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*Ultrafiltration of surface water by poly(vinylidene fluoride) (PVDF)/TiO<sub>2</sub>  
mixed matrix hollow fiber membranes (HFMs) with advanced antifouling  
properties under visible light irradiation*

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*A Thesis presented to the Faculty of the Graduate School of the  
University of Missouri-Columbia*

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*In Partial Fulfillment  
of the Requirements for the Degree*

*Master of Science*

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*By*

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*July 2014*

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*The undersigned, appointed by the Dean of the Graduate School, have examined*

*the thesis entitled:*

*Ultrafiltration of surface water by poly(vinylidene fluoride) (PVDF)/TiO<sub>2</sub>*

*mixed matrix hollow fiber membranes (HFMs) with advanced antifouling*

*properties under visible light irradiation*

*Presented by Xiaofeng Wang*

*A candidate for the degree of*

*Master of Science*

*And hereby certify that, in their opinion, it is worthy of acceptance*

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## LIST OF ABBREVIATIONS

|                    |                                    |
|--------------------|------------------------------------|
| PVDF               | Poly(vinylidene fluoride)          |
| HFM <sub>s</sub>   | Hollow fiber membranes             |
| N-TiO <sub>2</sub> | Nitrogen doped titanium dioxide    |
| SEM                | Scanning electron microscopy       |
| HA                 | Humic acid                         |
| TOC                | Total organic carbon               |
| TMP                | Transmembrane pressure             |
| UF                 | Ultrafiltration                    |
| DBPs               | Disinfection by-products           |
| VOC <sub>s</sub>   | Volatile organic compounds         |
| RO                 | Reverse osmosis                    |
| TIPS               | Thermally induced phase separation |
| DIPS               | Diffusion induced phase separation |
| PDMS               | Polydimethylsiloxane               |
| divinyl-PDMS       | divinyl-polydimethylsiloxane       |
| CA                 | Cellulose acetate                  |
| PES                | Poly(ethersulfone)                 |
| PEI                | Polyetherimide                     |
| PP                 | Polypropylene                      |
| PANi               | Polyaniline                        |

---

|                  |  |
|------------------|--|
| PMP              | Poly(4-methyl-1-pentene)   |
| PAN              | Polyacrylonitrile  |
| P4VP             | Poly(4-vinylpyridine)  |
| 6FDANDA/PES      | Poly(1,5-naphthalene-2,2'-bis(3,4-phthalic hexafluoropropane dimide)/polyethersulfone) |
| PBI              | Polybenzimidazoles   |
| NMP              | N-methyl-2-pyrrolidone   |
| DG               | Diethylene glycol  |
| HMSS             | Hollow mesoporous silica spheres   |
| BPPO             | Brominated polyphenylene oxide   |
| PSF              | Polysulphone   |
| H <sub>2</sub> S | Hydrogen sulfide   |
| H <sub>2</sub>   | Hydrogen   |
| N <sub>2</sub>   | Nitrogen   |
| EPS              | Extracellular polymeric substance  |
| FBP              | Feed-brine-pressure  |
| AA               | Acrylic acid   |
| AM               | Acryl amide  |
| MPC              | 2-methacryloyloxyethyl phosphorylcholine   |
| BMA              | Butyl methacrylate   |
| PEO              | Poly(ethylene oxide)   |

---

|                      |                                 |
|----------------------|---------------------------------|
| HMA                  | 2-hydroxy-4-(methylthio)butyric |
| PVP                  | Polyvinylpyrrolidone            |
| Mw                   | Molecular weight                |
| Ti(Obu) <sub>4</sub> | Tetrabutyl titanate             |
| DMAC                 | N,N-Dimethylacetamide           |
| DI                   | Deionized                       |
| NPs                  | Nanoparticles                   |
| LED                  | Light emitting diode            |

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## LIST OF SYMBOLS

|                      |   |
|----------------------|---|
| <b>J</b>             | Water flux (L/m <sup>2</sup> h)                   |
| <b>V<sub>p</sub></b> | Volume of water permeated (L)                     |
| <b>A</b>             | Effective membrane surface area (m <sup>2</sup> ) |
| <b>t</b>             | treatment time (h)                                |
| <b>R</b>             | Humic acid/total organic carbon rejection         |
| <b>C<sub>p</sub></b> | Permeate concentration (mg/L)                     |
| <b>C<sub>f</sub></b> | Feed concentration (mg/L)                         |
| <b>D</b>             | Decrease in water flux                            |

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## ABSTRACT

Nitrogen doped TiO<sub>2</sub> (N-TiO<sub>2</sub>), a hydrophilic and visible light-active photocatalyst, was applied to prepare poly(vinylidene fluoride) (PVDF)/N-TiO<sub>2</sub> mixed matrix hollow fiber membranes (HFMs) by the phase inversion method. The membranes were characterized by scanning electron microscopy (SEM), contact angle measurement and UV-Vis absorbance. The membrane performances for treating surface water were evaluated based on the water flux, humic acid (HA) rejection and total organic carbon (TOC) rejection in surface water. Different water samples were collected from Eagle Bluffs, Missouri River and McBaine Water Treatment Plant in Columbia, MO. The results showed the pure water flux of PVDF-NTiO<sub>2</sub> membranes, which was about 28.5 ± 0.3 L/m<sup>2</sup>h at the transmembrane pressure (TMP) of 8 psi under visible light which was slightly higher than the flux of pure PVDF membranes around 25.6 ± 0.4 L/m<sup>2</sup>h. The contact angle of the PVDF-NTiO<sub>2</sub> membranes (about 43 °) was smaller than the pure membranes' contact angle (about 55 °), suggesting that the membrane hydrophilicity was significantly improved by incorporating TiO<sub>2</sub> nanoparticles into the PVDF HFMs. The as-prepared PVDF-NTiO<sub>2</sub> mixed matrix membranes removed over 40% of humic acid and 20% of TOC in the water samples collected from the Eagle Bluffs and Missouri River and rejected 20% of HA and TOC in water from the McBaine Water Treatment Plant, which were comparable to pure PVDF membranes. The mixed matrix membrane with N-TiO<sub>2</sub>, however, showed much better resistance to membrane fouling. The study suggests that the PVDF-NTiO<sub>2</sub> membranes with enhanced water flux and anti-fouling characteristics could

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treat water more efficiently for control of natural organic matter.

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## **CHAPTER 1**

### **INTRODUCTION**

#### **1.1 Global water problem and surface water importance**

Water is the backbone of the global economy, and is vital for agriculture, industry, recreation, energy production, and domestic consumption(Gewin, 2005). In the past few decades, providing quality water supplies has increasingly become a challenge due to excessive use and widespread contamination of nature's water sources. It is estimated that over one billion people, or about one-seventh of world's population do not have access to fresh water; of these one billion, the vast majority are living in developing countries. Over 3.6 million people around the world die each year from drinking unsafe water(Prince, Bhuvana, Boodhoo, Anbharasi, & Singh, 2014).

Surface water is water on the surface of the planet such as in a lake, river or ocean and it is the main source of drinking water in many locations. Surface water often contains various constituents including natural organic materials that affect water quality, thus, it is vital to develop proper technologies to purify surface water so it can meet drinking water quality standards.

#### **1.2 Methods of surface water treatment**

Various approaches have been applied for surface water treatment depending on the source water quality characteristics. The conventional method is to use coagulation and

sedimentation, widely adopted by water plants in the world (Shannon et al., 2008). Another method is to use membrane filtration including microfiltration, ultrafiltration, nanofiltration, and reverse osmosis.

### 1.2.1 Coagulation and Sedimentation Plant

A typical coagulation and sedimentation plant for surface water treatment contains several important unit operations (Figure 1). Raw water is first drawn from a lake or river and transported to water treatment plants, then screened through a number of traveling screens resulting in removal of large debris, such as fish and seaweed.

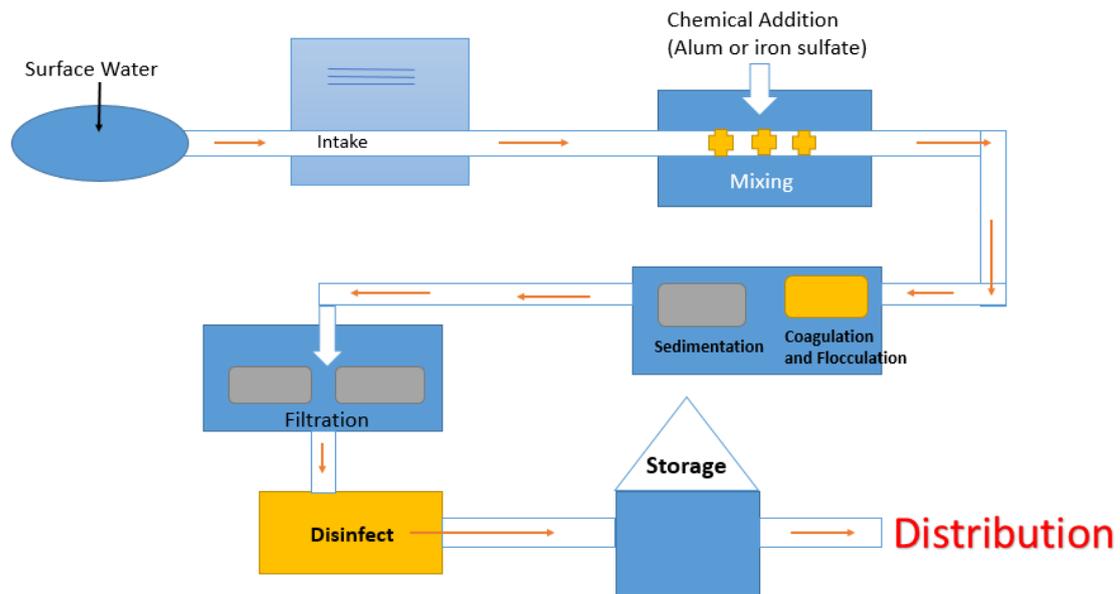


Fig. 1. Water Treatment Process

The water then enters the rapid mixers where polyaluminum chloride is added. Hydrolysis of polyaluminum chloride results in floc formation and charge neutralization of colloidal particles including clay minerals, bacteria, and virus, leading

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to their eventual settling and removal from the water. In coagulation and flocculation basins, large paddles gently stir the water that helps particle-particle interactions, causing the floc to increase in size and density and settle at the bottom of the basin. The sludge generated by sedimentation is removed by scrapers and sent to waste water plant or disposed of.

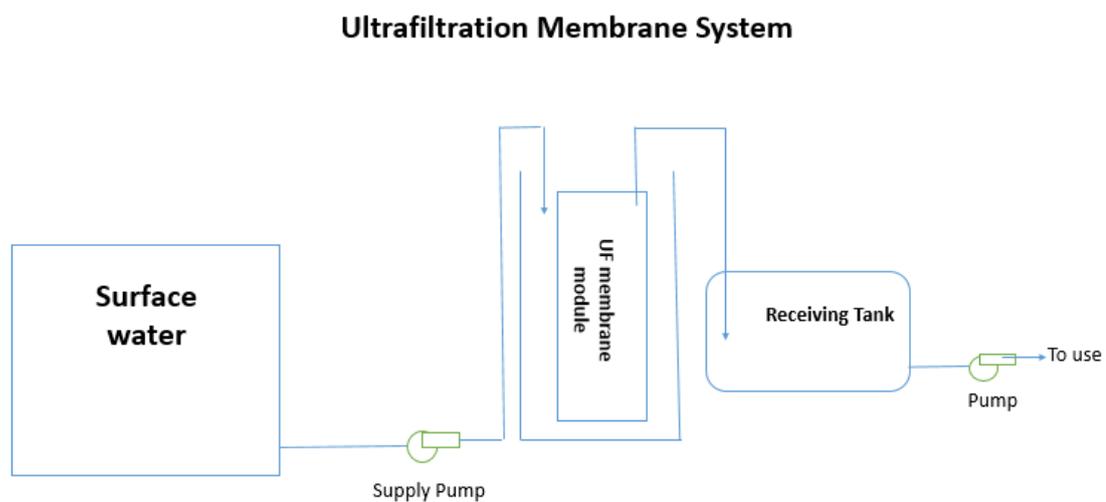
The water flowing out from the sedimentation process will be further treated by a filtration process through a granular medium, where any remaining particles such as viruses, cysts, bacteria and flocs are removed. The filtered water will be treated by a disinfectant (for example, chlorine, chloramine) so any remaining pathogens will be deactivated prior to the distribution of water to homes and businesses.

The coagulation/sedimentation treatment described above is very effective to provide quality water at large scale and has contributed in a major way to the improvement of public health to billions of people in the world. There are, however, some disadvantages and limitations for the technology. First, the system is complex and may fail if any one of these unit operations breaks down. Secondly, the disinfection by-products (DBPs) may form with negative impact to human health. The chlorine or chloramine added as disinfectants can react with natural organic matter in source water and result in formation of DBPs such as trihalomethane with reproductive toxicity, mutagenicity and carcinogenicity.

### **1.2.2 Membrane ultrafiltration**

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Fig.2 shows water treatment process by UF system. Surface water is drawn by supply pump and transported to the UF membrane module. There are about 1000 hollow fibers in an ultrafiltration membrane module. After the filtration process, the treated water flows to the receiving tank for distribution. Comparing to the conventional coagulation/sedimentation treatment, UF system offers several advantages including: (1) higher quality of treated water, (2) a much more compact system, (3) easier control of operation and maintenance, (4) fewer chemical components, and (5) less production of sludge(Guo, Zhang, Fang, & Su, 2009; Nakatsuka, Nakate, & Miyano, 1996).



**Fig.2.** UF Membrane System

### **1.3 Overview of hollow fiber membranes (HFMs)**

The technology of synthetic membranes have been developed more than 100 years ago and they were first applied as scientific tool in chemical and biomedical laboratories in the 1900s. According to different shapes membranes are classified as flat membranes, hollow fiber membranes (HFMs), capillary membranes and tubular membranes. And

they can also be classified as microfiltration, ultrafiltration, nanofiltration and reverse osmosis membranes by different pore sizes (Table 1).

**Table 1** Pressure-driven membrane process and their characteristics

|                | Microfiltration             | Ultrafiltration                              | Nanofiltration  | Reverse Osmosis |
|----------------|-----------------------------|--|---|-----------------|
| Pressure (bar) | 0.1-2                       | 0.1-5  | 3-20  | 5-120           |
| Pore size (nm) | 100-1000                    | 2-100  | 0.5-2   | <0.5            |
| Applications   | Clarification; pretreatment | Removal of macromolecules, bacteria, viruses | Removal of (multivalent) ions and relatively small organics | Desalination    |

Hollow fiber membranes are playing an important role in drinking water purification as well as in wastewater treatment. The excellent mass-transfer properties conferred by the hollow fiber configuration has led to numerous commercial applications in various fields such as the medical field (blood fractionation), water reclamation (purification and desalination), liquid/liquid or liquid/solid separation, gas separation, hemodialysis, removal of volatile organic compounds (VOCs) from water and so on (Feng, Khulbe, Matsuura, & Ismail, 2013).

In recent years, HFMs have become popular with great promises to improve the supply of clean water through the purification of nontraditional water sources such as brackish, sea, and waste water (Jang, Kim, Lee, & Lee, 2013). It is a pressure-driven process whereby a semi-permeable membrane rejects dissolved substances in the

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feeding water but allows water to pass through(Q. Yang & Mi, 2013). The progress in hollow fiber technology depends on the development of hollow fiber membranes because the membranes determine the technological and economic efficiency for the treatment process. Nanofiltration membranes' separation characteristics lie between ultrafiltration and reverse osmosis (RO) membranes for liquid separation, with relatively low investment cost with operating pressure lower than that of RO membranes, have high permeance and rejection performance of multivalent ions as well as organic compounds of molecular weight between 200~1000 g/mol(Jang et al., 2013). Therefore, the separation characteristics dominate HFMs field nowadays.

### 1.3.1 Membrane preparation

Spinning hollow fiber involves the following four steps: solution formulation, extrusion, coagulation and treatment of coagulated fiber(Feng et al., 2013). There are several critical parameters that need to be controlled during the spinning process including spinneret temperature, dope solution flow rate and bore fluid composition.

HFMs prepared via phase inversion methods exhibit specific surface and mechanical characteristics. HFMs formed by different polymers exhibit different properties. Table 1 shows the common polymers which were used for preparation of hollow fibers.

**Table 2** List of polymers

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| Polymer                 |      |
|-------------------------|------|
| Cellulose acetate       | CA   |
| Polyvinylidene fluoride | PVDF |

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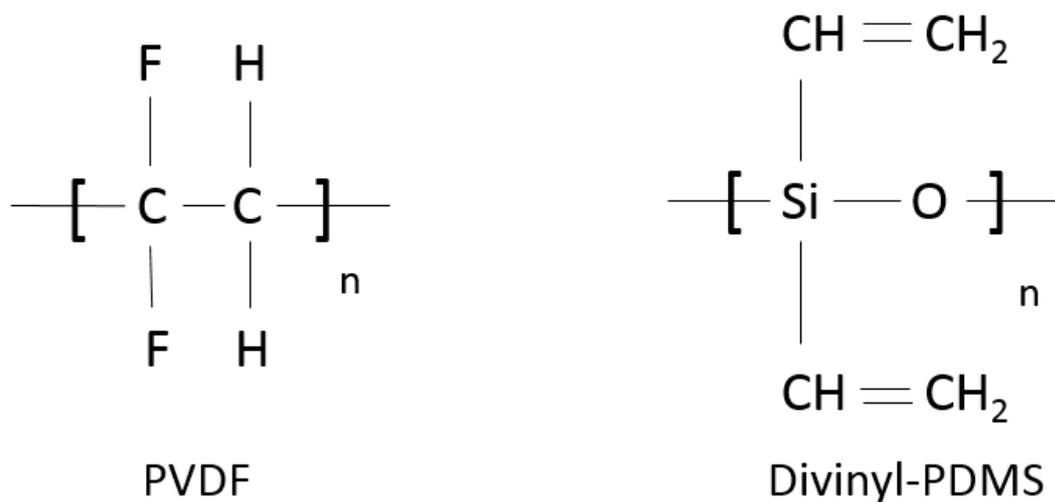
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|  |             |
|--|-------------|
| Poly(ethersulfone)   | PES         |
| Polyetherimide   | PEI         |
| Polypropylene  | PP          |
| Polydimethylsiloxane   | PDMS        |
| Polyaniline  | PAni        |
| Poly(4-methyl-1-pentene)   | PMP         |
| Polyacrylonitrile  | PAN         |
| Poly(4-vinylpyridine)  | P4VP        |
| Poly(1,5-naphthalene-2,2'-bis(3,4-phthalic)hexafluoropropane diimide/polyethersulfone) | 6FDANDA/PES |

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In the last 15 years, new polymer have been introduced for the preparation of hollow fibers. The structures of some of these polymers are discussed below.

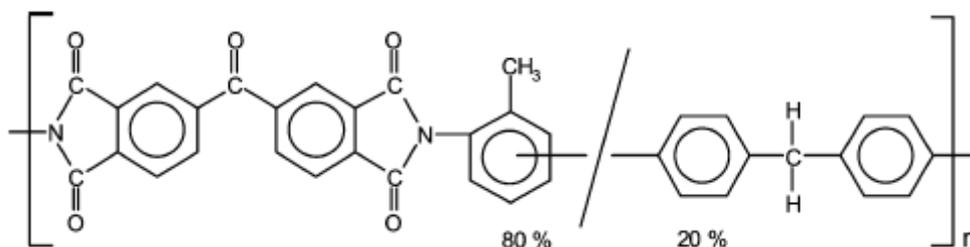
Yeow et al. fabricated PVDF HFMs using the dry-wet phase inversion method which were coated with cross-linkable divinyl-terminated silicone rubber, divinyl-polydimethylsiloxane (divinyl-PDMS)(Yeow, Field, Li, & Teo, 2002). Fig.3. shows the chemical structure of PVDF and divinyl-PDMS.



**Fig.3.** Chemical structure of PVDF and divinyl-PDMS

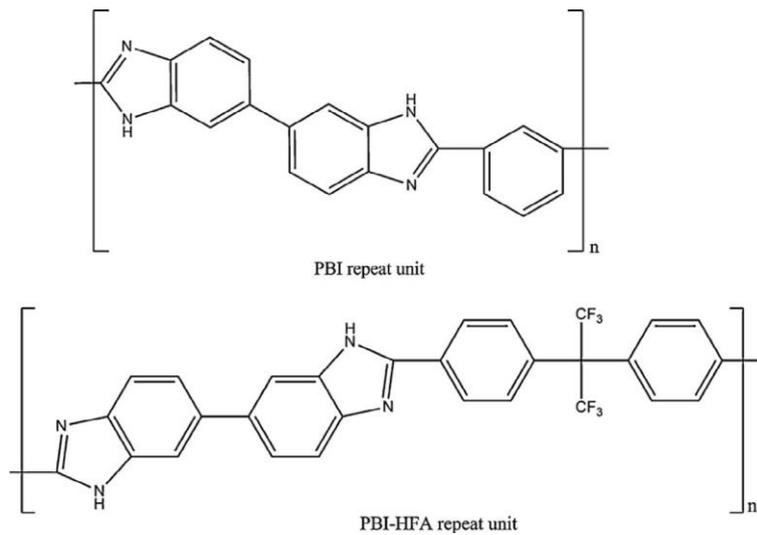
Barsema et al. prepared asymmetric hollow fiber membranes based on co-polyimide

BTDA-TDI/MDI which is a commercial polymer produced by Lenzing with the trade name P84 (Barsema, Kapantaidakis, van der Vegt, Koops, & Wessling, 2003). It showed good performance on the separation of a CO<sub>2</sub>/N<sub>2</sub> (80/20) mixture. The chemical structure of this polymer is shown in Fig. 4.



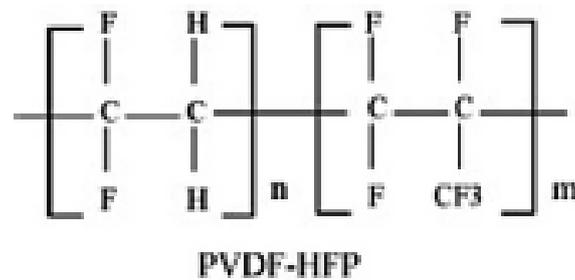
**Fig.4.** Chemical structure of BTDA-TDI/MDI co-polyimide

Organic–inorganic hybrid (mixed matrix) asymmetric hollow fiber membranes were spun via a dry jet-wet quench procedure using surface modified inorganic small pore size zeolite incorporated in an Ultem<sup>®</sup> 1000 polyetherimide matrix (Husain & Koros, 2007). The zeolites were modified via two separate techniques and termed as (1) Ultem<sup>®</sup> “sized” and (2) “Grignard treated”. Fig.5 shows the structure for repeat unit of PBI and PBI-HFA.



**Fig.5.** Structure for repeat unit of PBI and PBI-HFA

Shi et al. introduced PVDF-HFP for the preparation of asymmetric microporous hollow fiber membranes which were fabricated by dry-jet wet spinning processes (Shi, Wang, Cao, Liang, & Tay, 2008). Fig.6 shows the chemical structure of PVDF-HFP.



**Fig.6.** Chemical structure of PVDF-HFP

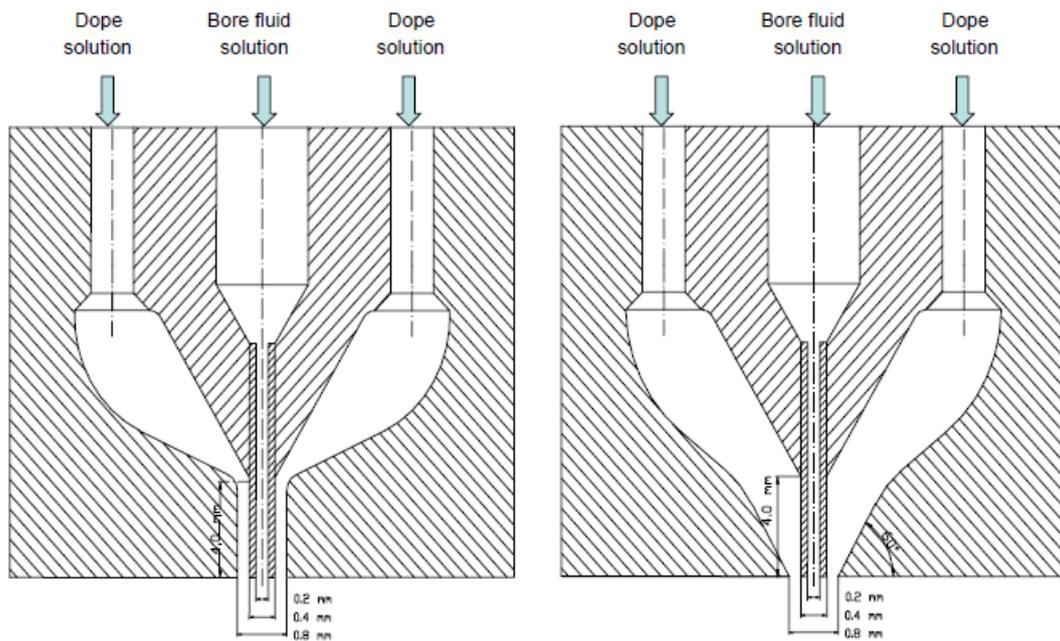
### 1.3.2 Spinneret design

Some variables can promote a visco-elastic polymer solution expansion which is called die-swell phenomenon (Feng et al., 2013). Die-swell phenomenon may result in low reproducibility of the permeation properties but it can be avoided by increasing the

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solvent concentration in bore liquid, as well as by increasing the distance spinneret-precipitation bath even with a high content of water in the bore liquid(Pereira, Nobrega, & Borges, 2000). All these factors result in the decrease of the mass transfer between the polymer solution and the coagulation bath. Therefore, the internal perimeter deformation is inhibited.

Wang et al. studied the effects of dope flow rate and flow angle within a spinneret during spinning hollow fiber membranes on the morphology, water permeability and separation performance of poly(ethersulfone) ultrafiltration HFMs(K. Y. Wang, Matsuura, Chung, & Guo, 2004). For this objective, two spinnerets with different flow angles were designed and used. The dope solution, containing PES/*N*-methyl-2-pyrrolidone (NMP)/diethylene glycol (DG) with a weight ratio of 23/41/36, which was very close to its cloud point (binodal line), was used in order to speed up the coagulation of nascent fibers so that the relaxation effect on molecular orientation was reduced. The wet-spinning process was purposely chosen to fabricate the hollow fibers without extra drawing. Fig.7 shows the schematic diagram with different flow angles (90 ° and 60 °).



**Fig.7.** Schematic diagram with different flow angles (90 ° and 60 °)

Reprinted with permission from Ref.(K. Y. Wang et al., 2004)

Therefore, the effects of gravity and elongation stress on fiber formation could be significantly reduced and the orientation induced by shear stress within the spinneret could be frozen into the wet-spun fibers. The results showed that higher dope flow rates (shear rates) in the spinneret produced UF HFMs with smaller pore sizes and denser skin layers due to the enhanced molecular orientation.

### 1.3.3 Hollow fiber applications

The excellent mass-transfer properties conferred by the hollow fiber configuration lead to many commercial applications in various fields such as water treatment and gas separation. For the water and other organic solutions purification, Wu et al. prepared a novel HFM by incorporating hollow mesoporous silica spheres (HMSS) into a polymer

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matrix of brominated polyphenylene oxide (BPPO) using triethanolamine as the amination agent(H. Wu, Tang, & Wu, 2012). The hybrid membrane showed improved water permeability, thermal stability, and water content, while the rejection to egg albumin was maintained at a high level (>90%). Loh. et al. fabricated intrinsically-skinned asymmetric PANi hollow fibers using a process of directly adding large organic acids to highly concentrated PANi solutions(Loh et al., 2008). The HFMs showed good stability in a wide variety of organic solvents and exhibited rejections of nanosolutes in acetone. In addition, Ghosh et al. used polysulphone (PSF) HFMs to purify lysozyme enzyme(Ghosh, Silva, & Cui, 2000). Praneeth et al. synthesized HFMs from PES and PAN polymers to fabricate modules for surface water treatment and clarification of fungal enzyme broth(Praneeth, Kalyani, Ravikumar, Tardio, & Sridhar, 2013). The PAN and PES membranes showed 54.9 and 69.3% xylanase enzyme recoveries from fungal broth at reasonable flux with turbidity rejection of 94.8 and 95.7% respectively.

For gas separation, Wang et al. used an asymmetric PVDF HFM module to remove H<sub>2</sub>S from a gas stream containing 17.9-1159 ppm H<sub>2</sub>S to low concentration(D. Wang, Teo, & Li, 2002b). The module showed excellent results in purification of gas streams containing soluble toxic gases. Wang et al. fabricated PEI asymmetric hollow-fiber membrane which was spun from a N-methyl-2-pyrrolidone/ethanol solvent system via a dry-wet phase-inversion method, with water as the external coagulant and 50 wt% ethanol in water as the internal coagulant(D. Wang, Teo, & Li, 2002a). The membrane showed sufficiently high selectivity (H<sub>2</sub>/N<sub>2</sub> selectivity > 50) at 25 °C. Besides water

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purification and gas separation, HFMs are also used on pervaporation, membrane distillation, and membrane contactor.

#### **1.4 Methods to improve HFMs antifouling properties**

Although HFM technology has many advantages over other separation technologies, its partial application is sometime limited by an issue of the so-called membrane fouling. Membrane fouling has been the “bottleneck” because it results in severe flux decline and needs for membrane cleaning and replacement. Thus, it raises cost on purification process, increase operation difficulty and shortens membrane’s life time. As a result, many efforts are made to solve the problem, including the design of new membrane modules in, combination with pretreatment processes(Huang, Schwab, & Jacangelo, 2009) and the development of antifouling HFMs. Among these methods the last one has been paid much attention by many researchers.

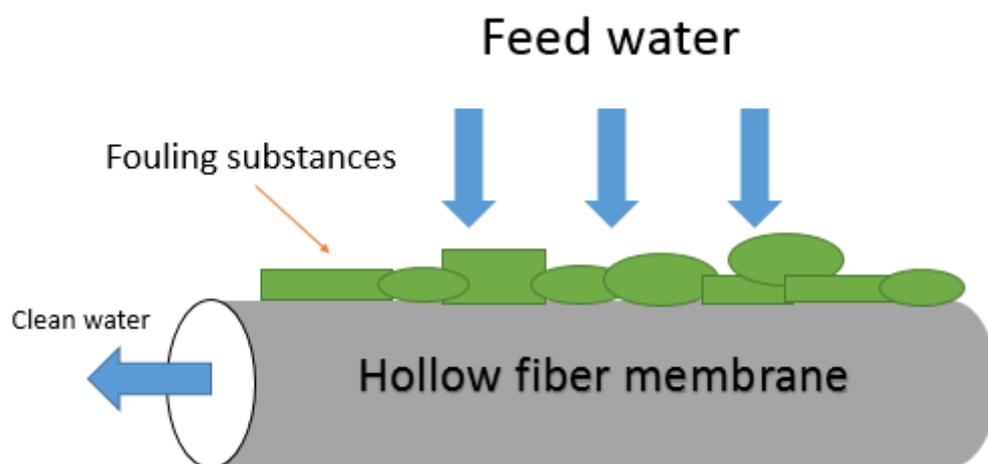
##### **1.4.1 Membrane fouling phenomena**

The mainly types of fouling in membranes include:

1. Crystalline: precipitative deposition of inorganic materials on a surface
2. Organic: deposition of organic substances (e.g. oil, proteins, humic substances) on the surface
3. Particulate and colloidal: deposition of clay, silt, and particulate humic substances

- 
4. Microbiological: biofouling, adhesion and accumulation of microorganisms, fouling biofilms(Flemming, 1997).

The natural organic matter (NOM) is a complex mixture of organic substances in natural water, containing humic acid, fulvic acid, proteins, colloidal polysaccharide, fatty acids that are the main substance for membrane fouling in surface water treatment(Amy, 2008; Kaiya, Itoh, Fujita, & Takizawa, 1996; Lee, Amy, Croué & Buisson, 2005; Sun, Liu, Chu, & Dong, 2013). On a separation membrane, the film matrix is a secondary membrane that participates dominantly in the separation process (Fig. 1). The gel-like structure of the extracellular polymeric substances (EPS) matrix reduces the efficiency of convectional transport processes and causes a transmembrane pressure (TMP) drop that results in flux decline. Moreover, the rough, viscoelastic surface of the film increases fluid frictional resistance and causes a feed-brine-pressure (FBP) drop.



**Fig.8.** Schematic sketch show the film acting as a secondary membrane

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## **1.4.2 Methods to enhance membrane antifouling properties**

### **1.4.2.1 Plasma Modification**

Many approaches have been explored for the control of membrane fouling. Plasma treatment is a technique for the surface modification of HFMs during which the hydrophilic monomers will be grafted on the HFM surface after the membrane surface is exposed to plasma with various free radicals. Plasma is a simple and convenient modification of membranes. When using plasma to trigger gas the purity and ratio of gases should be controlled rigorously so that simplex reaction groups are grafted on the surface. After being modified by plasma polymerization membrane surfaces' roughness will increase and the HFMs are more hydrophilic(Sun et al., 2013).

Yang et al. used acrylic acid (AA) as modified monomer and modified PVDF HFMs(Q. Yang et al., 2013). The results showed that membrane flux increased by 20%~30% and the pollution-resistant ability of modified membranes increase by 8.44% when they filtrated and separated attapulgitic suspension liquid after modified by low-temperature plasma.

Yang et al. used acryl amide (AM) to modify PP HFMs(Q. Yang, Chen, Chang, & Fan, 2009). The results indicated that the zeta potential of original membrane and 10% AM grafted membranes is -12.73 mV, -20.44 mV. The corresponding charge density is  $9.17 \times 10^{-6} \text{ C/m}^2$ ,  $14.7 \times 10^{-6} \text{ C/m}^2$ .

### **1.4.2.2 Radiation grafting modification**

Radical grafting is a useful method for polymer modification. In this process, the free radicals are produced from the initiators and transferred to polymer resulting in the modification of membrane material.

Junfu et al. grafted AA on the PVDF hollow fiber membrane by  $\gamma$ -radiation (Junfu et al., 2010). The results indicated that the modified HFMs had higher flux and flux recovery rate. And the grafted membrane was more hydrophilic than original PVDF. Fig.9 shows the schematic diagram of  $\gamma$ -radiation induced grafting polymerization.

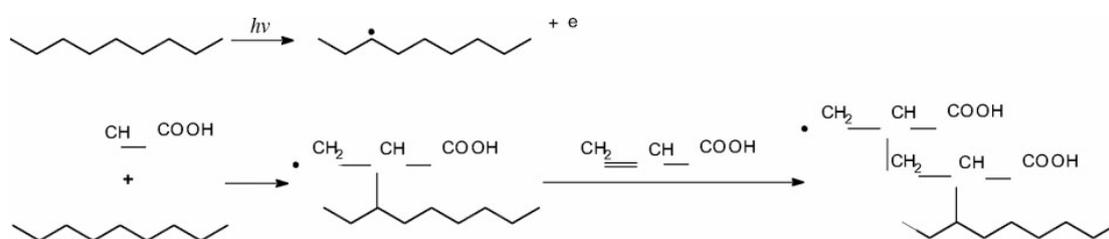


Fig.9. Schematic diagram of  $\gamma$ -radiation induced grafting polymerization

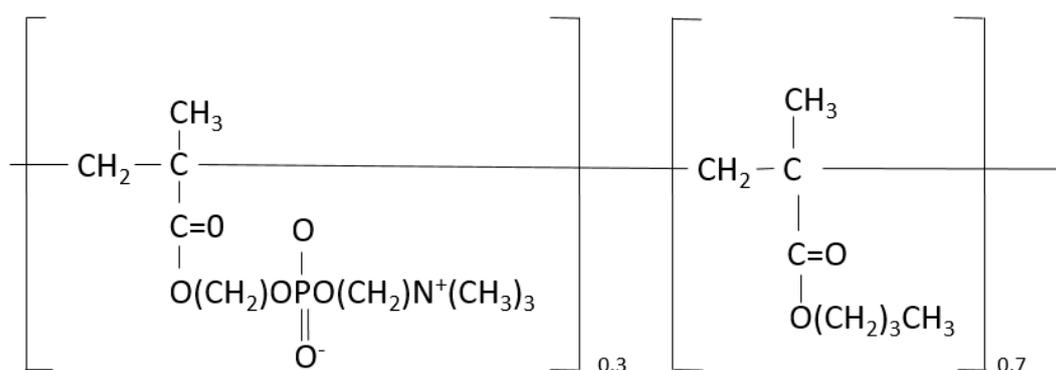
Reprinted with permission from Ref.(Junfu et al., 2010)

Yang et al. grafted 2-acrylamido-2-methylpropanesulfonic acid on the PSF ultrafiltration membrane by UV-irradiation (Y. M. Yang et al., 2010). The experiment showed that when the irradiation time was 2 min, the concentration of monomer and cross linker were 0.5% and 0.15%, the pure water flux of the modified membrane achieved the maximum of 92.46 L/ (m<sup>2</sup> h), which represented a significant increase of about 82.04%, when compared with the original membrane.

#### 1.4.2.3 Surface coating modification

Surface coating is an easy method to modify the surface of HFMs. By the way of coating a layer of hydrophilic substances the surface coating modification can help to improve the anti-fouling properties(Sun et al., 2013).

Shu et al. coated a copolymer of 2-methacryloyloxyethyl phosphorylcholine (MPC) and butyl methacrylate (BMA) (poly(MPC-co-BMA)) aqueous solution on the PVDF HFMs(Nishigochi et al., 2014). Fig.10 shows the structure of poly(MPC-co-BMA). The experiments showed that membranes coated with poly(MPC-co-BMA) exhibited higher water permeabilities after fouling.



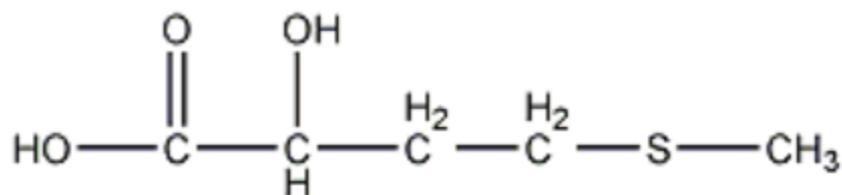
**Fig.10.** Chemical structure of poly(MPC-co-BMA)

Revanur et al. coated amphiphilic polymer of poly(ethylene oxide) (PEO) on the PVDF ultrafiltration membrane and found that the membranes prevented fouling of the membrane when exposed to oil-in-water emulsions and enhanced the antifouling properties(Revanur, McCloskey, Breitenkamp, Freeman, & Emrick, 2007). Remarkable differences in fouling between the coated and uncoated PVDF-UF membranes were shown.

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#### 1.4.2.4 Blending modification

Blending modification means that two or more kinds of polymeric materials were blended to prepare a new kind of material. The membrane prepared by polymer blending may have higher hydrophilicity and antifouling properties. For example, Cherdronek et al. blended 2-hydroxy-4-(methylthio)butyric acid (HMA) with PVP to fabricate a new membrane that has better hydrophilicity and antifouling capacity (Cherdronek et al., 1994). Fig.10 shows the chemical structure of HMA.



**Fig.11.** Chemical structure of HMA

Oh et al. modified PVDF UF membrane by dispersing nano-sized titanium(IV) oxide (TiO<sub>2</sub>) particles in a PVDF solution (Oh, Kim, & Lee, 2009). PVDF membranes were fabricated by a phase inversion method and the results showed that the contact angle of modified membrane was decreased indicating an enhanced hydrophilicity of the membrane.

#### 1.4.3 Brief summary

A variety of approaches have been developed for membrane modification and fabrication, including plasma modification, radiation grafting treatment, surface

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coating and blending. However, each may have its limitations. To illustrate, plasma modification needs vacuum equipment so it is not easy to apply for large-scale production. For the radiation grafting treatment, the reactions are non-selective and difficult to control (Sun et al., 2013).

### **1.5 TiO<sub>2</sub> nanoparticles (NPs) enhanced membrane**

Incorporation of nanoparticles such as TiO<sub>2</sub> to membrane a new approach for membrane preparation. There are two main ways for preparing of TiO<sub>2</sub> nanocomposite membranes: (1) depositing NPs onto membrane surface and (2) blending the NPs into the membrane.

In the depositing approach, TiO<sub>2</sub> NPs are coated on membrane surface. For instance, Kim et al. prepared one kind of hybrid composite membrane by self-assembly of TiO<sub>2</sub> NPs through interaction with the COOH functional group of an aromatic polyamide thin-film layer (Kim, Kwak, Sohn, & Park, 2003). The membrane possessed excellent anti-bacterial effect with *E. coli* and outstanding antifouling properties under UV light irradiation. Bae and Tak immobilized the TiO<sub>2</sub> NPs on membrane surface by dipping method to increase the surface hydrophilicity and antifouling properties. The results showed that TiO<sub>2</sub> immobilized membranes are simple to prepare and powerful for fouling mitigation in membrane bioreactor (MBR) applications (Bae & Tak, 2005).

In the blending approach, TiO<sub>2</sub> NPs are dispersed in a casting solution and then membranes are cast by the common phase separation method. For example, Wu et al.

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prepared PES/TiO<sub>2</sub> composite membranes and the results showed that the membrane enhanced hydrophilicity, thermal stability and anti-fouling ability (G. Wu, Gan, Cui, & Xu, 2008). To overcome agglomerations and also to improve the stability of particles in the casting solution, Razmjou et al. added Degussa P25 TiO<sub>2</sub> NPs to casting solution and synthesized UF membranes (Razmjou, Mansouri, & Chen, 2011). The incorporation of modified NPs into PES UF membranes showed a remarkable improvement in fouling resistance and a better hydrophilicity was the most probable reason for improvement in antifouling performance.

I thereby propose to prepare nitrogen-doped TiO<sub>2</sub> NPs and then adopt the blending approach to fabricate PVDF/N-TiO<sub>2</sub> mixed matrix HFMs that could be activated by visible light. PVDF was chosen as HFM material because of its outstanding chemical and thermal stabilities and corrosion resistance (Kelly, 1983; Yu, Shen, & Xu, 2009). Besides, water permeability and antifouling properties may be improved due to the enhanced hydrophilicity and photocatalytic properties of TiO<sub>2</sub> NPs. The potential of the membrane for effective water treatment will be explored.

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## CHAPTER 2

### MATERIALS AND METHODS

#### 2.1 Materials and chemicals

Chemicals used in this study were obtained from Sigma-Aldrich. Tetrabutyl titanate ( $\text{Ti}(\text{OBU})_4$ , 97%) and ammonia aqueous solution (28 - 30%) were used as titania precursor and nitrogen source. PVDF with an average molecular weight (MW) of 180 kDa was dried for 3 h at 120 °C before usage. The N,N-dimethylacetamide (DMAC, 99.5%) was selected as the solvent for the polymer. And polyvinylpyrrolidone (PVP) with an average MW of 10 kDa was used as porogen. Deionized water (DI) produced by Millipore DI system (Synergy 185, 18.2  $\text{M}\Omega\cdot\text{cm}$ ) was used for HFMs preparation and ultrafiltration study.

#### 2.2 Collection and characterization of water samples

Water samples were collected from three locations in central Missouri near the City of Columbia: Eagle Bluffs conservation area, Missouri River, and Columbia McBaine Water Treatment Plant, all at the same time in December, 2013. Water samples were stored in a refrigerator at 4 °C. The total organic carbon (TOC) of water samples were analyzed by a TOC analyzer (TOC-5000, Shimadzu Corp., Japan). UV254, which is generally a good indicator of humic acid content in water, was measured by a UV-Vis spectrophotometer (Lambda 25, PerkinElmer, Waltham, MA) at the wavelength of 254 nm. The water pH was measured by a pH meter (Thermo Orion) after 3 points

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calibration.

The UV-254 values suggested that the humic acid concentration was the lowest for water from the McBaine Water Treatment Plant, in the middle for the Missouri River water, and the highest for sample from the Eagle bluffs conservation area. The pH and TOC values were overall comparable for these three samples.

**Table 3** UV-254, TOC concentration and pH of three water samples

|            | Eagle bluffs | Missouri River | Water plant |
|------------|--------------|----------------|-------------|
| UV-254     | 0.162        | 0.107          | 0.043       |
| TOC (mg/L) | 9.49         | 7.87           | 8.17        |
| pH         | 7.52         | 7.67           | 7.15        |

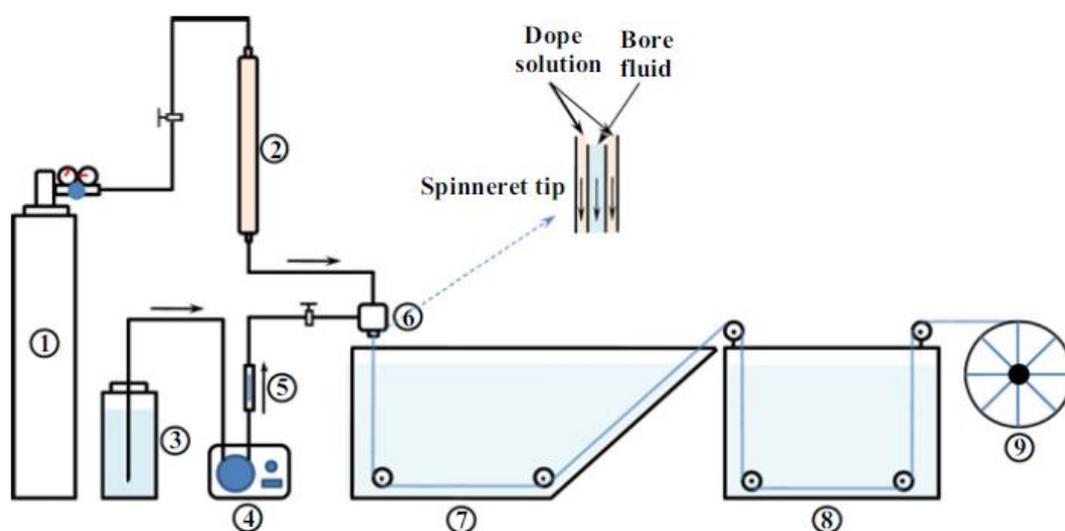
## **2.3 Preparation of polyvinylidene difluoride (PVDF) HFMs**

### **2.3.1 Synthesis of N-TiO<sub>2</sub> NPs**

N-TiO<sub>2</sub> NPs were synthesized by sol-gel method from Wang et al method (Z. Wang et al., 2005) with modifications. Firstly, a 10 ml ammonia aqueous solution was added dropwise into 20 ml Ti(OBu)<sub>4</sub> solution at room temperature with stirring to promote hydrolysis. Then the precursor was dried in an oven at 120 °C for 2 h after stirring for 10 min. At last, the TiO<sub>2</sub> precursor was calcinated at 400 °C for 1 h to obtain N-TiO<sub>2</sub> NPs with a brown color.

### 2.3.2 Spinning of hollow fiber membranes

The PVDF/N-TiO<sub>2</sub> mixed matrix HFMs were prepared by the phase inversion method on a custom-designed single-head spinning machine as reported previously (Yin, Zhu, & Deng, 2013). First, 5 wt% of N-TiO<sub>2</sub> NPs (0.4g) was dispersed in DMAC (30g) solvent and sonicated for 0.5 h to achieve dispersion. Then PVP was added to the solution and stirred for 0.5 h. Finally, PVDF was added and stirred at 45 °C for 7 h on a combined hot-plate magnetic-stirrer device to form casting solution. The dope solution was kept overnight for degassing before use.



**Fig.12.** Schematic diagram of the custom-designed single-head spinning system: (1) high purity nitrogen, (2) dope solution, (3) bore fluid, (4) gear pump, (5) flow meter, (6) spinneret, (7) coagulation bath, (8) washing bath, and (9) collecting drum

Reprinted with permission from Ref.(Yin et al., 2013)

As shown in Fig. 12, during the spinning process, the dope solution was added into the annulus of the spinneret under certain pressure provided by the high purity

nitrogen(Yin et al., 2013). When the dope and bore fluid mixed at the tip of the spinneret they entered the coagulation bath. Then the precipitated PVDF hollow fiber was prewashed in washing bath and collected by the collecting drum. At last, the HFMs were washed in the water for at least 24 h to remove the remnant solvent. Experimental parameters of spinning process were listed in Table 2. The membranes containing 5 wt% of N-TiO<sub>2</sub> NPs were labeled as PVDF-NTiO<sub>2</sub>.

**Table 4** Spinning conditions of pure PVDF HFMs

| Parameter                        | Condition     |
|----------------------------------|---------------|
| Spinneret DO/ID                  | 1.0 mm/0.6 mm |
| Spinneret temperature(°C)        | 25            |
| Dope solution                    | PVDF/PVP/DMAC |
| Concentration (wt %)             | 20/4/76       |
| Dope solution flow rate (mL/min) | 1.0           |
| Bore fluid composition           | DI water      |
| Bore fluid flow rate (mL/min)    | 0.6           |
| Range of air-gap distance (cm)   | 0             |
| Coagulant                        | Tap water     |
| Coagulant temperature (°C)       | 25            |
| Washing bath                     | Tap water     |
| Washing bath temperature (°C)    | 25            |
| Take-up speed (cm/min)           | 360           |

## 2.4 Methods of characterization techniques for HFMs

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### 2.4.1 Low pressure cross-flow filtration system

A custom-designed low pressure cross-flow filtration system was used to characterize the performance of PVDF HFMs. DI water was used to evaluate pure water flux and 3 different water samples were applied to evaluate humic acid rejection, total organic carbon rejection and fouling resistance of the membranes. The membrane performance under the influence of visible light was evaluated using a fluorescent light source(F32T8 fluorescent lights) with an output energy density of 10.9 mW/cm<sup>2</sup>. The membrane module's effective area is approximately 10 cm<sup>2</sup>. The flux, rejection and flux decrease were calculated with Equation 1-4:

$$J = \frac{V_p}{A \cdot t} \quad (1)$$

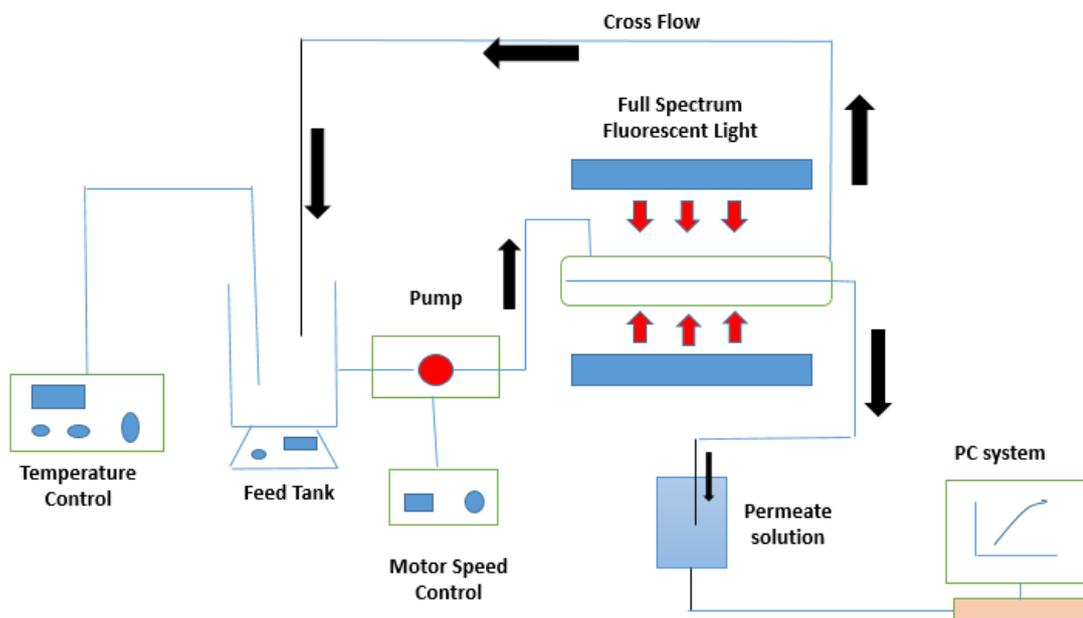
$$R = \left(1 - \frac{C_p}{C_f}\right) \times 100 \quad (2)$$

$$D = (1 - J_b/J_a) \times 100 \quad (3)$$

$$J_{av} = (J_a + J_b + J_c)/3 \quad (4)$$

where  $J$  is the water flux (L/m<sup>2</sup>h),  $V_p$ ,  $A$  and  $t$  are the permeate volume (L), membrane area (m<sup>2</sup>) and treatment time (h), respectively.  $R$  is the HA/TOC rejection and  $C_p$  and  $C_f$  are the concentrations of permeate and feed solution.  $D$  is the flux decrease and  $J_{av}$  is the average flux.  $J_a$ ,  $J_b$  and  $J_c$  are the water flux at the 5th min, 180th min and 90th min during water treatment tests, respectively. Fig.13 showed the schematic

diagram of the filtration system.



**Fig.13.** Schematic diagram of the hollow fiber membrane filtration system

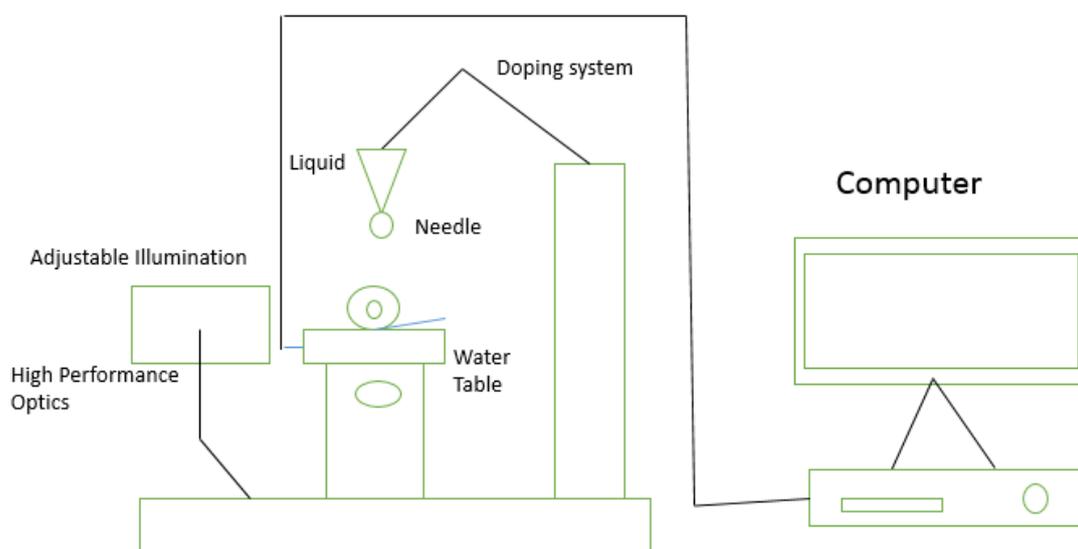
During the assessment of membrane performance, every membrane was compressed by DI water at the transmembrane pressure (TMP) of 8 psi for 2h prior to testing natural water samples. The LabVIEW automated system (National Instruments LabVIEW 8.2 with Ohaus digital balance) was applied to collect the pure water flux data by weighing the permeate water on a balance. After the pure water flux test, a water sample was pumped into the membrane module by a gear pump and the permeate flux was evaluated by weighing the permeate solution. The organic content in the permeate solution was measured by the UV-Vis spectrophotometer for UV 254 and TOC analyzer.

### 2.4.2 Contact angle of HFMs

Hydrophilicity of the HFMs can be evaluated via the contact angle measurement

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(VCA-2500 XE, AST products, Billerica MA) (sessile drop). First, several membrane fibers were cut into around 5 cm in length, and then tightly arranged, taped, and pressed onto a plastic tape. The contact angle measurement was conducted after the membrane was fully air-dried. Sessile drop method for contact angle test is limited by the camera resolution. The contact angles were measured as an average of the results from the left and right sides of a drop, but still subject to human detection errors. Fig.14 showed the schematic diagram of the contact angle measurement system.

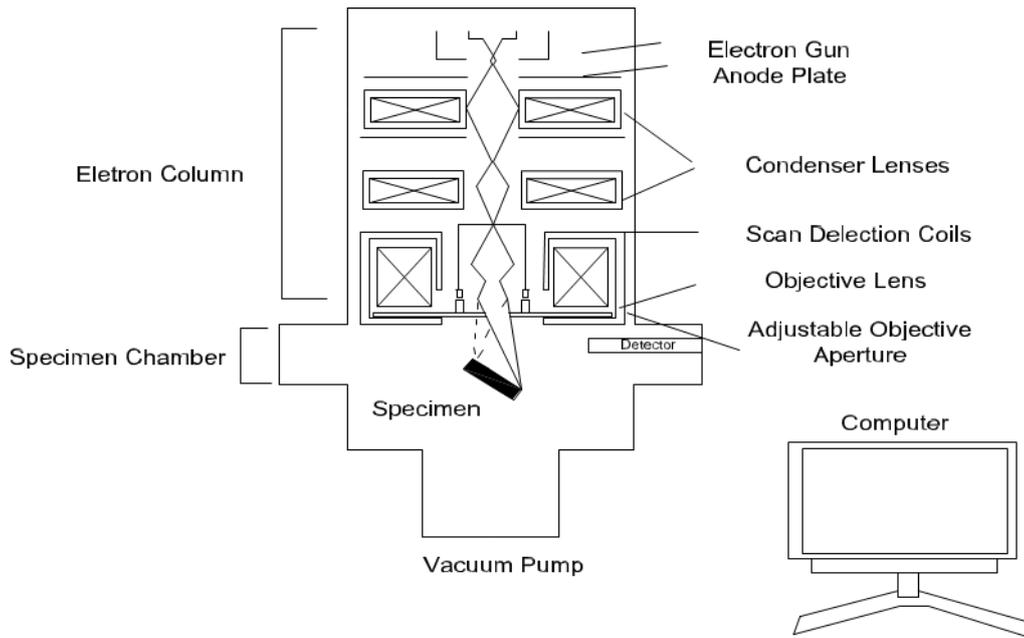


**Fig.14.** Schematic diagram of contact angle measurement

### 2.4.3 Scanning electron microscope (SEM) of HFMs

Scanning electron microscope (SEM) can show the structure of HFMs by scanning them with a beam of electrons. The membranes samples were first air-dried at room temperature. To obtain the membrane cross-section imaging, the membrane was freeze-

fracture in the liquid nitrogen. The samples were coated with platinum at 20 mA for 60s prior to evaluation by SEM on Quanta FEG 600. For SEM technology, the area for analysis is at micrometer scale so the sampling points may not be representative. Fig. 15 shows the schematic of the SEM instrument.



**Fig. 15.** A schematic diagram of SEM equipment

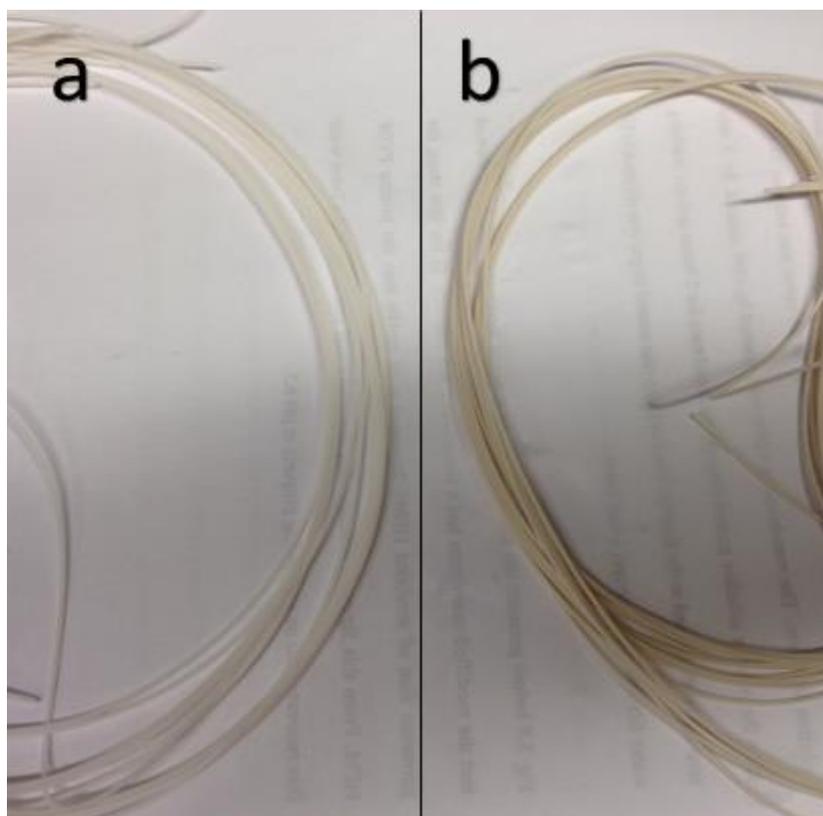
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## CHAPTER 3

### RESULTS AND DISCUSSION

#### 3.1 Characterization of PVDF-NTiO<sub>2</sub> membranes

As shown by Fig.16, the pure PVDF hollow fiber membranes showed white color, while the PVDF membranes with doped N-TiO<sub>2</sub> NPs exhibited a uniform gray tint. This color indicated there were N-TiO<sub>2</sub> NPs in the membrane matrix and the uniform color suggested a good dispersion of these NPs.

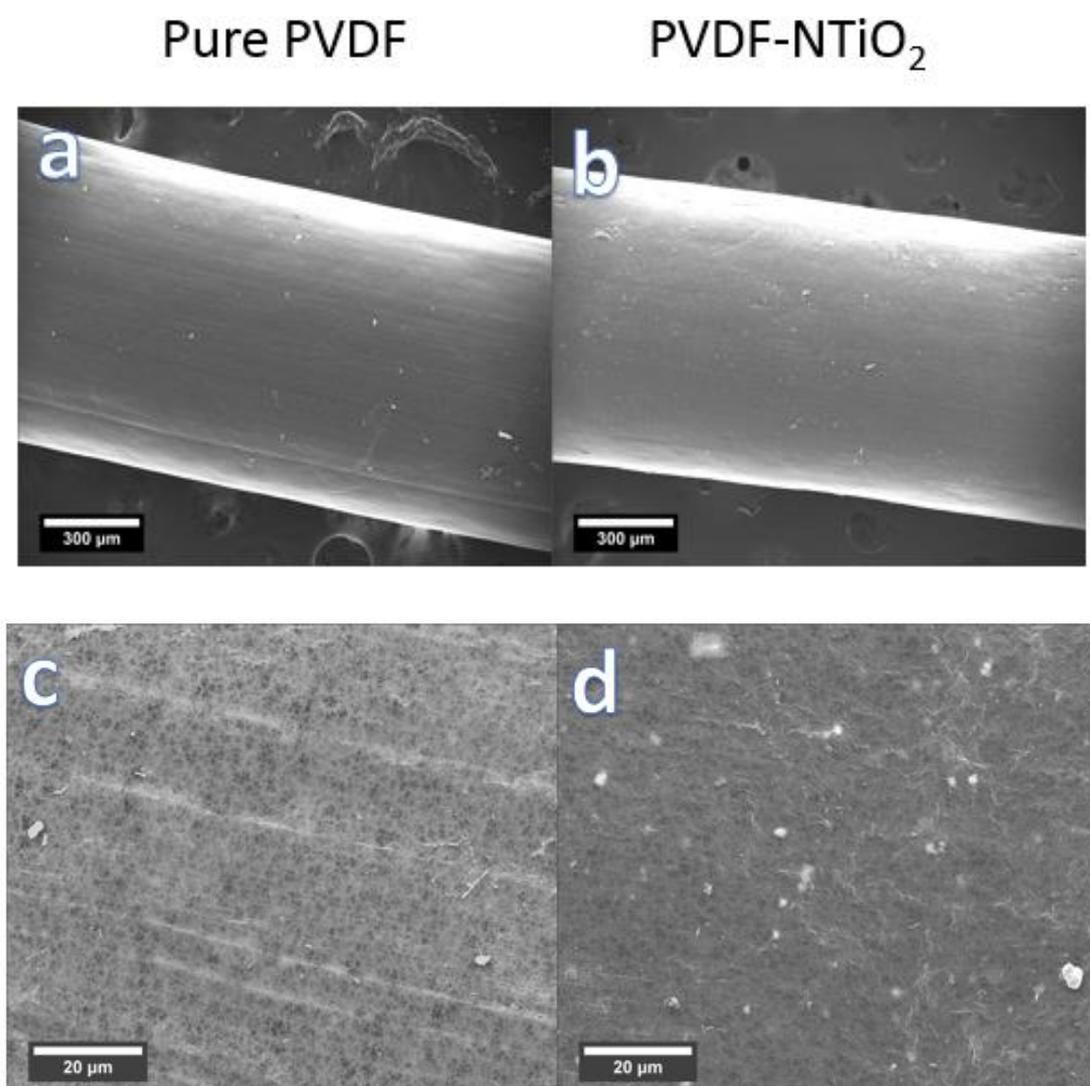


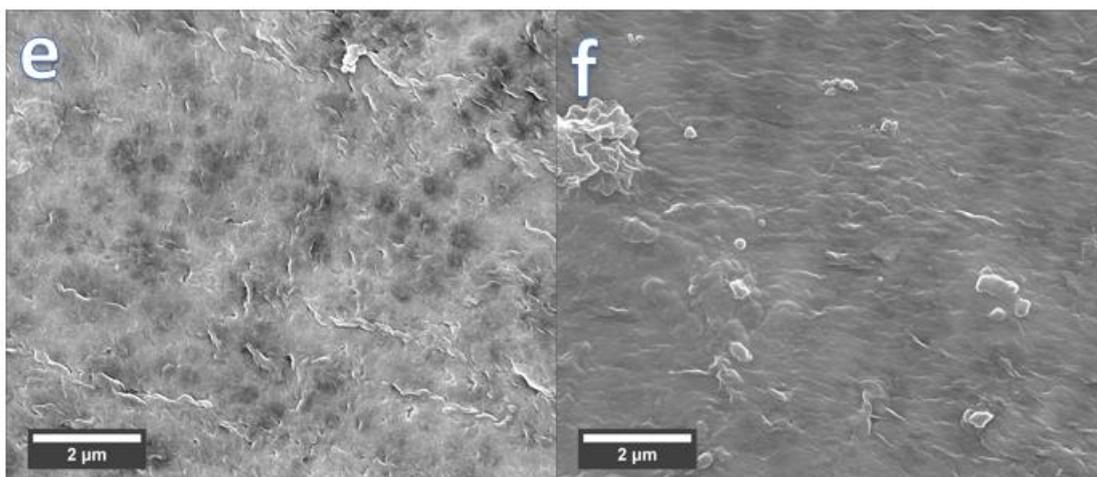
**Fig.16.** As-prepared PVDF/N-TiO<sub>2</sub> membranes: (a) Pure PVDF (b) PVDF-NTiO<sub>2</sub>

Representative SEM images of the pure PVDF membranes and PVDF-NTiO<sub>2</sub> membranes are shown in Fig.17 under different magnifications. As indicated by Fig.17

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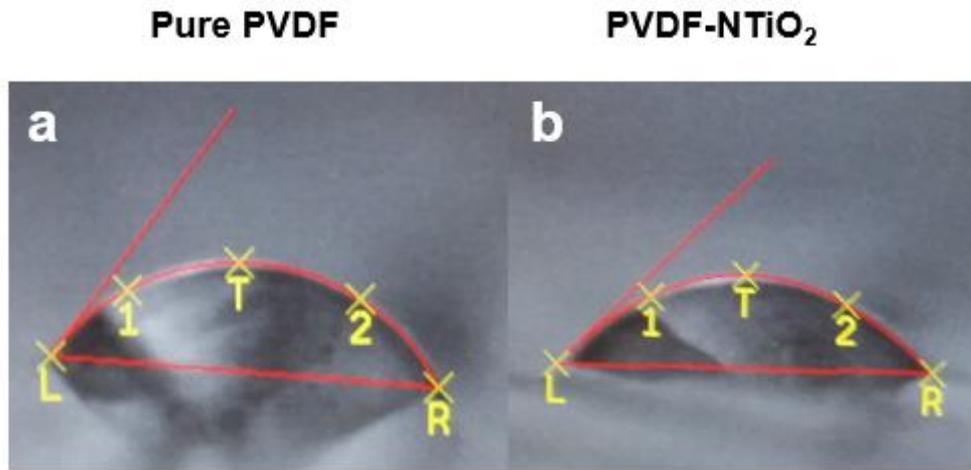
(a) and (b), all membranes had an outside diameter of about 500  $\mu\text{m}$ . Some particles existed on the surface of both pure PVDF and PVDF-NTiO<sub>2</sub> which are believed to be contamination of dust particles occurred during SEM sample preparation. Comparing the images at a higher resolution, it was clear that many NPs were imbedded inside the N-TiO<sub>2</sub> mixed HFMs as whit dots (Fig.17 (d)) whereas there was no white dot inside the pure PVDF (Fig.17 (c)). Fig.17 (e) and (f) indicated the diameters of the pores were in the 0.3 $\mu\text{m}$  range.





**Fig.17.** SEM images of PVDF/N-TiO<sub>2</sub> membranes: (a) (b) SEM images with magnification of 150×, (c) (d) SEM images with magnification of 2500×, (e) (f) SEM images with magnification of 25000×

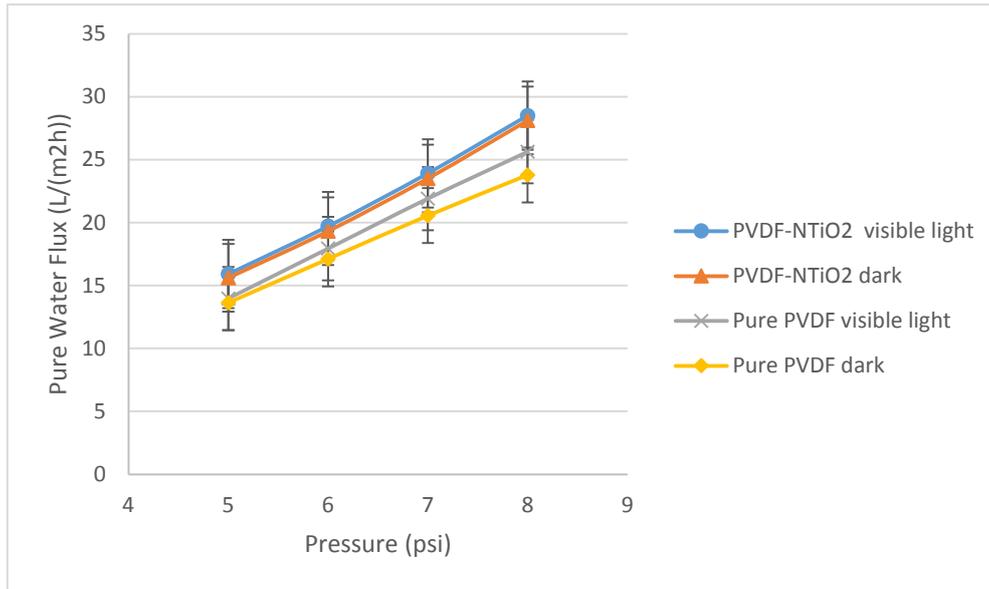
The membrane contact angles were measured under the dark condition, and as illustrated by Fig. 18, the contact angle  $55^{\circ} \pm 1^{\circ}$  (a) for of pure PVDF membrane and  $43^{\circ} \pm 2^{\circ}$  (b) for NTiO<sub>2</sub> mixed matrix membrane. The smaller contact angle of N-TiO<sub>2</sub> mixed matrix membranes could be attributed to the hydrophilicity nature of TiO<sub>2</sub>. Our preliminary study showed the contact angle decreased with increasing N-TiO<sub>2</sub> NPs concentrations, and PVDF membranes with 5% N-TiO<sub>2</sub> NPs presented best photocatalytic property. When the mixed matrix membranes were irradiated by visible light or UV light for over 30 min, the contact angle would slightly decrease.



**Fig.18.** Contact angles images of PVDF/N-TiO<sub>2</sub> membranes: (a) Pure PVDF (b) PVDF-NTiO<sub>2</sub>

### 3.2 Membrane performance

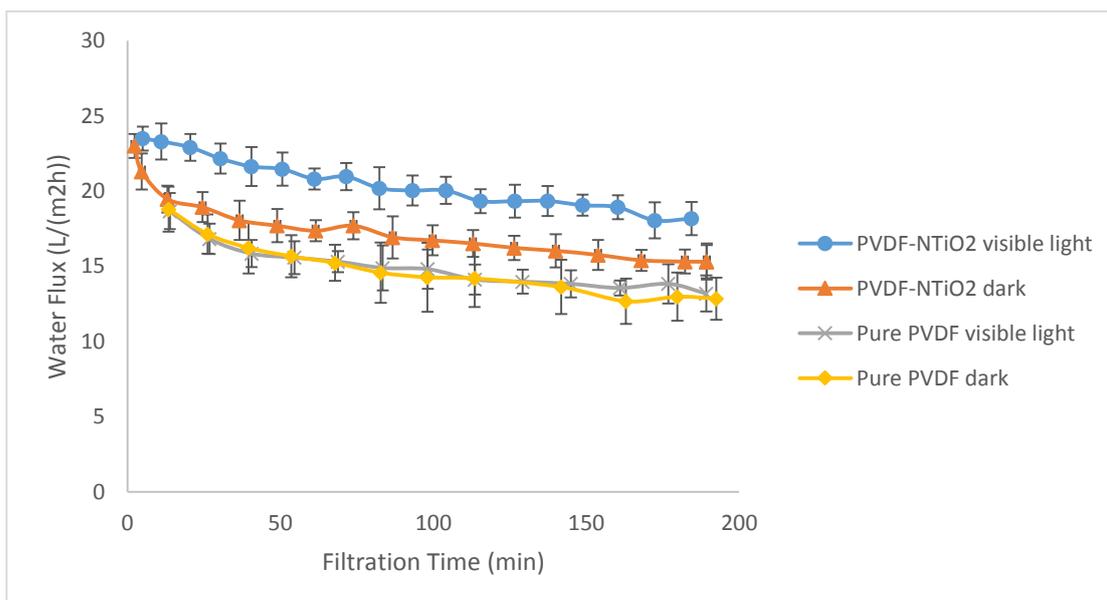
The pure water fluxes of all membranes as a function of TMP under various irradiation conditions are shown in Fig.19. The water flux of pure PVDF hollow fiber membranes without light (dark) was at around 23.8 L/m<sup>2</sup>h under 8 psi and was comparable to the flux under visible light irradiation. The water flux of the PVDF-NTiO<sub>2</sub> membranes was also similar with/without visible light irradiation, and slightly higher than water flux of pure PVDF membrane. The result is consistent with the higher hydrophilicity of the NTiO<sub>2</sub>-embedded membrane as indicated by the contact angle measurements.



**Fig.19.** Pure water flux of membrane samples under various irradiation conditions

Tests designed to evaluate the membrane fouling resistance were conducted by using surface water samples under different irradiation conditions (dark and visible light). The permeate fluxes of the Eagle Bluffs water sample at the TMP of 8 psi are presented in Fig.20. The average flux with PVDF-TiO<sub>2</sub> was 40% higher than the one with pure PVDF membranes, with or without visible light irradiation, respectively.

Pure PVDF membranes exhibited similar fouling behaviors with/without visible light, while PVDF-NTiO<sub>2</sub> membrane showed a significantly improved fouling resistance under visible light irradiation.



**Fig.20.** Fouling behaviors of membrane samples under various irradiation conditions for Eagle Bluffs water

samples treatment. The error bar represents the range of data from triplicate tests.

The results above on the water flux as well as organic solute data during the testing time period of 3 hrs were summarized in Table 5. The pure PVDF membranes and PVDF-NTiO<sub>2</sub> membranes had demonstrated similar rejections for HA and TOC with/without visible light. The rejections of HA (as indicated by UV 254) and TOC were about 40% and 20%, respectively. Changes of water flux with time is an indicator of membrane fouling. Under the dark condition, the flux decrease for both membranes was the same. With visible light irradiation, the water flux decrease was only about 21% for the PVDF-NTiO<sub>2</sub> membrane during the test time period, which was less than the 29% decrease for the pure PVDF membrane, suggesting that the incorporation of N-TiO<sub>2</sub> nanoparticles had resulted in a membrane with better anti-fouling characteristics. Please note that even under dark condition, PVDF-NTiO<sub>2</sub> membranes still showed

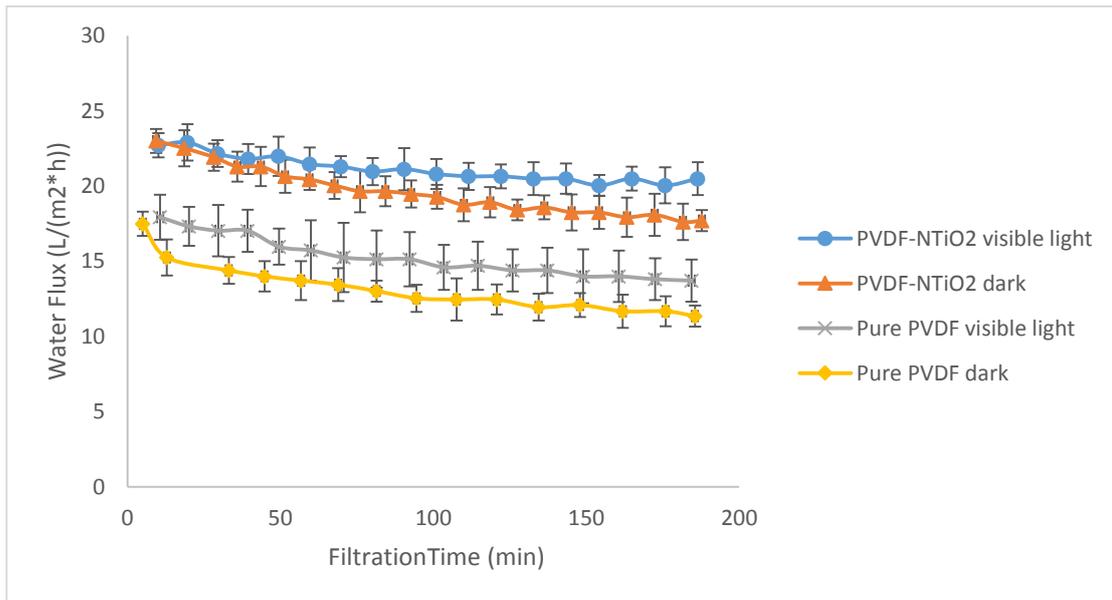
higher water flux than the pure PVDF membrane, which could be attributed to the hydrophilicity property of TiO<sub>2</sub> NPs.

**Table 5** Eagle Bluffs water samples treatment results by different membrane samples under various irradiation conditions

|                                      | Dark      |                        | Visible light |                        |
|--------------------------------------|-----------|------------------------|---------------|------------------------|
|                                      | Pure PVDF | PVDF-NTiO <sub>2</sub> | Pure PVDF     | PVDF-NTiO <sub>2</sub> |
| UV-254                               | 47%       | 41%                    | 42%           | 39%                    |
| Rejection of TOC                     | 22%       | 20%                    | 24%           | 18%                    |
| Flux decrease                        | 32%       | 33%                    | 29%           | 21%                    |
| Average flux (L/(m <sup>2</sup> *h)) | 14.9      | 17.4                   | 15.0          | 20.4                   |

The testing results with the water samples collected from Missouri River are in general consistent with those from the Eagle Bluffs sample (Fig.21). As summarized in table 6, the average flux with PVDF-TiO<sub>2</sub> showed was 61% higher than that of pure PVDF membranes under visible light and 38% higher than without light irradiation.

The water flux decrease was about 10% for PVDF-NTiO<sub>2</sub> membranes and 24% for the pure PVDF membrane, indicating that there was much less membrane fouling for the PVDF-NTiO<sub>2</sub> membrane under the visible light irradiation. There were also some differences between the Eagle Bluff and Missouri River water samples, for example, the flux decrease with PVDF-NTiO<sub>2</sub> membrane was less than with pure PVDF membrane even in the dark, suggesting that the concentration and nature of natural organic matters in water also play a role for membrane fouling.



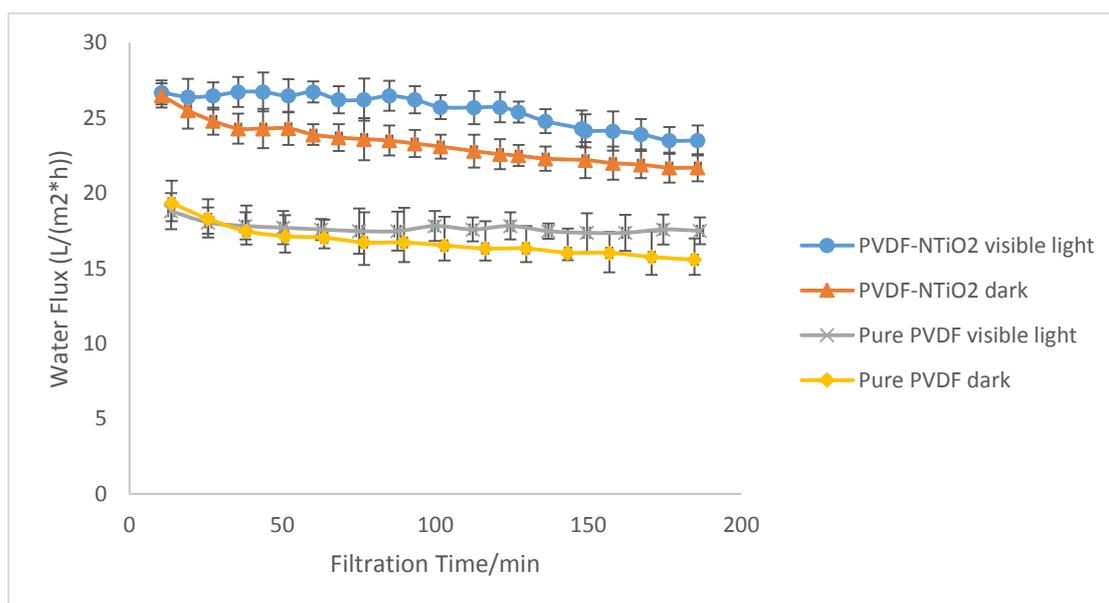
**Fig.21.** Fouling behaviors of membrane samples under various irradiation conditions for Missouri River water samples treatment. The error bar represents the range of data from triplicate tests.

**Table 6** Missouri River water samples treatment results by different membrane samples under various irradiation conditions

|                                      | Dark      |            | Visible light |            |
|--------------------------------------|-----------|------------|---------------|------------|
|                                      | Pure PVDF | PVDF-NTiO2 | Pure PVDF     | PVDF-NTiO2 |
| UV-254                               | 44%       | 40%        | 42%           | 41%        |
| Rejection of TOC                     | 22%       | 20%        | 21%           | 19%        |
| Flux decrease                        | 35%       | 23%        | 24%           | 10%        |
| Average flux (L/(m <sup>2</sup> *h)) | 12.4      | 18.8       | 14.5          | 20.0       |

The results with the third water sample, which was collected from the McBaine Water Treatment Plant with a shallow aquifer near the Missouri River as the water source, were summarized in Figure 22 and Table 7. The average water flux was slightly higher than the previous two samples and the flux decrease was smaller under all conditions, which was consistent with the fact that the water sample from McBaine water treatment

plant had a much lower organic content than the other two water samples. Table 7 showed a reduction of UV-254 at about 20% for both membranes and with or without light irradiation. This is much lower than the 40% for the Eagle Bluffs and Missouri River water samples treatment. However, the rejection based on TOC were all comparable and at approximately 20%. These results suggest water from the McBaine water treatment plant may contain less high molecular weight, color-forming humic substances than the other two water samples. This was also consistent with the very low flux reduction for pure PVDF membranes (about 7%) and the PVDF-NTiO<sub>2</sub> membranes (11%) under the visible light.



**Fig.22.** Fouling behaviors of membrane samples under various irradiation conditions for McBaine Water Treatment Plant water sample treatment. The error bar represents the range of data from triplicate tests.

**Table 7** McBaine Water Treatment Plant water samples treatment results by different membrane samples under various irradiation conditions

|                                      | Dark      |                        | Visible light |                        |
|--------------------------------------|-----------|------------------------|---------------|------------------------|
|                                      | Pure PVDF | PVDF-NTiO <sub>2</sub> | Pure PVDF     | PVDF-NTiO <sub>2</sub> |
| UV-254                               | 20%       | 20%                    | 21%           | 19%                    |
| Rejection of TOC                     | 21%       | 20%                    | 21%           | 19%                    |
| Flux decrease                        | 20%       | 18%                    | 7%            | 11%                    |
| Average flux (L/(m <sup>2</sup> *h)) | 16.8      | 23.4                   | 17.7          | 25.6                   |

### 3.3 Discussions

A novel PVDF hollow fiber membrane with integrated N-TiO<sub>2</sub> NPs was prepared by the phase inversion method. The contact angle of PVDF-NTiO<sub>2</sub> membranes was smaller than the pure PVDF membrane due to the hydrophilicity nature of the TiO<sub>2</sub> NPs. Under visible light the pure water flux was increased from 25.6±0.4 to 28.5±0.3 L/m<sup>2</sup>h at the TMP of 8 psi with the incorporation of N-TiO<sub>2</sub> NPs. The antifouling properties of the N-TiO<sub>2</sub> doped PVDF membranes were improved due to the enhanced-hydrophilicity and photocatalytic properties of membrane. The average water permeability for the three natural water samples increased from 14.3, 14.7 and 15.7 to 20.1, 20.6 and 25.7 L/m<sup>2</sup>h, respectively, when visible light was applied for the N-TiO<sub>2</sub> doped PVDF membranes. These results demonstrate that the new N-TiO<sub>2</sub> PVDF membrane has an enhanced water permeability and antifouling properties especially under the light irradiation. It is envisioned that the membrane could be applied in places where light is available or could be supplied, for example, for surface water treatment, wastewater

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treatment, and algae membrane bioreactor.

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## Chapter 4

### FUTURE WORK

This study has demonstrated that antifouling properties of PVDF-NTiO<sub>2</sub> mixed matrix HFMs are improved under visible light irradiation during the membrane filtration of natural water with natural organic matters. Approximately 20% reduction of TOC and 20-40% reduction of UV 254 are observed. Since natural organic matter largely controls the formation of disinfection by products (DBPs) in drinking water system, it is important to evaluate the impact of the organic removal by the ultrafiltration process on the control of the DBP formation. For membrane fabrication more compact membranes with higher rejection of humic acid and total organic carbon. Increasing the amount of PVDF and decreasing the amount of PVP in the dope solution may achieve this aim. Further improvement on the TiO<sub>2</sub>-based catalyst should also be explored. There are reports on N-F-codoped TiO<sub>2</sub> (Li, Haneda, Hishita, & Ohashi, 2005), CdS/TiO<sub>2</sub> coupled semiconductor (Ghows & Entezari, 2011), and black hydrogenated TiO<sub>2</sub> (Chen, Liu, Yu, & Mao, 2011). Some of these may be used for the development of visible light activated hollow fiber membranes. In addition, more N-TiO<sub>2</sub> nanoparticles could be added to the membrane doping solution to raise the amount of surface located TiO<sub>2</sub>, of course, there is an upper limit for the percentage of TiO<sub>2</sub> nanoparticles that could be incorporated and beyond which it may not be possible to prepare functional membranes.

When the practical industrial application is the final goal, there is a need to optimize

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the design of membrane modules as the light is a new parameter for consideration. The focus should be on maintaining membrane's exposure to visible light irradiation without losing too much membrane surface area in unit volume. Therefore, novel optical materials could be applied on membrane module design and preparation. In addition to sun light, energy efficiency light source like light-emitting diode (LED) could be explored to generate light inside the module (Li et al., 2005; X. Wang & Lim, 2010).

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