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REMOVAL OF HUMIC ACID IN WATER USING AN INTEGRATED TiO₂ PHOTOCATALYTIC OXIDATION AND MEMBRANE SYSTEM

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A thesis submitted to the Nanyang Technological University
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SUMMARY

In order to conciliate the more and more outstanding conflict between water shortage and the severer water pollution situations, it is of significance to increase the process of wastewater purification. However, natural organic matter (NOM), for which humic acid accounts a major part having been demonstrated to be a key issue for water pollution. It is necessary to remove humic acid in waters to ensure safe water accessibility to all the populations. In this study, TiO_2/UV photocatalytic oxidation and membrane filtration process (MF/UF) was integrated to remove humic acid. Some conclusions are summarized:

Firstly, MF (0.2 μm) process could not remove humic acid in waters in terms of UV_{254} (absorbance at 254 nm), color_{436} (absorbance at 436 nm), and TOC. UF (20 kDa CA, 30 kDa PS, 30 kDa PVDF, 60 kDa PS and 100 kDa Ultrafluc) process could remove color_{436} , UV_{254} over 90%, but the low TOC removal efficiency could not reach the drinking water standards. The obvious flux reduction was major attributed to the pore blocking and cake layer formation due to the wide distribution of humic acid in molecular weight or particle sizes.

Secondly, the integrated TiO_2/UV photocatalytic oxidation and MF processes (PCO-MF) on removal of humic acid was investigated. It clearly proved that the integrated PCO-MF was able to improve the removal of humic acid in comparison to MF process, with regards to the removal efficiencies of UV_{254} , color_{436} and TOC, which was mainly removed by the adsorption and degradation by TiO_2 under UV irradiation and the rejection by membrane. Molecular weight distribution of humic acid analyzed by HPSEC demonstrated that humic acid with large molecular weights was degraded into smaller ones which become biodegradable and easily to be adsorbed by TiO_2 . SEM images of fouled membrane displayed that membrane

fouling was controlled by the transition from irreversible phase (pore blocking) to reversible phase (cake layer), removed by physical cleaning lightly.

Thirdly, the concurrent TiO_2 /UV photocatalytic oxidation and UF process (PCO-UF) on humic acid removal was evaluated. It demonstrated that PCO-UF processes used with five kinds of UF membranes all were able to remove UV_{254} and color_{436} completely under different pH conditions of feedwater. The removal efficiency of TOC could reach more than 95%, implying that nearly all the organic matters have been removed in the concurrent PCO-UF process. But it also witnessed that the influence of different UF membranes regarding membrane materials, molecular weight cutoff, thickness, hydrophobicity/hydrophilicity on removal efficiencies and flux performances was complicated and needed to be investigated in details. In the concurrent PCO-UF process, humic acid was adsorbed and degraded into smaller ones by TiO_2 , while UF membranes reject humic acid adsorbed TiO_2 particles which were recycled back into feedwater tank by the cross flow velocity. Therefore, in this process, membrane fouling was reduced to the least extent, and TiO_2 was recovered by UF membranes, which are very convenient for practical engineering application. But, due to poor energy input, the humic acid feedwater of this study could not be degraded completely. However, an obvious change of molecular weight distribution of humic acid was found eventually.

In summary, this study proved that the integration of TiO_2 /UV photocatalytic oxidation and membrane filtration processes (MF/UF) were able to remove humic acid with high efficiency and are worth to be developed continuously for practical engineering application.

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NOMENCLATURE

AOPs	advanced oxidation processes
BOD	biological oxygen demand
CA	cellulose acetate
COD	chemical oxygen demand
Color ₄₃₆	absorbance at wavelength of 436nm
DBPs	disinfection by-products
DC	digital camera
DI	deionized
FESEM	field emission scanning electron microscope
FTIR	fourier transform infrared spectroscopy
HA	humic acid
HAAs	haloacetic acids
HPLC	high performance liquid chromatography
HPSEC	high performance size exclusion chromatography
MF	microfiltration
MW	molecular weight
MWCO	molecular weight cutoff
MWD	molecular weight distribution
NOM	natural organic matter
PCO	TiO ₂ /UV photocatalytic oxidation
PCO-MF	TiO ₂ /UV photocatalytic oxidation and microfiltration process
PCO-UF	TiO ₂ /UV photocatalytic oxidation and ultrafiltration process
PS	polysulphones
PSA	particle size analysis/analyzer
PSD	particle size distribution
PSS	styrenesulfonic acid sodium salt

PVDF	polyvinylfluoride
PZC	point of zero charge
SEC	size exclusion chromatography
SEM	scanning electron microscope
TMP	transmembrane pressure (MPa)
THMs	trihalomethans
TOC	total organic carbon
UF	ultrafiltration
UV ₂₅₄	absorbance at wavelength of 254nm
WHO	world health organization

CAPTER 1 INTRODUCTION

1.1 Background

With the increasing demand in industrial, agricultural production and our daily lives, water has been a valuable, precious but scarce resource (Kolpin, Furlong et al. 2002). Water reclamation and recovery is a feasible and necessary approach to increase water supply and safety. NOM is complex macromolecular products of the chemical and biological degradation of plant and animal residuals. And it includes lignin, carbohydrate and proteins, which universally exist in surface and ground waters (Yuan and Zydney 1999). With a complex nature composed of carboxylic, phenolic and carbonyl functional groups, humic acid accounts for a 40-90% of dissolved organic matters in nearly all the water supplies (Kilduff, Karanfil et al. 1996) and has been indicated to react with the major disinfectants (chlorine, ozone, chlorine dioxide, chloramines) to produce a host of DBPs (Krasner et al., 2006). On the other hand, MF has been widely used in drinking water treatment for the removal of particles, turbidity, and microorganisms to meet the stringent water quality requirements as an effective alternative to conventional water treatment processes with several advantages including superior water quality, easier control or operation, lower maintenance, lower operational pressure, and less sludge production (Bian, Watanabe et al. 1999; Yuan and Zydney 1999; Yuan and Zydney 1999). However, the membrane fouling during the filtration, greatly reducing permeate flux and increasing operational pressure, leads to a high operational cost, and a short membrane lifespan. Humic acid has been demonstrated to be the major constituent causing membrane fouling during the drinking water treatment process by a number of previous studies (Hane et al., 2004; Chae et al., 2007).

Since 1996 (Bekbolet and Balcioglu 1996), PCO has been applied to photocatalytic oxidation of humic acid (Eggins, Palmer et al. 1997; Fukushima, Tatsumi et al. 1998; Bekbolet, Suphandag et al. 2002; Li, Fan et al. 2002; Al-Rasheed and Cardin 2003; Al-Rasheed and Cardin 2003; Liu, Lim et al. 2008). Most of the previous studies proved that PCO was an effective approach to remove and degrade humic acid, and also many factors like catalyst (Bekbolet, Suphandag et al. 2002) and dosage (Le-Clech, Lee et al. 2006), pH (Chin, Lim et al. 2007), membrane materials (Domany, Galambos et al. 2002), TMP, UV light intensity etc. needed to be addressed, however, an unavoidable issue is the recovery of catalyst (TiO_2) which may result in a safe problem of water accessibility. UF membrane had been investigated to separate TiO_2 particles in drinking water treatment process and demonstrated to be an effective method to recover TiO_2 catalysts (Soo-Ah Lee and Wonyong Choi 2001). Therefore, it becomes natural to make full use of the advantages of PCO and membrane filtration process to increase the degradation of NOM and separate TiO_2 catalysts at the same time.

Recently, the integration of TiO_2 photocatalysis with membrane filtration has demonstrated to be an advanced water treatment technology for removal of humic acid (Le-Clech, Lee et al. 2006; Huang, Leal et al. 2008; Syafei, Lin et al. 2008) and other pollutants (Choo, Chang et al. 2008). Huang (Huang, Leal et al. 2008) reported that PCO was effective in NOM removal and membrane fouling control which mainly attributing to the molecular weight changes. Whereas on the contrary, Syafei (Syafei, Lin et al. 2008) claimed that TiO_2 -coated membrane under UV irradiation did not perform any better in removing NOM and reducing fouling. Obviously, there exists a disagreement on whether PCO is concurrently active in humic acid removal and membrane fouling control and it is necessary to clearly investigate some factors on removal of NOM and fouling control during the integrated process. Hence, it is of interest to study the removal of humic acid in

water using an integrated PCO and membrane filtration system.

1.2 Objectives

In order to investigate the effectiveness of integrated PCO and membrane filtration process on humic acid removal in waters and membrane fouling control, this research project aims:

- (1) To develop the integration of PCO and membrane filtration technologies used for humic acid removal in waters;
- (2) To investigate the effectiveness of integrated PCO and MF (PCO-MF) membrane filtration technologies on humic acid removal and membrane fouling control under different UV wavelengths and irradiation time;
- (3) To evaluate the effectiveness of concurrent PCO and UF (PCO-UF) membrane filtration technologies on humic acid removal and membrane fouling control by different UF membranes under different pH values of humic acid feedwater; and
- (4) To provide some meaningful recommendations for practical engineering application of the integrated PCO-MF and concurrent PCO-UF processes on humic acid removal in waters.

1.3 Scopes of Study

The first part of this study focused on investigating the effectiveness of PCO-MF on humic acid removal. Before the integrated process was investigated, the MF process and PCO was used to remove humic acid in waters, to work as the foundation of the further study.

The second part of this study centered on evaluating the effectiveness of concurrent PCO-UF on humic acid removal. In this part, the influences of some factors, such as

pH of humic acid, membrane materials, and MWCO of UF membranes were evaluated.

Analytical methods like UV-Visible spectrometry, measurement of TOC, and turbidity; and some advanced instrumentation like HPSEC, SEM, FESEM and PSA were used to obtain enough and variable witnesses for a confirmable conclusion.

1.4 Organization of Thesis

The thesis is divided into 7 chapters. Chapter 1 provides a general background of study, in respect to some issues related to NOM, especially caused by humic acid, wastewater discharge rules and drinking water quality standards, and some methods regarding the removal of humic acid including conventional water treatment technologies, membrane filtration, PCO and other AOPs.

A comprehensive literature review was presented in Chapter 2. Apart from the introduction of fundamental knowledge about humic acid in waters due to its wide existences, molecular structure and molecular weight, removal methods like membrane filtration process and PCO were also particularly highlighted.

The materials and experimental methodologies, procedures in analyzing experimental trends from HPSEC, SEM/FESEM and PSA were included in Chapter 3. It is followed by the detailed procedures and sample preparation methods.

Chapter 4 presented the results of humic acid removal by MF/UF processes, two major aspects of removal efficiency and permeate flux were considered under different conditions including pH of humic acid feedwater, membrane materials and MWCO of UF membranes.

Chapter 5 discussed the effectiveness of integrated PCO-MF on removal of humic acid and membrane fouling. The effectiveness was discussed in term of the removal efficiency, while the membrane fouling control was explained through the MWD of humic acid before and after PCO and membrane filtration process as analyzed by HPSEC; the fouled membrane surfaces and cross sections were scanned by SEM/FESEM, and the size of aggregated particles of TiO_2 and humic acid was obtained by the PSA.

The effectiveness and permeate flux performances of concurrent PCO-UF on humic acid removal were discussed in Chapter 6. In this chapter, the influence of pH, membrane materials and MWCO were studied. The MWD of humic acid was analyzed by HPSEC, fouled membranes were scanned by FESEM, and the aggregated particles sizes of TiO_2 and humic acid were also measured by the PSA to explain the change in membrane resistance.

Lastly, the conclusion and recommendations were reported in Chapter 7, with the projection of future works also included.

CHAPTER 2 LITERATURE REVIEW

2.1 Introduction

The aim of a literature review is to provide a concrete and logical background for this study by reviewing the latest technologies and discoveries and trends to date and hence, identify the purpose and significance of this study.

Safe and available water accessibility has been a crucial issue to increasing populations throughout the world due to increasing pollution of water sources with the global trend of industrialization and capitalization. Among all these issues, NOM has become one of the most significant pollutants that affect human lives and industrial production.

It is important to have a fundamental understanding of NOM, its composition and characteristic before any method can be proposed to remove the humic acid from water. Hence, in the following parts, NOM and humic substance in waters will be reviewed with regards to their compositions, structures, MWD and some other properties. Subsequently some available methods to remove humic acid, such as membrane filtration process and PCO were particularly emphasized. At the same time, membrane fouling brought by humic acid is also one important factor that needs to be reviewed; lastly, the integration of PCO and membrane filtration to remove humic acid is discussed.

2.2 NOM and Humic Substances

Most of NOM originate from soils, and some come from aqueous solution

(Leenheer; and Rostad 2004), thus NOM are ubiquitous in both ground water and surface water bodies and varies in concentration with seasonal changes. The existence of NOM in waters has an adverse effect on water quality and drinking water safety, such as color problem and interactions with other contaminations. Meanwhile, drinking water standards are becoming much more stringent, therefore it is imperative to remove NOM contents in waters via an efficient and cost effective method.

A major fraction of NOM is humic substances, which are a series of high molecular weight, yellow to black substances formed by secondary synthesized reactions (F.J.Stevenson 1994). They can be generally characterized as being rich in oxygen-containing functional groups like carboxylic, carbonyl, methoxyl, hydroxyl and phenolic function groups (Wiszniewski, Robert et al. 2002), notably COOH but also phenolic and/ or enolic OH, alcoholic OH, and C=O of quinines. Stevenson (1994) has done a great deal of investigations on humic substance, and classified humic substance into two parts: non-humic and humic substance. The detailed classification and chemical properties of humic substances is listed in Table 2.1.

Table 2.1 Classification and chemical properties of humic substances*

* Information from Stevenson, 1994.

In recent years, the below classification method of humic substances was agreed generally and used widely. According to the solubility in water under different pH conditions and molecular weight, humic substances can be divided into three categories (Lee, Zhang et al. 2008): 1) humic acid, 2) fulvic acid, and 3) humins.

Humic acid comprises of a mixture of weak aliphatic (carbon chains) and aromatic (carbon rings) organic acids which are not soluble in water under acidic conditions but are soluble in water under alkaline conditions. Humic acid accounts for that fraction of humus substances that are precipitated from aqueous solution when the pH is below 2. A typical model structure of humic acid is shown in Figure 2.1.

Figure 2.1 Model structure of humic acid (Stevenson, 1982)

The molecular weight of humic acid ranges from approximately 10,000 to 100,000 Da. Humic acid is thought to be poly-disperse because of their chemical features. From a three-dimensional aspect, they are coiled, long chain molecules which may be slightly cross-linked (Yoon, Lee et al. 1998). On average 35% of the humic acid molecules are aromatic (carbon rings), while the remaining compounds are in the form of aliphatic (carbon chains) molecules (Leenheer, Wershaw et al. 2003).

Fulvic acid is a mixture of weak aliphatic and aromatic organic acids which are soluble in water at all pH conditions (acidic, neutral and alkaline). Their compositions and shapes are quite variable. The size of fulvic acid is smaller than humic acid, with molecular weight ranging from approximately 1,000 to 10,000. The model structure of fulvic acid is shown in Figure 2.2.

Figure 2.2 Model structure of fulvic acid (Buffle, 1997)

Humins are the fractions of humic substances which are not soluble in water at any pH. Humin complexes are considered as macro-organic (very large) substances because their molecular weights range from approximately 100,000 to 10,000,000. In comparison, the molecular weights of carbon-hydrates (complex sugars) range from approximately 500 to 100,000.

Except that molecular weight of NOM is related to its solubility, Cabaniss et al., (2000) also reported that molecular weight played a great role on NOM properties and reactivity. Figure 2.3 (Cabaniss, Zhou et al. 2000) showed the effect of molecular weight on NOM properties and reactivity, assuming consistent chemical composition across the MW range. From Figure 2.3, it is known to us that the greater the molecular weight, the more non-soluble the NOM will be, which is in agreement with the above principle of classification.

Figure 2.3 Effect of molecular weight on NOM properties and behavior, assuming consistent chemical composition across the MW range

2.3 Humic Acid in Water Treatment

Humic acid accounts for a major fraction (40-90%) of the dissolved organic matter in nearly all water supplies (Kilduff, Karanfil et al. 1996), and widely exist in surface water and ground water (J. I. Kim 1990) resulting in pollution problems that can affect water quality and drinking water safety. The removal of humic acid has been studied by many researchers all over the world, because humic acid causes undesirable color and taste of waters, and can also act as food for bacterial growth in waters. Humic acid in waters can also interact with other organics and metals like pesticides, insecticides and herbicides (Pinger, 1999; Krasner et al., 2006) to attain a high concentration to ease their transportation, and their adverse effects on water quality and human drinking water safety will be magnified or enhanced.

Another issue of humic acid in waters is that it can react with oxidants like chlorine, which is widely used as water disinfectant, and form different kinds of DBPs, such as THMs and HAAs (Richardson, Thruston Jr et al. 2003; Leenheer; and Rostad 2004; Sohn, Amy et al. 2004; Krasner, Weinberg et al. 2006). These DBPs are toxic and degrade the water quality causing them to be unsuitable for human drinking to some extent. USEPA (2006) has established the maximum contaminant levels for

the sum of four THMs and five HAAs at 40 and 30 $\mu\text{g/L}$, respectively. Studies have also indicated that a high intake of humic acid might be an etiological factor for the Blackfoot disease (Hseu and Yang, 2002). Therefore, it is of great importance to minimize the humic acid presence in potable waters.

2.4 Removal of Humic Acid in Water

2.4.1 Conventional Water Treatment Technologies

Conventional water treatment technologies like adsorption, coagulation (Melia, W.C.Becker et al. 1999), ion-exchange and biological degradation (Graham 1999) (Hallvard Ødegaard 1999) have been utilized to remove and degrade humic acid in water. However, these technologies have all been proved to be restricted by certain limitations in one way or another. For example, in many countries, humic acid is usually removed from water before chlorination by coagulation using aluminum sulphate ($\text{Al}_2(\text{SO}_4)_3$) or ferric chloride (FeCl_3), but humic acid can not be removed completely via this technique. Wang et al., (2000) reported that only 10-50% removal of TOC by coagulation. And also, it generates large volumes of sludge with high concentration of aluminum/iron content, which requires further treatment and disposal. Moreover, the treated water by coagulation requires careful monitoring of dissolved aluminum/iron concentration. According to the World Health Organization (WHO)'s regulations and standards (1993), water containing more than 0.2 g/L Al is not recommended for drinking purposes. It has also been suspected that human exposure to aluminum has a role to play in the onset of Alzheimer's disease (WHO, 1998).

Some researchers developed plenty of enhanced coagulation processes to remove NOM in the past years (Garca and Moreno 2007) (Yu, Sun et al. 2003). Most of processes have been utilized to remove NOM under different conditions. Chang et

al (Chang, Chiang et al. 2005) investigated the performance of enhanced coagulation by alum and polyer on synthetic water including humic acid and other pollutants; Park et al evaluated the effect of iron species and inert minerals on coagulation and direct filtration for humic acid removal (Park and Yoon 2009). Coagulation and powdered activated carbon was integrated to remove organic matter by some researchers (Tomaszewska, Mozia et al. 2004). The effect of preozonation on humic acid removal by coagulation was also investigated (Li, Yan et al. 2009). Some hybrid system of coagulation and membrane filtration processes were developed to remove humic acid in waters or used for drinking water treatment (Konieczny, Sakol et al. 2009; Zularisam, Ismail et al. 2009). Ghernaout et al also investigated the removal of humic acid by continuous electromagnetic treatment followed by electrocoagulation in batch using aluminium electrodes (Ghernaout, Ghernaout et al. 2009). All of those developed enhanced coagulation processes demonstrated to be able to remove humic acid to some extent. However, the disadvantages such as sludge treatment, secondary pollutants and strict conditions control were hard to be neglected.

2.4.2 Membrane Filtration Technology

According to the definition given by the European Membrane Society, the membrane is an intervening phase separating two phases and or acting as an active or passive barrier to the transport of matters between phases (S.Judd and B.Jefferson 2003). Basically, a membrane can act as a thin layer to separate materials depending on their physical or chemical properties when a driving force, either a gradient of chemical potential (concentration or pressure gradient) or electrical potential, is applied across the membrane. So naturally, there are some basic requirements for a membrane:

- High flux of product

- Good mechanical strength for supporting the physical structure
- Good selectivity for the desired substances.

Membrane filtration process exhibits the promising technology in water and wastewater purification due to its many advantages in water treatment like fewer chemicals, lower operating and maintenance costs, easier operation, more compact and modular construction, better water quality and quantity to meet stringent water standards (Chen, Kim et al. 2003; K.Wang, Hung et al. 2006).

Membrane filtration technologies have been widely used in many fields. Membrane processes are used to produce potable water from surface water (Domany, Galambos et al. 2002), ground water (Buchanan, Roddick et al. 2005), brackish water and seawater (Afonso and Borquez 2002) or to treat real industrial wastewater before its discharge or reuse. Also, membrane technologies can be used to treat secondary or tertiary municipal wastewater or oil field wastewater. To date, membrane filtration has been established as an important element in water and wastewater treatment. Figure 2.4 (K.Wang, Hung et al. 2006) showed the application range of various membrane processes, from which was clear that membrane processes had occupied a wide share in the market and has the potential of further expansion in the future years to come.

Bian et al (1999) investigated the removal of humic acid by UF and NF membranes. The results demonstrated that the same humic acid removal efficiency of 30% could be achieved by 50 kDa PAN, 150 kDa CA and 200 kDa PAN (poly acril nitoril) UF membranes in a cross flow mode with a TMP of 100 kDa. Maartens et al (1999) indicated that a capillary polysulphone membrane was able to remove commercial humic acid with removal efficiency of UV_{254} more than 80% at a TMP of 150 kPa. But all the researchers indicated that humic acid became into a major factor to result

in membrane fouling.

Figure 2.4 Application range of various membrane processes

In the past decades, membrane applications in removing humic substances are spread wide and fast. Figure 2.5 shows an example of a membrane treatment plant for removal of humic substances (Thorsen, 1999). These plants are used for a number of treatment purposes, like disinfection, removal of turbidity, hardness, micro-pollutants and NOM. Based on the similar basic principle, different treatment needs demand membranes of different optimum pore diameters. Due to the fact that dead end filtration had been proved to be unsuitable for humic acid removal, thus in the designed plant of figure 5, cross flow mode was applied to remove humic acid (Thorsen 1999).

Figure 2.5 Typical diagram of a membrane filtration plant for humic substances removal

However, membrane fouling which occurs on the membrane surface or in membrane pores can be a bottle-neck problem that jeopardizes further applications of membrane processes (Fan, Harris et al. 2001). Generally, membrane fouling can be caused by 1) particulate deposition (colloidal fouling); 2) adsorption of organic molecules (organic fouling); 3) inorganic deposits (scaling); and 4) microbial adhesion and growth (biofilm formation). However, umic acid has been recognized as a significant foulants (Nystrom, Ruohomaki et al. 1996), which causes reduction in permeate flux, damage membrane surface, shorten life span of membrane and increase operational costs. And above all, these effects of fouling are deemed irreversible (Yuan and Zydney 1999; Yuan and Zydney 2000).

Many processes have been implemented to mitigate fouling, for example, pretreatment, coagulation/flocculation, ozonation and PAC or GAC adsorption (Howe 2001; Wei 2001; Judd and Judd 2007). All these have been proven to be effective, but more works are needed to seek the optional method to prevent or control membrane fouling. The best way to solve membrane fouling completely is first to investigate the fouling mechanism. Thus, in this study, one aim is to investigate the membrane fouling mechanism clearly so as to propose a reasonable

advice to prevent or control membrane fouling.

2.4.3 Advanced Oxidation Processes

Through the production of hydroxyl radicals, advanced oxidation processes (AOPs) are able to degrade organic and inorganic impurities in waters into lower molecular weight fractions of better biodegradability (Bekbolet and Balcioglu 1996; Bekbolet, Suphandag et al. 2002). It is the photogeneration of electron-hole pairs that plays a role in the degradation process of NOM. These photo-generated species constitute a redox pair and take part in photo redox reaction. The holes react with the electron donors in the electrolyte to produce powerful oxidizing free radicals such as $\cdot\text{OH}$ (Bekbolet and Ozkoşemen 1996). According to Hoffmann's publication (Hoffmann, Martin et al. 1995), the general mechanism of TiO_2 photocatalysis was shown in figure 2.6 and can be summarized as follows:

Figure 2.6 Mechanism of TiO_2 photocatalysis

- (1) Formation of charge carriers by a photon;
- (2) Charge carrier recombination to liberate heat;
- (3) Initiation of an reductive pathway by a valence-band electron;
- (4) Initiation of an reductive pathway by a conduction-band electron;
- (5) Further thermal (hydrolysis or reaction with active oxygen species) and photocatalytic reactions to yield mineralization products;
- (6) Trapping of a conduction-band electron to yield Ti(III) ; and
- (7) Trapping of a valence-band hole at a surface titanol group.

In the area of water and wastewater treatment, AOPs including O_3 , O_3/H_2O_2 , O_3/UV , UV/H_2O_2 and TiO_2/UV have been developed to remove humic acid in waters in the past decades. Among all the AOPs that were used, PCO has gained considerable attention in the field of water treatment. Water purification by TiO_2 photocatalysis has been attracting immense research interests, especially in the removal of toxic pollutants and bacteria (Sun, Tay et al. 2003) in the beginning stages. However, few studies were done on removal of humic acid by TiO_2 photocatalysis due to its complexity. In 1996, for the first time, Bekbolet and Ozkosemen (1996) did a preliminary investigation on the photocatalytic degradation of humic acid using TiO_2 . In this study, humic acid of 50 mg/L could be removed with a TiO_2 dosage of 1 g/L in an acidic medium. It also indicated that humic acid could be destructed sufficiently to keep the THMs level below the limit of 80 μ g/L. Eggins et al (Eggins, Palmer et al. 1997) also suggested TiO_2 photocatalysis as an alternative for the degradation of aquatic humic substances. It took approximately 12 minutes to reduce the humic acid concentration by half and 60 minutes to achieve 50% complete mineralization for an initial humic acid concentration of 100 mg/L. Al-Rasheed and Cardin (Al-Rasheed and Cardin 2003; Al-Rasheed and Cardin 2003) explored the effectiveness of photocatalysis of humic acid in saline water.

Further investigation was also done on the relative changes in humic acid and its biodegradability by Bekbolt et al., (1996). BOD_5/COD ratio was found to increase with irradiation time and more biodegradable substances formed (Wiszniewski, Robert et al. 2002). Thus, PCO was suggested to use as a pretreatment process for the preceding biological treatment process on humic acid removal. Photocatalysis was able to break long organic molecules into smaller biodegradable compounds and could make their biological treatment eligible.

Concerning the photocatalytic reaction rate, H_2O_2 , as an electron scavenger and bicarbonate as a hole scavenger was added to increase the degradation rate of humic acid (Bekbolet and Balcioglu 1996). In this study, it was found that bicarbonate ion slow down the degradation rate by scavenging the hydroxyl radicals when with a high concentration. And also found that H_2O_2 could not improve the photocatalytic reaction rate on humic acid removal anymore. But Wang et al., (Wang, Hsieh et al. 2000; Wang and Hubbe 2001) found that H_2O_2 could promote the photo-degradation efficiency of humic acid. The low concentration of H_2O_2 was able to accelerate the reaction rate greatly, but over dosage lead to a negative effect (Tay, Chen et al. 2001). Hence, it is clear that the catalyst dosage had a major effect on the efficiency of humic acid removal.

UV light is strong enough to produce hydroxyl radicals to oxidize humic acid, however it is necessary to note that UV light is energy-consuming and can pose as a health hazard due to its strong intensity. Visible light sources are abundant and harmless, therefore some researchers investigated the feasibility of humic acid removal by TiO_2 with the irradiation of visible light. However, Cho and Choi (Cho and Choi 2002) found out that the visible light-induced reactions of humic acid in the TiO_2 suspension did not lead to a decrease in dissolved organic matter concentration.

Currently, TiO_2 photocatalysis is still a debatable topic due to the fact that many influencing factors have not been evaluated and explained distinctly. What's more, most applications of photocatalysis were only limited as pretreatment processes. Considering the current situation of limited knowledge, much more investigations are required to focus on research areas such as chemical reactivity and interactions between humic acid and catalysts, efficiency improvement of catalysts, and other optimum reaction conditions.

2.5 Integrated Processes of PCO and Membrane Filtration for Humic Acid Removal

PCO is effective in the degradation of organic matters, but the recycle and regeneration of TiO_2 have caused another issue. Since membrane filtration is not only able to reject humic acid, but also recycle TiO_2 particles, therefore, many researchers have tried to integrate membrane filtration process and PCO together to remove humic acid. In the new integrated system, TiO_2 will adsorb and degrade humic acid under UV irradiation, while membrane recycles and regenerates TiO_2 catalysts.

In recent years, the integrated photocatalysis/membrane filtration processes have been tested for removal of various organics from waters (Sopajaree, Qasim et al. 1999; Molinari, Borgese et al. 2002; Fang, Sun et al. 2005; Fu, Ji et al. 2006; Le-Clech, Lee et al. 2006; Molinari, Pirillo et al. 2006). Some publications have reported that TiO_2 photocatalysis was effective in removal of humic acid (Tay, Chen et al. 2001; Fang, Sun et al. 2005), NOM (Doll and Frimmel 2005; Fu, Ji et al. 2006; Le-Clech, Lee et al. 2006) and organic dye pollutants (Konstantinou and Albanis 2004; Grzechulska-Damszel, Tomaszewska et al. 2009). But not all have clearly reported the extent of membrane fouling control and also certain debating points still exist.

Huang et al., (2008) investigated the fouling control potential by the integrated PCO and MF/UF processes. This study proved that PCO was an effective process for NOM removal, although a small fraction of refractory NOM remained. The study also evaluated the influence of TiO_2 dosage on membrane fouling control with a conclusion that negligible change was found for the TiO_2 dosage above 0.3 g/L. The membrane fouling control by PCO was mainly attributed to the changes in NOM molecules resulting from preferential removal of high molecular weight

hydrophobic molecules, which are the major fractions responsible for membrane fouling.

On the contrary, Syafei et al (2008)) investigated the humic acid removal by UF with TiO₂ coated membrane under UV irradiation. The study found that the use of an UV₂₅₄ illuminated TiO₂ coated membrane system in UF did not enhance the flux and humic acid removal efficiency in comparison to the original membrane. But, the study did achieve similar phenomenon as Huang et al (2008) experienced, that the molecular weight of humic acid was changed with the UV illumination on TiO₂ coated membrane.

Except the TiO₂ coating on membrane surface, novel TiO₂ membranes were also fabricated to remove humic acid with the irradiation of UV light. Zhang et al (2008) tested the efficiency of humic acid removal by the fabricated TiO₂ nanowire membrane and reported that humic acid were removed nearly 100% and the fouling was alleviated by the concurrent photocatalytic degradation.

From the above views, we found it was still a debatable point that needed to be further investigated whether the combined PCO and membrane filtration was effective in humic acid removal definitely, and the membrane fouling control mechanism has not been precisely understood. Considering the amount of uncertainties revolving this area, this study was proposed and carried out for the purpose of promoting the understanding of certain fundamental principles and mechanisms.

2.6 Summary

This chapter reviewed some pertinent literatures in relation to the scope of the thesis. The increasingly severe situation of water accessibility and water pollution caused

by the prevalent existence of NOM in waters was first discussed in this chapter. The origin of humic substances and its characteristics were then reviewed, followed by the introduction of available technologies for humic acid removal in recent years. Conventional water treatment process was limited by its own deficiency; membrane fouling is inevitable when used to remove humic acid. With the rapid development of AOPs, greater attention was focused on the integration of PCO and membrane filtration process to remove humic acid. Although, fruitful results have been achieved by such an integrated method, much works are needed to fully understand the fouling control mechanisms. From the practical engineering perspective, this study was hopefully to carry out fundamental investigation of the integrated PCO and membrane filtration process on humic acid removal.

CHAPTER 3 MATERIALS AND METHODOLOGIES

3.1 Introduction

This chapter presents some materials and methodologies used in this thesis. More detailed procedures used for specific experiments are described in appropriate chapters necessarily.

3.2 Preparation of Humic Acid Stock Solution

3.2.1 Materials

- **Humic Acid**

Commercially available humic acid powder was obtained from Aldrich Chemicals with a reported purity >97% for the study. The powder was derived from decomposition organic materials of mining excavation, particularly dead plants and can be found in vegetable soil, peat, and/or soft coal in Germany.

- **Deionized Ultrapure Water**

ELGA ultra pure water machine, model UHQ was used to produce ultra pure water for this study.

- **Sodium Hydroxide (NaOH)**

Analytical grade NaOH pellets, obtained from MERCK, Germany, were used for adjusting pH of the solution.

- **Hydrochloric Acid (HCl)**

Analytical grade HCl, obtained from APS AJAX Finechem, Australia, was used for

adjusting pH of the solution.

3.2.2 Preparation of Humic Acid Stock Solution

Humic acid are readily soluble in alkaline conditions, thus NaOH is used to improve dissolution in water. At pH>12, 1 g humic acid powder was added and stirred to 100 mL of 0.1 Mol/L NaOH solution and kept overnight. After dissolution, dilute it to 1000 mL with Deionized water (DI) (MilliQ). Then the dissolved humic acid solution was filtered by 1.22 μ m glass fibre filter paper (Advantec) and 0.45 μ m cellulose acetate filter paper (Sartorius, Germany). The residue humic acid remaining on filter paper was dried at 103 °C and weighted to calculate the final concentration as follows:

$$\text{Humic acid (mg/L)} = (\text{humic acid}_{\text{initial}} - \text{humic acid}_{\text{residue}}) \text{ mg/L} \quad (3.1)$$

The pH of prepared humic acid stock solution was around 1 L, and it needed to be stored in the dark refrigerator at 4 °C before usage.

3.2.3 Characterization of Humic Acid

In order to evaluate its influence on membrane filtration and photocatalytic oxidation concretely and precisely, humic acid used in this study were characterized by three methods subsequently: Firstly, the C.N.H.S and O contents of humic acid were determined by an elemental analyzer; Secondly, FTIR spectrum provides the chemical bonds and their relative contents in humic acid; Lastly, humic acid powders were scanned by SEM to display an observable and direct image.

3.2.3.1 C.N.S.H/O Elemental Analysis

Humic acid in this study were analyzed by CNSH/O elemental analyzer, Perkin

Elmer 2400 II. The CHNS/O analyzer is ideal for rapid, simultaneous determination of carbon, hydrogen, nitrogen and sulphur content in humic acid. As shown in Table 3.1, the predominant elements are carbon and oxygen. However, the carbon content is lower than that reported by Stevenson et al.,(1994) and Schnitzer and Khan, (1972) but with an increase of oxygen content, the reason maybe lie in the different humic acid used in this study. Humic acid used in this study were same as the one used in Lee's study, so the carbon content distributes in the same range. The sulfur content of humic acid (0.89-1.09%) here was similar with the content (1.05%) provided by manufacturer.

Table 3.1 Elemental analysis of humic acid

	Humic acid range (Stevenson, 1994)	Lake sediment humic acid (Schnitzer and Khan,1972)	Laurentian humic acid (Kilduff, 1996) ^a	Aldrich humic acid (Lee Peifung 2008)	Aldrich humic acid range (in this study)
C	53.8-58.7	53.7	51.9	42.66	41.42-43.56
H	3.2-6.2	5.8	5.5	5.07	6.55-7.21
N	0.8-4.3	5.4	2.3	1.23	0.90-0.91
S	0.1-1.5	N/A	N/A	1.35	0.89-1.09
O*	32.8-38.3	35.1	39.9	50.31	47.44-50.03

*Oxygen%=100%-Carbon%-Hydrogen%-Nitrogen%-Sulfur%;

^a Datum reported by manufacturer.

3.2.3.2 FTIR Spectrum of Humic Acid

In order to study the functional groups of humic acid, the FTIR instrument (Perkin Elmer) with a detector in a wave number range of 370-7800 cm⁻¹ was used in this study. It has been indicated that the main functional groups of humic acid were carboxylic and phenolic at the wavelength of 3439 and 1575 cm⁻¹, respectively. The Figure 3.1 obtained in this study is similar to the results obtained by Lin et al (Lin,

Liu et al. 2001) and Lee et al (2008). This further confirmed that humic acid were oxygen containing organic matter.

Figure 3.1 FTIR spectra of Aldrich humic acid

Table 3.2 General assignments of the FTIR spectra of humic acid

Wavelength (cm^{-1})	Assignment
3600-3000	Hydrogen-bonded OH groups, free OH, intermolecular-bonded OH
3077-3030	Aromatic C-H stretching
2950-2850	Aliphatic C-H, C-H ₂ , C-H ₃ stretching
2850-2500	Carboxylate ion
1725-1640	C=O stretching of carboxylic acids
1640-1585	C=O stretching vibration of double bonds in cyclic and acyclic compounds, ketones and quinines
1515	C=C stretching vibration of benzene, pyridines
1470-1420	Aliphatic C-H deformation
1400-1390	OH deformation and C-O stretching of phenolic OH, C-H deformation of CH ₃ groups
1390-1332	Salts of carboxylic groups
1280-1137	C-O stretching of esters, ethers and phenols
1090-1040	C-O stretching of alcoholic compounds
880-750	Hydrogen-bonded OH stretching vibration of carboxylic groups
650-510	Deformation of COOH

3.2.3.3 SEM Images of Humic Acid

In this study, humic acid powder (before preparation of stock solution) was characterized by the EVO SEM microscope and shown in Figure 3.2. Figures 3.2a and 3.2b were taken without any pretreatment, while Figure 3.2c was taken after being vacuum (30 Pa) treated by a freeze drier (-61 °C) for 24 h to remove the moisture of humic acid totally. However, it can be found that there was no difference between with and without pretreatment. Figure 3.2a showed the plane, while b and c shows the cross section morphology of humic acid powder. Humic

acid powder aggregated together in the layer-formed with some fiber-like stuff appearance.

Figure 3.2 SEM images of Aldrich humic acid powder

3.3 Membrane Filtration Process

As an important part of this study, MF and UF membrane filtration process was conducted in a cross-flow membrane test mode under different operational conditions.

3.3.1 Membrane Filtration Experimental Setup

As shown in Figure 3.3, membrane filtration experiments were carried out in a laboratory-scale cross-flow membrane test unit, Model C10-T (Nitto Denko Co., Japan), the cell designed in rectangular form (46 mm × 180 mm with a 60 cm² effective membrane surface (Hane et al., 2004; Wu and Sun, 2005). Feedwater was prepared by diluting humic acid stock solution and stored in a large beaker (5 L) when used, permeate is collected by a beaker locating on a balance connected with one computer to record the permeate weight automatically during the experimental period.

Figure 3.3 Experimental setup for cross-flow membrane filtration

3.3.2 MF Membrane

Cellulose Acetate MF membrane, with a pore size of 0.2 μm purchased from Sartorius, Germany was used here. Additional limited information (Table 3.3) was provided by the manufacturer.

Apart from the provided information from manufacturer, the clean MF membrane was also scanned by SEM and shown in Figure 3.4. From this figure of surface and cross section of virginal MF membrane, multiple thin layers with uniformed pores were observed acting as the functional layer.

Figure 3.4 SEM image of MF membrane, (a) surface and (b) cross section

Table 3.3 Characteristics of cellulose acetate membrane

Adsorption	Bovine serum albumin < 10 µg/L
Bubble point	Minimum value For 0.2 µm >2.9 bar when measured with an automatic integrity tester,
Chemical compatibility	Resistant to aqueous solutions, pH 4-8,
Extractable with water	Less than 1%
Flow rate for water	Average value per cm ² area at Δp=1 bar (100 kPa, 14.5 psi): 24 mL/min for 0.2 µm,
Material	Cellulose acetate
Sterilization	By autoclaving at 121 °C or 134 °C with γ-radiation, dry heat or ethylene oxide
Sterilization filtration	Filters with 0.2 µm pore sizes are validated by Bacteria Challenge Tests.
Thermal stability	Max.180 °C
Thickness	Average value 120 µm
Pore size	0.2 µm
Diameter	293 mm
Pack size	25, non sterile

3.3.3 UF Membrane

Five kinds of flat sheet UF membranes with different MWCO and different materials were purchased from GE Company to carry out UF experiments in this study. Also, additional limited information was obtained from GE company website and listed out as follows:

Table 3.4 Characteristics of UF membranes

MWCO	Material	Hydrophobic/ Hydrophilic	Thickness (μm)	pH range
20 kDa	Cellulose acetate (CA)	hydrophilic	200	2-9
30 kDa	Polysulphones (PS)	hydrophobic	250	0.5-13
30 kDa	Polyvinylfluorides (PVDF)	hydrophilic	200	1-11
60 kDa	Polysulphones (PS)	hydrophobic	250	0.5-13
100 kDa	Ultrafluc	hydrophilic	200	1-10

Figure 3.5 displays the FESEM images of some of the UF membranes, it was found that the membrane pores on virginal membrane surfaces. But these membrane pores are not as uniformed as the MF membranes as shown in Figure 3.4.

Figure 3.5 FESEM images of virginal UF membrane, (a)30 kDa PS and (b)30 kDa PVDF

3.3.4 Pretreatment of Membranes

As the effective surface of membrane test unit is 60 cm^2 , both MF and UF membranes have to be cut into appropriate sizes to suit into the size of the test unit. The membranes were easily broken when dry, and the pore sizes can be extended, which is convenient for separation when wetted with DI water. Thus, the MF

membrane was immersed in DI water for 30 minutes before being installed into the test unit; while the UF membranes were cut into suitable sizes and immersed in DI water overnight (around 24 h) before usage. Except immersing the membranes in DI water, no other pretreatment was used to pre-treat the membranes in this study.

3.3.5 Operational Conditions

Considering the difference between MF and UF membranes and limited by experimental equipments, different operational conditions were designed to conduct MF and UF experiments, shown in Table 3.5.

Table 3.5 Operational conditions for MF and UF experiments

	TMP	Retentate flow rate
MF	0.2 MPa	0.56-0.64 L/min
UF	0.05 MPa	1.72-1.84 L/min

3.4 PCO

3.4.1 TiO₂

Commercially available TiO₂ P25 (Degussa Corp., Germany), containing 70% anatase and 30% rutile with an average particle size of 30 nm and surface area of 50m²/g, was used as catalyst in the photocatalytic oxidation process of this study.

3.4.2 UV Lamp

Two Pen-Ray lamps (Figure 3.6) with different wavelength 254 and 365 nm purchased from UVP, acted as the UV irradiation source. Together with the UV lamps, two designated power supply were also recommended.

- (1) UV₂₅₄ nm Lamp, Model 3SC9 PEN-RAY LAMP, with a lighted length of 9.0" (228.6 mm) and outside diameter of 0.375" (9.5 mm), the recommended power supply was PS-4 PEN-RAY POWER SUPPLY, AC, 220V/50HZ.
- (2) UV₃₆₅ nm, Model 11SC1L PEN-RAY Lamp, with a lighted length of 2.25", the outside length diameter is 0.375" (9.5 mm), the recommended power supply was Model PS-1 PEN-RAY Power Supply, 220/50HZ.

Figure 3.6 Illustration diagram of UVP lamp

3.4.3 PCO-MF

In the PCO-MF period, PCO experiment was first carried out in a separate reactor as Figure 3.7 shown, then the effluent of PCO was used as feedwater to carry out MF experiment in the forenamed cross-flow filtration setup.

A glass bottle (1 L) locating on the stirrer used as the reactor to hold the mixed solution of TiO₂ (0.5 g/L) and humic acid (50 mg/L). UV lamp was suspended in the middle of reactor to insure an even light distribution to all the directions, one pump continually supplies air into the reactor to provide enough oxygen for PCO and at the same time to ensure uniform mixing situation during the whole process.

Figure 3.7 Schematic diagram of PCO

3.4.4 Concurrent PCO-UF

During this period, PCO-UF was carried out concurrently in the concurrent setup as shown in Figure 3.8. A 5 L glass bottle containing 50 mg/L humic acid and 0.5 g/L TiO₂ was used as the filtration feedwater tank and as PCO reactor. Other instructions were similar as PCO-MF process as above.

Figure 3.8 Experimental setup of concurrent PCO-UF

3.5 Test Analysis

3.5.1 pH

A pH meter (HORIBA pH/ion meter, F-53) was used to measure the pH of humic

solution to observe whether there is an obvious difference before and after PCO and membrane filtration process so as to determine the physiochemical parameters of humic acid solution immediately.

3.5.2 Turbidity

In this study, turbidity was measured by a HACH 2100N Turbidity meter to observe the removal of particles by membrane filtration.

3.5.3 UV₂₅₄ and Color₄₃₆ Analysis

It is due to the dark color of humic acid solution that scientists are using color as a criterion to investigate humic acid content in an aqueous solution. It was found that absorption in the UV and visible region is useful for quantitative analysis, and herefore a UV-Vis 2401 PC double-beam spectrophotometer (Shimadzu Corporation, MD) was used to measure the absorption of humic acid at wavelength of 254 nm and 436 nm. A correlation exists between absorption and concentration given by the Beer-Lambert law:

$$\text{Absorbance} = \log_{10} \frac{I}{T_t} = \epsilon c L \quad (3.2)$$

Where, A is absorbance, I is the incident light, T_t is transmitted intensity, ϵ , $\text{m}^2 \text{mol}^{-1}$, is molecular absorptivity of the sample at this wavelength, c , mol/L , is the concentration, L , cm , is the path length through the sample. From the above equation, it is known that molecular absorptivity ϵ is a numerical measure of absorption at a given wavelength. It has also been witnessed that the absorptivity ϵ of humic acid to increase with the increase in: (a) molecular weight, (b) carbon content percentage, (c) degree of condensation, and (d) ratio of C aromatic rings to C in aliphatic structures (Lee, Zhang et al. 2008).

Figure 3.9 The molar absorptivity of humic acid at wavelength of 254 nm and 436 nm at pH 9.5

The absorptivity ϵ of humic acid is different depending on the pH conditions of solution. Figure 3.9 shows the relationship between absorptivity of humic acid at wavelength of 254 nm and 436 nm and the concentration at pH of 9.5. From the graph, the absorptivity ϵ of humic acid is 0.023 and 0.004 at wavelength 254 nm and 436 nm with a good linear regression agreement ($R^2=0.999$), respectively. However, both of these values are smaller than 0.0336 at 254 nm and 0.0067 at 436 nm as reported by Lee at pH=9 (Lee, Zhang et al. 2008).

Using these two equations, concentration of humic acid can be calculated quantitatively, and humic acid removal efficiency can be reflected effectively.

3.5.4 TOC Analysis

TOC is a significant indicator to reflect the removal effect of humic acid by membrane filtration and PCO. In this study, TOC was measured by a TOC analyzer, TOC-5000, SHIMADZU. The TOC of humic acid solution before and after PCO and membrane filtration were monitored to observe the removal effect.

3.6 Particle Size Analysis

Particle size is an important factor to influence the membrane fouling situation, especially to affect the formation of different fouling, so it is quite necessary to determine the size of aggregated particle of TiO_2 and humic acid after each experiment. In this study, Malver Mastersizer 2000 was used to measure the aggregated particles size.

3.6.1 The Principle of Particle Size Analysis

The analyzer (Malver Mastersizer 2000) determines PSD based on the principle of laser diffraction in the range of 0.02 to 2000 μm of particulate materials including powders, suspensions and emulsions by wet measurements only.

Laser particle size analysis consists in measuring the size of particles (powders, suspensions and emulsions) using the diffraction and diffusion of a laser beam. During the laser diffraction measurement, particles are passed through a focused laser beam. These particles scatter light at an angle that is inversely proportional to their size. The angular intensity of the scattered light is then measured by a series of photo-sensitive detectors. The map of scattering intensity versus angle is the primary source of information used to calculate the particle size. The Mie scattering model accurately predicts the scattering of particles. The schematic of the laser diffraction measurement is displayed in Figure 3.10.

Figure 3.10 Schematic diagram of the laser diffraction measurement

(http://www.beckman.com/coultercounter/homepage_tech_laserdiff.jsp, DEC 2008)

Instrument consists of:

- A He-Ne gas laser ($\lambda=0.63 \mu\text{m}$) as a source of coherent intense light of fixed wavelength, Which is the most common as they offer the best stability (especially with respect to temperature) and better signal to noise than the higher wavelength laser diodes.
- A suitable detector. Usually this is a slice of photosensitive silicon with a number of discrete detectors. It shows that there are an optimum number of detectors (16-32)-increased numbers do not mean increased.
- Some means of passing the sample through the laser beam.

3.6.2 Analytical Procedures

3.7 High Performance Size Exclusion Chromatography

High performance size exclusion chromatography (HPSEC) is a type of high performance liquid chromatography (HPLC) and is effective in measuring the MWD of organic matters. In this study, the MWD of humic acid before and after PCO and membrane filtration process, will be monitored to provide sufficient evidence to validate and explain the membrane fouling mechanism.

3.7.1 HPSEC Principle

HPLC is one mode of chromatography that is widely used as an analytical technique.

The basic principle of HPLC is to utilize a liquid mobile phase to separate the components of a mixture. These components (or analyte) are first dissolved in a solvent, and then forced to flow through the specific chromatographic column under high pressure. In the column, the mixture is resolved into its components.

In size exclusion chromatography the column is filled with materials having precisely controlled pore sizes, and the sample is simply screened or filtered according to its solvated molecular size. When mixed samples containing different molecular weight components pass through the column under given pressure, larger molecules are rapidly washed or excluded from the gel pores and are carried in the flow through the interest volume only and elutes first, while the smaller ones penetrate the pores and stay longer in the column. Thus different molecular components have different elution time in the column and then are separated. The basic principle schematic diagram of HPSEC is shown in Figure 3.11.

Elution order: larger molecules elute first, smaller ones elute later

Figure 3.11 Schematic principle of HPSEC

(<http://www.forumsci.co.il/HPLC/topics.html>, OCT 2008)

3.7.2 HPSEC System

HPSEC system consists of the following instruments:

- Perkin Elmer Series 200 pump
- Perkin Elmer 900 Series interface
- Perkin Elmer 785 UV/Vis detector
- Perkin Elmer Vacuum Degasser series 200
- Perkin Elmer series 200 column oven
- Perkin Elmer series 200 auto-sampler
- Perkin Elmer 600 series Link
- Total-chrom Software to analyze datum

Apart from the above basic system instrumentations, the detailed information related to SEC column, guard column and vials is listed out as follows:

1) SEC Column:

One Shodex Protein KW 802.5 (Shodex, Japan) column was used to determine the MWD of humic acid. Detailed information was provided by the supplier as from Table 3.6.

2) Guard Column:

One pre-guard column (Protein WS-800P) also was used to remove impurities (ash contents and other metals ions) contained in the sample before the column. The pre-guard column size is 6 mm ID × 50 mm, the pore size and particle size is 500 Å and 7 µm, respectively.

3) Vials:

1.5 mL Screw Neck Vial, 32 × 11.6 mm, clear, 1st hydrolytic class, with Screw Thread 10/245

4) Caps:

10 mm combination seal, PP screw Cap, yellow, centre hole, 10-425 thread, Silicone white/PTFE blue, 55 shore A, 1.5 mm slitted.

Table 3.6 Detailed SEC column information

% Carbon Load	N/A
Brand	Shodex
Chemistry	Diol (OH)
Endcapped	N/A
Endfitting Type	Shodex Internally-threaded type
Format	Column
Ion Exchange Capacity	N/A
Length (mm)	300 mm
Internal Diameter (mm)	8 mm
Mode	Gel Filtration (aqueous)
Molecular Weight Range	100-50,000
pH Range	2-8
Particle Shape	Spherical
Particle Size	5 μ m
Particle Substrate	Silica
Pore Size	250 Å
Column Material	SUS 316
Packing Material	Porous silica gel covered with chemically-bonded hydroxyl groups
Usable Temperature	10 to 45 °C
Max. Pressure	50 kg/cm ²
Max.Flow rate	For the analysis: 1.5 mL/min For the replacement of eluent: 0.5 mL/min
Silanol Activity	N/A
Solvent	Water
Surface Area	N/A
USP Classification	L20

Units in Package	1/pkg

5) Mobile Phase:

It is of great importance to select one kind of suitable mobile phase as carrier to carry the sample passing through the column to achieve reasonable separation effect. Three commonly used buffer solution recommended by the manufacturer are (1) phosphate buffer solution, (2) tris hydrochloric solution, and (3) acetate buffer solution. As indicated by other researches (Chin, Aiken et al. 1994; Pelekani, Newcombe et al. 1999; Huang, Leal et al. 2008), the ionic strength and pH value of mobile phase has a notable impact on the column effect, it has been demonstrated and widely applied that 0.02 Mol/L phosphate buffer solution with an ionic strength of 0.1 Mol/L and pH of 6.8 can act as a suitable carrier for the HPSEC analysis of humic acid. A flow rate of 1.0 ml/min was used to carry the samples through the column.

Preparation of Mobile Phase:

Dilute 1.51 mL 85% (Volume/Volume) Ortho-phosphate with DI water in a 1 L flask and mix it uniformly. Adjust the pH value to 6.8 using NaOH and HCl, then adjust the ionic strength to 0.1 Mol/L using NaCl solution. Lastly the prepared phosphate buffer solution is needed to be filtered by 0.2 µm filter paper (Adventc). Store the phosphate buffer solution in a refrigerator for use.

3.7.3 Operational Conditions

After being connected to the HPLC system, the column should be conditioned for 30 minutes, depending on the experimental condition, the flow rate for column conditioning is designated as 0.2 mL/min. At the same time, the UV detector and

oven should be switched on to attain the steady-state condition for analysis.

Basic operational conditions are shown in Table 3.7.

Table 3.7 Operational conditions for HPSEC

Wavelength of UV detector	224 nm
Column temperature	30 °C
Operational Pressure	560-960 psi, depending on the column situation
Mobile phase	100% Phosphate buffer solution
Concentration of mobile phase	0.02 Mol/L
Ionic strength of mobile phase	0.1 Mol/L
pH value of mobile phase	6.8
Flow rate of mobile phase for column conditioning	0.2 mL/min
Flow rate of mobile phase for sample analysis	1 mL/min

3.7.4 PSS Standard Calibration

Poly (Styrenesulfonic acid Sodium salt) (PSS) standards with molecule of 210, 4300, 1300, 32000 and 77,000 Da obtained from Fluka and acetone were used to calibrate the HPSEC system before samples analysis with the concentration of 33 mg/L. PSS standards were detected by UV detector at wavelength of 224 nm for 20 min with the injection volume of 100 µl. Detailed methods to calibrate the system can be found elsewhere (Becher, Carlberg et al. 1985); (Leung, Pandey et al. 1987; Chin, Aiken et al. 1994; Pelekani, Newcombe et al. 1999; Sanly, Lim et al. 2007).

From Figure 3.12, it is observed that all the PSS standards appeared with good

peaks with specified different elution time.

Figure 3.12 HPSEC diagram for PSS standards

Different from PSS standards, the acetone HPSEC peak does not appear in good condition due to the existence of some impurities. But the dominant peak indicates clearly that the elution time of acetone is 15.94 min.

Figure 3.13 HPSEC diagram for acetone

Table 3.8 Elution time of PSS standards and acetone

Category	MW (Da)	Log (MW)	Elution time (min)
PSS	210	2.322219	17.63
PSS	4,000	3.633468	9.49
PSS	13,000	4.113943	8.20
PSS	32,000	4.50515	7.39
PSS	77,000	4.886491	6.84
Acetone	58		15.94

The calibration curve can be drawn out on the basis of concrete elution time in Table 3.8. Here, two methods were used to calibrate the HPSEC system: one is the narrow molecular weight range method, the other one is the wide molecular weight range method. The calibration curves are shown in Figure 3.14.

According to the HPSEC calibration principle, HPSEC systems should be calibrated with a series of known molecular weight standards in a narrow molecular weight distribution range with a good co-relationship. And also in many other researches (Chin, Aiken et al. 1994; Huang, Leal et al. 2008), the molecular weight range of PSS standards used to calibrate the HPSEC system is less than 50,000 Da. The difference between the above two curves' co-relationships proved that the narrow molecular weight range method was more suitable for HPSEC system calibration.

Figure 3.14 Calibration curve, (a) narrow MW range and (b) wide MW range

3.8 Scanning Electron Microscope

The scanning electron microscope (SEM) is one type of electron microscope that images the sample surface by scanning it with a high-energy beam of electrons in a raster scan pattern. The electron interact with the atoms that make up the sample producing signals that contain information about the sample's surface topography, composition and other properties such as electrical conductivity. SEC used in this study was EVO 65 ZESIS.

Sample preparation

All samples should be scanned in a dry and gold coated environment under vacuum, so samples should be freeze-dried in a freeze-drier (-61 °C and 30 Pa) for 24 hours to remove the moisture completely, and then coated with a gold layer before the sample is scanned.

3.9 Field Emission Scanning Electron Microscope

FESEM works under vacuum condition, the FESEM principle is displayed as Figure 3.15. Electrons generated by a field emission source are accelerated in a field gradient. The beam passes through electromagnetic lenses, focusing onto the specimen. The bombardment different types of electrons are emitted from the specimen. A detector catches the secondary electrons and an image of the sample surface is constructed by comparing the intensity of these secondary electrons to the scanning primary electron beam. Finally the image is displayed on a monitor. FESEM used in this study was Jeol JSM-6340F.

Sample Preparation

Likewise with the SEM, samples should be scanned in a dry and platinum coated environment under vacuum. Hence, the samples should be coated with a platinum layer under vacuum situation (< 3 Pa) before it is scanned.

Figure 3.15 FESEM Principle

(<http://infohost.nmt.edu/~maximino/FESEM%20principle.htm>, SEP 2008)

3.10 Summary

All fundamental materials and general methods used in this study have been explained and listed out in this chapter, except for some specific methods which would be described in details in the appropriate places. All the contents of this chapter lay a solid groundwork for the entire study, and provide a capacious field to undertake further research endeavors. Firstly, the experimental plan was established, some necessary materials were purchased immediately and the basic experimental setup was built up from scratch. Subsequently, many advanced techniques and equipments such as the SEM/FESEM and HPSEC were used to explain or investigate certain theories or phenomena.

CHAPTER 4   REMOVAL OF HUMIC ACID BY MEMBRANE FILTRATION PROCESS

4.1 Introduction

As the first part of this study, only membrane filtration (MF/UF) was used to remove humic acid in water. The UV_{254} , $color_{436}$ and organic substances represent for UV absorbance at 254 nm, 436 nm, and TOC, respectively, were used to evaluate the humic acid removal efficiency. The flux performance was measured, and the fouled membranes were scanned by SEM/FESEM to characterize its fouling situations.

4.2 Experimental Procedures

The basic operational conditions for membrane filtration experiments have been introduced in Chapter 3. The sampling interval for MF experiments (0.2 μ m CA membrane) was 5 minutes. The total running time for UF experiments was 1-2 hours. The feedwater volume for MF experiments was 1 L, while for UF experiments were 5 L. A higher TMP at 0.2 MPa and a larger retentate flowrate at 1.76-1.84 L/min were used to conduct the UF experiments compared to that of MF experiments (TMP and retentate flow rate were 0.05 MPa and 0.56-0.60 L/min, correspondingly). The detailed experimental results are discussed in the following chapters.

4.3 Results and Discussion

In this chapter, the removal efficiency and flux performance of MF/UF process of humic acid were investigated and acted as the background for further investigation of integrated PCO-MF and concurrent PCO-UF processes of humic acid. At the

same time, the membrane fouling situation and MWD of humic acid before and after the membrane filtration process was inspected to provide evidences to membrane fouling phenomenon, together with the images of fouled membranes scanned by SEM and FESEM.

4.3.1 Flux Performance

4.3.1.1 Flux Performance of MF Process

At the beginning of this study, MF was evaluated to remove humic acid. The different effects on flux performance by pretreatment of humic acid stock solution, TMP, filtration time and the concentration of humic acid feedwater, were investigated individually.

Figure 4.1 Effect of filtration time on flux performance

Most experiments of this study were conducted in a short time period, but Figure 4.1 showed the flux performance in a long filtration time situation under a constant TMP of 0.05 MPa condition. This experiment lasted for 32 h and the flux reached a steady situation after 24 h which meant the steady fouling layer was formed after 24

h. In the first 2 h, the flux reduced quickly, and then reduced to a gradual reduction rate during the period between 2-h and 24-h, before finally reaching the steady-state situation.

Figure 4.2 Effect of pretreatment of humic acid stock solution on flux performance

In the preparation of humic acid stock solution, two different humic acid stock solutions were prepared: (1) the humic acid stock solution was filtered by 1.22 μm and then 0.45 μm filter paper, referred to as “filtered”; (2) the humic acid stock solution was filtered by 1.22 μm filter paper but unfiltered by 0.45 μm , referred to as “unfiltered”. The difference between these two kinds of stock solution lies in the different composition of humic acid. Unfiltered stock solution contains part of humic acid with particle size less than 1.22 μm , while the filtered stock solution has only a narrow particle size of less than 0.45 μm .

From the Figure 4.2, it is obvious that the unfiltered humic acid feedwater showed a heavier flux reduction than that of filtered humic acid, but both were higher than that of 0.5 g/L TiO₂ solution used as feedwater. This might suggest that: (1) the amount

of humic acid with particle size between 1.22 μm and 0.45 μm need to be considered and have a great influence on flux performance; (2) it was the large particles between 1.22 μm and 0.45 μm that increased pore blocking and resulted in greater reduction of flux; (3) this partially proved the fact that humic acid had a wide range of particle size. TiO_2 particles was uniformly distributing in water and aggregate into large particles (Le-Clech, Lee et al. 2006) sedimentating on membrane surface to lead to a severe flux reduction.

Figure 4.3 Effect of TMP on flux performance

TMP is an important operational parameter of membrane filtration process in relation to the permeate production, operating cost, membrane fouling situation, life span of membrane.

From figure 4.3, it can be seen that the higher the TMP, the faster the rate of flux reduction when a 50 mg/L humic acid feedwater was used. And furthermore, high TMP promotes severe membrane fouling in a short period of time, because of that, higher TMP would push or compress more particles into membrane pores to block them.

Figure 4.4 Effect of initial concentration of humic acid on flux performance

The flux performance depends on the initial concentration of humic acid (Figure 4.4). Under the same condition of 0.05 MPa TMP, the higher the initial concentration of humic acid, the easier the membrane pores were blocked and the rate of flux reduction were faster.

4.3.1.1 Flux Performance of UF Process

The effect of pH of humic acid feedwater on UF process has been investigated widely by some researchers (Jones and O'Melia 2000; Garcia-Molina, Lyko et al. 2006), and had been pointed to be an important factor affecting flux performance and removal efficiency.

In the UF experiments, the influence of pH of humic acid feedwater was investigated to study the interactions between different membrane materials and humic acid. Humic acid was only soluble in alkaline conditions, while insoluble at acidic conditions, thus the composition of humic acid feedwater greatly depends on

its pH. The interactions between humic acid and membrane materials affected flux performance and was elucidated in this study.

In this study, five types of UF membranes of different materials were tested in order to compare the flux performance at different pH conditions. The materials, thickness, MWCO, and hydrophobicity/hydrophilicity all affect permeate quality and flux performance under given TMP and retentate flow rate.

Figure 4.5 Flux performance of UF membranes (pH=3)

Figure 4.5 showed the flux performance of five types of UF membranes at pH 3 of humic acid feedwater. From figure 4.5, it was seen that the 100 kDa ultrafluc membrane displayed the highest flux but with an obvious reduction; followed by the 20 kDa CA membrane nearly without reduction; the third was the 30 kDa PVDF membrane with a slow and stable reduction; the least reduction of flux appeared to the 30 kDa and 60 kDa PS membrane. Both of which were hydrophobic surface activity. The 20 kDa CA membrane was hydrophilic membrane and was the thinnest among the five types of membranes examined by a vernier caliper; therefore its flux was smaller than that of 100 kDa ultrafluc membrane, but greater than that of other

three types of membranes even with the smallest MWCO. PVDF material was less hydrophobic than PS, and PVDF membrane was also thinner than PS membrane, therefore even with the identical MWCO, the flux of 30 kDa PVDF was still higher than that of PS membrane.

Figure 4.6 Flux performance of UF membranes (pH=7)

When the pH of humic acid feedwater was adjusted to 7, the flux performances seemed to be different slightly. The flux of 100 kDa membrane was reduced to some extent gradually, which meant that the pH of feedwater had certain influence on flux performance to a given UF membrane. Another different point lied in that the flux of 60 kDa PS membrane was less than that of 30 kDa PS membrane at this pH condition. This indicated that the absolute permeate flux of UF membrane was affected by pH of humic acid feedwater more than by MWCO of membrane. As all the factors like MWCO, materials, thickness, surface charge of membrane, physico-chemical properties and operational conditions affect flux performance, so it was necessary to investigate and analyze the different influences under given conditions.

Figure 4.7 Flux performance of UF membranes (pH=9)

From figure 4.7, it was seen that the flux reduction of 100 kDa ultraflic membrane was less than that under the conditions of pH 3 and 7, which demonstrated that the flux reduction decreased following the increase of pH of humic acid feedwater. This was because humic acid was easily soluble in high pH solution, and certain time was in need for the sedimentation of humic acid on membrane surface. At the same time, experimental datum also proved that the fluxes of other four membranes at pH 9 were higher than that under the conditions of pH 3 and 7.

4.3.2 Removal Efficiency

4.3.2.1 Turbidity Removal

As shown in Table 4.1, all five types of UF membranes had higher turbidity removal efficiency than 0.2 μm MF membrane. But it needed to be pointed that the used UF membranes still could remove the turbidity of humic acid completely under any pH condition. This was because humic acid distributed in a very wide molecular weight range, part of smaller molecular weight humic acid was able to

pass through the UF membranes, and was able to pass through MF membrane without much difficulties. This is also a motivation for further investigation of other combined processes to remove humic acid completely. This directly points to the significance of carrying out the investigation of integrated PCO-MF and concurrent PCO-UF processes on humic acid removal.

Table 4.1 Turbidity removal efficiency

	Turbidity removal efficiency (%)		
	pH=3	pH=7	pH=9
20 kDa CA	—	86.23	—
30 kDa PS	85.8	87.22	83.66
30 kDa PVDF	81	84.81	82.56
60 kDa PS	—	82.03	88.27
100 kDa Ultrafluc	60.01	92.52	—
0.2 μ m MF	—	—	65.53

4.3.2.2 Color₄₃₆ Removal

Table 4.2 showed the color removal efficiency of humic acid by UF and MF membranes. From this Figure, it was known to us that UF membranes were effective in color removal of humic acid (Maartens, Swart et al. 1999), but the color removal efficiency of MF membrane was relative low at alkaline conditions. Likewise turbidity, the organic matters with large molecular weight or molecular size were accountable for colour of humic acid, so it was convenient to be removed by UF membranes.

Table 4.2 Color₄₃₆ removal efficiency

	Color ₄₃₆ removal efficiency (%)		
	pH=3	pH=7	pH=9
20 kDa CA	—	98.98	97.58
30 kDa PS	100	98.98	98.56
30 kDa PVDF	97.14	98.94	99.04
60 kDa PS	95.71	98.36	99.26
100 kDa Ultraflc	92.99	99.05	—
0.2 µm MF	—	—	69.95

4.3.2.3 UV₂₅₄ Removal

UV₂₅₄ removal efficiencies of humic acid by UF and MF membranes were listed out in Table 4.3, from which we knew that at pH 9, UV₂₅₄ was mostly removed by UF membranes, but MF membrane displayed very low removal efficiency. When the pH was reduced, the removal efficiency of UV₂₅₄ by UF membranes decreased, this indicated that higher pH resulted in more humic acid dissolving in water and was convenient for removal by UF membranes. And also, it found that with the increase of pH, higher removal efficiency of UV₂₅₄ was observed to all the five types of UF membranes. This was attributed to the solubility of humic acid in alkaline environment.

Table 4.3 UV₂₅₄ removal efficiency

	UV ₂₅₄ removal efficiency (%)		
	pH=3	pH=7	pH=9
20 kDa CA	—	97.07	97.6
30 kDa PS	93.36	96.96	96.3
30 kDa PVDF	88.66	98.21	97.85
60 kDa PS	—	95.47	99.47
100 kDa Ultraflc	85.28	98.55	—
0.2 μm MF	—	—	30.72

4.3.2.4 TOC Removal

TOC removal efficiencies of humic acid by UF and MF membranes were showed in Table 4.4. Comparing to the removal efficiencies of color₄₃₆ and UV₂₅₄, TOC was the most difficult to be removed by UF and MF process, even at pH 9. What’s more, MF membrane showed the lowest removal efficiency of TOC. This was because TOC included all the organic matters of humic acid in a wide and broad molecular weight and size distribution and there were still a few parts of organic matters with small molecular weight that could pass through the membranes. Another point was that 30 kDa PS UF membrane showed the least removal efficiency of TOC among the three preset pH conditions, and further investigation was needed to uncover the behind reasons.

Table 4.4 TOC removal efficiency

	TOC removal efficiency (%)		
	pH=3	pH=7	pH=9
20 kDa CA	—	84.23	92.04
30 kDa PS	54.85	54.56	70.99
30 kDa PVDF	90.43	89.79	84.6
60 kDa PS	—	70.67	98.28
100 kDa Ultrafluc	64.08	91.78	—
0.2 μ m MF	—	—	33.47

4.3.3 SEM/FESEM Images of Membranes

SEM/FESEM provided a clear and morphological image of membrane surfaces, from which we could analyze the severity of membrane fouling situations and could scrutinize the accumulation of pollutants and the fouling distribution on membrane surface. When the MF membrane was used, one part of humic acid entered and permeated through membrane pores, although most parts of humic acid were rejected to sediment on membrane surface as shown in Figure 4.8a, this Figure also indicated that not all the membrane pores were blocked by humic acid meaning both pore blockages and cake layer accounted for membrane fouling and the flux reduction.

Figure 4.8b provided the FESEM image of 60 kDa PS membrane contaminated by humic acid at pH 9, this image clearly indicated that humic acid was rejected to sediment on membrane surface by UF membrane. At the same time, it was found that membrane pores had not been blocked by humic acid completely. It was suspected that the interactions between humic acid and UF membrane surfaces resulted in the un-uniformed distribution of humic acid on UF membrane surfaces,

but more works needed to verify such a hypothesis.

Figure 4.8 Images of fouled membranes, (a)SEM image of MF membrane fouled by humic acid (pH=9), and (b)FESEM image of 60 kDa PS UF membrane fouled by humic acid (pH=9)

4.3.4 MWD of Humic Acid by HPSEC

The MWD of humic acid after UF membrane was analyzed by HPSEC in Figure 4.9. From which, it was found that after UF process, most of humic acid had been removed and the molecular weight of remained humic acid was reduced to smaller ones. But it should be indicated that there was still a few part of humic acid with relative large molecular weight in the permeate water after UF membrane, and this was suspected to be responsible for the low TOC removal efficiency. Same as other study (Laabs, Amy et al. 2006), UF membrane only reduced the amount of humic acid but could not change molecular weight and structures of humic acid, due to its only physical function.

Figure 4.9 MWD of humic acid after UF

Many researchers have reported that UF membrane is effective to separate humic acid into different molecular weight fractions (Fan, Harris et al. 2001). The results of this study also were in accordance with this publication's statement, the direct proof was that large molecular weight fraction of humic acid had been removed while the remained fractions were of smaller molecular weight.

4.4 Conclusion

In this chapter, the removal efficiency of humic acid by MF and UF process was evaluated through the investigations of flux performance, removal efficiency, membrane fouling situation and MWD of humic acid.

(1) The flux of MF membrane when used to filtrate humic acid (50 mg/L) was reduced close to 35%, and affected by the filtration time, pretreatment of humic acid feedwater, TMP and the initial concentration. Except the 100 kDa ultrafiltration membrane, the fluxes of other four types of UF membranes kept constant during the experimental processes under all pH conditions. Because the solubility of humic

acid was different under different pH conditions, the flux reduction of 100 kDa ultraflic UF membrane at pH 9 was the least significant among three pH conditions.

(2) MF membrane was not able to remove the turbidity, color₄₃₆, UV₂₅₄ and TOC of humic acid completely because of the wide distribution of molecular weight; while UF membrane had the ability in removing turbidity, color₄₃₆ of humic acid completely, and also was effective on removing the UV₂₅₄ and TOC to certain high extent, but could not remove TOC completely. So it was necessary to further develop integrated PCO-MF process and concurrent PCO-UF process to remove humic acid totally and provide an available technology for practical engineering application.

(3) SEM/FESEM images of fouled MF membrane proved that part of humic acid were rejected to sediment on membrane surface, still part of humic acid could pass through membrane pores to block them. While, the FESEM images of fouled UF membrane demonstrated that humic acid were rejected to sediment on UF membrane surfaces, but some membrane pores were not blocked, a possible reason may be attributed to the interactions between humic acid and the surface charges of UF membrane under different pH conditions.

(4) MWD of humic acid analyzed by HPSEC proved that most of humic acid had been removed by UF membranes, but UF membrane couldn't reject all humic acid due to its complex compositions.

This chapter laid a solid foundation for the further investigation of integrated PCO-MF process and concurrent PCO-UF process on humic acid removal and membrane fouling control.

CHAPTER 5 REMOVAL OF HUMIC ACID BY INTEGRATED TiO_2 PHOTOCATALYTIC OXIDATION AND MF MEMBRANE

5.1 Introduction

As the second part of this study, the integrated PCO-MF was investigated to remove humic acid and control membrane fouling. Compared with MF filtration process, PCO demonstrated to be an impetus to adsorb and degrade humic acid into carbon dioxide and water. The integrated effect was evaluated by the way of the removal efficiencies of UV_{254} , color_{436} , TOC and flux performance. The fouling control mechanism was explained and proposed on the basis of MWD of humic acid analyzed by HPSEC and images of fouled membranes examined by SEM/FESEM.

5.2 Experimental Procedures

PCO and MF filtration process on humic acid removal was carried out separately in this part. Firstly, 1 L humic acid feedwater (50 mg/L) was photocatalytically oxidized by TiO_2 under UV irradiation for different time. For the sake of practical engineering application, the effluent of PCO was directly used as feedwater to carry out MF experiments without removing TiO_2 particles (Huang, Leal et al. 2008). The removal efficiencies of UV_{254} , color_{436} , TOC and flux performance were investigated with the variance of UV light of different wavelength and irradiation time to provide evidences for the development of this technology in water and wastewater treatment field.

5.3 Results and Discussion

In this chapter, the effect of integrated PCO and MF process on humic acid removal was investigated through the observations of flux performance and removal efficiency. Meanwhile, the effect of PCO on membrane fouling control was also evaluated and the control mechanism was also proposed through the analysis of MWD of humic acid by HPSEC.

5.3.1 Flux Performance

For the sake of practical engineering application, the effluent of PCO was used as feedwater to conduct MF experiments without removing TiO_2 particles by centrifugations (Huang, Leal et al. 2008) or other methods. The permeate fluxes of MF for different feedwater were displayed in Figure 5.1. 50 mg/L humic acid solution (pH=9.5) showed the lightest flux reduction, followed by the TiO_2 solution (0.5 g/L), the largest flux reduction appeared to be by the mixed humic acid (50 mg/L, pH=9.5) and TiO_2 (0.5 g/L) solution (mixed for 1.5 h without UV irradiation before MF). This indicated that humic acid particles could not block membrane pores and only part of humic acid with smaller molecular weight passed through MF membrane into permeate, that was also the reason for low UV_{254} , color_{436} and TOC removal efficiencies of MF membranes (explained in later section). After adsorption of humic acid, TiO_2 particles aggregated together and formed into thick cake layer on membrane surface causing severe flux reduction compared to that of TiO_2 solution. PCO could eliminate membrane fouling and improve permeate flux (Huang, Leal et al. 2008), the PCO effluent after being irradiated by UV light for 8 h displayed similar flux reduction as that of TiO_2 solution. It was observed that the more powerful the UV light source was (UV light at wavelength of 254nm), the smaller the flux reduction would be. This meant that UV light at a wavelength of 254 nm irradiation was able to promote larger part of humic acid degradation,

which was in agreement with the removal efficiency of UV_{254} , $color_{436}$ and TOC explained in 5.3.2.

Figure 5.1 Effect of PCO on MF flux performance

The effect of PCO on flux is related to UV irradiation time. As Figure 5.2 shown, in the comparison with the flux of humic acid (50 mg/L, pH=9.5), the flux of humic acid (50 mg/L, pH=9.5) and TiO_2 (0.5 g/L) mixed solution was improved with the extension of UV irradiation time. Longer UV irradiation time led to more humic acid adsorbed and degraded into smaller molecular ones which resulted in the change of interactions between TiO_2 and humic acid degraded products.

Figure 5.2 Effect of UV irradiation time on MF flux performance

5.3.2 Removal Efficiency

In this part, the humic acid feedwater of each experiment consisted of humic acid (50 mg/L, pH=9.5) and TiO₂ (0.5 g/L). TMP and retentate flow rate of MF process was 0.05 MPa and 0.56 L/min.

5.3.2.1 TiO₂ Recovery

Although PCO has proved to be able to degrade and remove NOM like humic acid in waters (Eggins, Palmer et al. 1997; Al-Rasheed and Cardin 2003; Choo, Tao et al. 2008), the safety problems caused by the presence of TiO₂ particles in drinking water has become into a debating point. So it was a critical issue to ensure all the TiO₂ particles were removed from treated water when PCO was applied for drinking water treatment.

In this study, the recovery efficiency of TiO₂ particles by MF membrane was investigated both in the dead end and cross flow membrane filtration mode. Figure 5.3 has indicated that TiO₂ recovery efficiency by 0.2 µm MF membrane in this study could attain more than 99.99% in both dead end and cross flow modes, which

meant that TiO_2 particles in this study were recovered completely by the used MF membrane. This put up a safe premise for further application of integrated PCO-MF process on removal of humic acid.

Figure 5.3 TiO_2 recovery by MF membrane

5.3.2.2 Color₄₃₆ Removal

Figure 5.4 showed the removal efficiency of color₄₃₆ by the integrated PCO-MF process. After being treated by PCO for 5 h and MF for 2 h, color₄₃₆ of humic acid has been completely removed (>99%), indicating that the integrated PCO-MF process was effective in removal of color₄₃₆ of humic acid. Besides, it was found that with the extension of PCO action time, PCO removal efficiency increased, MF removal efficiency decreased, while accompanied by the increase of total removal efficiency. This was because humic acid was adsorbed and degraded by TiO_2 under UV light irradiation, the degraded products after PCO were too small to be rejected by followed MF process. However, the increase of total removal efficiency still indicated that integrated PCO-MF process was effective in removal of color₄₃₆ of humic acid.

Figure 5.4 Color₄₃₆ removal by PCO-MF

5.3.2.3 UV₂₅₄ Removal

Same as color₄₃₆, UV₂₅₄ removal efficiency was also investigated and shown in Figure 5.5. UV₂₅₄ removal is generally more difficult to be removed than color₄₃₆. But, after 8 h of PCO and 2 h of MF, it was possible to attain UV₂₅₄ removal efficiency more than 95%. Similar changing trend of PCO removal efficiency and MF removal efficiency was observed along the extension of PCO time. The longer the PCO time was, the higher the PCO removal efficiency was, but the lower the MF removal efficiency was, due to the molecular weight change of humic acid in the integrated PCO-MF process. Nevertheless, total removal efficiency of UV₂₅₄ could be ensured to a high level.

Figure 5.5 UV₂₅₄ removal by PCO-MF

5.3.2.4 TOC Removal

Figure 5.6 TOC removal by PCO-MF

TOC, including all the organic matters is the most difficult to be removed by MF process. Figure 5.6 showed the removal efficiency of TOC by integrated PCO-MF process. Compared with the removal efficiency of color₄₃₆ (Figure 5.4) and UV₂₅₄ (Figure 5.5), TOC removal efficiency was the lowest under the same conditions.

Even after 8 h of PCO and 2 h of MF process, the total removal efficiency of TOC was approximately 85%, thus longer PCO action time was needed to improve TOC removal. In conclusion, it was apparent that the integrated PCO-MF process was effective in color₄₃₆, UV₂₅₄ and TOC removal. It expected to be a very promising technology for water and wastewater treatment.

5.3.3 SEM Images of Fouled Membrane

Figure 5.7 showed the SEM images of membranes under different conditions. After contaminated by the aggregated particles of TiO₂ and humic acid, a compact fouling layer formed on membrane surface (a1) resulting in a severe flux reduction, in contrast to the surface (a2) and cross section (a3) of clean membrane. While the membrane surfaces (b) seemed much looser and rougher and not all the pores were blocked, only thin layer formed in a random manner after filtration of humic acid, this indicated that humic acid particles was partly rejected by MF membrane, but there were still parts of humic acid that passed through membrane, leading to flux reduction and low removal efficiency of UV₂₅₄. However, in the process of PCO-MF, the formed cake layer of aggregated TiO₂ and humic acid on membrane surface (c) became looser and thinner after irradiation of UV light. And what's more important was that few particles entered into membrane pores to block them under cake layer, the cross section of fouled membrane (d) confirmed this obviously. This indicated that it was the cake layer rather than pore blocking that has become into the dominant factor of membrane fouling to cause flux reduction. At the same time, further SEM images also demonstrated that the cake layer formed on the membrane surfaces in the PCO-MF process become looser and thinner because humic acid was degraded and removed under a long time or more powerful UV light irradiation, which proved that the flux reduction become lighter with the extension of UV irradiation time.

Figure 5.7 SEM images of fouled membranes

(a1) membrane surface contaminated by mixture of TiO_2 and humic acid without UV irradiation, (a2), (a3) surface and cross-section of virgin membrane; (b) membrane surface contaminated by humic acid solution; (c), (d) surface and cross-section of membrane contaminated by mixture of TiO_2 and humic acid with UV irradiation)

5.3.4 Aggregated Particle Size

In the PCO process, humic acid was adsorbed on the surface and inner pores of TiO_2 to aggregate into large particles. The sizes of these aggregated particles of TiO_2 and humic acid would dominate the type of membrane fouling and the fouling degree. And also, the particle size has a direct influence on membrane resistance which affected permeate flux. In the serial membrane filtration process, the relationship between the resistance in serial model and permeate flux is normally described as follows:

$$J = \frac{\Delta P}{\mu R_t} = \frac{\Delta P}{\mu(R_m + R_p + R_c + R_{cp})} = \frac{\Delta P}{\mu(R_m + R_r + R_{irr})} \quad (5.1)$$

Where, J is the permeate flux, ΔP is the TMP, μ is the water viscosity, R_t is the total resistance, R_m is the membrane resistance, R_p is the pore blocking resistance, R_c is the cake resistance, R_{cp} is the concentration polarization resistance, R_r is the reversible resistance ($R_c + R_{cp}$), R_{irr} is the irreversible resistance (equal to R_p here). R_m is assumed to keep constant, R_{cp} can be eliminated or minimized by the cross flow velocity in the cross flow mode, thereby, R_c is the major inducement to cause flux reduction and determine the fouling situation.

The specific cake resistance (α) is an effective parameter to reflect the resistance of cake layer and it is related to cake porosity (ε) and the density (ρ_d) and the diameter (d_p) of particles forming a cake by the Carman-Kozeny relationship for special particles (Boerlage, Kennedy et al. 2003):

$$\alpha = \frac{180(1-\varepsilon)}{\rho_p d_p^2 \varepsilon^3} \quad (5.2)$$

Regarding constant TMP and constant cross flow velocity here, the retention of particles is assumed to be constant, the cake resistance is proportional to the amount of cake deposited on the membrane and is described as the following equation:

$$R_c = \frac{V}{A} \times \alpha \times C_b \quad (5.3)$$

Where, V is the filtration volume of feedwater, m^3 ; A is the effective membrane surface m^2 .

Combining the equation (5.2) and (5.3) gives:

$$R_c = C_b \frac{180(1-\varepsilon)}{\rho_p d_p^2 \varepsilon^3} \quad (5.4)$$

The size of aggregated TiO_2 and humic acid after each integrated PCO-MF experiment was measured and an obvious changing trend was found as Figure 5.8. It could be seen that with the increase of UV irradiation time, the aggregated particle size increased. Thus the fouling resistance should be decreased. And the flux reduction should be slowed down, which had been demonstrated in Figure 5.1. This figure also indicated that the size of aggregated particles was larger than the pore size of MF membrane ($0.2 \mu\text{m}$), which meant little membrane pores would be blocked, but the aggregated particles were rejected to form cake layer on membrane surface. So, it could be concluded that membrane resistance had been changed from an irreversible resistance (pore blocking) into a reversible resistance (cake layer). In a further step, the greater the aggregated particle size was, the larger the void spaces between the particles, eventually, the looser the formed cake layer would be. All these had been witnessed by the SEM images of fouled membranes (Figure 5.7).

Figure 5.8 Aggregated particle size of humic acid and TiO₂

5.3.5 Effect of PCO on pH Change

Accompanying the increase of aggregated particle size of TiO₂ and humic acid, pH of feedwater also was changed during the PCO-MF process. With the extension of PCO action time, more humic acid were adsorbed and degraded into smaller ones, till carbon dioxide and water, which naturalized the alkalinity of feedwater. And longer PCO action time led to fierce decrease of pH as Figure 5.9 shown. The interactions between TiO₂ and humic acid were weakened following the change of pH, therefore more TiO₂ and humic acid were aggregated into together to increase their size. The pH change of humic acid feedwater in the PCO-MF process re-confirmed the increase of aggregated particle size of TiO₂ and humic acid.

Figure 5.9 pH change of feedwater in the integrated PCO-MF process

5.3.6 MWD of Humic Acid by HPSEC

PCO can degrade humic acid into intermediate products and change the MWD of humic acid (Eggins, Palmer et al. 1997; Le-Clech, Lee et al. 2006; Huang, Leal et al. 2008). After PCO, MWD of degraded humic acid was analyzed by HPSEC as shown in Figure 5.10. Most of humic acid were removed by adsorption and mineralized into CO_2 and H_2O . But there was still little refractory fractions remained in the PCO effluent. Taking the relative low TOC removal efficiency into consideration, these remaining fractions were considered as organic compounds and very difficult to be removed. In reference to Huang's (Huang, Leal et al. 2008)) research, longer UV irradiation time and powerful UV light irradiation can both promote removal and degradation of humic acid.

Figure 5.10 also indicated that the difference between the oxidation function of PCO and the rejection function of MF membrane which can only reduce the amount of humic acid content but not change the MWD of humic acid (Laabs, Amy et al. 2006).

Figure 5.10 MWD of humic acid during the PCO-MF process

5.4 Conclusion

It was found in this chapter that the integrated PCO-MF process was effective in humic acid removal and could transfer the irreversible fouling (pore blocking) into reversible fouling (cake layer) to reach the aim of controlling membrane fouling and with better removal efficiency than MF process. Experimental datum indicated that TiO_2 particles could be recovered by $0.2\ \mu\text{m}$ MF membrane to avoid the adverse effect of TiO_2 on permeate quality. Longer irradiation time and greater UV light intensity (UV light at wavelength of 254 nm) was able to improve the removal efficiency of humic acid and decompose most of the humic acid into smaller, simpler molecular compounds as shown in Figure 5.10. The SEM images witnessed that a compact cake layer of aggregated TiO_2 and humic acid formed on membrane surface without entering into the membrane pores under cake layer. The size of aggregated TiO_2 and humic acid particles increased and resulted in a loose and thin cake layer with the increase of irradiation time. Lastly, the flux performance was improved due to control of membrane fouling by conversion of irreversible fouling into reversible fouling that was easily rectified by physical cleaning methods.

CHAPTER 6   REMOVAL OF HUMIC ACID BY CONCURRENT TiO₂ PHOTOCATALYTIC OXIDATION AND UF MEMBRANE

6.1   Introduction

As the third section of this study, the concurrent PCO-UF process was developed to remove humic acid. This technology is closer to practical engineering applications comparatively. From the previous investigations of PCO-MF process, it has witnessed that PCO had a great potential on the degradation of humic acid and the improvement of MF on removal of humic acid. Therefore, it is of great significance to investigate the concurrent PCO-UF process on removal of humic acid furtherly.

6.2   Experimental Procedures

The investigation of humic acid removal by concurrent PCO-UF process was conducted herein. One point different with the integrated PCO-MF in this part was that the effect of MWCO and materials of UF membranes on humic acid removal were investigated.

A 5 L glass bottle containing humic acid feedwater (50 mg/L humic acid and 0.5 g/L TiO₂) acted as both the reactor of PCO and the feedtank of UF process. Unless stated specifically at appropriate places, detailed experimental conditions such as 0.2 MPa TMP and 1.80 L/min retentate flow rate have been explained in Chapter 3.

6.3 Results and Discussion

6.3.1 Flux Performance

The flux performances were showed in Figure 6.1 under the same operational conditions, when humic acid feedwater (pH=3) was filtrated by different UF membranes, It was clear that the 100 kDa UF membrane showed an obvious flux reduction among the five types of membranes because of its largest pore size. While, the 30 kDa and 60 kDa PS membranes displayed the smallest permeate flux due to their hydrophobic properties and the thickest membrane among all five kinds of membranes. Owing to the different materials and different thickness, 30 kDa PVDF (weak hydrophobic) and 20 kDa CA membrane (hydrophilic and the thinnest) demonstrated constant permeate fluxes between that of 100 kDa ultrafllic and 30 kDa PS membrane. This indicated that permeate flux was affected significantly by membrane material and thickness.

When pH of humic acid feedwater was adjusted to 7, some differences appeared on flux performances. Under this condition, the flux of 30 kDa PVDF membrane was higher than that of 20 kDa CA membrane, possibly because of the different hydrophobic/hydrophilic properties of PVDF and CA membranes. The different hydrophobic/hydrophilic properties of membranes led to different interactions with the adsorbed humic acid on TiO_2 particles, henceforth, different fluxes were recorded.

Figure 6.1 Flux performance of PCO-UF (pH=3)

Figure 6.2 Flux performance of PCO-UF (pH=7)

Compared with the above two different conditions, when pH of humic acid feedwater was 9, the flux of 100 kDa ultraflow membrane showed the least reduction since that humic acid dissolved in water under this pH. The fluxes of 30 kDa PVDF and 20 kDa CA membranes seemed close to each other. The interactions between

UF membranes and aggregated particles of humic acid and TiO_2 should be a significant factor influencing flux performance under different conditions.

Figure 6.3 Flux performance of PCO-UF (pH=9)

From the above flux performances under different pH conditions, a straightforward conclusion was that the fluxes of UF membranes were correlative to the properties of membranes itself, physico-chemical properties of humic acid feedwater and operational conditions. Under different conditions, the flux was affected by dominant factors like MWCO, materials, pH of humic acid feedwater. However, more work is required to validate the effect of each factor and its influencing extent on the flux in details.

6.3.2 Removal Efficiency

In the concurrent PCO-UF process, UF membrane not only rejected pollutants, but also recycled TiO_2 particles and carried the accumulated pollutants on membrane surface into feedtank. In the feedtank, TiO_2 adsorbed humic acid and oxidized them into smaller molecular weight ones until complete mineralization into CO_2 and H_2O .

under UV irradiation. Herewith, PCO and UF worked together to remedy their respective disadvantages by expanding their common advantages. On the one hand, humic acid were rejected and oxidized, on the other hand, the high flushing cross-flow velocity carried away the sedimentated pollutants on membrane surface.

Flux performance reflected the permeate production of membrane process. The removal ability of humic acid was the crucial indicator to estimate whether the proposed concurrent PCO-UF process was able to remove humic acid in water. Wherefore, the following section displayed the investigations of humic acid removal by concurrent PCO-UF process under different conditions.

6.3.2.1 Turbidity Removal

Same as previous MF and PCO-MF process, to make sure safe water accessibility for human beings is the premise to use PCO-UF process in purification of water and wastewater. And TiO_2 catalysts are important for recycle and reuse so as to reduce operational cost and improve the sustainability of PCO-UF process in the field of water and wastewater treatment. Some researcher (Le-Clech, Lee et al. 2006) have found that once in aqueous solution, TiO_2 forms large agglomerations, which size varies from 0.2 to $1.2\mu\text{m}$ for pH of 3 and 8, respectively. In this study, the size aggregated particles of humic acid and TiO_2 was larger than $0.2\mu\text{m}$ under pH of 3, 7 and 9. So this would be enough to make sure TiO_2 catalysts recycle and recovery without penetration through membranes to cause a safety problem.

6.3.2.2 Color₄₃₆ Removal

Denoted as the absorbance at wavelength of 436nm, color₄₃₆ was measured by a UV/Vis photo-spectrometer. The relative content of color₄₃₆ reflects the large organic compound of humic acid (Fan, Harris et al. 2001; Huang, Leal et al. 2008).

Figure 6.4 displayed the removal efficiency of color₄₃₆ by different UF membranes, all the UF membranes removed color₄₃₆ of humic acid completely (>97%) under different pH conditions.

Figure 6.4 Color₄₃₆ removal efficiency

6.3.2.3 UV₂₅₄ Removal

As shown in Figure 6.5, it was seen that over 90% UV₂₅₄ of humic acid was removed by used UF membranes under different pH conditions. However, at pH 9, the highest removal efficiency of UV₂₅₄ appeared, which agreed with the least flux reduction at this condition considering the fact that humic acid were easily soluble in water and to be adsorbed and oxidized by TiO₂ under UV irradiation. TiO₂ adsorbed and degraded humic acid into smaller ones which belonged to UV₂₅₄. While, few parts of smaller degraded humic acid passed through UF membrane and resulted in lower removal efficiency at pH 3 and 7.

Figure 6.5 UV₂₅₄ removal efficiency

6.3.2.4 TOC Removal

Under UV irradiation, the organic matters of humic acid were adsorbed by TiO₂ and oxidized into smaller molecular weight substances till complete mineralization into CO₂ and H₂O in the concurrent PCO-UF process. Compared to the TOC removal efficiency by UF process in Chapter 4, TOC removal efficiency was improved greatly in PCO-UF process. Whereas the datum in Table 6.6, it can be seen that all the TOC removal efficiencies of each membrane under different pH conditions reached more than 80%, this meant that most of TOC had been removed, however longer time was needed for complete removal. The minor differences of TOC removal efficiencies between different UF membranes under different pH conditions were suspected to attribute to the different and complex interactions occurred in the concurrent PCO-UF process. More work is required and necessary to investigate it, and this work will be the further research plan of author.

Figure 6.6 TOC removal efficiency

6.3.3 Images of Fouled Membranes

Distinct images of fouled membranes were observed by DC after each experiment, Figure 6.7 displayed the DC images of fouled UF membranes under different pH conditions. From this figure, it was found that under pH 3, both 30 kDa PS and 60 kDa PS UF membranes were contaminated by humic acid adsorbed TiO_2 particles and dense cake layers formed on membrane surfaces. When pH of humic acid feedwater increased, it was seen that UF membranes were contaminated slighter with thin cake layers accumulated on surfaces. These phenomena could also be explained by the size of aggregated particles of humic acid and TiO_2 . The size of aggregated particles of humic acid and TiO_2 reduced with the pH increase of humic acid feedwater. The size reduction of aggregated particles of humic acid and TiO_2 meant a lower potential of particles sedimentation and thin cake layer formation.

Figure 6.7 DC images of fouled membranes, (a) 30 kDa PS UF under pH=9.64, (b) 30 kDa PS UF under pH=3.06, (c) 60 kDa PS UF under pH=9, and (d) 60 kDa PS UF under pH= 3.19.

Except the above obvious DC images, UF membranes scanned by FESEM provided clear images about the surface and cross section in the Figure 6.8.

Figure 6.8 FESEM images of fouled membranes

(a) virgin 20 kDa CA UF, (b) virgin 30 kDa PVDF UF, (c) fouled 30 kDa PVDF UF at pH=3, (d) fouled 60 kDa PS UF at pH=3, (e) cross section of fouled 100 kDa ultrafiltration UF at pH=3, (f) cross section of fouled 100 kDa ultrafiltration UF at pH=3, (g) cross section of fouled 100 kDa ultrafiltration UF at pH=7, and (h) cross section of fouled 100 kDa ultrafiltration UF at pH 9.

Figures 6.8a and b showed the virgin membrane surfaces of 20 kDa CA and 30 kDa PVDF UF membranes, respectively, which clearly revealed that membrane pores were not blocked. From Figures 6.18c and d, it was seen that cake layer formed on 30 kDa PVDF and 60 kDa PS UF membrane surfaces when pH of humic acid feedwater was 3, cake layers were also formed on the surfaces of other UF membranes. But the cake layer seemed to be the thickest at pH 3, and thinnest at pH 9 due to the difference of humic acid solubility under different pH conditions, which was also in agreement with the aggregated particle size of humic acid and TiO_2 .

From Figures 6.8e and f, it was not found that membrane pores were blocked, and it was also observed that the functional layer of 100 kDa ultrafiltration UF membrane were not blocked even under pH 3. The inserted image in Figure 6.8f revealed the cake layer formed upon the functional layer clearly. Figure 6.8d showed the cross section of 100 kDa ultrafiltration UF membrane at pH 7, little particles were found to enter into membrane pores, but also an obvious space between functional layer and supporting layer appeared clearly. Figure 6.8h showed the cross section of 100 kDa ultrafiltration UF membrane at pH 9, membrane pore blocking seemed as that at pH 3 and 7. At the same time, the difference between functional layer and supporting layer was clearly found as the inserted image shown.

From the above images, it was known that in the PCO-UF process, cake layer with different thickness formed on UF membrane surfaces under different pH conditions, but no membrane pores were blocked by humic acid and TiO_2 particles. And the severest fouling occurred when pH of humic acid feedwater was 3, the lightest fouling occurred when pH was 9 as a result of the different solubility of humic acid.

6.3.4 Aggregated Particle Size

In the concurrent PCO-UF process, humic acid was adsorbed by TiO_2 and aggregated into large particles which being easily rejected by UF membranes and recycled into feedtank by cross-flow velocity. The sizes of these aggregated particles were larger than UF membrane pore sizes. So, few particles passed through UF membranes, and in this way high removal efficiencies were achieved.

Figure 6.9 Aggregated particle size of TiO_2 and humic acid (pH=3)

After each experiment of PCO-UF process on humic acid removal in this study, the size of aggregated particles of humic acid and TiO_2 was measured as the shown in Figure 6.9, 6.10 and 6.11. It was found that the aggregated particle size was affected by pH of humic acid feedwater and was explained in details as follows.

Figure 6.9 showed the aggregated particle size of humic acid and TiO_2 in the different PCO-UF process when pH=3, it was seen that the aggregated particle sizes of humic acid and TiO_2 when different UF membranes used were larger than that of respective UF membrane pore sizes, though differences existed among these

PCO-UF processes. This was resulted by different interactions between UF membrane and aggregated particles with different surface charges. From the membrane materials, it is known that PS and ultraflic material are strongly hydrophobic, while CA is strongly hydrophilic, but PVDF is relative weakly hydrophobic. This means that both the strongly hydrophobic and the strongly hydrophilic materials can react with humic acid adsorbed TiO_2 to aggregate into larger ones, while the interaction between relative weakly hydrophobic PVDF and aggregated particles of humic acid and TiO_2 in acidic environment was relatively weak and hence smaller particles were aggregated.

Figure 6.10 Aggregated particle size of TiO_2 and humic acid (pH=7)

When pH of humic acid feedwater was adjusted to neutral condition (pH=7) as Figure 6.10 shown, it revealed that the sizes of aggregated particle of TiO_2 and humic acid seemed to be without any relations with pH. This implied that under neutral condition, the interaction between aggregated particles of humic acid TiO_2 and the membrane surface was very weak, so the size of aggregated particles of TiO_2 and humic acid looked like to be close to one another, among all the membrane materials.

Figure 6.11 Aggregated particle size of TiO_2 and humic acid (pH=9)

From Figure 6.11, which was about the size of aggregated particles of humic acid and TiO_2 under alkalinity condition (pH=9), it was seen that the size of aggregated particle of TiO_2 and humic acid when hydrophilic CA membrane used was larger than that of the other four types of membranes. The reason lied in the positively charged hydrophilic CA membrane. But the aggregated particle of humic acid TiO_2 was negatively charged under pH 9, so the interaction between CA membrane and aggregated particle of humic acid was more forceful than that between other membranes and aggregated particles of humic acid TiO_2 . Hence, more humic acid was adsorbed by TiO_2 and easily aggregated together into larger particles. However, more detailed work is needed to confirm the mechanism about how humic acid and TiO_2 interact when different membrane materials are used under different pH conditions.

6.3.5 Surface Charge

The surface charge of aggregated particles of humic acid and TiO_2 was measured according to titration method (Stumm 1992) to evaluate the influence of PCO on

TiO₂ surface charge which was helpful to prove the interactions between humic acid and TiO₂ to explain the change of aggregated particle size.

Figure 6.12 revealed the surface charge (Q (mmol/g TiO₂) in the x-axis) curves of TiO₂ solution, TiO₂ and humic acid solution without UV irradiation and TiO₂ and humic acid with UV irradiation, all of which seemed very familiar. But the PZC was different. PZC of TiO₂ solution was around 5.6, which was acidic, PZC of TiO₂ and humic acid solution without UV irradiation was 9.0, which was alkalinity, and PZC of TiO₂ and humic acid solution with UV irradiation was around 7.10, which was neutral, respectively. The PZC change of TiO₂ and humic acid mixed solution was in line with the degradation of humic acid during the PCO-UF process, in which, humic acid was degraded and oxidized into smaller molecular weight ones like CO₂ and H₂O dissolving into the solution to reduce pH.

Figure 6.12 Surface charge of aggregated particle of humic acid and TiO₂ in the PCO-UF process, insert was the enlarged part

Discussed from another view, it demonstrated the surface charge of the aggregated particle of humic acid TiO_2 , the original pH of TiO_2 and humic acid mixed solution was around 9.6, while after 10 h of PCO-UF, pH became into 7.63, very close to the PZC at this moment. However, it was known that the surface charge had been reduced by UV irradiation in the PCO-UF process, and the interactions between aggregated particles of humic acid TiO_2 with UF membranes had also been changed, both of which were two main factors affecting fouling trends.

6.3.6 MWD of Humic Acid by HPSEC

Figure 6.13 MWD of humic acid feedwater with elution time

In the PCO-UF process, the MWD of humic acid also changed with the irradiation of UV light. As shown in Figure 6.13, MWD of humic acid feedwater at different time was analyzed. A very strange phenomenon appeared that after 2 h of PCO-UF, the amount of humic acid in feedwater was greatly reduced to a low level, while in later period, the measured amount of humic acid seemed to recover, this was because that the capacity of TiO_2 arrived in the first 2 h. So in the following period,

TiO₂ could not adsorb humic acid, thus, the degradation rate of humic acid by TiO₂ was slower than the recycle rate by cross flow velocity. Except the change of humic acid content in feedwater, also it was also found that molecular weight of humic acid was changed, which witnessed the presence of degradation of humic acid in the PCO-UF process. The incomplete degradation of humic acid was as a result of poor energy input, which could not provide enough energy to excite the release of hydroxide radicals ($\cdot\text{OH}$) to oxidize humic acid.

Figure 6.14 MWD of humic acid feedwater in the PCO-UF process

In order to observe MWD of humic acid clearly, the MWD of humic acid was transferred from following elution time to following molecular weight as shown in Figure 6.14. From this Figure, it was easily found that most humic acid had been removed (adsorbed and degraded by TiO₂). However, in the period between 4 h and 10 h of the PCO-UF process, it was found that although humic acid with large molecular weight had been reduced into smaller molecular weight ones with a clear elution peak transition, most of humic acid in feedwater had not been degraded by TiO₂ adsorption and degradation for the lack of energy input.

Figure 6.15 MWD of permeate in the PCO-UF process

Different from the MWD of humic acid in feedwater, most humic acid had been removed after PCO-UF. Figure 6.15 showed the MWD of permeate after PCO-UF, through which, it was known that most of humic acid were removed by UF membrane and few degraded products of humic acid passed through UF membrane. So, in the PCO-UF process, humic acid were removed by UF mostly, although PCO played a role in humic acid degradation. However, as a result of the insufficient energy input, humic acid could not be degraded by TiO_2 within the experimental period of this study.

6.4 Conclusion

In this chapter, a novel concurrent PCO-UF process was developed to remove humic acid in water. We investigated the removal efficiencies of humic acid by PCO-UF process with different UF membranes used under different pH conditions, and the flux performance of each experiment. Apart from the removal of humic acid, membrane fouling situations were also evaluated through the observations of

FESEM images, size of aggregated particle of humic acid and TiO_2 , surface charge, and MWD by HPSEC. On the ground of above experimental datum and analysis, some conclusions were summarized as follows:

The developed concurrent PCO-UF process was able to remove UV_{254} , color_{436} and turbidity of humic acid (50 mg/L) completely, and was also able to remove TOC of humic acid with removal efficiency over 85%. When the influence of pH of humic acid feedwater was concerned, the highest removal efficiencies of UV_{254} , color_{436} and TOC of humic acid by PCO-UF process appeared to that of pH 9, and lowest appeared to pH 3, the reason was that humic acid were soluble in alkalinity condition but not soluble in acidic condition.

The fouling cake layers formed on UF membrane surfaces at pH 3 seemed to be the thickest; at pH 9 was the slightest both by obvious DC images and FESEM images. At the same time, the FESEM images witnessed that UF membrane pores were not blocked by aggregated particles of humic acid and TiO_2 .

Through the measurement of size of aggregated TiO_2 and humic acid, it was found that the size of aggregated particle of TiO_2 and humic acid was the largest at pH 3, and smallest at pH 9, also because of the different solubility of humic acid under different pH conditions. Meanwhile, it was know to us that the hydrophobic/hydrophilic properties of membrane materials played a crucial role in the formation of aggregated particle.

The surface charge measured by titration method indicated that the PZC of the aggregated particle of humic acid TiO_2 was changed in the PCO-UF process. In the feedtank of PCO-UF process, humic acid were adsorbed and oxidized by TiO_2 under UV irradiation, at the same time, the TiO_2 and humic acid were rejected by

membranes and recycled by the cross flow velocity into feedtank. The surface charge was changed by the way of degradation of humic acid into smaller molecular weight ones like CO_2 , which dissolved to reduce pH and change the surface charge of aggregated particle of humic acid and TiO_2 . Subsequently, the interactions between membranes and aggregated particles of humic acid and TiO_2 were affected.

The MWD of humic acid in the PCO-UF process was analyzed by HPSEC. It was seen that humic acid had been removed by the rejection of UF membranes. However, in the feedtank, humic acid could not be adsorbed and oxidized completely by TiO_2 due to insufficient energy input. But it was noticed that humic acid were adsorbed and oxidized by TiO_2 in the first 2 h of PCO-UF process, while, in the subsequent period between 2 h to 10 h, the degradation rate of humic acid by PCO was not up to the recycle of humic acid by cross velocity, and thus the reduction of humic acid was not observed objectively.

In summary, PCO-UF process demonstrated to be effective in removal of humic acid and control of membrane fouling. And this process was definitely worthwhile to be developed for practical engineering applications after more testing works.

CHAPTER 7 CONCLUSION AND RECOMMENDATION

7.1 Conclusion

In this study, PCO and MF/UF process were used to remove humic acid in waters. The investigation of MF/UF, integrated PCO-MF and concurrent PCO-UF on humic acid removal were carried out and the following major findings were made:

The removal of humic acid by MF (0.2 μm) in a lab-scale cross flow filtration mode was conducted with the TMP and retentate flow rate of 0.05 MPa and 0.56 L/min, respectively. Experiments proved that humic acid could not be removed by MF. The removal efficiencies of turbidity, color₄₃₆, UV₂₅₄ and TOC were low since humic acid distributed in a wide range of molecular weights. Meanwhile, we found that obvious flux reduction was induced by humic acid in this study, SEM images witnessed that both pore blocking and cake layer caused by pollutants reduced the flux.

The removal of humic acid by UF in a lab-scale cross flow filtration mode was conducted with the TMP and retentate flow rate of 0.2 MPa and 1.80 L/min, respectively. Five types of UF membranes namely 20 kDa CA, 30 kDa PVDF, 30 kDa PS, 60 kDa PS and 100 kDa ultraflic were used to remove humic acid. Experiments demonstrated that all the used UF membranes were able to remove turbidity and color₄₃₆ of humic acid completely; the removal of UV₂₅₄ and TOC was different for each kind of UF membrane. The flux performances of different UF membranes used also were affected by pH of humic acid feedwater to some extent. However, it was found that the largest flux reduction was recorded for 100 kDa ultraflic UF membrane, next for 20 kDa CA and 30 kDa PVDF UF membranes, and

there were almost no obvious flux reductions on the 30 kDa and 60 kDa PS UF membranes. This indicated that the membrane material, MWCO, thickness and hydrophobicity/hydrophilicity and other membrane characteristics might have influenced the removal efficiencies and flux reduction of humic acid.

For practical engineering applications, integrated PCO-MF process was used to remove humic acid in this study. Through the investigations of removal efficiencies and flux performance affected by UV light with different wavelengths, and UV irradiation time, it was found that the integrated PCO-MF process was able to remove turbidity, color₄₃₆ and UV₂₅₄ of humic acid totally, and also was effective in improving the removal efficiency of TOC to more than 85% (PCO (254 nm) 8 h+MF 2 h). But an unavoidable fact was that longer UV irradiation time was still needed to make sure the complete removal of degraded organic products in the PCO-MF process. With the help of UV irradiation, humic acid was degraded into smaller molecular weight ones till complete mineralization into CO₂ and H₂O, and the MWD of humic acid was found to be changed by HPSEC. SEM images also proved that cake layer formed on membrane surface without pore blocking in the PCO-MF process, which meant that fouling was transferred from irreversible pore blocking to reversible cake layer phase. Besides, the size of aggregated particle of TiO₂ and humic acid was also found to be larger than MF membrane pore (0.2 μm) and increased with the extension of UV irradiation time. The size increase of aggregated particle of TiO₂ and humic acid led to the decrease of total membrane resistance, therefore, the flux reduction was reduced and fouling was controlled. All these have been witnessed in this study.

Subsequently, the concurrent PCO-UF process was developed to remove humic acid. Different UF membranes were used to remove humic acid at pH 3, 7 and 9 respectively. Membrane materials, MWCO, hydrophobicity/hydrophilicity,

thickness all demonstrated to affect the removal efficiencies, flux performance, fouling situation, size of aggregated particles TiO_2 and humic acid, and surface charge of those aggregated particles in the PCO-UF process.

Firstly, compared with the removal of humic acid by UF, concurrent PCO-UF process improved the removal efficiency of humic acid obviously, except 100% removal efficiencies of turbidity, color_{436} , UV_{254} , TOC removal efficiencies were also improved to more than 90%. But there still existed some differences between different UF membranes under different pH conditions. All the experiments witnessed that greater pH was, the higher the removal efficiencies of humic acid by PCO-UF processes were, and the lesser the membrane fouling were. Different from UF processes, in the PCO-UF process, the reduction of fluxes were improved slightly, which meant the fouling was controlled to certain extents. However, it was found that the flux of 100 kDa was the highest, next was 20 kDa CA and 30 kDa PVDF UF membranes, the 30 kDa and 60 kDa PS UF membranes all displayed the lowest fluxes. This proved that membrane materials, MWCO, hydrophobicity/hydrophilicity and thickness interrelated properties all played roles in humic acid removal, flux performance, surface charge and fouling situation.

Secondly, DC and FESEM images of membranes witnessed that only cake layer formed on UF membrane surfaces without aggregated particles of humic acid TiO_2 entry into membrane pores. And the size of aggregated TiO_2 and humic acid at different pH conditions were different but larger than membrane pore sizes as a result of the different interactions between UF membranes and aggregated particles of humic acid and TiO_2 . The surface charge measured by through titration method indicated that the PZC of aggregated particle of humic acid and TiO_2 was reduced to around 7 in the PCO-UF process and this affected the aggregation of TiO_2 and humic acid, as well as the fouling situation of UF membranes and performance of

flux.

Thirdly, it was known that in the PCO-UF process, humic acid was degraded and oxidized by TiO_2 into smaller molecular weight ones with the irradiation of UV light; on the other hand, the aggregated particles of humic acid TiO_2 were rejected by UF membranes and recycled to feedtank by cross flow velocity. The MWD of humic acid analyzed by HPSEC witnessed that humic acid was adsorbed and oxidized by TiO_2 in the first 2 h, however, in the period between 2 h and 10 h, TiO_2 could not oxidize the recycled humic acid adsorbed onto TiO_2 particles completely due to the insufficient energy input, thus the MWD of humic acid in the feedwater was not found to be changed. But through the observation of MWD of PCO-UF permeate, it was also known that most of humic acid had been removed by PCO-UF process. This proved that the PCO-UF process was able to remove humic acid, and also effective in checking membrane fouling.

In summary, this study provided good examples of humic acid removal by integrated PCO-MF and concurrent PCO-UF, which both have demonstrated to be able to remove humic acid and control membrane fouling to improve the flux performances.

7.2 Recommendation

Although some meaningful and significant conclusions were obtained in the study, much more work is to be carried out in the future.

Firstly, in order to explain membrane fouling control mechanism, membrane fouling resistances are necessary to be monitored after each experiment to make sure the major dominant factors of the total resistance. And also the effect of pH of humic acid feedwater on the integrated PCO-MF process should be evaluated more clearly.

The zeta potential change of membranes also should be measured to demonstrate the interactions between membrane and aggregated particles of humic acid and TiO_2 .

Secondly, in the PCO-UF process, much detailed work is needed to investigate the effect of membrane materials, thickness, hydrophobicity/hydrophilicity and other physical properties on humic acid removal, flux performance, formation of aggregated particles, surface charge, zeta potential of UF membranes and membrane fouling. Due to the differences among five kinds of UF membranes used, there are still some phenomena that can not be explained clearly currently. The membrane fouling formed on the membrane surfaces should be scanned more clearly by FESEM, or AFM, especially about the cross sections of fouled UF membranes under different pH conditions. Hence, further investigations are necessary to be conducted.

Thirdly, in order to be as close to the practical engineering applications as possible, this research work should be testified in a pilot-scale plant if possible. However, before constructing a pilot-scale testing, the above stated investigation works should be conducted in prior.

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