Comparative Study on Performance and Organic Fouling of ZrO$_2$ Ceramic Membranes in Ultrafiltration of Synthetic Water and Wastewater Treatment Plant Effluent

Thesis by

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ABSTRACT

Comparative study on performance and organic fouling of ZrO$_2$ ceramic membrane in ultrafiltration of synthetic water and wastewater treatment plant effluent

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Adsorption of organic matter on ceramic membrane can lead to hydraulic-irreversible fouling, which decreases the permeate flux and the cost-efficiency of membrane devices. In order to optimize the filtration process, detailed information is necessary about the organic fouling mechanisms on ceramic membranes. In this study, dead-end filtration experiments of both synthetic water and secondary effluent from a wastewater treatment plant (WWTP) were conducted on a ZrO$_2$ ceramic membrane.

The experiment results of synthetic water showed that humic acid (HA) was able to be adsorbed by the ZrO$_2$ membrane and cause permeate flux decline; and that HA-tryptophan mixture, at the same DOC level, promoted the filtration flux decline. DOC removal in the case of HA-tryptophan was lower than that of HA alone. It seems that hydrophilic organic matter with low molecular weight have some specific contribution to the organic fouling of the ZrO$_2$ membrane. The results also suggest that tryptophan molecules were preferentially adsorbed on the membrane at the beginning, exposing their hydrophobic sides which might further adsorb HA from the...
feed water. During the filtration of WWTP effluent, protein-like substances (mainly tryptophan-like) were also preferentially adsorbed on the membrane compared with humic-like ones in the initial few cycles of filtration. More humic-like substances were adsorbed in the following filtration cycles due to the increase of membrane hydrophobicity.

A significant rise in hydraulic-irreversible flux decline was obtained by decreasing pH from near pH\textsubscript{pzc} to below pH\textsubscript{pzc} of the membrane. It suggests that a positively charged surface is preferred for HA adsorption. Ionic strength increase did not affect the filtration of HA, but it lessened the hydraulic-irreversible flux decline of HA-tryptophan filtration. The adsorption of HA-tryptophan can be attributed to outer-sphere interaction while HA adsorption is mainly caused by inner-sphere interaction.

The results of pre-ozonated HA filtration showed that pre-ozonation lowered the proportion of potential hydraulic-reversible foulants in HA. Filtration of pre-ozonated WWTP effluent was also performed. Flux decline phenomenon similar to that of pre-ozonated HA was observed, and it is confirmed that smaller molecules have a stronger affinity to ZrO\textsubscript{2} membrane and tend to form hydraulic-irreversible fouling.
ACKNOWLEDGEMENTS

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LIST OF ABBREVIATIONS

- **ATR**  Attenuated total reflection
- **COD**  Chemical oxygen demand
- **DOC**  Dissolved organic carbon
- **DOM**  Dissolved organic matters
- **DBPs**  Disinfection by-products
- **EfOM**  Effluent organic matters
- **FTIR**  Fourier transform infrared Spectrometry
- **FA**  Fulvic acid
- **F-EEM**  Fluorescence excitation emission matrix
- **HA**  Humic acid
- **HPLC**  High performance liquid chromatography
- **LMW**  Low molecular weight
- **NOM**  Natural organic matters
<table>
<thead>
<tr>
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<th>Description</th>
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<tr>
<td>PAC</td>
<td>Powdered activated carbon</td>
</tr>
<tr>
<td>SMP</td>
<td>Soluble microbial products</td>
</tr>
<tr>
<td>SOC</td>
<td>Synthetic organic compounds</td>
</tr>
<tr>
<td>SPF</td>
<td>Specific permeate flux</td>
</tr>
<tr>
<td>SUVA</td>
<td>Specific Ultraviolet absorbance</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscope</td>
</tr>
<tr>
<td>TOC</td>
<td>Total organic carbon</td>
</tr>
<tr>
<td>Trp</td>
<td>Tryptophan</td>
</tr>
<tr>
<td>UV</td>
<td>Ultraviolet</td>
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<td>WWTP</td>
<td>Wastewater treatment plant</td>
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Chapter I

Introduction

I.1 Ceramic membrane filtration of secondary effluent

The reuse of wastewater treatment plant (WWTP) effluent as a water resource for beneficial purposes offers an effective mean of solving water problems, especially in arid areas. A very important part in WWTP effluent is the effluent organic matter (EfOM), which is of high concern for human and environmental health. The understanding of EfOM is essential for optimum treatment of the secondary effluent. EfOM consists of natural organic matter (NOM), soluble microbial products (SMPs), and a few trace chemicals. The treatment methods of EfOM includes coagulation and flocculation, activated carbon adsorption, biofiltration, ionic exchange, advanced oxidation processes and membrane filtration.

Low pressure membrane filtration is a potential technology for advanced treatment of secondary effluent. Some have already been applied in tertiary treatment in wastewater reuse. Microfiltration (MF) and ultrafiltration (UF) membranes have been proved to be able to remove suspended matters, large dissolved or colloid organic compounds and pathogens, bacteria and viruses from WWTP effluent. Ultrafiltra-
tion membranes are able to remove EfOM within size range of 10-10³ μm. Compared with polymeric membranes, ceramic membranes have longer life, higher permeability, better resistance towards high temperature, erosion and microbial influence, as well as good performance on continuous operation with better recovery (3). Their applications in water reclamation are becoming more and more important.

Although ceramic membranes were proved to have potential in improving water quality of WWTP effluent for water reclamation, organic fouling is still a fundamental drawback for its utilization like other filtration technologies. There are two kinds of organic fouling of ceramic membranes, hydraulic-reversible and hydraulic-irreversible fouling. Hydraulic-irreversible fouling is the major concern, since it reduces membrane permeate flux and filtration efficiency permanently (4). The cause of organic fouling on ceramic membranes varies, including particles deposition, the interaction between dissolved or colloid substances with metal oxides, and the electrostatic effect, etc. The essential characteristics of secondary EfOM that affects membrane fouling includes the molecular weight distribution, hydrophilicity (aliphatic) and hydrophobicity (aromatic) nature, also the aquatic charge of the EfOM. For ceramic membranes, surface charge and hydrophilicity play an important role in organic matter adsorption. As a result, water pH, ionic strength and calcium concentration all influent the filtration performance of ceramic membranes.

I.2 Research objectives

The objective of this study was to investigate the organic fouling mechanisms of a 60 nm ZrO₂ ceramic membrane using synthetic water and WWTP effluent. According to the experimental study on the impact of HA, tryptophan, water pH, ionic strength, and also ozone dose in pretreatment on the permeability and organic fouling of the membrane, we can propose an organic fouling mechanism for the 60 nm ZrO₂ ceramic
membrane in water/effluent filtration.
Chapter II

Literature review

Water scarcity has always been a major issue in many places all over the world due to climate change, industrial and domestic consumption and agriculture irrigation. Increasing water cost forces people to figure out new ways in getting sustainable fresh water, and brings intense necessity in water reuse and reclamation. As knowledge about emerging contaminants grows, legislation limit over WWTP effluent quality has become more and more stringent, leading to great demand for advanced water treatment technologies.

II.1 Water scarcity and water reuse

II.1.1 Water scarcity

Nowadays, water shortage is the most challenging problem human beings are facing, especially in developing countries where most of the world’s population growth occurs. Scientists have estimated that by the year 2025, global water need will grow by 3,800 km$^3$/yr, and the major water source for that is still nature system. In this case, countries with large population like China and India will deplete all their nature water very soon. Moreover, over 1 billion people in the world have no access to clean
drinking water sources, and about twice that many are provided with inadequately disinfected water. Health risk arising from low drinking water quantity and quality put great pressure on scientists, urge them to find solutions to deal with obtaining sufficient water at an affordable price[5]. One of the major solutions is wastewater reuse, which can provide sustainable water resource, meanwhile reduce the pollutant amount discharged into the nature water body.

II.1.2 Water reuse

Water reuse is becoming increasingly popular as an approach to solve world water scarcity issue. In developed countries, planned water reuse projects are applied for municipal and industrial purposes in order to keep water an sustainable resource. On the other side, in developing countries, unplanned water reuse is necessary especially in arid areas and for human health consideration[6]. One possible sources of water reuse is WWTP effluent, which is produced in large amount and would be discharged into the environment only if being recycled. Previous studies have shown that the expel of WWTP effluent into the environment will change the organic and inorganic nutrients in nature water and may cause problems like eutrophication. Although there are some risks for using reused water, such as the exposure of human or animals to pathogens in the effluent, they can be controlled by applying proper treatment methods such as membrane filtration.

II.2 Wastewater organic matters characteristics

II.2.1 General properties

The major objectives of wastewater treatment are non-specific parameters. Therefore, target contaminants need to be removed from wastewater are usually mixtures of several substances. Characterizing wastewater is essential for the design of collecting,
treatment and disposal processes, wastewater quality includes physical, chemical and biological properties.

- The physical properties of wastewater mainly include temperature, color, odor and solids.
- Chemical properties concern about inorganic matters, organic pollutants and also gases.
- Biological properties are levels of bacteria, viruses, protozoa and so on.

### II.2.2 Organic matters

Organic matters, dissolved or particular, present in all kinds of water. In wastewater, the organic matters groups usually have 40% to 60% of protein, 25% to 50% of carbohydrates and about 10% fats and oils. In addition, a small amount of various synthetic organic molecules are also a very important part of wastewater. Level of organic matters in water is important for several reasons. First of all, their direct toxicity, for example, residuals of pesticides may cause health problem to living organisms in the water. Also organic matters can react with other aquatic species and their toxicity may be enhanced. The third property of organic matters is that their degradation may consume the oxygen in the water body, and the loss of oxygen make aquatic organisms like fish in danger, therefore change the feature of the entire system(7).

The major method to remove organic matters in wastewater is biodegradation by conventional wastewater treatment processes, but there are still refractory organic matters which are resistant to biological methods, such as surfactants, phenols and pesticides(8). DOM was differentiate from organic matters by an universal consensus filtration size limit of 0.45µm(9). A gradually accumulation of the refractory DOM was observed in many lakes all over the world(10). These complex and heterogeneous
DOM in natural water are, in most cases, represented by effluent organic matters (EfOM), and they come from three major sources:

- Refractory NOM coming from drinking water.
- Synthetic organic compounds (SOCs) derived from domestic wastewater and disinfection processes in water treatment.
- Soluble microbial products (SMPs) produced during bioprocesses of water treatment, which was found to be the majority of DOM in wastewater effluent.

EfOM can affect all the chemical and biological processes in water environment. Most of EfOM in WWTP effluent water is in dissolved form. DOC in EfOM consists of the following components:

- Hydrophobic compounds, including humic, fulvic, Alkyl monocarboxylic, dicarboxylic substances.
- Transphilic compounds, including hydroxyl, sugar acid and sulfonic acid.
- Hydrophilic compounds, including polysaccharides, amino acid, alkyl alcohol, amide, alkyle amine.

Identification of DOM

A number of measurements were described by researchers to characterize wastewater DOM. The characterization of DOM can be based on TOC level with upper size limit of 0.45 µm. Particle distribution and UV absorption spectra can be utilized to measure non-fractionated DOM. Fujita et al. used ¹H NMR spectra and gas chromatography-mass spectrometry to classify the DOC in reclaimed wastewater, fulvic and humic acid ratio was found, and trace organic residue was also characterized. Excitation-emission matrix (EEM) fluorescence spectroscopy
is also a common method to identify DOM. The three-dimensional spectra has been divided into five regions and associated with humic like, phenol like, protein like (tryptophan and tyrosine) organic compounds. Kalbitz et al. applied synchronous fluorescence and UV absorption spectroscopy, and proved it is a simple way to distinguish aromatic structures and degree of humidification of DOM. Attenuated total reflection and Fourier transform infrared (ATR-FTIR) spectrometry can analyze the foulants on the membrane and is a useful tool to study membrane fouling. High performance liquid chromatography (HPLC) allowed the separation of different components in DOM. Capillary electrophoresis (CE) also showed possibility to fingerprint and identify different NOM.

Effect of ozonation on DOM

Ozone is a common oxidant for disinfection and order taste removal. In aqueous phase, the ozone will react with water molecular to form hydroxyl radicals. By ozonation, the electrophilic center of organic matters will be broke in to smaller molecules. Ozone can also react with aromatic moieties and produce hydroxylated organic compounds. The loss of aromaticity will end up with a decrease in UV adsorption near wavelength of 260 nm. A slightly reduction of TOC can be observed because of the complete degradation of some small molecules, but by ozonation only is unlikely to degrade the large molecular weight DOM in water totally. Studies about NOM being oxidized by O₃ observed a significant decline of hydrophobic acid and humic acid which was made up by the increase in percentage of hydrophilic acid, hydrophilic base and hydrophilic neutral.
II.3 Membrane filtration for water reuse treatment

Membranes can be flexibly applied in different stages of wastewater treatment as well as reuse processes, collaborating with other methods like bioreactors in order to treat the effluent to a higher level. Although membrane technologies haven’t dominated wastewater treatment and reuse processes, its wide application in these domains is quite prospective with more experience gained(25).

II.3.1 Polymer membrane filtration

Development and function in water treatment

Membrane technologies development can be traced back to the eighteenth century, early philosopher scientists got the idea of a semipermeable membrane. Started from 1930s, early microfiltration polymer membrane technology found their significant application in drinking water testing. By the year 1960, although modern membrane technologies had made some progress, no industry usage existed. Between 1960 and 1980, with the improvement of interfacial polymerization and multi-layer coating, high-performance membranes were built. Also spiral-wound, hollow fiber, capillary modules were used in order to increase membrane surface area. After that, membrane technologies were industrialized and expanded rapidly(26). The role membranes play in water and wastewater treatment is becoming increasingly important, they are now being widely used in desalination, disinfection by products (DBPs) control and removal of inorganic and synthetic organic matters(27).

Problems in practical application

At early stage of membrane development, polymer membranes are commonly used. Technology on organic membranes was well developed and has many advantages, such as good tenacity, applicability to various particle separation, simple production
procedure, low price, etc. But it still has shortcomings that cannot be overcome; high temperature, erosion, acid, base and organic solvent all have a adverse effects on the membrane life. Therefore, study on inorganic membranes had attracted more research attention.

II.3.2 Ceramic membrane filtration

Development and function in water treatment

After the year of 1980, research on inorganic membranes has grown significantly, and their potential application started emerging. Ceramic membranes is arousing long-term interesting in gas and liquid separation. Compared with organic membranes, inorganic ceramic membranes have longer life, better resistance towards high temperature, erosion and microbial influence, as well as good performance on continuous operation with better recovery. With these advantages, ceramic membrane separation was widely used in a wide range of industries such as petrochemical, food production and pharmaceutical.

The fabrication of ceramic membranes usually involves the assembly of agglomerate particles and formation of porous compacts with different shapes. Therefore, the organization of particle size and shape results in a statistical distribution of porosity, and the pore size is inhomogeneity. In the last stage, the compacts will be treated at high temperature (calcination process), making the pore size shrink to the final values of the ceramic membranes. Since the porosity of products after the first two stages are not easily reproducible, the last step is used to control the quality of surface and dimension quality. Table lists the various ceramic membrane pore size and the corresponding permeability.
Table II.1: Clean water permeability at 20 °C

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Permeability (L/m²-h-bar)</th>
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<tr>
<td>Microfiltration</td>
<td></td>
</tr>
<tr>
<td>0.1 µm</td>
<td>1500</td>
</tr>
<tr>
<td>0.2 µm</td>
<td>2000</td>
</tr>
<tr>
<td>0.5 µm</td>
<td>4500</td>
</tr>
<tr>
<td>0.8 µm</td>
<td>7500</td>
</tr>
<tr>
<td>1.4 µm</td>
<td>11000</td>
</tr>
<tr>
<td>2.0 µm</td>
<td>15000</td>
</tr>
<tr>
<td>Ultrafiltration</td>
<td></td>
</tr>
<tr>
<td>20 nm</td>
<td>300</td>
</tr>
<tr>
<td>50 nm</td>
<td>900</td>
</tr>
<tr>
<td>100 nm</td>
<td>1800</td>
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</table>

Prospect in practical application

The major research fields on ceramic membranes functioning are the preparation, separation application and catalytical membranes. For large scale commercial use of ceramic membranes, only microfiltration, ultrafiltration and bio-separation are successfully achieved, while other applications like gas separation and membrane reactor are only available in small scale lab use. Problems like relatively high cost and long-term reliability still needs further study on process conditions and membrane design in order to broaden commercial applications of ceramic membranes. Reports have shown that catalytic reactors have the potential of being applied in large scale, and will allow operation conditions which cannot be used in conventional processes. Once the membrane reactor is being properly designed, it is possible to reduce the reactor volume and also energy balance can be improved.
II.3.3 Major aspects for the application of ceramic membrane filtration

Ceramic membranes are being used in desalination, drinking water and wastewater treatment. Larbot et al. demonstrated that it is possible to use ceramic membranes to get a high salt rejection in water desalination, also metal oxide ceramic membranes were characterized by contact angle to be hydrophilic. The large scale use of microfiltration and ultrafiltration membranes in drinking water treatment is because of their ability to remove pathogenic microorganisms and DBPs precursors. Bottino et al. performed microfiltration using ceramic membranes on lake water, and the water quality was improved with complete removal of suspend solids along with microorganism, and retention of 64% TOC. Mavrov et al. added powdered activated carbon (PAC) in feed water, proving that the membranes can function on turbidity and microorganism removal without being blocked in the test period. Ceramic alumina microfiltration membranes were used to treat petrochemical wastewater, the effluent showed significant decrease in oil and grease, and this method was confirmed cost efficient compared with other membrane units. Cross-flow microfiltration was applied after activate sludge reactor to enhance the TOC removal capacity, since it enabled operating at high biomass concentration. Even at high wastewater organic load, membrane bioreactor with a ultrafiltration module still can achieve a high COD and suspended particles removal.

II.4 Fouling mechanism and antifouling methods

Membrane fouling is a common phenomenon during pressure driving filtration processes. Although membrane separation technology has been used in practical industrial processes, the continuous permeability reduction due to fouling still incumber the widespread application of membrane. The flux decline that could not be recovered...
by hydraulic backwash is called irreversible fouling\textsuperscript{(41)}, which is caused by precipitation or adsorption of organic or inorganic matters. Irreversible fouling will reduce membrane productivity, add to costs in operation and maintenance.

**Fouling mechanisms**

Direct observation method of membrane fouling usually involves electron microscopy. Cheryan et al. presented micrographs to show both surface and internal fouling for ultrafiltration membranes\textsuperscript{(42)}. Kim et al. demonstrated the disadvantage of conventional scanning electron microscope (SEM) as the low resolution attainable while working at the beam energy that won’t spoil the sample\textsuperscript{(43)}. They found that field emission-SEM can be used as a better way to exam surface of ultrafiltration membranes with higher resolution and less risk in damaging the sample\textsuperscript{(44)}. Flux decline is also an indirect way to analyze fouling materials on the membrane.

**Substances lead to fouling**

Particulate matter was relatively unimportant in fouling as compared to dissolved matter. Small colloids with sizes between 3-20 nm in diameter, were confirmed to be important membrane foulants\textsuperscript{(4)}. Membrane properties will be influenced from the beginning of filtration because of the fouling layer formed on the surface\textsuperscript{(45)}. Solute deposition, pore blocking, adsorption and irreversible changes to the membrane layer were demonstrated to be important mechanisms for fouling by colloids\textsuperscript{(46-48)}.

Humic substances, are surface reactive electrolytes of weak acidic\textsuperscript{(49)}. Jucker used hydrophilic cellulose acetate membranes to filter humic acid and fulvic acid. Zeta potential of the membranes increased as they adsorbed humic acid and fulvic acid. Zeta potential of the membranes increased as they adsorbed humic substances (they became less negative), and as humic substance adsorption increased, contact angle test showed more hydrophobic\textsuperscript{(50)}. Some studies suggested that the adsorption of humic substances prefer the membrane pores before the membrane zeta potential reach
maximum, after zeta potential reaches the plateau humic substances will basically being adsorbed by the surface\(^{(49)}\).

Proteins, an important factor of ultrafiltration membrane fouling, were found to form a monolayer covering the membrane during the first seconds of a filtration process\(^{(51)}\), then the flux rate will be limited by hydraulic resistance of the layer\(^{(52)}\). Protein adsorption is strongly related with type of membranes, membrane surface chemistry and morphology like porosity, pore size distribution\(^{(53, 54)}\). Several studies have observed severe fouling at the iso-electric point of protein\(^{(55, 56)}\). Since protein is strong hydrophobic, their adsorption onto the membrane can lead to hydrophobic interaction\(^{(57)}\). Hydrophobic membranes are more rapidly fouled compared with hydrophilic ones. After the formation of the protein layer, more adsorption will be hindered electrostatic repulsion except for at the pH of iso-electric point\(^{(51)}\). The transmission of protein through the membrane is found to reach corresponding maximum at iso-electric point\(^{(58)}\). Some interpret this phenomena as the result of charge effect\(^{(59)}\), since at that pH electrostatic repulsion is absent. Others argued protein molecules are smaller at iso-electric point, which result in more pass through\(^{(60)}\).

**Factors affect fouling**

It is well known that irreversible membrane fouling can be affected by many factors, for instance, membrane material, water constituent, and also solution chemistry and operating parameters. In order to prevent irreversible fouling, it is important to study the factors that influence absorption.

The interaction among membrane, solute and solution which lead to adsorption is a very complex process, by changing any of the factors may tremendously change the fouling behavior. The Humic substances will become more hydrophilic when increasing pH, and their solubility will be greater and adsorption onto the hydrophilic cellulose acetate membranes will decrease\(^{(52)}\). Calcium is found to be able to enhance
the humic acid adsorption onto XM50 and PM30 membranes, but it does not have the same effect on fulvic acid adsorption. Calcium salts may even compete with fulvic acid for activated sites (49).

Absorption behavior of protein and humic acid on a type of hydrophilic ultrafiltration membrane was studied under different pH and ionic strength. When pH increase, both the adsorption of protein and humic acid decreased due to electrostatic repulsion, while increased ionic strength can shield the electrostatic strength and made the adsorption increase (61). It is also shown that if salt was removed before filtration, less flux decline would happen to the membrane (62). Absorption of protein reached maximum when at isoelectric pH, and will increase significantly with increasing salt concentration in the solution (56). The sorption of DOM onto metal oxide was also found to be influenced by pH and calcium ion concentration (63).

As for inorganic metal oxide membranes, different chemical composition will lead to various adsorption pattern, includes competition among types of DOM. The adsorption of large molecular weight organic particles on aluminum oxide surface is greater than small molecular weight organic particles (64). Compounds with molecular weight between 1000 and 3000 g/mol were significantly removed (65). Assumption was made that limitation of activated sites on metal oxide surfaces induce competition among different organic fractions in water, and the competition may be corresponding to carboxyl groups and the molecular structures (66). McKnight et al. demonstrate the preference of iron and aluminum oxide on adsorbing aromatic moieties, carboxyl groups and amino acid (67). Conclusion was made that high molecular weight hydrophobic DOM fractions with more aromatic or carboxyl groups are preferred to be adsorbed by minerals (68) (69). Absorption of organic matters with carboxylic groups are found to be more likely being affected by pH increasing compared with those with phenolic groups (70).
Antifouling methods

Several studies have discussed strategies on membrane in order to reduce fouling and improve flux, such as increase the membrane hydrophilicity and modify the surface charge\cite{71}. Pretreatment of membrane using enzymes\cite{72}, carbon coating\cite{53} or surfactants\cite{73} are also effective in improve filtration performance. Fane et al. used nonionic nonyl phenol polyethoxylates as surfactants on ultrafiltration membranes, and less irreversible deposit of protein was observed on the treated membrane. The deposition rate was reduced from 0.09 $\mu$g/s to 0.06 $\mu$g/s, meanwhile the cleaning effect was enhanced\cite{74}. It is also found that membranes with the lowest contact angle appeared to have the lowest flux loss, so that the flux decline of is linked with the hydrophilization of the membrane surfaces\cite{72}.

Fouling control techniques related with water being investigated include low-flux operation, high-shear slug flow aeration in submerged configuration, periodical aeration, permeate backwash, intermittent suction operation and adding powdered activated carbon (PAC). Among all these methods, only PAC addition is not in large-scale application at present\cite{75}.

Ultrasound was also a effective method to remove particle-fouled membranes without making damaging the surface or enlarge pore size\cite{76}. But ultrasound was found to be able to increase water mass transfer coefficient through the membrane, while not suitable for removing fouling substances inside pores\cite{77}. Polymeric membranes which have less resistance to high temperature are more easily significant damaged by ultrasound\cite{78}. However studies have shown that no evidence of damage, nor increase in flux, was observed by sonicating ceramic membrane for a properly short time (five seconds)\cite{79}.
II.5 Organic absorption characteristics of metal oxides

The adsorption of organic matter by ceramic membranes depends greatly on the properties of metal oxides. The major mechanisms by which organic matter adsorb onto metal oxides surface involve: anion exchange (electrostatic interaction), ligand exchange surface complexation, hydrophobic interaction, cation bridging, hydrogen bonding and entropic effects (80). However, due to the complex physicochemical and structural characteristics of NOM and metal oxides, a discrepancy exists in demonstrating the interaction mechanisms between the two. Previous studies found that pH increase always accompanied organic acids adsorption, indicating the complexation of COO$^-$ groups of organic acid and OH$^-$ of oxides (81). Humic acid adsorption onto aluminum oxides was through an anion exchange process (82). The adsorbed NOM covers the membrane surface and might dominate the surface physicochemical property. NOM coating can render the hydrophilic metal oxides surface into hydrophobic and more capable in adsorbing hydrophobic organic compounds (83). The charge of metal oxides is also controlled by the adsorbed layer of organic matter. Due to the polyelectrolyte property of organics, spare carboxyl groups on the same organic matter that didn’t bounded to the metal oxides have increased the surface negative charge(84).

Aqueous condition and metal oxide surface properties have impact on organic adsorption. Gu et al. (85) found that under acidic or slightly acidic water pH, the ligand exchange interaction between carboxyl/hydroxyl groups of NOM and iron oxides are more significant. Adsorption behavior was also found being limited by adsorption sites available on organic matter and metal oxides(85). The adsorption of hydrophobic organic compound onto HA bonded mineral surface was proved to be less at higher ionic strength(86). This was interpreted that at low pH and high ionic
strength, the adjacent carboxyl and hydroxyl groups of HA have charge repulsion, result in a "coiled" structure which has less attachment sites to the mineral surface.

As a result of the interaction between organic matter and metal oxides, the organic fouling on ceramic membrane is a complex process involving deposition affected by membrane surface properties, aqueous condition and organic constituent.
Chapter III

Methods and Materials

III.1 Water samples

The secondary effluent was collected from a WWTP in Jeddah, Saudi Arabia. The samples were pre-filtrated through a 1.2 \( \mu \)m filter in the lab to remove solid particles and some bacteria, and then stored at 4 °C in the cold room. WWTP effluent samples were replaced once every two weeks. Major characteristics of the WWTP effluent was shown in Table III.1.

<table>
<thead>
<tr>
<th>pH</th>
<th>Temperature</th>
<th>TDS</th>
<th>Conductivity</th>
<th>Turbidity</th>
<th>Alkalinity (CaCO(_3))</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.61</td>
<td>21 °C</td>
<td>2.61 ppm</td>
<td>5.49 ( \mu )S</td>
<td>1.15 NTU</td>
<td>80 mg/L</td>
</tr>
</tbody>
</table>

Synthetic water was prepared with dissolved Aldrich-HA. Since the solubility of HA is not known, a stock solution was prepared by introducing 1 g HA into 1 L NaHCO\(_3\) solution (200 mg/L as HCO\(_3^-\)). The mixture was then filtered through 0.45 \( \mu \)m acetate fiber filter and stored at 4 °C. Synthetic water samples for the filtration experiments were prepared each time before filtration by diluting the stock solution 50 times. The pH and TOC of the synthetic water was 8.7 and in the range of 3.5 to 4.5 mg/L, respectively.
Tryptophan (Trp) stock was prepared in 100 mg/L, stored in dark at 4 °C and replaced every week. Trp was added into the synthetic water as a typical small molecule to see its influence on HA adsorption onto the membrane.

Since water temperature greatly affects membrane permeability\(^{(28)}\), before used for filtration, both the WWTP effluent and the synthetic water were taken out from the cold room and kept for over 10 hours in the lab room until reached room temperature (around 21 °C).

### III.2 Ceramic membrane

Zirconium (ZrO\(_2\)) ceramic disk membranes with nominal pore diameter of 60 nm were used for filtration experiments. These disk membranes were 47 mm in diameter and have a effective filtration area of 13.2 cm\(^2\). Scanning electronic microscopy (SEM) images of the cross section and surface of ZrO\(_2\) membrane are shown in Fig.\(\text{III.1}\). The membrane is consist of three layers, at the bottom is the silica support, which was covered by a layer of Al\(_2\)O\(_3\), on top of the membrane is ZrO\(_2\). The particle size is decreasing from bottom to top. The zero point charge pH \((\text{pH}_{\text{pzc}})\) of the membrane is 8.5-9.0, determined by acid-base titration.

![Figure III.1: SEM images of ZrO\(_2\) membrane (A) cross section and (B) surface.](image)

III.3 Ceramic membrane filtration set-up

Filtration experiments were carried out in a dead-end flow filtration process. Dead-end filtration (Fig. III.2) allows all the fluid pass through the membrane and trap all the particles with larger sizes than the pore size on the membrane surface. As a consequence, the trapped particles will form a cake layer on the membrane exerting a higher resistance for water permeation. The efficiency of the filtration will be decreasing until the cake layer is removed by backwash, so it is an discontinuous process. Filtration and hydraulic cleaning should take turns in operation.

![Dead-end filtration](image)

Figure III.2: Dead-end filtration

The filtration feed pressure was controlled by a pump, and kept constant at 2.5 bar, while backwash pressure was 3 bar. During the filtration, water was pressed through the membrane. The membrane fouling can be directly reflected by the decline of specific permeate flux (SPF, L/m²-h-bar) with time. An electronic balance (Mettler Toledo ML3002/01, Switzerland) connected with a computer recorded total weight of the permeate every 10 s, a decline curve of specific permeability was drawn according to the permeate weight data. Fig. III.3 shows the scheme of the filtration system. Two water tanks were connected with the pump, one for feed water, the other for milli-Q water for backwash. Each filtration cycle lasted for 20 mins, then the ceramic disk was turned over, reconnected and backwashed with 50 mL milli-Q water. Both the permeate and the backwash was collected, stored in dark glass bottles at 4 °C for
further analysis.

![Filtration set-up scheme](image)

**Figure III.3: Filtration set-up scheme**

### III.4 Analytical methods

In order to evaluate the permeate quality and organic fouling mechanism of ZrO$_2$ membrane. The raw water, permeates and sometimes backwash water were measured with UV$_{254}$, DOC, LC-OCD and Fluorescence-EEM. Fouled membrane surface was characterized with ATR-FTIR and contact angle.

#### III.4.1 UV$_{254}$ and DOC

UV absorption at 254 nm (UV$_{254}$) is representative for the unsaturated structures (i.e. double bonds and aromatics) of the organic matter in water. UV$_{254}$ is a practical, economic and typically method to measure organics, compared with TOC instruments. In this study, UV$_{254}$ of the water samples was measured on a DR/5000 spectrophotometer (HACH, 254 nm, 1 cm quartz cell) as soon as the sample was collected.

DOC was measured by the non-purgeable organic carbon (NPOC) method on Shimadzu TOC analyzer equipped with an auto sampler. Each sample was measured.
three times and the average value of TOC was ourput automatically. The range of the calibration curve was 0.5-12 mg/L.

### III.4.2 Liquid chromatography-organic carbon detection (LC-OCD)

LC-OCD (DOC-LABOR model 8, Dr.Huber, Germany) was used in this study to characterize the molecular size distribution. The equipment was installed with a chromatographic column for the separation of organic matter according to their molecular size and ion-exchange ability. In LC-OCD system, the major part is the organic carbon detector (OCD), which is based on the infrared detection of CO$_2$ generated in the calcination of organic matter in water. It is also equipped with an organic nitrogen detector (OND) and a UV detector (UVD) at 254 nm.$^{[1]}$

LC-OCD has a high potential in the identification of organic matter fractions in water. From LC-OCD results, a lot of information on compound quantification and characterization can be obtained, and the sensitivity is low to µg/L range. LC-OCD system is used by about 20 research groups all over the world, its major application includes studying membrane performance and fouling, monitoring pre-treatment of seawater and municipal water quality.$^{[1]}$. A typical LC-OCD output of wastewater sample is shown in Fig. [III.4]. The first peak at about 32 min after injection is biopolymers, followed by humic substances at about 61 min. Low molecular weight (LMW) organic acid has a retention time of about 55 min. The peak that follows the acid peak is attribute to neutral and amphiphilic compounds. Organic carbon concentrations can be calculated by integrating the area below the peaks and the resulting peak area is related to carbon concentration by using a calibration curve of potassium hydrogen phthalate. The UVD chromatograms shows similar distributions except for biopolymers and LMW neutrals, since they do not have double bounds necessary for light absorption at a wavelength of 254 nm.$^{[87]}$. 
III.4.3 Fluorescence excitation emission matrix (F-EEM)

F-EEM has been used by researchers as an analytical tool to characterize NOM in water for many years. During a F-EEM process, the sample will firstly absorb energy from by a high energy light source (like xenon lamp) and the electrons may be excited to occupy a higher energy orbital, which lead the sample to reach several exited singlet states, this change in states of sample is called excitation. After being excited, the sample will be deactivated from the lowest singlet state to ground state, emitting UV or visible fluorescence, which is called fluorescence emission. In order to presenting an fluorescence data, it is essential to build an excitation-emission matrix (EEM). Fluorescence emission intensity is shown corresponding with excitation wavelengths, producing a contoured map showing peak locations and intensities.

The substances in nature water DOM that can be detected by F-EEM are differentiated into humic-like and protein-like matters. Humic-like matters consists of humic acid (humic-like 1) and fulvic acids (humic-like 2). Protein-like groups includes two dissolved amino acids: tryptophan-like (protein-like 2) and tyrosine-like (protein
like 1). Table. III.2 provides the classical locations of these peaks. In this study, a FluoroMax-4 spectrofluorometer with a 150 W xenon lamp (HORIBA Scientific, France) was used to detect DOM components in water samples.

<table>
<thead>
<tr>
<th>Table III.2: Peak locations of DOM substances of F-EEM contour map</th>
</tr>
</thead>
<tbody>
<tr>
<td>Humic-like 1</td>
</tr>
<tr>
<td>Excitation</td>
</tr>
<tr>
<td>230-260 nm</td>
</tr>
<tr>
<td>Emission</td>
</tr>
<tr>
<td>420-450 nm</td>
</tr>
</tbody>
</table>

### III.4.4 Attenuated total reflection Fourier transform infrared Spectrometry (ATR-FTIR)

FTIR is a preferred method for organic analysis. When infrared radiation passes through the sample, some of it will be absorbed and some will transmit. The ATR-FTIR spectrum presents molecular absorption and transmission, which creates a sample molecular structure fingerprint. The information that FT-IR can provide includes: Identification of unknown materials, determine the quality or consistency of a sample, determine components of a mixture.

FTIR is very fast and sensitive in detection, with simple mechanism. It is very reliable for identification of any samples. In this study, FTIR (Spectrum 100, PerkinElmer, U.S.) equipped with an universal ATR accessory of a ZnSe crystal was used to characterize the organic foulants on the membrane.

### III.4.5 Contact angle

Contact angle was measured by a optical tensiometer (KSV Theta, Finland) using the sessile drop method, in order to test membrane hydrophobicity. A drop of 50 µL milli-Q water was dropped onto the surface of dry membrane and a sequence of 2D frames were taken to record contact angle and its decreasing trend, then the contact
angle value on both side of the water drop was calculated and the average is recorded. Larger contact angle presents higher surface hydrophobicity of the membrane.
Chapter IV

Results and Discussion

IV.1 The filtration of synthetic water and WWTP effluent

HA is a predominant component of nature organic matter in water. Investigation on its contribution to ceramic membrane permeability decline is essential in understanding the organic fouling on the membrane. Tryptophan-like substance is a major part of the protein-like substances in effluent organic matter according to the peak intensities of F-EEM contour map. Tryptophan was also selected to test the effect of protein-like organic fouling on ZrO$_2$ membranes. The DOC level of synthetic water was controlled between 3-5 mg/L, about 200 mg/L NaHCO$_3$ was added into the synthetic water in order to achieve the alkalinity approximating normal water.

IV.1.1 Specific permeate flux (SPF) of synthetic water

According to F-EEM analysis of natural DOM, organic substance can be divided into humic-like and protein-like species. Tryptophan, an aromatic amino acid, is proved to have the same peak center location as one of the protein-like peaks in EEMs. In order to study whether there is synergetic effect of these substances on
ZrO$_2$ membrane filtration, HA mixed with tryptophan was prepared as a synthetic water.

**Flux decline**

Fig. IV.1 shows the filtration performance of HA and the HA-tryptophan mixture on ZrO$_2$ membrane. Although the three synthetic water have the same amount of DOC, the filtration performance varied from each other significantly. Without addition of tryptophan, the hydraulic-irreversible flux drop was 15% after the first cycle of filtration. It was 19% and 15% in synthetic water with 1 mg/L and 2 mg/L tryptophan, respectively. After 8 cycles of filtration, the hydraulic-irreversible flux reduction compared with initial flux are 29%, 31% and 45% for HA, HA with 1 mg/L tryptophan and 2 mg/L tryptophan respectively. The total hydraulic-irreversible fouling rised with the increase of tryptophan proportion in the synthetic water.
Organic matter removal

UV$_{254}$ of the permeates of three synthetic waters are shown in Fig. IV.2(A). For the filtration of HA alone, a steady UV$_{254}$ removal was achieved from the beginning, indicating that there was a continuous adsorption of HA on the membrane. For the filtration of HA-tryptophan mixture, UV$_{254}$ of the permeates continued to decrease as filtration cycles increased. The mixture with higher proportion of tryptophan lost more UV$_{254}$ than that with a lower tryptophan content. This result means that the adsorbed organic matter from the HA-tryptophan mixture can promote
further organic adsorption more than that from HA alone. Tryptophan might play an important role in this enhanced adsorption phenomenon. DOC removal in the filtration of the HA-tryptophan mixture was less than that of HA alone. With the rise of tryptophan proportion in the mixture, even less DOC was removed. It is likely that tryptophan might compete with HA, when they coexist, for adsorptive sites of the membrane. Since tryptophan is a smaller molecule compared with HA, the adsorption of tryptophan would reduce DOC removal capacity. It was also noticed that the increase of tryptophan proportion in synthetic water led to lower specific UV absorption (SUVA) values of the synthetic water, indicating that the synthetic water is more hydrophilic when replacing some of the HA with tryptophan. Since the more hydrophilic the water was, the more hydraulic-irreversible fouling was obtained on the membrane, hydrophilic organic matter might be the major organic foulants for ZrO₂ membranes.

Figure IV.2: Organic matter removal during ZrO₂ membrane filtration of synthetic water. (A) UV₂₅₄; (B) DOC.

LC-OCD results (Fig. IV.3) displayed 96% and 100% removal of the small molecule peak for mixtures with 1 mg/L and 2 mg/L tryptophan, respectively. The same peak removal for HA was much less, proved that tryptophan was preferentially adsorbed by ZrO₂ membrane. Accordingly, tryptophan-like small molecules might have a com-
peting effect with HAs in adsorbing on the membrane for the real WWTP effluent.

![Figure IV.3: LC-OCD analysis for raw water and permeates of (A) synthetic HA alone (DOC = 3.7 mg/L); (B) synthetic HA-tryptophan mixture (1 mg/L tryptophan, DOC = 3.7 mg/L); (C) synthetic HA-tryptophan mixture (2 mg/L tryptophan, DOC = 3.7 mg/L).]

**IV.1.2 Filtration of WWTP effluent**

The WWTP effluent contains more complex organic components compared with the synthetic water. The filtration performance on ZrO$_2$ membrane for the effluent was compared with that of the synthetic mixture to see if any common organic fouling properties exist.
Permeate flux decline

The SPF decline curve of the effluent (Fig. IV.4) was different from the synthetic water. The hydraulic-irreversible flux drop after the first cycle of filtration was 30% of the initial flux, the overall hydraulic-irreversible flux decline after the eight filtration cycles was 70%. The flux drop rate which can be expressed by the slope of filtration curve is maximum at the initial phase of each filtration cycle.

![Figure IV.4: SPF decline of ZrO$_2$ membranes during the filtration of a secondary effluent.](image)

Organic matter removal

UV$_{254}$ and DOC removal by ZrO$_2$ membrane from WWTP effluent are shown in Fig. IV.5. Average UV$_{254}$ removal was 5.6% while average DOC removal was 16%.
Figure IV.5: UV$_{254}$ (A) and DOC (B) removal of WWTP effluent by ZrO$_2$ membrane filtration.

Four typical components (Table III.2) of raw effluent, permeates and backwash water were measured by F-EEM (Fig. IV.6). The relative intensities of the four peaks in F-EEM were calculated into ratios to the four corresponding peaks in raw WWTP effluent.

Relative intensity decrease of each component by the first and fifth filtration compared with that of raw effluent is displayed in Fig. IV.7, which also includes the components removed by backwash. In the first cycle of the filtration, tyrosine-like was removed the most (26%), followed by tryptophan-like (8.4%), which also confirms a preferential adsorption of protein-like substances on ZrO$_2$ membrane described in Section IV.1.1. As filtration cycle increased, organic matter removal changed. Over twice of both the humic-like substances were found adsorbed on the membrane in the fifth filtration cycle compared with the first cycle. The adsorption of protein-like substances increased only slightly. This result can be interpreted as that the membrane preferentially adsorbs protein-like substances in the first few filtration cycles. These protein-like substances would bond the membrane surface with their hydrophilic side and expose their hydrophobic side. Those hydrophobic groups might have stronger affinity for humic-like substances than the membrane.
Figure IV.6: 3D fluorescence spectra of (A) WWTP raw effluent, (B) permeate 1, (C) permeate 2, (D) backwash.
Figure IV.7: Intensity ratio removal of the four fluorophores by the membrane in 1\textsuperscript{st} and 5\textsuperscript{th} filtration and flushed off by 1\textsuperscript{st} backwash. (P1: Peak intensity ratio of organic matter the membrane removed by 1\textsuperscript{st} filtration; P2: Peak intensity ratio of organic matter the membrane removed by 5\textsuperscript{th} filtration; B1: Peak intensity ratio of organic matter removed by 1\textsuperscript{st} backwash.)

Contact angle values of the membrane surface during the filtration process are shown in Fig. IV.8. The slope value in contact angle displays the resistance for water to permeate through the membrane. The greater contact angle is, the more hydrophobic is the membrane surface. In the first few filtration cycles, hydrophilicity didn’t change significantly, only increase of resistance occurred. It is possible that the protein-like substances not only absorbed on the membrane surfaces but also into pores. As the membrane underwent more filtration cycles, the hydrophobicity enhanced, which is possibly correlated with the adsorption of hydrophobic humic-like substances.
IV.2 Effects of pH and ionic strength on the filtration

IV.2.1 Influence of water pH

HA fouling is reported to be strongly influenced by membrane surface charge, since HA is either not charged or little negatively charged, and a gel-like layer was formed on the surface of positively charged filters with metals\(^{90}\). The ZrO\(_2\) membrane is positively charged when pH is lower than its pH\(_{pzc}\) (around 8.5-9.0). Water pH was adjusted by 1 M HCl and 1 M NaOH to see the influence of pH on the flux and membrane fouling.

Permeate flux decline

Specific flux decline of the ZrO\(_2\) membranes at different pHs are shown in Fig. IV.9. It is quite obvious that the filtration performance at pH 8.7 differed from that at pH 4.5, 5.5 and 6.5. At pH 8.7, the flux decreased by about 40% in the first cycle, and
hydrodynamic-flux was 15%; while at lower pHs, flux dropped by around 65% in the first cycle, the hydraulic-irreversible flux increased to 40%. The pH$_{pzc}$ of ZrO$_2$ membrane was at around pH 8.5-9.0. The membrane is almost neutrally charged at pH 8.7, and positively charged at lower pHs. The result indicates that positively charged surface has significant adverse effects on the fouling of ZrO$_2$ membrane during the filtration of synthetic water.

Figure IV.9: SPF decline of ZrO$_2$ membrane in the filtration of synthetic water (DOC around 4 mg/L) at (A) pH 8.7; (B) pH 6.5; (C) pH 5.5; (D) pH 4.5.

**Organic matter removal**

UV$_{254}$ and DOC results are shown in Fig. IV.10. It’s quite clear that as pH dropped, both DOC and UV$_{254}$ removal promoted. According to the DOC removal performance, hydraulic-irreversible fouling increasing with lowering pH is possibly caused
by HA adsorption. The DOC removal results consisted with the fouling trend. When aqueous pH was near pH_{pzc} of the membrane, the membrane was in neutral charge stage, which resulted in less adsorption and low DOC removal for HA. When water pH was lower than the membrane pH_{pzc}, electrostatic interaction was enhanced between carboxylic and/or phenolic groups of HA and the metal oxide of the membrane. PH decline in the range below pH_{pzc} was not as significant as that from near pH_{pzc} to below pH_{pzc} in changing DOC removal removal rate, which is possibly related to the limited adsorptive capacity of the membrane. Furthermore, the cake layer formed on membrane surface in the first cycle of filtration was very difficult to be hydraulic removed when pH was below pH_{pzc}. In the following filtration cycles, this layer tended to further react with HA, leading to further HA deposition on the fouling layer and causing more hydraulic resistance[91]. This phenomenon is shown in Fig. IV.10 in which DOC of the permeates decreased continuously until the 3rd cycle.

Figure IV.10: UV\_254 (A) and DOC (B) decline of raw water and permeates from each filtration cycle of ZrO\_2 membrane filtration at different pHs.

The LC-OCD results in Fig. IV.11 was correlated with DOC removal. Each component had different degree of decrease at different filtration pHs. As pH of the feed water decreased from 8.7 to 4.5, the removal of humic substances were significantly enhanced, from 8% to 67%. Also 20% removal of low molecular weight neutrals was
observed in the pH 4.5 filtration, compared with only 6% when pH was 8.7. Low molecular weight acid decreased by 67% at pH 8.7 compared with 75% at pH 6.7. The negative charge density of large molecules tends to be lower than small ones. Therefore, the significant HA adsorption increase at lower pH is possibly due to the more positive surface charge of the ZrO$_2$ membrane.

Figure IV.11: LC-OCD results of raw water and permeate of HA at (A) pH 8.7; (B) pH 4.5.

IV.2.2 Influence of ionic strength

The filtration of HA and HA-tryptophan mixture at different ionic strength adjusted by NaCl was performed. The flux decline is shown in Fig IV.12 and Fig. IV.13, respectively. For HA alone, the overall hydraulic-irreversible permeability loss after filtration were 21%, 23% and 28% for synthetic water with 0 M NaCl, 0.01 M NaCl and 0.1 M NaCl, respectively. As for the HA-tryptophan mixture, hydraulic-irreversible permeability loss changed to 22%, 20% and 9% for water with 0 M NaCl, 0.01 M NaCl and 0.1 M NaCl, respectively. The increase in ionic strength has an almost negligible adverse effect on HA filtration, but it decreased the hydraulic-irreversible fouling of HA-tryptophan mixture significantly. This result indicates that HA-tryptophan adsorption on ZrO$_2$ membranes is possibly due to electrostatic interaction. HA ad-
sorption is more like an inner-sphere bonding.

The difference between the HA and HA-tryptophan mixture adsorption on the membrane might be related to the interactions between HA and tryptophan molecules such as encapsulation through electrostatic attraction(61). These kinds of interaction might reduce the availability of the adjacent carboxylic groups or carboxylic-phenolic groups which are responsible for the inner-sphere interaction with metal oxides in the aryl structures of the HA(49).

Figure IV.12: SPF decline of ZrO$_2$ membrane filtration of HA at (A) 0 M NaCl; (B) 0.01 M NaCl; (C) 0.1 M NaCl.
IV.3 Effect of pre-ozonation on the filtration

IV.3.1 Filtration of pre-ozonated HA synthetic water

Effect on permeability

After being treated by a dosage of 5 mg/L O₃, the DOC of raw HA solution dropped from 3.26 mg/L to 2.94 mg/L. Ozonation removed 10% DOC of the HA. In comparison to non-ozonated water, permeability decline of ozonated water was apparently much slower in each filtration cycle (Fig. IV.14). However, nearly 85% of the organic fouling caused by ozonated water was hydraulic-irreversible. Table IV.1 lists the initial flux of each cycle after backwash. The reduction in initial flux of each cycle was caused
by irreversible fouling. The reversible fouling of ozonated HA decreased only a little, possibly because that some of this kind of foulant was degraded by ozone. Ozonation is very efficient in destructing aromatic and double bond structures in organic matter, increasing hydrophilicity of the organic matter in water\(^\text{(92)}\). It can be conjectured that backwash tends to remove foulants that are more hydrophobic. Hydrophilic fouling seems to be more critical in hydraulic-irreversible organic fouling of \(\text{ZrO}_2\) membrane. This trend was also found by the following filtration experiments on WWTP effluent.

Figure IV.14: SPF decline of \(\text{ZrO}_2\) membranes filtration with (A) HA alone; (B) HA ozonated with 10 mg/L \(\text{O}_3\).

Table IV.1: Comparison of the initial flux of each cycle between non-ozonated HA and ozonated HA.

<table>
<thead>
<tr>
<th>Initial SPF (L/m(^2)-h-bar)</th>
<th>First cycle</th>
<th>Second cycle</th>
<th>Third cycle</th>
<th>Fourth cycle</th>
</tr>
</thead>
<tbody>
<tr>
<td>HA alone</td>
<td>641</td>
<td>571</td>
<td>526</td>
<td>518</td>
</tr>
<tr>
<td>Ozonated HA</td>
<td>643</td>
<td>589</td>
<td>567</td>
<td>517</td>
</tr>
</tbody>
</table>

**Organic matter removal**

As is shown in Fig. IV.15 after pre-ozonation, \(\text{UV}_{254}\) of the HA dropped by about 50%. The filtration of pre-ozonated HA only reduce 5.0% of the \(\text{UV}_{254}\), compared
with the 20% removal in non-ozonated HA. DOC removal of the water also reduced from 16% to 6.0% after being pretreated with O₃. The removal of organic matter deceased significantly, while the degree of irreversible fouling didn’t change much. It can be assumed that ozonation reduced the proportion of HA constituents that can cause reversible fouling on ZrO₂ membrane. Furthermore, DOC removal of the pre-ozonated water dropped slightly with more filtration cycles performed, which indicates the hydrophilic matter adsorbed on the membrane surface from pre-ozonated water can lessen the affinity between aqueous organic matter and the membrane. In the case of non-ozonated HA, the interaction between the absorbed HA and the organic matter in solution was probably much stronger, which could be interpreted that the adsorbed organic molecules exposed their hydrophobic side to the water which made the membrane surface more likely to adsorb hydrophobic organic matter. That might be the reason why TOC removal was greater in the later cycles for non-ozonated HA than that for ozonated HA.

Figure IV.15: UV₂₅₄(A) and DOC (B) removal during ZrO₂ membrane filtration of HA and pre-ozonated HA.
IV.3.2 Filtration of pre-ozonated WWTP effluent

WWTP effluent was pretreated with 5, 10 and 15 mg/L $O_3$, respectively. Then these pre-ozonated water along with the unpreozonated WWTP effluent were filtered with the $\text{ZrO}_2$ membrane, to test the influence of ozone dose on fouling behavior.

Permeate flux decline

Fig. IV.16 shows the specific flux drop of $\text{ZrO}_2$ membrane filtration of the four waters samples. The decline of hydraulic-reversible fouling was observed for the pre-ozonated water. Hydraulic irreversible fouling and reversible fouling are compared in Fig. IV.17. Apparently, the degree of hydraulic-reversible fouling decreased when increasing the $O_3$ dose applied in the pretreatment (Fig. IV.17B). Irreversible fouling increased significantly in the first cycle of filtration, after which no more big difference in it can be observed between the pre-ozonated and non-ozonated water (Fig. IV.17A).
Figure IV.16: SPF decline of ZrO$_2$ membrane filtration of (A) WWTP effluent; (B) WWTP effluent pre-treated with 5 mg/L O$_3$; (C) WWTP effluent pre-treated with 10 mg/L O$_3$; (D) WWTP effluent pre-treated with 15 mg/L O$_3$.

Figure IV.17: Hydraulic-irreversible (A) and hydraulic-reversible (B) SPF decline.
Organic matter removal

The UV$_{254}$ removal in five cycles of ZrO$_2$ membrane filtration of the ozonated effluent was stable (Fig. [IV.18A]), indicating that components with unsaturated structures in the ozonated water was adsorbed by ZrO$_2$ membrane. Average UV$_{254}$ removal rate increased from 6.3% (Fig. [IV.5A]) to 11%, 18%, 11% when ozone dose was 5, 10 and 15 mg/L, respectively. The result implies that pre-ozonation increased the proportion of the unsaturated components adsorbed on the membrane. Similar to UV$_{254}$ removal, DOC removal rates of the ozonated effluent in the five cycles of ZrO$_2$ membrane filtration were also relatively constant (Fig. [IV.18]). Average DOC removal was 3.2%, 4.3%, 4.1% for ozone dose of 5, 10 and 15 mg/L, respectively, compared with 13% for untreated WWTP effluent. This result means that pre-ozonation decreased the proportion of the organic matter that can cause hydraulic-reversible fouling on the membrane surface.

Figure IV.18: UV$_{254}$ (A) and DOC (B) of raw water and permeates.

LC-OCD results (Fig. [IV.19]) indicate that by increasing ozone dose in pre-ozonation of WWTP effluent, the ratio of humic substances in total DOC decreased and that of the lower molecular weight components increased (building blocks and LMW neutrals). As ozone dose increased, LMW neutrals removal were 0.5%, 9.5%,
23%, building blocks removal were 0.6%, 1.9%, 14%, humic substances removal were 0.2%, 4.7%, 5.2%, biopolymer removal were 30%, 29%, 21% for 5, 10, 15 mg/L ozone applied, respectively. These results indicate that during the filtration of pre-ozonated water, higher ozone dosage results in more LMW organic matter deposition on the membrane.

Figure IV.19: LC-OCD results for raw water and permeate of (A) WWTP effluent; (B) WWTP effluent treated with 5 mg/L O$_3$; (C) wastewater effluent treated with 10 mg/L O$_3$; (D) WWTP effluent treated with 15 mg/L O$_3$.

Fig. IV.20 displays the F-EEM results of DOM components in water samples treated by different ozone dose before and after filtration. The intensity ratio to the initial peak height of each component was computed and compared in Fig. IV.21. The effluent composition changed greatly through ozonation. As for ozonation at 5
mg/L O₃, HA-like and FA-like decreased by 8.3% and 26% while tyrosine-like and tryptophan-like substances increased by 6.6% and 55%. After raising O₃ applied to 10 mg/L, more humic substances were transformed into smaller molecules and the increment of tyrosine-like and tryptophan-like were both 72%. It implies that with more abundant O₃ in the pretreatment process, the production of HA-like will be enhanced. The decline of reversible fouling with higher ozone dose may also be interpreted by the increasing ratio of protein-like components in total DOM. Small molecules with carboxyl groups in it can be regarded as irreversible foulants, since increment in irreversible fouling always happens when membrane adsorbed more of those substances. There’s also a probability that competition for the membrane activated sites exists between the humic-like and protein-like substance, in which smaller protein-like matter has advantages to be absorbed. At O₃ concentration of 10 mg/L, more protein-like matter is bonded with membrane sites, resulting in lack of interaction between humic substances and the membrane. Humic foulant from ozonated water were easier to be removed by hydraulic backwash at O₃ dose of 10 mg/L, nearly 80% of the FA-like and 40% of HA-like adsorbed was flushed off by milli-pore water, much higher than it did at lower or no ozone dose. In a word, large complex molecules tend to be hydraulic backwashed off, while smaller molecules have stronger interaction with ZrO₂ membrane, they are likely to form irreversible fouling.
Figure IV.20: 3D fluorescence of (A) WWTP effluent treated with 5 mg/L O₃; (B) permeate of WWTP effluent treated with 5 mg/L O₃; (C) backwash water of WWTP effluent treated with 5 mg/L O₃; (D) WWTP effluent treated with 10 mg/L O₃ raw water; (E) permeate of WWTP effluent treated with 10 mg/L O₃ permeate; (F) backwash water of WWTP effluent treated with 10 mg/L O₃ backwash.

Figure IV.21: Intensity removal ratio of the four fluorophores by ZrO₂ membrane and flushed off by backwash (P0: ratio of material removed by membrane in each filtration when ozone dose applied was 0 mg/L; B1: Ratio of material flushed off by each backwash when ozone dose was 0 mg/L).
Absorbance ATR-FTIR results on fouled ZrO$_2$ membrane are displayed in Fig. IV.22. It is well known that C=C bending absorption takes place at wave number of 1,700-1,500 cm$^{-1}$, a significant signal was observed after the membrane being contaminated, which is probably caused by unsaturated structure in organic matter. Another peak at the wave number of 1,000-1,200 cm$^{-1}$ was possibly caused by sugar.

Figure IV.22: ATR-FTIR absorbance spectra for virgin and contaminated membrane after filtration (A) and backwash (B) of WWTP effluent treated with different O$_3$ dose. P0: membrane after filtration of WWTP effluent treated with 0 mg/L O$_3$, B0: backwashed membrane after filtration of WWTP effluent treated with 0 mg/L O$_3$. 
Chapter V

Conclusions

This study focused on the organic fouling on ZrO$_2$ ceramic membranes, during the ultrafiltration of synthetic water and WWTP effluent. Dead-end filtration performances of the membrane on several water samples were tested and compared. Organic fouling mechanisms were proposed. The surface chemistry of ZrO$_2$ membrane was proved to have significant influence on the filtration performance and the organic fouling.

In comparison to the filtration of HA alone, HA mixed with tryptophan at a similar DOC level had some negative effect on ZrO$_2$ membrane filtration performance, i.e. a severe hydraulic-irreversible fouling. As tryptophan proportion in the mixture increased, more hydraulic-irreversible fouling was observed; while DOC removal by the membrane was reduced. It can be interpreted that tryptophan may compete with HA for adsorptive sites on the membrane. Hence hydrophilic organic matter with low molecular weight has specific contribution to the organic fouling of the ZrO$_2$ membrane. Similar result was also observed during the filtration of WWTP effluent. The removal of protein-like (mainly tryptophan-like) substances was dominant in the first few cycles of the filtration. However, more humic-like substances were adsorbed by the membrane as the filtration went on. Due to the adsorption of humic-like substances, the membrane surface became more hydrophobic. It can be assumed
that after the preferential adsorption of protein-like substances, the membrane had a more hydrophobic surface, leading to more adsorption of humic-like substances in the following filtration cycles.

HA adsorption on ZrO$_2$ membrane was significantly enhanced by reducing water pH below pH$_{pzc}$ of the membrane, when the membrane surface became more positively charged. The removal of DOC increased from 6.2% to 79% when pH changed from 8.7 to 4.5. High ionic strength had no apparent negative effect on HA filtration. However, it improved the filtration of HA-tryptophan mixture by cutting down hydraulic-irreversible flux decline. This result implies that the adsorption of HA-tryptophan on ZrO$_2$ membrane is controlled by electrostatic interaction.

Pre-ozonation of both synthetic water and WWTP effluent reduced hydraulic-reversible flux decline of the filtration. This can be explained that ozonation broke down HA constituents that could cause reversible fouling to ZrO$_2$ membrane. Membrane irreversible flux decline of ozonated water was much higher in the first cycle, probably caused by LMW organic products of ozonation. No significant change in flux decline was observed in the following filtration cycles, suggests that adsorption of LMW molecules is preferred for ZrO$_2$ membrane, but also limited by the amount of adsorptive sites available.

To sum up, organic fouling on ZrO$_2$ membranes is a complicated process caused by the interactions between different organic groups and the membrane surface. Water pH, ionic strength and the organic constituents all have influences on the filtration performance. Protein-like molecules seem to be preferentially adsorbed by the membrane at the beginning of the filtration, which in turn enhance the membrane hydrophobicity, resulting in more adsorption of humic-like substances. Ozonation can break down the unsaturated structures of organic matters, producing hydrophilic LMW organics. The adsorption of the ozonation products on the membrane leads to hydraulic-irreversible fouling.
Chapter VI

Future Research Work

The work presented in this thesis can be extended in the following aspects:

- Investigating the impacts of other aromatic small molecules addition to HA solution on membrane fouling, to further discuss the interaction between organic matters and ZrO$_2$ membrane surface.

- Use H$_2$SO$_4$ or NaOH solution as cleaning agent instead of milli-Q water to study the changing in characteristics of foulants removed from membrane by backwash with different solution.

- Modification of the membrane surface charge to study how membrane fouling is affected.
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