the ecosystem due to its biological accumulative effect (Grieken *et al.,* 2009). To overcome these problems, the immobilized TiO_2 catalyst on the support material has been introduced. Compared to the suspended applications, the immobilized TiO_2 photocatalyst on the support requires only one-step process. This kind of configuration exhibits a major drawback such as low photocatalytic activity due to the less active surface area of the attachment of the TiO_2 catalyst on the support (Gao and Liu, 2005).

There are several methods can be used to immobilize the TiO_2 photocatalyst on the membrane support (Chong *et al.,* 2010). Dip coating or spinnng, blending, hot pressing, and physical or chemical cross-linking are some of the methods incorporating hybrid membrane (Bonchio *et al.,* 2006; Mohamed *et al.,* 2015a; Okur *et al.,* 2013; Romanos *et al.,* 2013). In several studies, hot pressing methods were done by applying both pressure and heat to improve the connectivity between fiber and membrane intersection (Lu *et al.*, 2002; Yuliwati *et al.*, 2011). Membrane compactness, mechanical properties and chemical stabilities of membrane will be improved by applying the concurrent application of pressure and heat (Na *et al.,* 2009). The losses strands of the nanofibers that are present on the top of the surface would also be eliminated as reported by Na *et al.* (2009) who studied the effect of hot press treatment on the electrospun PVDF membrane.

The current conventional methods used for wastewater treatment incapable for treating micropollutants such as EDCs and this might due to the compounds complexity and persistence. There is no such technology approach or treatment method that applies the same to all EDCs removal. Due to its high surface area, nanofibers have been used in this technique as it can enhance the filtration efficiency. Therefore, the current research was conducted to explore the possibility and effectiveness of EDCs removal in wastewater by using nanofiber coating on the membrane for membrane separation and photodegradation applications.

1.3 Objective of Study

The aim of this study is to investigate the removal efficiency of Bisphenol A (BPA) via photocatalytic process using the developed hybrid membrane made of PVDF-based membrane coated with TiO_2 nanofibers. The specific objectives of this study are:

1) To study the effect of TiO_2 precursor solution concentrations on the physical properties of TiO_2 nanofibers

2) To study the effects of hot pressing temperature on morphological structure of TiO_2 nanofibers coated onto PVDF membrane

3) To investigate the photocatalytic performances and membrane separation properties of flat sheet PVDF/e-spun TiO_2 nanocomposite membrane towards BPA removals

1.4 Scope of Study

In order to achieve the above mentioned objectives, the following scopes are outlined:

1) Preparing TiO_2 precursor solution by varying the concentration of (0.5g, 1.0g and 1.5g) polyvinylpyrrolidone, PVP in 1.6mL of titanium tetraisopropoxide (TTIP) under electrospinning process.

2) Analysing the morphological structure and the diameter of the resultant TiO_2 nanofibers using scanning electron microscope (SEM).

3) Preparing the polyvinylidene fluoride (PVDF) flat sheet membrane using phase inversion technique as a nanocomposite membrane support.

4) Developing the coating process of PVDF membrane with as-spun TiO_2 nanofibers using hot press method at temperature of 100°C, 160°C and 180°C for 30 minutes.

5) Characterizing the PVDF/e-spun TiO_2 nanofibers in terms of morphological structures and structural properties towards photocatalytic process by using field electron scanning electron microscope (FESEM), energy dispersive X-ray analysis (EDX), thermal properties by differential scanning calorimetry (DSC) and optical absorption behaviour by ultraviolet-visible-near-infrared spectrophotometry (UV-VIS-NIR).

6) Investigating the photocatalytic performance of the prepared PVDF/e-spun TiO_2 nanofibers for the photodegradation of BPA by using high performance liquid chromatography (HPLC) coupled with a programmable UV detector.

7) Examining the performance of the PVDF/e-spun TiO_2 nanofibers toward membrane separation through the membrane physical characteristics in terms of membrane hydrophilicity, pure water flux, membrane porosity, membrane mean pore size, and membrane rejection.

1.5 Significance of Study

In recent years, membrane based photocatalytic technology was nominated as an Advanced Oxidation Process (AOP) owing to its promising ability to degrade trace level environmental pollutants via hybrid technology approach such as photodegradation and membrane separation. The utilization of TiO_2 nanofibers as the photocatalyst was found to be interesting due to the flexibility in its surface function, high mechanical stability, and very large surface area to volume ratio towards the light irradiation. These properties are significantly meaningful for a maximum light absorption and simultaneously improved the photocatalytic activity. Furthermore, the immobilization of TiO_2 nanofibers on the PVDF membrane support can simplify the conventional photocatalytic process by eliminating the post treatment of catalyst separation process. The significant improvement in this study, indicated that the photocatalytic membrane is vital to sustain a clean and safer environment.

REFERENCES

Ahmed, S., Rasul, M. G., Brown, R., and Hashib, M. A. (2011). Influence of Parameters on the Heterogeneous Photocatalytic Degradation of Pesticides and Phenolic Contaminants in Wastewater : A Short Review. *Journal of Environmental Management* 92(3):311–30.

Akpan, U. G. and Hameed, B. H. (2009). Parameters Affecting the Photocatalytic Degradation of Dyes Using TiO_2-Based Photocatalysts : A Review. *Journal of Hazardous Materials* 170:520–29.

Amjad, Z., Zibrida, J. F., and Zuhl, R. W. (1998). Reverse Osmosis Technology : Fundamentals and Water Applications. *Association of Water Technologies,Inc 1998 Annual Convention & Exposition*. 24-28 October 1998, Washington, DC.

Arruda, L. B., Santos, C. M., Orlandi, M. O., Schreiner, W. H., and Lisboa-Filho, P. N. (2015). Formation and Evolution of TiO_2 Nanotubes in Alkaline Synthesis. *Ceramics International* 41(2):2884–2891.

Baker, R. W. (1985). Membrane Technology and Applications. (2nd Edition). Technology and Research, Inc. Menlo Park, California: Wiley.

Bhattarai, P., Thapa, K. B., Basnet, R. B., and Sharma, S. (2014). Electrospinning: How to Produce Nanofibers Using Most Inexpensive Technique? An Insight into the Real Challenges of Electrospinning Such Nanofibers and Its Application Areas. *International Journal of Biomedical and Advance Research* 05(09):401–405.

Bjorge, D., Daels, N., Vrieze, S. D., Dejans, P., Camp, T. V., Audenaert, W., Hogie, J., Westbroek, P., de Clerck, K., and Hulle, S. W. H. (2009). Performance Assessment of Electrospun Nanofibers for Filter Applications. *Desalination* 249:942–948.

Bonchio, M., Carraro, M., Gardan, M., Scorrano, G., Drioli, E., and Fontananova, E. (2006). Hybrid Photocatalytic Membranes Embedding Decatungstate for Heterogeneous Photooxygenation. *Topics in Catalysis* 40(1-4):133–140.

Braga, F. J. C., Rogero, S. O., Couto, A. A., Marques, R. F. C., Ribeiro, A. A., and Campos, J. S. de C. (2007). Characterization of PVDF/HAP Composites for Medical Applications. *Materials Research* 10(3):247–251.

Busca, G., Berardinelli, S., Resini, C., and Arrighi, L. (2008). Technologies for the Removal of Phenol from Fluid Streams : A Short Review of Recent Developments. *Journal of Hazardous Materials* 160:265–288.

Cai, Y. B., Zhang, J. J., Sun, G. Y., Wang, Q. Q., Ye, H. P., Qiao, H., and Wei, Q. F. (2014). Fabrication, Structural Morphology and Photocatalytic Activity of Porous TiO_2 Nanofibers through Combination of Sol–gel, Electrospinning and Doping removal Techniques. *Materials Technology* 29(1):40–46.

Cao, X., Ma, J., Shi, X., and Ren, Z. (2006). Effect of TiO_2 Nanoparticle Size on the Performance of PVDF Membrane. *Applied Surface Science* 253(4):2003–2010.

Cheng, C., He, A., Nie, C., Xia, Y., He, C., Ma, L., and Zhao, C. (2015). One-Pot Cross-Linked Copolymerization for the Construction of Robust Antifouling and Antibacterial Composite Membranes. *Journal of Material Chemistry B* 3:4170–4180.

Chin, S. S., Chiang, K., and Fane, A. G. (2006). The Stability of Polymeric Membranes in a TiO_2 Photocatalysis Process. *Journal of Membrane Science* 275(1-2):202–211.

Choi, Hyeok, Stathatos, E., and Dionysiou, D. D. (2006). Sol–gel Preparation of Mesoporous Photocatalytic TiO_2 Films and TiO_2/Al_2O_3 Composite Membranes for Environmental Applications. *Applied Catalysis B: Environmental* 63(1-2):60–67.

Chong, M. N., Jin, B., Chow, C. W. K., and Saint, C. (2010). Recent Developments in Photocatalytic Water Treatment Technology: A Review. *Water Research* 44(10):2997–3027.

Colmenares, J. C., Luque, R., Campelo, J. M., Colmenare, F., Karpinski, Z., and Romero, A. A. (2009). Nanostructured Photocatalysts and Their Applications in the Photocatalytic Transformation of Lignocellulosic Biomass: An Overview. *Materials* 2(4):2228–2258.

Crain, D. A., Eriksen, M., Iguchi, T., Jobling, S., Laufer, H., LeBlanc, G. A., and Guillette, L. J. J. (2007). An Ecological Assessment of Bisphenol-A: Evidence from Comparative Biology. *Reproductive Toxicology* 24(2):225–239.

Dai, Y., Liu, W., Formo, E., Sun, Y., and Xia, Y. (2011). Ceramic Nanofibers Fabricated by Electrospinning and Their Applications in Catalysis, Environmental Science, and Energy Technology. *Polymer Advanced Technology* 22:326–338.

Damodar, R. A., You, S. J., and Chou, H. H. (2009). Study the Self Cleaning, Antibacterial and Photocatalytic Properties of TiO_2 Entrapped PVDF Membranes. *Journal of Hazardous Materials* 172(2-3):1321–1328.

Destrée, C., and Nagy, J. B. (2006). Mechanism of Formation of Inorganic and Organic Nanoparticles from Microemulsions. *Advances in Colloids and Interface Science* 126:353–367.

Ding, Y., Zhang, P., Long, Z., Jiang, Y., Xu, F., and Di, W. (2008). Preparation of PVDF-Based Electrospun Membranes and Their Application as Separators. *Science and Technology of Advanced Materials* 9(1):1-4.

Doh, S. J., Kim, C., Lee, S. G., Lee, S. J., and Kim, H. (2008). Development of Photocatalytic TiO_2 Nanofibers by Electrospinning and Its Application to Degradation of Dye Pollutants. *Journal of Hazardous Materials* 154(2008):118–127.

Dzinun, H., Othman, M. H. D., Ismail, A. F., Puteh, M. H., Rahman, M. A., and Jaafar, J. (2015). Photocatalytic Degradation of Nonylphenol by Immobilized TiO_2 in Dual Layer Hollow Fibre Membranes. *Chemical Engineering Journal* 269:255–261.

Ellison, C. J., Phatak, A., Giles, D. W., Macosko, C. W., and Bates, F. S. (2007). Melt Blown Nanofibers: Fiber Diameter Distributions and Onset of Fiber Breakup. *Polymer* 48(11):3306–3316.

Fazeli, S., Fatehizadeh, A., Hassani, A. H., Torabian, A., and Amin, M. M. (2012). Evaluation of Flat Sheet Membrane Bioreactor Efficiency for Municipal Wastewater Treatment. *International Journal of Environmental Health Engineering* 1(2):2–6.

Feng, C., Khulbe, K. C., Matsuura, T., Table, S., and Ismail, A. F. (2013). Preparation and Characterization of Electrospun Nanofiber Membranes and

Their Possible Applications in Water Treatment. *Separation and Purification Technology* 102:118–135.

Fischer, K., Grimm, M., Meyers, J., Dietrich, C., Glaser, R., and Schulze, A. (2015). Photoactive Microfiltration Membranes via Directed Synthesis of TiO_2 Nanoparticles on the Polymer Surface for Removal of Drugs from Water. *Journal of Membrane Science* 478:49–57.

Fridrikh, S. V., Yu, J. H., Brenner, M. P., and Rutledge, G. C. (2003). Controlling the Fiber Diameter during Electrospinning. *Physical Review Letters* 90(14):1–4.

Fujishima, A., Rao, T. N., and Tryk, D. A. (2000). Titanium Dioxide Photocatalysis. *Journal of Photochemistry and Photobiology C: Photochemistry Reviews* 1:1–21.

Gaber, A., Rahim M. A. A., and Salam, M. N. A. (2014). Influence of Calcination Temperature on the Structure and Porosity of Nanocrystalline SnO_2 Synthesized by a Conventional Precipitation Method. *International Journal of Electrochemical Science* 9:81–95.

Ganguli, A. K., Ahmad, T., Vaidya, S., and Ahmed, J. (2008). Microemulsion Route to the Synthesis of Nanoparticles. *Pure Applied Chemical 80*(11):2451–2477.

Gao, Y., and Liu, H. (2005). Preparation and Catalytic Property Study of a Novel Kind of Suspended Photocatalyst of TiO_2-Activated Carbon Immobilized on Silicone Rubber Film. *Materials Chemistry and Physics* 92(2-3):604–608.

Gaya, U. I. and Abdullah, A. H. (2008). Heterogeneous Photocatalytic Degradation of Organic Contaminants over Titanium Dioxide: A Review of Fundamentals, Progress and Problems. *Journal of Photochemistry and Photobiology C: Photochemistry Reviews* 9(1):1–12.

Ghemati, D., and Aliouche, D. (2013). Study of the Kinetics Adsorption of Organic Pollutants on Modified Cellulosic Polymer Using Ultraviolet-Visible Spectroscopy. *Journal of Spectroscopy* 1(1):1-7.

Gomes, A. L., Zakia, M. B. P., Filho, J. G., Armelin, E., Aleman, C., and Campos, J. S. de C. (2012). Preparation and Characterization of Semiconducting Polymeric Blends. Photochemical Synthesis of poly(3-Alkylthiophenes) Using Host Microporous Matrices of Poly(vinylidene Fluoride). *Polymer Chemistry* 3(5):1334-1343.

Gondal, M. A., Sadullah, M. S., Dastageer, M. A., McKinley, G. H., Panchanathan, D., and Kripa, K. V. (2014). Study of Factors Governing Oil–Water

Separation Process Using TiO_2 Films Prepared by Spray Deposition of Nanoparticle Dispersions. *ACS Applied Materials & Interfaces* 6(16):13422–13429.

Gopal, R., Kaur, S., Ma, Z., Chan, C., Ramakrishna, S., and Matsuura, T. (2006). Electrospun Nanofibrous Filtration Membrane. *Journal of Membrane Science* 281(1-2):581–586.

Grafe, T., and Graham, K. (2002). Polymeric Nanofibers and Nanofiber Webs : A New Class of Nonwovens. *International Nonwovens Technical Conference.* 24-26 September 2002. Atlanta, Georgia.

Grieken, V., Rafael, J. M., Sordo, C., and Pablos, C. (2009). Comparison of the Photocatalytic Disinfection of E. Coli Suspensions in Slurry, Wall and Fixed-Bed Reactors. *Catalysis Today* 144(1-2):48–54.

Gruber-Woelfler, H., Radaschitz, P. F., Feenstra, P. W., Haas, W., and Khinast, J. G. (2012). Synthesis, Catalytic Activity, and Leaching Studies of a Heterogeneous Pd-Catalyst Including an Immobilized Bis(oxazoline) Ligand. *Journal of Catalysis* 286:30–40.

Hanaor, D. A. H., and Sorrell, C. C. (2010). Review of the Anatase to Rutile Phase Transformation. *Journal of Materials Science* 46(4):855–874.

Hashimoto, K., Irie, H., and Fujishima, A. (2005). TiO_2 Photocatalysis : A Historical Overview and Future Prospects. *Japanese Journal of Applied Physics* 44(12):8269–8285.

Heikkila, P. (2009). Electrospinning of Polyacrylonitrile (PAN) Solution: Effect of Conductive Additive and Filler on the Process. *eXPRESS Polymer Letters* 3(7):437–445.

Heo, J., Joseph, L., Yoon, Y., Park, Y. G., Her, N., Sohn, J., Yoon, S. H. (2011). Removal of Micropollutants and NOM in Carbon Nanotube-UF Membrane System from Seawater. *Water Science & Technology* 63(11):2737-2744.

Herrmann, J. M. (1999). Heterogeneous Photocatalysis : Fundamentals and Applications to the Removal of Various Types of Aqueous Pollutants. *Catalysis Today* 53:115–129.

Huang, X., Meng, Y., Liang, P., and Qian, Y. (2007). Operational Conditions of a Membrane Filtration Reactor Coupled with Photocatalytic Oxidation. *Separation and Purification Technology* 55:165–172.

Huang, Z. M., Zhang, Y., Kotaki, M., and Ramakrishna, S. (2003). A Review on Polymer Nanofibers by Electrospinning and Their Applications in Nanocomposites. *Composites Science and Technology* 63(2003):2223–2253.

Hwang, K., Kwon, B., and Byun, H. (2011). Preparation of PVDF Nanofiber Membranes by Electrospinning and Their Use as Secondary Battery Separators. *Journal of Membrane Science* 378(1-2):111–116.

Kamat, P. V. (1993). Photochemistry on Nonreactive and Reactive (semiconductor) Surfaces. *Chemical Reviews* 93(1):267–300.

Kaneco, S., Rahman, A. M., and Suzuki, T., Katsumata, H., and Ohta, K. (2004). Optimization of Solar Photocatalytic Degradation Conditions of Bisphenol A in Water Using Titanium Dioxide. *Journal of Photochemistry and Photobiology A: Chemistry* 163:419–424.

Kanki, T., Hamasaki, S., Sano, N., Toyoda, A., and Hirano, K. (2005). Water Purification in a Fluidized Bed Photocatalytic Reactor Using TiO_2 Coated Ceramic Particles. *Chemical Engineering Journal* 108:155–160.

Kavitha, T., Rajendran, A., and Durairajan, A. (2012). Synthesis, Characterization of TiO_2 Nano Powder and Water Based Nanofluids Using Two Step Method. *European Journal of Applied Engineering and Scientific research* (4):235–240.

Khayet, M., Feng, C. Y., Khulbe, K. C., and Matsuura, T., (2002). Preparation and Characterization of Polyvinylidene Fluoride Hollow Fiber Membranes for Ultrafiltration. *Polymer* 43: 3879-3890.

Kim, J. H., Park, P. K., Lee, C. H. and Kwon, H. H. (2008). Surface Modification of Nanofiltration Membranes to Improve the Removal of Organic Micro-Pollutants (EDCs and PhACs) in Drinking Water Treatment: Graft Polymerization and Cross-Linking Followed by Functional Group Substitution. *Journal of Membrane Science* 321(2):190–198.

Kimura, K., Toshima, S., Amy, G., and Watanabe, Y. (2004). Rejection of Neutral Endocrine Disrupting Compounds (EDCs) and Pharmaceutical Active Compounds (PhACs) by RO Membranes. *Journal of Membrane Science* 245(1-2):71–78.

Kriklavova, L. and Ledere, T. (2011). A Review Study of Nanofiber Technology For Wastewater Treatment. *Nanocon 2011*. 21-23 September 2011. Brno, Czech republic, EU.

Lalia, B. S., Kochkodan, V., Hashaikeh, R., and Hilal, N. (2013). A Review on Membrane Fabrication: Structure, Properties and Performance Relationship. *Desalination* 326:77–95.

Le-clech, P., Lee, E. K., and Chen, V. (2006). Hybrid Photocatalysis/Membrane Treatment for Surface Waters Containing Low Concentrations of Natural Organic Matters. *Water Research* 40:323–330.

Leong, S., Razmjou, A., Wang, K., Hapgood, K., Zhang, X., and Wang, H. (2014). TiO_2 Based Photocatalytic Membranes: A Review. *Journal of Membrane Science* 472:167–184.

Lev, J., Holba, M., Kalhotka, L., Szostková, M. and Kimmer, D. (2011). Application of The Electrospun Nanofibers In Wastewater Treatment. *Nanocon 2011*. 21-23 September 2011. Brno, Czech republic, EU.

Li, D., and Xia, Y. (2003). Fabrication of Titania Nanofibers by Electrospinning. *Nano letters* 3(4): 555-560.

Li, D., McCann, J. T., and Xia, Y. (2006). Electrospinning: A Simple and Versatile Technique for Producing Ceramic Nanofibers and Nanotubes. *Journal of American Ceramic Society* 89(6):1861–1869.

Li, Q., Sun, D., and Kim, H. (2011). Fabrication of Porous TiO_2 Nanofiber and Its Photocatalytic Activity. *Materials Research Bulletin* 46(11):2094–2099.

Li, J., Qiao, H., Du, Y., Chen, C., Li, X., Cui, J., Kumar, D., and Wei, Q. (2012). Electrospinning Synthesis and Photocatalytic Activity of Mesoporous TiO_2 Nanofibers. *The Scientific World Journal* 2012:1-7.

Li, M., Wang, D., Xiao, R., Sun, G., Zhao, Q., and Li, H. (2013a). A Novel High Flux Poly(trimethylene Terephthalate) Nanofiber Membrane for Microfiltration Media. *Separation and Purification Technology* 116:199–205.

Li, M., Katsouras, I., Piliego, C., Glasser, G., Lieberwirth, I., Blom, P. W. M., and de Leeuw, D. M. (2013b). Controlling the Microstructure of Poly(vinylidene-Fluoride) (PVDF) Thin Films for Microelectronics. *Journal of Materials Chemistry C* 1(46):7695–7702.

Li, M., Huang, G., Qiao, Y., Wang, J., Liu, Z., Liu, X., and Mei, Y. (2013c). Biocompatible and Freestanding Anatase TiO_2 Nanomembrane with Enhanced Photocatalytic Performance. *Nanotechnology* 24(30):1-8.

Liang, S., Kang, Y., Tiraferri, A., Giannelis, E. P., Huang, X., and Elimelech, M. (2013). Highly Hydrophilic Polyvinylidene Fluoride (PVDF) Ultrafiltration

Membranes via Post fabrication Grafting of Surface-Tailored Silica Nanoparticles. *Applied Materials and Interfaces* 5:6694–6703.

Liao, Y., Rong, W., M, Tian., Qiu, C., and Fane, A. G. (2013). Fabrication of Polyvinylidene Fluoride (PVDF) Nanofiber Membranes by Electro-Spinning for Direct Contact Membrane Distillation. *Journal of Membrane Science* 425-426:30–39.

Ling, C. M., Mohamed, A. R., and Bhatia, S. (2004). Performance of Photocatalytic Reactors Using Immobilized TiO_2 Film for the Degradation of Phenol and Methylene Blue Dye Present in Water Stream. *Chemosphere* 57(7):547–554.

Linh, N. T. B., Lee, K. H., and Lee, B. T. (2011). A Novel Photoactive Nano-Filtration Module Composed of a TiO_2 Loaded PVA Nano-Fibrous Membrane on Sponge Al_2O_3 Scaffolds. *Materials Transactions* 52(7):1452–1456.

Litter, M. I. (1999). Heterogeneous Photocatalysis Transition Metal Ions in Photocatalytic Systems. *Applied Catalysis B: Environmental* 23:89–114.

Liu, F., Hashim, N. A., Liu, Y., Abed, M. R. M., and Li, K. (2011). Progress in the Production and Modification of PVDF Membranes. *Journal of Membrane Science* 375:1–27.

Liu, S., Liu, B., Nakata, K., Ochiai, T., Murakami, T., and Fujishima, A. (2012). Electrospinning Preparation and Photocatalytic Activity of Porous TiO_2 Nanofibers. *Journal of Nanomaterials* 2012:1–5.

Lu, X., Bian, X., and Shi, L. (2002). Preparation and Characterization of NF Composite Membrane. *Journal of Membrane Science* 210(1):3–11.

Madaeni, S. S., Ghaemi, N., Alizadeh, A., and Joshaghani, M. (2011). Applied Surface Science Influence of Photo-Induced Superhydrophilicity of Titanium Dioxide Nanoparticles on the Anti-Fouling Performance of Ultrafiltration Membranes. *Applied Surface Science* 257(14):6175–6180.

Martins, P. M., Gomez, V., Lopes, A. C., Tavares, C. J., Botelho, G., Irusta, S., and Mendez, S. L. (2014). Improving Photocatalytic Performance and Recyclability by Development of Er-Doped and Er/Pr-Codoped TiO_2/Poly(Vinylidene Fluoride)−Trifluoroethylene Composite Membranes.” *Journal Physical Chemistry C* 118:27944–27953.

Masakazu, A. (2000). Use of Visible Light, Second-Generation Titanium Oxide Photocatalysts Prepared by the Application of an Advanced Metal Ion-Implantation Method. *Pure and Applied Chemistry* 72(9):1787–1792.

Meng, F., Chae, S. R., Drews, A., Kraume, M., Chae, S. R., Drews, A., Kraume, M., Shin, H. S., and Yang, F. (2009). Recent Advances in Membrane Bioreactors (MBRs): Membrane Fouling and Membrane Material. *Water Research* 43(6):1489–1512.

Mihaich, E. M., Friederich, U., Caspers, N., Hall, A., T., Klecka, G. M., Dimond, S. S., Staples, C. A., Ortego, L. S., and Hentges, S. G. (2009). Acute and Chronic Toxicity Testing of Bisphenol A with Aquatic Invertebrates and Plants. *Ecotoxicology and Environmental Safety* 72(5):1392–1399.

Min, B. J., Sun, P. P., Kim, T. Y., Kim, S. S., and Kim, S. J. (2013). The Effects of Temperature and Pressure on Membrane Electrode Assemblies for Polymer Electrolyte Membrane. *Advanced Science and technology Letters* 38:10–14.

Mohamed, M. A., Salleh, W. N. W., Jaafar, J., Ismail, A. F., Mutalib, M. A., and Jamil, S. M. (2015a). Incorporation of N-Doped TiO_2 Nanorods in Regenerated Cellulose Thin Films Fabricated from Recycled Newspaper as a Green Portable Photocatalyst. *Carbohydrate Polymers* 133:429–437.

Mohamed, M. A., Salleh, W. N. W., Jaafar, J., Ismail, A. F., Mutalib, M. A., and Sani, N. A. A. (2015b). Physicochemical Characteristic of Regenerated Cellulose/N-Doped TiO_2 Nanocomposite Membrane Fabricated From Recycled Newspaper with Photocatalytic Activity under UV and Visible Light Irradiation. *Chemical Engineering Journal* 284:202–215.

Mohamed, M. A., Salleh, W. N. W., Jaafar, J., Ismail, A. F., and Nor, A. M. N. (2015c). Photodegradation of Phenol by N-Doped TiO_2 Anatase/rutile Nanorods Assembled Microsphere under UV and Visible Light Irradiation. *Materials Chemistry and Physics* 162:113–123.

Molinari, R., Grande, C., Drioli, Enrico., Palmisano, L., and Schiavello, M. (2001). Photocatalytic Membrane Reactors for Degradation of Organic Pollutants in Water. *Catalysis Today* 67:273–279.

Mollaesmail, S., Moghaddam, J., and Karimi, S. (1996). The Influence of Morphology on Photo-Catalytic Activity and Optical Properties of Nano-Crystalline ZnO Powder. *Nano-micro Letters* 4(4):1–11.

Morales, A. E., Mora, E. S., Pal, U. (2007). Use of Diffuse Reflectance Spectroscopy for Optical Characterization of Unsupported Nanostructures. *Revista Mexicana de Fisica S* 53(5):18–22.

Morihama, A. C. D., and Mierzwa, J. C. (2014). Clay Nanoparticles Effects on Performance and Morphology of Poly(vinylidene Fluoride) Membranes. *Brazilian Journal of Chemical Engineering* 31(1):79–93.

Mozia, S. (2010). Photocatalytic Membrane Reactors (PMRs) in Water and Wastewater Treatment. A Review. *Separation and Purification Technology* 73(2):71–91.

Musson, S. E., and Townsend, T. G. (2009). Pharmaceutical Compound Content of Municipal Solid Waste. *Journal of Hazardous Materials* 162(2-3):730–735.

Na, H., Zhao, Y., Zhao, C., Zhao, C., and Yuan, X. (2008). Effect of Hot-Press on Electrospun Poly(Vinylidene Fluoride) Membranes. *Polymer Engineering and Science* 2008:934-940.

Na, H., Li, Q., Sun, H., Zhao, C., and Yuan, X. (2009). Anisotropic Mechanical Properties of Hot-Pressed PVDF Membranes with Higher Fiber Alignments via Electrospinning. *Polymer engineering and science* 2009:1291-1298.

Na, H., Zhao, Y., Liu, X., Zhao, C., and Yuan, X. (2011). Structure and Properties of Electrospun Poly(vinylidene Fluoride)/polycarbonate Membranes after Hot-Press. *Journal of Applied Polymer Science* 122(2):774–781.

Nghiem, L. D., Vogel, D., and Khan, S. (2008). Characterising Humic Acid Fouling of Nanofiltration Membranes Using Bisphenol A as a Molecular Indicator. *Water Research* 42(15):4049–4058.

Nguyen, H. Q., and Deng, B. (2012). Electrospinning and in Situ Nitrogen Doping of TiO_2/PAN Nanofibers with Photocatalytic Activation in Visible Lights. *Materials Letters* 82:102–104.

Nor, N. A. M., Jaafar, J., Othman, M. H. D., and Rahman, M. A. (2013). A Review Study of Nanofibers in Photocatalytic Process for Wastewater Treatment. *Jurnal Teknologi* 65(4):83–88.

Nowotny, M. K., Bogdanoff, P., Dittrich, T., Fiechter, S., Fujishima, A., and Tributsch, H. (2010). Observations of P-Type Semiconductivity in Titanium Dioxide at Room Temperature. *Materials Letters* 64:928–930.

Ochiai, T., and Fujishima, A. (2012). Photoelectrochemical Properties of TiO_2 Photocatalyst and Its Applications for Environmental Purification. *Journal of Photochemistry & Photobiology, C: Photochemistry Reviews* 13(4):247–262.

Oh, S. J., Kim, N., and Lee, Y. T. (2009). Preparation and Characterization of PVDF/ Organic-Inorganic Composite Membranes for Fouling Resistance Improvement. *Journal of Membrane Science* 345(1-2):13–20.

Ohno, T., Akiyoshi, M., Umabeyashi, T., Asai, K., Mitsui, T., and Matsumura, M. (2004). Preparation of S-Doped TiO_2 Photocatalysts and Their Photocatalytic Activities under Visible Light. *Applied catalysis A General* 265:115–121.

Okur, O., Karadağ, Ç. I., San, F. G. B., Okumuş, E., and Behmenyar, G. (2013). Optimization of Parameters for Hot-Pressing Manufacture of Membrane Electrode Assembly for PEM (polymer Electrolyte Membrane Fuel Cells) Fuel Cell. *Energy* 57:574–580.

Padron, S., Fuentes, A., Caruntu, D., and Lozano, K. (2013). Experimental Study of Nanofiber Production through Forcespinning. *Journal of Applied Physics* 113(2):1-9.

Panigrahi, A., Pilli, S. R. and Mohanty, K. (2013). Selective Separation of Bisphenol A from Aqueous Solution Using Supported Ionic Liquid Membrane. *Separation and Purification Technology* 107:70–78.

Park, J. K., Myoung, J. J., Kyong, J. B. and Kim, H. K. (2003). Reaction Mechanism for the Hydrolysis of Titanium Alkoxides. *Bulletin of the Korean Chemical Society* 24(5):671–673.

Park, J. Y. and Kim, S. S. (2009). Effects of Processing Parameters on the Synthesis of Nanofibers by Electrospinning. *Metals and Materials International* 15(1):95–99.

Parmar, K. P. S., Ramasamy, E., Lee, W., and Sung, J. (2010). A Simple Method for Producing Mesoporous Anatase TiO_2 Nanocrystals with Elevated Photovoltaic Performance. *Scripta Materialia* 62(5):223–226.

Phonthammachai, N., Gulari, E., Jamieson, A. M., and Wongkasemjit, S. (2006). Photocatalytic Membrane of a Novel High Surface Area TiO_2 Synthesized from Titanium Triisopropanolamine Precursor. *Applied Organometallic Chemistry* 20:499–504.

Qin, X. H., and Wang, S. Y. (2006). Filtration Properties of Electrospinning Nanofibers. *Journal of Applied polymer Science* 102:1285-1290.

Qu, J., Cong, Q., Luo, C., and Yuan, X. (2013). Adsorption and Photocatalytic Degradation of Bisphenol A by Low-Cost Carbon Nanotubes Synthesized Using Fallen Leaves of Poplar. *RSC Advances* 3(3):961–965.

Rahimpour, A., Jahanshahi, M., Mollahosseini, Arash., and Rajaeian, B. (2012). Structural and Performance Properties of UV-Assisted Deposited Nano-Composite PVDF/SPES Membranes. *Desalination* 285:31–38.

Ramasundaram, S., Yoo, H. N., Song, K. G., Lee, J., Choi, K. J., and Hong, S. W. (2013). Titanium Dioxide Nanofibers Integrated Stainless Steel Filter for Photocatalytic Degradation of Pharmaceutical Compounds. *Journal of Hazardous Materials* 258-259:124–132.

Romanos, G. E., Athanasekou, C. P., Likodimos, V., Aloupogiannis, P., and Falaras, P. (2013). Hybrid Ultrafiltration/Photocatalytic Membranes for Efficient Water Treatment. *Industrial & Engineering Chemistry Research* 52:13938–13947.

Rykowska, I. and Wasiak, W. (2006). Properties , Threats, and Methods of Analysis of Bisphenol A And Its Derivatives. *Acta Chromatographica* 16:1-27.

Saljoughi, E., Sadrzadeh, M., and Mohammadi, T. (2009). Effect of Preparation Variables on Morphology and Pure Water Permeation Flux through Asymmetric Cellulose Acetate Membranes. *Journal of Membrane Science* 326(2):627–634.

Sarlak, N., Amin, M., Nejad, F., Shakhesi, S., and Shabani, K. (2012). Effects of Electrospinning Parameters on Titanium Dioxide Nanofibers Diameter and Morphology : An Investigation by Box-Wilson Central Composite Design (CCD). *Chemical Engineering Journal* 210:410–416.

Shen, S., Sun, K., Zhang, H., and Liang, Y. (2014). Advanced Catalysis and Nanostructure Design for Solar Energy Conversion. *Advances in Condensed Matter Physics* 2014:1–3.

Shon, H. K., Phuntsho, S., and Vigneswaran, S. (2007). Effect of Photocatalysis on the Membrane Hybrid System for Wastewater Treatment. 1–17.

Singh, K. S., Mi, Z., and Grant, S. R. (2008). Stress Effects on Fouling of Flat Sheet Membrane Bioreactor Treating Biodegradable Wastewater. *World Environmental and Water Resources Congress 200,* Ahupua'a:1-22.

Singh, P., Mondal, K. and Sharma, A. (2013). Reusable Electrospun Mesoporous ZnO Nanofiber Mats for Photocatalytic Degradation of Polycyclic Aromatic

Hydrocarbon Dyes in Wastewater. *Journal of colloid and interface science* 394:208–215.

Su, C., Hong, B., and Tseng, C. (2004). Sol – Gel Preparation and Photocatalysis of Titanium Dioxide. *Catalysis Today* 96:119–126.

Takeuchi, K., Nakamura, I., Matsumoto, O., Sugihara, S., Ando, M., and Ihara, T. (2000). Preparation of Visible-Light-Responsive Titanium Oxide Photocatalysts by Plasma Treatment. *Chemistry Letters* 2000:1354–1355.

Teh, C. M. and Mohamed, A. R. (2011). Roles of Titanium Dioxide and Ion-Doped Titanium Dioxide on Photocatalytic Degradation of Organic Pollutants (Phenolic Compounds and Dyes) in Aqueous Solutions : A Review. *Journal of Alloys and Compounds* 509(5):1648–1660.

Vahtrus, M., Sutka, A., Vlassov, S., Sutka, A., Polyakov, B., Saar, R., Dorogin, L., and Lohmus, R. (2015). Mechanical Characterization of Nanofibers Produced by Different Electrospinning Techniques. *Materials Characterization* 100:98–103.

Vonch, J., Yarin, A., and Megaridis, C. M. 2007. Electrospinning : A Study in the Formation of Nanofibers. *Journal of Undergraduate Research* 1 1:1–6.

Wang, Y. H., Liu, X. Q., and Meng, G. Y. (2007). Preparation of Asymmetric Pure Titania Ceramic Membranes with Dual Functions. *Materials Science and Engineering: A* 445-446:611–619.

Wei, W., Zhang, H., Li, X., Zhang, H., Li, Y., and Vankelecom, I. (2013). Hydrophobic Asymmetric Ultrafiltration PVDF Membranes: An Alternative Separator for VFB with Excellent Stability. *Physical Chemistry Chemical Physics : PCCP* 15(6):1766–1771.

Wei, Z., Kowalska, E., Verrett, J., Justin, C. C., Remita, H., and Ohtani, B. (2015). Morphology-Dependent Photocatalytic Activity of Octahedral Anatase Particles Prepared by Ultrasonication–hydrothermal Reaction of Titanates. *Nanoscale* 7:12392-12404.

Wu, N., Shao, D., Wei, Q., Cai, Y., and Gao, W. (2009). Characterization of PVAc / TiO_2 Hybrid Nanofibers : From Fibrous Morphologies to Molecular Structures. *Journal of Applied Polymer Science* 112(2008):1481–1485.

Yan, L., Li, Y., Xiang, C., and Xianda, S. (2006). Effect of Nano-Sized Al_2O_3 Particle Addition on PVDF Ultrafiltration Membrane Performance. *Journal of Membrane Science* 276(1-2):162–167.

Yang, Y., Zhong, H., and Tian, C. (2011). Photocatalytic Mechanisms of Modified Titania under Visible Light. *Research on Chemical Intermediates* 37:91–102.

Yoon, Y., Westerhoff, P., Snyder, S. A., Wert, E. C., and Yoon, J. K. (2007). Removal of Endocrine Disrupting Compounds and Pharmaceuticals by Nanofiltration and Ultrafiltration Membranes. *Desalination* 202(1-3):16–23.

Yu, Ji., Yu, J. C., Ho, W., and Jiang, Z. (2002). Effects of Calcination Temperature on the Photocatalytic Activity and Photo-Induced Super-Hydrophilicity of Mesoporous Thin Films. *New Journal of Chemistry* 26(5):607–613.

Yu, L. Y., Shen, H. M., and Xu, Z. L. (2009). PVDF–Composite Hollow Fiber Ultrafiltration Membranes Prepared by Sol–Gel Method and Blending Method. *Journal of Applied Physics* 113:1763–1772.

Yu, Y., Wang, E., Yuan, J., and Cao, Y. (2013). Applied Surface Science Enhanced Photocatalytic Activity of Titania with Unique Surface Indium and Boron Species. *Applied Surface Science* 273:638–644.

Yuliwati, E., Ismail, A. F., Matsuura, T., Kassim, M. A., and Abdullah, M. S. (2011). Characterization of Surface-Modified Porous PVDF Hollow Fibers for Refinery Wastewater Treatment Using Microscopic Observation. *Desalination* 283:206–213.

Zaleska, A. (2008). Doped-TiO_2 : A Review. *Recent Patents on Engineering* 2:157–164.

Zargham, S., Bazgir, S., Tavakoli, A., Rashidi, A. S., and Damerchely, R. (2012). The Effect of Flow Rate on Morphology and Deposition Area of Electrospun Nylon 6 Nanofiber. *Journal of Engineered Fibers and Fabrics* 7(4):42–49.

Zhang, L., Kanki, T., Sano, N., and Toyoda, A. (2003). Development of TiO_2 Photocatalyst Reaction for Water Purification. *Separation and purification Technology* 31:105–110.

Zhang, J., Yin, G. P., Wang, Z. B., Lai, Q. Z., and Cai, K. D. (2007). Effects of Hot Pressing Conditions on the Performances of MEAs for Direct Methanol Fuel Cells. *Journal of Power Sources 165*(1):73–81.

Zhang, X., Xu, S., and Han, G. (2009). Fabrication and Photocatalytic Activity of TiO_2 Nanofiber Membrane. *Materials Letters* 63(21):1761–1763.

Zhang, Y, Liu, P., and Wu, H. (2015). Development of High Efficient Visible Light-Driven N, S-Codoped Nanowires Photocatalysts. *Applied Surface Science* 328:335–343.

Zhou, F. L., and Gong, R. H. (2008). Review Manufacturing Technologies of Polymeric Nanofibres and Nanofibre Yarns. *Polymer International* 57:837–845.

Zhou, X., Lu, J., Jiang, J., Li, X., Lu, M., Yuan, G., Wang, Z., Zheng, M., and Seo, H. J. (2014). Simple Fabrication of N-Doped Mesoporous Nanorods with the Enhanced Visible Light Photocatalytic Activity. *Nanoscale Research Letters* 9(1):1-7.

Zori, M. H. (2011). Synthesis of TiO_2 Nanoparticles by Microemulsion Heat Treated Method and Photodegradation of Methylene Blue. *Journal of Inorganic Organometallic Polymer* 21:81–90.