Development of Combination Processes Consisting of Ozonation, Coagulation and Ceramic Membrane Filtration for Water Reclamation based on Evaluation of Risk and Energy

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Development of Combination Processes Consisting of Ozonation, Coagulation and Ceramic Membrane Filtration for Water Reclamation based on Evaluation of Risk and Energy

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By

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ABSTRACT

Water scarcity has become a significant issue nowadays. Almost one-fifth of the world's population, live in areas of physical scarcity, one quarter of the world's population face economic water shortage. And the water scarcity will be more serious in the future for population growth, urbanization and water pollution. But water that was once used can be reclaimed and used again for mainly non-potable use such as, irrigation use, urban reuse and environmental and recreational reuse, etc. Considering untreated wastewater contains a wide variety of contaminants that may be hazardous to human health and the environment, suitable treatment is needed to reduce such risks. There have been lots of studies on water reclamation from secondary effluent but little research on treating primary effluent by ozonation, membrane filtration processes. Nevertheless, little work has been reported about combination processes based on ozonation and ceramic membrane filtration (CMF). Moreover, no study was found on such combination processes from comprehensively evaluation of both product water quality and energy consumption. According to the above background, the feasibility of water reclamation from primary effluent and secondary effluent was studied with consideration of product water quality and energy consumption in this study.

Firstly, the removal of various contaminants by ozonation was studied. Ozonation could effectively remove most PPCPs, except antiarrhythmic agents, ketoprofen, caffeine, bezafibrate, DEET, clofibric acid. The reaction rate in liquid phase was 1.35 times as high as reaction rate in solid phase. For pathogen disinfection, ozonation showed effectiveness on MS2 disinfection, but showed weaker effect on bacteria disinfection compared with MS2, especially in primary effluent. Efforts were tried to improve the ozonation efficiency by pretreatments. CMF and PAC+CMF pretreatments could show tiny effect on PPCPs degradation and MS2 inactivation enhancement. And CMF pretreatment showed no effect on bacteria inactivation in secondary effluent, but obvious enhancement was found in primary effluent case. In addition, it was found CMF and

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PAC+CMF pretreatments could save O_3 dose through removing certain amount of organic carbons.

Secondly, CMF-based processes were conducted to remove contaminants from wastewater. It was found CMF showed excellent effect on removing bacteria, but with less than 1 logs removal of MS2. For effectively controlling MS2, CMF should be incorporated with coagulation. And in order to remove PPCPs, ozonation was needed.

Then CM fouling mitigation was examined by ozonation or ozonation +coagulation pretreatments. In case of treating secondary effluent, coagulation effectively mitigated CMF fouling. Obvious enhance on membrane fouling control by coagulation was achieved with 6 mg/L dose ozonation pretreatment. While ozonation pretreatment with 2 and 4 mg/L dose showed negative effect on enhancing coagulation for membrane fouling mitigation.

The mechanisms for change membrane fouling by pretreatments were investigated through characterization of particles and certain dissolved organic matters, such as sugar, proteins and humic substances. For membrane fouling resulted from particles, it was found coagulation pretreatment could mitigate membrane fouling significantly through forming larger size particles. And ozonation pretreatment could enhance coagulation effect on alleviating membrane fouling caused by particles.

For membrane fouling resulted from dissolved organic matters, it was found 20.3%, 29.8%, 8.7% and 23.2% of tyrosine-like organic matter, tryptophan-like compounds, phenol-like organic compounds and fulvic-like material in wastewater contributed to membrane fouling during filtrating secondary effluent using single CMF. The ratio decreased continuously with increasing PAC doses. It decreased to to 9.7%, 0.6%, 6.6% and 8.6%, respectively with 50mg/L PAC dose. It was interesting to find the fouling tendency of these components increased by ozonation pretreatment. Ozonation with 4mg/L dose O_3 could remove around 80% of these components. The residual organic matters would be accumulated inside of CM during filtration, followed by transmembrane pressure increasing sharply after 76-90 hours. After increasing the O_3 dose to 6 mg/L, over 90% of them were degraded. Although the fouling tendency increased, the amount of residual organic matters was too tiny to cause more serious fouling.

For treating primary effluent, ozonation was found not effective to control fouling. And coagulation with 50 mg/L dose of PAC was necessary to mitigate membrane fouling. Similar reasons with ones in secondary effluent case for control membrane fouling by PAC were found. Moreover, it was found there was relative larger amount of other organic matters in primary effluent except sugar, protein and humic substances could result in ceramic membrane fouling. But the membrane fouling caused by these potential organic foulants could be easily alleviated by coagulation taking PAC as coagulant.

Finally, technical rout for various usages was proposed based on evaluation of risk and energy. For treating primary effluent, coagulation, ceramic membrane filtration and post ozonation was suitable process for crop irrigation usage. The energy consumption was 0.390 kWh/m^3, much lower than power required by MBR. In secondary effluent case, coagulation, ceramic membrane filtration and ozonation showed advantages with low energy consumption and high enough water quality.

The works presented in this dissertation have elucidated that performance of O_3-based and CMF-based processes on removing contaminants. Beside, pretreatments effect on CM fouling control was examined, and fouling mechanisms were explored. Moreover, appropriate process for water reuse of secondary effluent and primary effluent was proposed based on comprehensive considering the disinfection effectiveness, decreasing ecological risk and saving energy consumption. Applicability of coagulation and CMF combination process with post ozonation was confirmed for various water usages through this study.

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CHAPTER I

Introduction

1.1   Research background

Water scarcity has become significant issue nowadays. Water reuse projects were established all over the world to solve such problem (Bixio et al., 2005; Godfrey et al., 2009; Zhang et al., 2007). The reclaimed water can be applied in urban usage, industry usage, agriculture usage, environmental and recreational usage, groundwater recharge, and augmentation of potable supplies, etc. (EPA, 2004). Thus water amount needed to meet demand is reduced by water reclamation. Also contaminants amount delivered to environment will decrease correspondingly.

Due to its specific origin, reclaimed water presents hazards and risks. Both are related to the presence of microbes and chemicals capable to cause illnesses and the toxicity for human, animals and plants, and negative impacts on the environment. Pathogenic microorganisms represent the most common threat to the reuse of water, due to the high concentration of potentially infectious species that routinely are present in the wastewater. Nowadays, further widespread attention has been given to the broad range of pharmaceutical and personal care products (PPCPs) for their various known and unknown negative effects on human, animal, plants and environment (Khetan et al., 2007). Such contaminants should also be removed as much as possible in order to conserve water resource, and to assure adequate future water supplies (Daughton et al., 1999).

Treatments employed to meet pathogen and PPCPs removal target can be categorized into either filtration, disinfection or oxidation. Among these technologies, membrane filtration with pore size less than 0.1 μm attracted many attentions for completely rejection of bacterial. Currently, ceramic membrane filtration (CMF) was tried to used,

due to high flux, mechanically superior and chemical resistance. Besides, ozonation has been reported as effective process for both disinfection and PPCPs removal (Beltrán, 2005; Hollender et al., 2009; Huber et al., 2003; Hunt et al., 1997; Ishida et al., 2008; Kim et al., 2010; Wert et al., 2011; Xu et al., 2002; Zimmermann et al., 2011). Thus CMF-based and O_3-based technologies are very promising for removing contaminants from wastewater. However, most of the studies using these technologies focused on treating secondary effluent. Besides, under proper treatment, primary effluent could be good water resource for crop growing due to high nutrients concentration. Study about removal of contaminants by water reclamation processes in treating primary effluent will show significant meanings.

In addition, membrane fouling was an inevitable problem during membrane filtration. It increases operation cost and reduce treatment stability. Some research have been done to mitigate fouling using ozone and coagulation pretreatment (Karnik et al., 2005b; Kim et al., 2008; Lehman et al., 2009; Schlichter et al., 2004). But mechanisms were not clear until now, and all these works was focused on treating secondary effluent and natural water. Further work should be done to investigate reasons of mitigation fouling by pretreatments during filtrating secondary and primary effluent. Last, in order to apply technologies to the real case, energy and risk evaluation should be taken into consideration.

1.2　Research objectives

According to the above research background, detailed objectives of this research are listed as follows:

1) To study O_3-based and CMF-based processes performance on contaminants removal from secondary effluent and primary effluent

2) To investigate the effect of O_3 and coagulation pretreatment on CMF fouling mitigation

3) To propose suitable water reclamation processes for several water reuse scenarios from product water quality and energy consumption aspects

1.3 Research structure
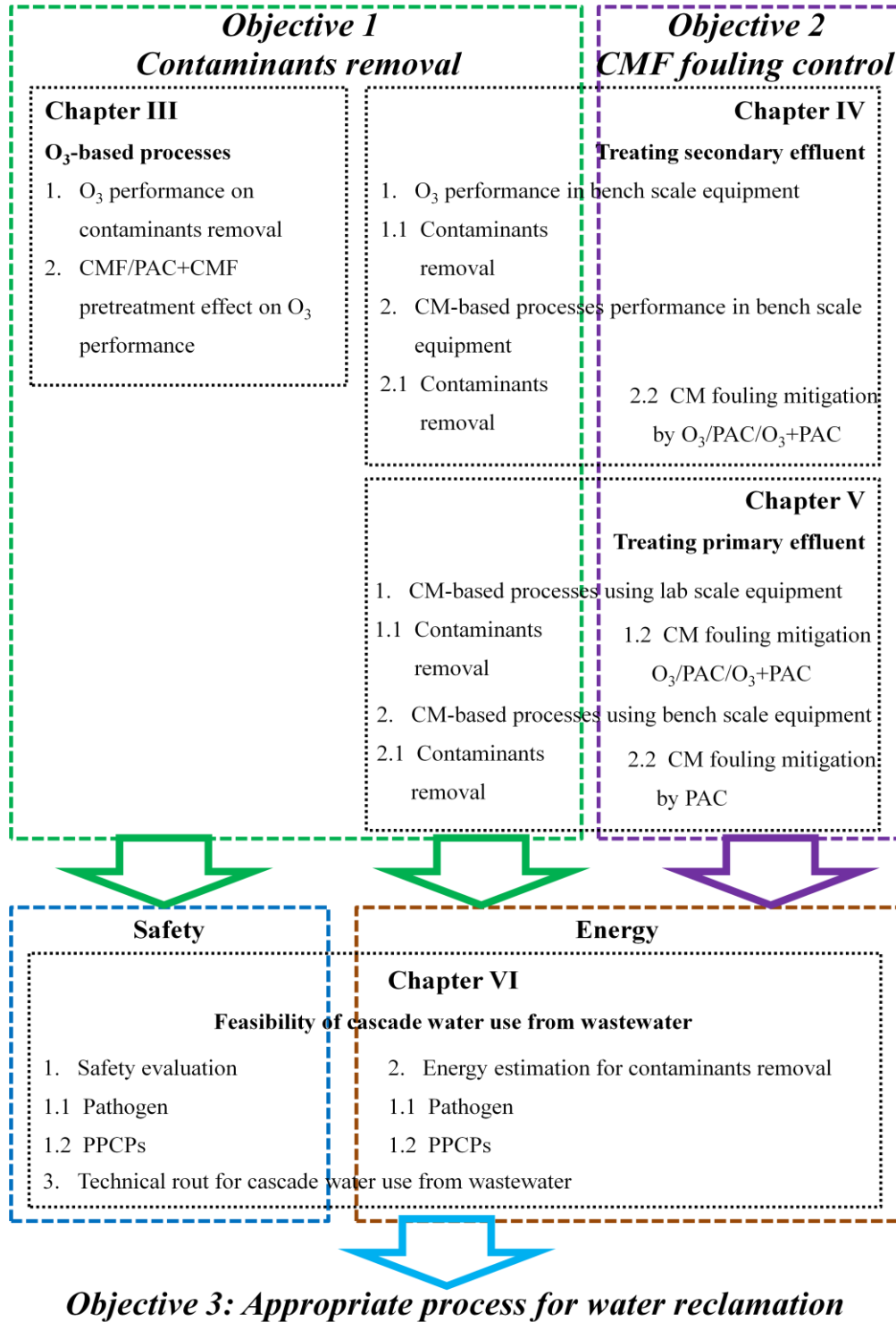
Figure 1.1   Schematic diagram of research structure

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CHAPTER II

Literature Review and Research Scope

2.1   Introduction of water reclamation and reuse

As defined in "Water reuse issues, technologies, and applications" (Asano et al., 2007), "water reclamation is the treatment or processing of wastewater to make it reusable with definable treatment reliability and meeting water quality criteria. Water reuse is the use of treated wastewater for beneficial uses, such as agricultural irrigation and industrial cooling, et al."

2.1.1   Cascade water use

Cascade water use means the fullest utilization of water as a resource in an environmentally friendly way. Raw wastewater or treated wastewater (secondary effluent) will be treated to reclamation grade water for various usages, such as irrigation, groundwater recharge, recreational uses, toilet flushing, and etc. This will decrease the volume of wastewater delivered to centralized treatment plants or the amount of contaminants discharged to water environment. At the same time, the number of water resource needed to meet water demand will be reduced. Thus, one of most important characteristics of cascade is long-term planning to ensure sustainable, safe, cost-effective water utilization.

2.1.2   Important role of water reuse

Water scarcity has become a significant issue nowadays. The renewable freshwater in global hydrologic cycle can provide several times what is required to sustain the current world population. However, only about 31 percent of the annual renewable water is accessible for human consumption due to geographical and seasonal variations (Postel, 2000; Shiklomanov, 2000). Water is a very complex resource. Contrary to a static resource

such as land, water occurs in a very dynamic cycle of rain, runoff, and evaporation, with enormous temporal, spatial, and quality variations that completely govern its value to people and ecosystems (Rijsberman, 2006). As a result, one country can encounter drought and flood in different locations at the same time.

Population growth and urbanization increase water demand. The world population in 2002 was estimated at 6.2 billion with an annual growth rate of 1.2 percent. It is projected that the world population in 2050 will be between 7.9 billion and 10.3 billion (UN, 2003). Urban populations are expanding, not only in developing countries, but also in developed countries. This expansion intensifies the effect of population growth on water resources due to the imbalance between water demands and the proximity of water sources (Asano et al., 2007).

Another major concern is water pollution. Two million tons of sewage, industrial, and agricultural wastes are discharged daily into the world's water resources. The UN estimated that wastewater is produced annually is at approximately 1,500 km^3, six times higher than the amount of river water on Earth combined.(UN et al., 2003). Untreated municipal wastewater typically contains a variety of biological and chemical constituents that may be hazardous to human health and the environment.

Unsafe or inadequate water, sanitation, and hygiene cause approximately 3.1 percent of all deaths and 3.7 percent of DALYs (disability adjusted life years) worldwide (WHO 2002). Unsafe water caused 4 billion cases of diarrhea each year, which resulted in 2.2 million deaths, mostly of children under five. This means that 15% of child mortality each year, which equals one death every 15 seconds, is attributed to diarrhea.(WHO et al., 2000).

Contaminants in the wastewater exert a negative effect on the ecosystem. There has been widespread decline in biological health in inland (non-coastal) waters. Globally, 24 percent of mammals and 12 percent of birds connected to inland waters are considered threatened by this situation (UN et al., 2003).

With water scarcity and water pollution problems in mind, water reuse becomes an attractive solution. Water reuse will reduce the amount of water resource needed to meet water demand, as well as the amount of contaminants entering the environment.

2.1.3   Types of water reuse

Water that was once used can be reclaimed and used again for different beneficial purposes. The quality of the wastewater and the reuse objective define the extent of subsequent treatment and the cost associated with the treatment. The basic classification of reclaimed water application can be divided as follows: urban reuse, industry reuse, agriculture reuse, environmental and recreational reuse, groundwater recharge, and augmentation of potable supplies (EPA, 2004).

2.1.4   Current situation

Recently, over 3,300 water reclamation facilities were identified, mostly in Japan and the United States, with 450 and 230 projects in Australia and the EU, respectively. The United States was by far the largest producer of reclaimed water, with an estimate close to 6.5 million cubic meters per day (Bixio et al., 2005). The current production capacity must be much larger than this figure for this data was summarized in 2005. Developing countries also conducted water reclamation projects (Godfrey et al., 2009; Zhang et al., 2007). The distribution of municipal wastewater reuse is shown in Figure 2.1. Wastewater reuse is mainly utilized in industrial cooling (20%), urban miscellaneous use (20%), scenic environment use (13%), irrigation (10%), and other purposes (37%) (Yannian Zhou et al., 2011).
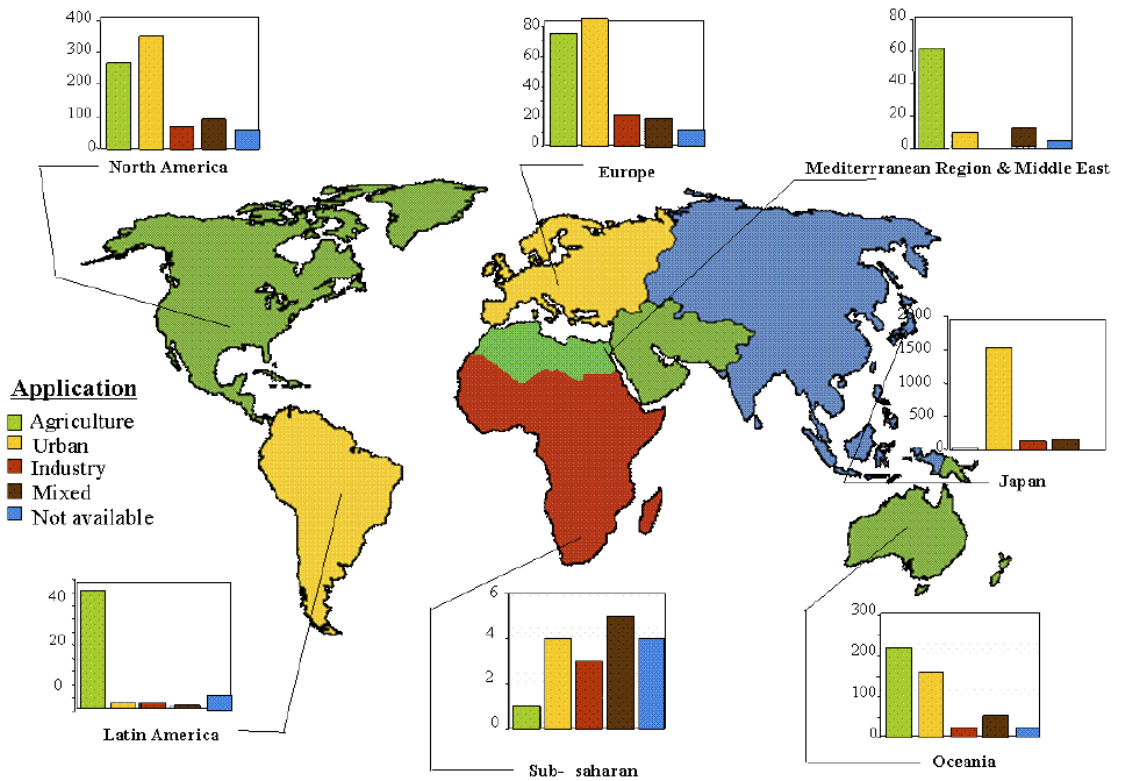
Figure 2.1   Number of identified municipal water reuse schemes per field of application in seven regions of the world (Bixio et al., 2005)

2.2   Introduction of contaminants

Municipal wastewater is a collection of wastewater from a variety of sources including households, offices, hospitals, commercial facilities, and industrial facilities. Thus, untreated municipal wastewater contains a wide variety of contaminants that may be hazardous to human health and the environment. Suitable treatment is needed to reduce such risks.

Before selecting processes and risk assessment, initial evaluation of risk associated with reclaimed water should be carried out. The hazards associated with the use of wastewater are listed in table 2.1.

Table 2.1   Hazards associated with the use of wastewater (Asano et al., 2007; Bruno, 1999; EPA, 2004; WHO, 2006)

Category	Constituents	Parameters of interest	Comments
Pathogenic organisms	Bacteria	*Shigell; Salmonella; Escherichia coli; Yersinia enterocolitica; Campylobacter jejuni*	Infectious dose highly variable (10-10^7) Survival time in water between 10-60 days Commonly used a indicator
	Protozoa	*Giardia lamblia; Cryptosporidium parvum; Entamoeba histolytica;*	Single-celled organisms; Larger than bacteria; Common in fresh and marine water; Enteric protozoan parasites produce cysts or oocysts; Survival time in water between 10-30 days
	Helminths	*Ascaris lumbricoides; Schistosoma mansoni*	Parasitic worms; One of the principal causative agents of human disease; Infectious dose 1-10 helminth eggs
	Viruses	*Hepatitis A; Noroviruses and Other Caliciviruses; Rotaviruses; Enterovisuses; Adenoviruses*	Survival time in water between 50-120 days; Infectious dose 1-10 viruses
General parameters	Suspended solids	*Total Suspended Solids (TSS)*	Sorb organic pollutants and heavy metals; Shield microorganisms; Plug irrigation systems and soil
	Nutrients	*Nitrogen; Phosphorus*	Might induce eutrophication; Nitrogen can lead to nitrate build-up in groundwater after leaching
	Hydrogen ion concentration	*pH*	Impact on coagulation, disinfection, metal solubility and soils; Toxicity with low or high concentrations
	Physical properties	*Color; turbidity*	Aesthetic and nuisance problems
Inorganic constituent	Dissolved inorganics	*Total Dissolved solids(TDS) Specific elements (Ca, Na…)*	High salinity may damage crops; Destabilize soil structure, decrease productivity in the long term; Accumulation on the cooling equipment
	Heavy metals	*Specific elements (Cd, Zn…)*	Accumulate in certain plants and animals; Limit suitability of the reclaimed water
Organic constituent	Biodegradable organics	*Biochemical oxygen demand (BOD); Chemical oxygen demand (COD); Total organic carbon (TOC)*	Aesthetic and nuisance problems; Provide food for microorganisms; Contribute to chlorine demand; Formation of disinfection byproducts
	Emerging contaminants	*pharmaceuticals and personal care products (PPCPs) Endocrine disrupting compounds (EDCs)*	Toxic to the environment and public health

2.3   Introduction of water reuse regulations

The development of water reuse was typically driven by water scarcity, water sources augmentation, and water pollution control. At the same time, discharged wastewater quality,

economic evaluation, public health protection, and public support and acceptance should be taken into consideration. It was difficult to decide a common global regulation for wastewater reuse. At present, water reuse regulations are developed and implemented based on actual situation in each country or state.

2.3.1   WHO regulations

Over the years, World Health Organization (WHO) has provided guidance for the safe use of wastewater, including "Reuse of Effluents: Methods of Wasteater Treatment and Health Safeguards" (WHO, 1973), "Health Guidlines for the Use of Wasteater in Agriculture and Aquaculture" (WHO, 1989) and "WHO Guidlines for the Safe Use of Wasteater, Excreta and Greywater" (WHO, 2006).

The guidelines are based on the development and the use of health-based targets, which are used to established a certain level of health protection in an exposed population. The guideline established by WHO in 2006 (WHO, 2006) stated that wastewater for agricultural applications has to meet a tolerable additional disease burden standard of $<10^{-6}$ DALYs per person per year, as safe as, which is equivalent to drinking water standard.

Table 2.2   Microbial reduction targets for treated wastewater use in agriculture (WHO, 2006)

	Health-based target (DALY per person per year)[a]	Helminths eggs (number per gram total solids or per liter)	*E. coli* (number per 100ml)	Log 10 pathogen reduction needed[a]
Unrestricted irrigation	$<10^{-6}$	<1	$<10^3$	6-7
Restricted irrigation	$<10^{-6}$	<1	$<10^5$	3-4
Localized (drip) irrigation	$<10^{-6}$	<1	-	2-4

a Rotavirus reduction. The health-based target can be achieved, for unrestricted and localized irrigation, by a 6-7 log unit pathogen reduction (obtained by a combination of wastewater treatment and other health protection measures, including an estimated 3-4 log unit pathogen reduction as a result of the natural die-off rate of pathogens under field conditions and the removal of pathogens from irrigated crops by normal domestic washing and rinsing; for restricted irrigation, It is achieved by a 2-3 log unit pathogen reduction;

The concentration limit of many chemicals in wastewater is determined based on crop's requirements, not health concerns. Common water quality parameters limitations for irrigation were shown in Table 2.3.

Table 2.3   Water quality for irrigation (WHO, 2006)

parameter	Units	Degree of restriction on use		
		None	Slight to moderate	Severe
Salinity EC	dS/m	<0.7	0.7-3.0	>3.0
TDS	mg/L	<450	450-2000	>2000
TN	mg/L	<5	5-30	>30
pH		Normal range 6.5-8.0		

Table 2.4   U.S. EPA water reuse guidelines (EPA, 2004)

Types of reuse	Reclaimed water quality
Urban reuse all types of landscape irrigation Agricultural reuse-food crops not commercially processed Recreational impoundments	• pH=6-9 • $\leq$ 10mg/L BOD • $\leq$ 2 NTU • No detectable fecal coli/100ml • 1mg/L Cl_2 residual
Restricted access area irrigation Agricultural reuse - food crops (not commercially processed) -Non-food crops Industrial reuse once-through cooling	• pH=6-9 • $\leq$ 30mg/L BOD • $\leq$ 30mg/L TSS • 200 fecal coli/100ml • 1mg/L Cl2 residual
Landscape impoundments Construction use	• $\leq$ 30mg/L BOD • $\leq$ 30mg/L TSS • 200 fecal coli/100ml • 1mg/L Cl_2 residual
Industrial reuse-cooling towers	• pH=6-9 • $\leq$ 30mg/L BOD • $\leq$ 30mg/L TSS • 200 fecal coli/100ml • 1mg/L Cl2 residual
Environmental reuse	• $\leq$ 30mg/L BOD • $\leq$ 30mg/L TSS • 200 fecal coli/100ml
Indirect potable reuse	• pH=6.5-8.5 • $\leq$ 2 NTU • No detectable fecal coli/100ml • 1mg/L Cl_2 residual • $\leq$ 3 mg/L TOC • Meet drinking water standards

2.3.2   U.S. EPA water reuse guidelines

U.S. Environmental Protection Agency (EPA) Guidelines for Water Reuse was first developed in 1980 and updated in 1992 and 2004. The guidelines cover water reclamation

for nonpotable urban, industrial, and agricultural reuse, as well as augmentation of potable water supplies through indirect reuse. Table 2.4 presents suggested guidelines by U.S. EPA for various water reuses.

2.3.3 California Title 22

In the U.S., there are no federal regulations directly governing water reuse practices. Water reuse regulations have been developed by many individual states. Among these states, California Department of Health Services (CDHS) compiled comprehensive regulations named "Title 22" (CDHS, 2008) based on inventories of reuse projects. This regulation mainly suggests microorganism index concentration in product water or removal rate by water reclamation processes for various water reuses. These information are summarized in Table 2.5.

Table 2.5   California Title 22 water reuse guidelines (CDHS, 2008)

a)   Use of recycled water for irrigation

Types of reuse	Reclaimed water quality
• Food crops, including all edible root crops • Parks and playgrounds • School yards • Residential landscaping • Unrestricted access golf courses	Disinfected tertiary recycled water • The wastewater is filtered before disinfection • 5 log F-specific bacteriophage MS2 removal rate • Total coliform bacteria ≤ 2.2/100ml
• Food crops, where the edible portion is produced above ground and not contacted by the recycled water	Disinfected secondary-2.2 recycled water • Total coliform bacteria≤ 2.2/100ml
• Cemeteries • Freeway landscaping • Restricted access golf courses • Ornamental nursery stock and sod farms where access by the general public is not restricted • Pasture for animals producing milk for human consumption • Any nonedible vegetation where access is controlled	Disinfected secondary-23 recycled water • Total coliform bacteria≤ 23/100ml
• Orchards, Vineyards where the recycled water does not come into contact with the edible portion of the crop • Non food-bearing trees • Fodder and fiber crops and pasture for animals not producing milk for human consumption • Seed crops not eated by humans • Food crops that must undergo commercial pathogen-destroying processing before being consumed by humans • Ornamental nursery stock and sod farms provided no irrigation with recycled water occurs for a period of 14 days prior to harvesting	Undisinfected secondary recycled water

b) Use of recycled water for impoundments

Types of reuse	Reclaimed water quality
Nonrestricted recreational impoundments	Disinfected tertiary recycled water *The wastewater is filtered before disinfection* *5 log F-specific bacteriophage MS2 removal rate* *Total coliform bacteria ≤ 2.2/100ml*
Restricted recreational impoundments	Disinfected secondary-2.2 recycled water *Total coliform bacteria≤ 2.2/100ml*
Landscape impoundments that do not utilize decorative fountains	Disinfected secondary-23 recycled water *Total coliform bacteria≤ 23/100ml*

c) Use of recycled water for cooling

Types of reuse	Reclaimed water quality
Industrial or commercial cooling or air conditioning that involves the use of any mechanism that creates a mist	Disinfected tertiary recycled water *The wastewater is filtered before disinfection* *5 log F-specific bacteriophage MS2 removal rate* *Total coliform bacteria ≤ 2.2/100ml*
Industrial or commercial cooling or air conditioning that does not involves the use of any mechanism that creates a mist	Disinfected secondary-23 recycled water *Total coliform bacteria≤ 23/100ml*

d) Use of recycled water for other purposes

Types of reuse	Reclaimed water quality
Flushing toilets and urinals Priming drain traps Industrial process water that may come into contact with workers Structural fire fighting Decorative fountains Commercial laundries Consolidation of backfill around potable water pipelines Artificial snow making for commercial outdoor use Commercial car washes	Disinfected tertiary recycled water *The wastewater is filtered before disinfection* *5 log F-specific bacteriophage MS2 removal rate* *Total coliform bacteria ≤ 2.2/100ml*
Industrial boiler feed Nonstructural fire fighting Backfill consolidation around nonpotable piping Solid compaction Mixing concrete Dust control on roads and streets Cleaning roads, sidewalks and outdoor work areas Industrial process water that will not come into contact with workers	Disinfected secondary-23 recycled water *Total coliform bacteria≤ 23/100ml*
Flushing sanitary sewers	Undisinfected secondary recycled water

2.3.4 Water reuse regulations in Australia

In Australia, the Environment Protection and Heritage Council, the Natural Resource Management Ministerial Council, and the National Health and Medical Research

Council have developed several guidelines for the safe use of recycled water. The guidelines include:

1. Australian Guidelines for Water Recycling: Managing Health and Environmental Risks (Phase 1). Sewage Effluent and Greywater

2. Australian Guidelines for Water Recycling: Managing Health and Environmental Risks (Phase 2): Augmentation of Drinking Water Supplies

3. Australian Guidelines for Water Recycling: Managing Health and Environmental Risks (Phase 2): Stormwater Harvesting and Reuse

4. Australian Guidelines for Water Recycling: Managing Health and Environmental Risks (Phase 2): Managed Aquifer Recharge

"Australian Guidelines for Water Recycling: Managing Health and Environmental Risks (Phase 1) Sewage Effluent and Greywater" provides a generic framework for management of recycled water quality and use. It provides specific guidance on the use of treated sewage and grey water for purposes other than drinkin. In this guideline, human health-based targets for pathogenic microorganisms and chemicals are comprehensively established. The log reductions for pathogen needed to meet the requirement are calculated based on the tolerable risk of 10^{-6} DALYs. Table 2.6 shows health-based targets, which are calculated based on the 95th percentiles of pathogen concentrations in raw sewage.

Table 2.6   Microbial health-based targets for recycling from treated sewage (NRMMC et al., 2006)

			Health-based target (DALY per person per year)[a]	Log reduction		
				Cryptosporidium[a]	Rotavirus[b]	Campylobacter[c]
Irrigation for commercial food crops			<10^{-6}	4.8	6.1	5.0
Dual reticulation	Garden irrigation		<10^{-6}	4.4	5.8	4.6
	Garden food crops		<10^{-6}	4.0	5.3	4.2
	Internal uses	Toilet flushing	<10^{-6}	3.1	4.5	3.3
		Washing machine	<10^{-6}	2.1	3.5	2.3
		Cross-connections	<10^{-6}	4.7	6.1	4.8
	Total internal use (no garden use)		<10^{-6}	4.7	6.1	4.8
	Total residential use (garden plus internal)		<10^{-6}	4.9	6.3	5.1
Municipal irrigation			<10^{-6}	3.7	5.2	4.0
Dual reticulation plus municipal irrigation			<10^{-6}	5.0	6.4	5.1
Fire fighting			<10^{-6}	5.1	6.5	5.3

a Cryptosporidium was chosen as indicator for bacteria
b Rotavirus was chosen as indicator for viruses
c Campylobacter was chosen as indicator for protozoa and helminths

For chemical hazards, 2004 Australian Drinking Water Guidelines (NHMAR et al., 2004) are used to assess potential health risks. Based on preliminary calculation, nine environmental hazards are identified as priorities for assessing the risk associated with specific recycled water usage (e.g. agricultural, municipal, residential, and fire control). The nine hazards are boron, cadmium, chlorine disinfection residuals, hydraulic loading, nitrogen, phosphorus, salinity, chloride and sodium.

"Australian Guidelines for Water Recycling: Managing Health and Environmental Risks (Phase 2):Augmentation of Drinking Water Supplies"(NRMMC et al., 2008) extends the guidance to the augmentation of drinking water supplies. The "Australian Guidelines for Water Recycling: Managing Health and Environmental Risks (Phase 2): Stormwater Harvesting and Reuse"(NRMMC et al., 2009b) extends the guidance to cove the harvest and reuse of stormwater. The "Australian Guidelines for Water Recycling: Managing Health and Environmental Risks (Phase 2): Managed Aquifer Recharge"(NRMMC et al., 2009a) focuses primarily on the protection of aquifers and the quality of recovered water in

managed aquifer recharge projects using various water sources, including recycled water. All these three guidelines were compiled based on general principles described in Phase 1 guidelines (NRMMC et al., 2006).

2.3.5   Water reuse standards in Japan

In Japan, The Ministry of Land, Infrastructure, Transport and Tourism (MLITT) compiled "Manual for Water Reclamation and Reclaimed Water Quality Standard" in 2005. General principles, such as microorganism safety, pleasant appearance and process reliability were considered in this standard. The reclaimed water qualities requirements are summarized in Table 2.7.

Table 2.7   Water reuse standard in Japan (MLITT, 2005)

Items	Washing	Landscape irrigation	Impoundments	Recreational water
E. Coli	No detected/100ml	No detected/100ml	≤1000CFU/100mL	No detected/100ml
Turbidity	<2 NTU	<2 NTU	<2 NTU	<2 NTU
pH	5.8-8.6	5.8-8.6	5.8-8.6	5.8-8.6
Appearance	Not discomfort	Not discomfort	Not discomfort	Not discomfort
Color	-[a]	-[a]	<40	<10
Odor	Not discomfort	Not discomfort	Not discomfort	Not discomfort
Residual chlorine	<0.1mg/L	<0.1mg/L	No restriction	<0.1mg/L

a: data will be set by consumers

2.3.6   Water reuse standards in China

In order to alleviate water pollution, save water and rational and sustainable utilize of water resource, Ministry of Housing and Urban-Rural Development of the People's Republic of China (MOHURD) compiled serial standards for water reclamation, containing:

1. The reuse of urban recycling water: Classified standard (GB/T 18919-2002)
2. Reuse of recycling water for urban: Water quality standard for urban miscellaneous water consumption (GB/T 18920-2002)
3. The reuse of urban recycling water: Water quality standard for scenic environment use (GB/T 18921-2002)

4. The reuse of urban recycling water: Water quality standard for groundwater recharge (GB/T 19772-2005)

5. The reuse of urban recycling water: Water quality standard for industrial uses (GB/T 19923-2005)

6. The reuse of urban recycling water: Water quality standard for farmland irrigation (GB/T 20922-2007)

7. The reuse of urban recycling water: Water quality standard for green space irrigation (GB/T 25499-2008)

Based on these standards, the Ministry of Water Resources of the People's Republic of China (MWR) developed " Standards of Reclaimed Water Quality" (MWR, 2007)in 2006, which is listed in table 2.8.

Table 2.8   Water reuse standard in China (MWR, 2007)

a)   Use of recycled water for urban reuse

Unit: mg/L

Items	Toilet flushing	Cleaning roads, Fire fighting, Construction	Landscape irrigation	Car wash
Basic requirement [a]	Yes	Yes	Yes	Yes
DO$\geq$	1.0	1.0	1.0	1.0
SS$\leq$	10	5	10	5
BOD5$\leq$	10	15	20	10
TDS$\leq$	1500	1500	1500	1000
LAS$\leq$	1.0	1.0	1.0	0.5
Fe$\leq$	0.3	0.3	0.3	0.3
Mn$\leq$	0.1	0.1	0.1	0.1

b) Use of recycled water for agricultural using

Unit: mg/L

Items	Farm irrigation	Forestation irrigation	Pasture irrigation	Aquaculture
Basic requirement [a]	Yes [b]	Yes [b]	Yes [b]	Yes [b]
DO≥	1.0	1.0	1.0	1.0
SS≤	30	30	30	30
BOD$_5$≤	80	150	5	5
TDS≤	1000	1000	1000	1000
NH4-N≤	10.0	20.0	5.0	5.0
TP≤	1.0	1.0	0.5	0.5
Hg≤	0.001	0.001	0.0005	0.0005
Cd≤	0.005	0.005	0.005	0.005
As≤	0.05	0.10	0.05	0.05
Cr≤	0.10	0.10	0.10	0.10
Pb≤	0.10	0.10	0.05	0.05
CN≤	0.05	0.05	0.005	0.005

c) Use of recycled water for landscape using

Unit: mg/L

Items	Ornamental landscape using		Recreational landscape using		Wetland
	River	Lake	River	Lake	
Basic requirement [a]	Yes [b]	Yes [b]	Yes [b]	Yes [b]	Yes
DO≥	1.0	1.0	2.0	2.0	1.0
SS≤	20	10	20	10	10
BOD5≤	10	6	6	6	6
LAS≤	0.3	0.3	0.3	0.3	0.3
NH4-N≤	5.0	5.0	5.0	5.0	5.0
TP≤	0.5	0.5	0.5	0.5	0.5
petroleum-related pollutants≤	1.0	1.0	1.0	1.0	1.0

d) Use of recycled water for aquifer recharge

Unit: mg/L

Items	Basic requirement a	DO≥	BOD$_5$≤	TDS≤	Hg≤	Cd≤	As≤	Cr≤	Pb≤	CN≤
	Yes	1.0	10	1000	0.001	0.005	0.05	0.05	0.01	0.05

a: Color≤30, Turbidity≤3 NTU, Odor: Not discomfort, Ph:6.5-9.0, Total hardness (mgCaCO3/L) ≤450, Total coliform≤3 CFU/L

b: meet the requirement

2.4   Introduction of treatments for water reclamation application

In order to ensure the safety of reclaimed water, it is critical to meet water quality requirements as described in 2.3. Different technologies are utilized, either singly or in combination, to achieve desired levels of constituent removal. Figure 2.3 shows the matrix of alternative treatment processes that have been applied in wastewater reclamation and reuse field.
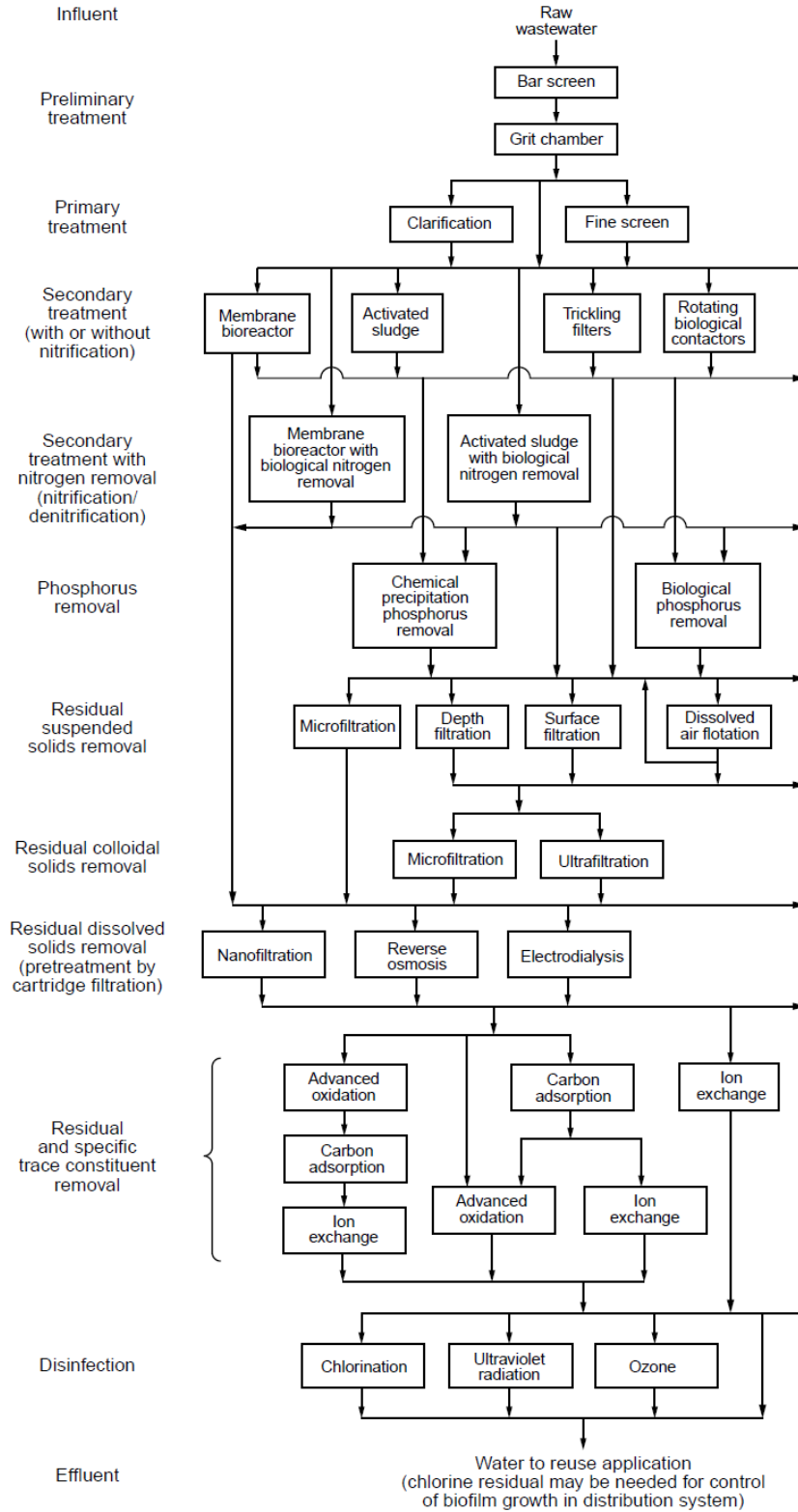
Figure 2.2   Matrix of alternative treatment processes that have been applied in wastewater reclamation (Asano et al., 2007)

2.4.2   Secondary treatments

Secondary treatments are processes aimed for the removal of biodegradable organic matter (in solution or suspension) and suspended solids. Disinfection is typically included in the definition of conventional secondary treatment. (Asano et al., 2007) The common secondary treatments used are conventional activated sludge and membrane bioreactor.

2.4.2.1   Conventional activated sludge

Activated sludge processes are used to grow biomass of aerobic organisms that can breakdown and convert wastes into slugs. Conventional activated sludge has aeration basin detention time of 4-6 hours. During this time, the microorganisms will completely stabilize the BOD before the mixed liquor leaves the basins. The advantages of using conventional activated sludge reactor are listed as follows: 1) The technology is well understood; 2) Skilled operation and maintenance personnel are widely available; 3) Large wastewater treatment facilities make use of conventional activated sludge, with plant capacities exceeding 2.5×10^6 m^3/d. At the same time, several disadvantages are shown: 1) Limitations in suspended solids removal resulting in a high level of disinfection dose; 2) Greater sludge production increases biosolids handling requirements and costs; 3) Large process footprint is needed.

2.4.2.2   Membrane bioreactor

Membrane bioreactor (MBR) is the combination of a membrane process with a suspended growth bioreactor. It is currently widely used in municipal and industrial wastewater treatment plant with a capacity up to 40,000m^3/d. The membranes have porosities range between micro and ultra filtration, from 0.04 microns to 0.4 microns (depending on the manufacturer). The product water is low in BOD, TSS, turbidity and bacteria, which is similar to effluent from secondary clarification followed by MF. The advantages of using membrane bioreactor are: 1) High water quality with greater reuse potential; 2) Low suspended solids concentration in water enables effective disinfection; 3) Reduced footprint; 4) Modular construction allows future expansion; 5) Process is relatively easy to automate. The disadvantages compared with conventional activated sludge are: 1) Pretreatment is required to avoid damages and clogging of membrane

elements; 2) Greater consumption of energy for effective operation; 3) Mechanisms and control of membrane fouling still under investigation; 4) Membrane replacement is relatively expensive; 5) Smaller capacity.

2.4.3 Tertiary and advanced treatments

Tertiary and advanced treatments are aim at the removal of residual suspended solids, dissolved constituents, and pathogen after secondary treatment (Asano et al., 2007). Table 2.9 summarizes some features, product water quality and disadvantages of several commonly utilized tertiary and advanced treatments.

Table 2.9   Features of each tertiary and advanced treatment

Contaminants removed	Technologies	Features	Product water qualities	Disadvantages
Particulate matter	Depth filtration	*The most common method* *A pretreatment step for membrane filtration* *A conditioning step for effective disinfection*	Turbidity: 0.3-4.0 NTU Removal rate of coliform bacteria: 0-1.0 logs Removal rate of viruses: 0-0.5 logs	*Poor product water qualities* *Performance changed greatly with influent water quality changing* *Loss of filter medium or media* *Development of cracks and contraction of the filter bed* *Backwashing water treatment*
	Surface filtration	*Specific refer to cloth-medium surface filtration with pore size from 10 to 30 μm*	Turbidity: 0.5-2.0 NTU Removal rate of coliform bacteria: 0-1.0 logs Removal rate of viruses: 0-0.5 logs	*Poor product water qualities* *Little data are available on the life of the filter cloth* *Backwashing water treatment*
	Membrane filtration	*Categories:* *Microfiltration (MF)* *Ultrafiltration (UF)*	Turbidity: <1.0 NTU Removal rate of coliform: 2->5logs for MF; 3->6logs for UF Removal rate of viruses: 0-2logs of MF; 2-7logs for UF	*Pretreatments are needed to mitigate fouling* *Low rejection of small molecular size pollutants, such as pharmaceuticals and personal care products (PPCPs), Endocrine disrupting compounds (EDCs)* *Low rejection of viruses using large pore size membrane* *Backwashing water treatment*
	Dissolved air flotation	*Removing oil, grease and algae* *Thickening of waste-activated sludge*	Turbidity: 0.5-2.0 NTU Efficient for separating low density floc particles	*Flotation is very dependent on the type of surface of the particulate matter* *Poor at process reliability when influent solids concentration changes greatly*

Table 2.8 Features of each tertiary and advanced treatments (continued)

Dissolved constituents	Membrane filtration	*Categories* *Nanofiltration (NF)* *Reverse osmosis (RO)* *Electrodialysis (ED)*	Removal rate of coliform: 3-6logs for NF; 4-7logs for RO Removal rate of viruses: 3-5logs for NF; 4-7 logs for RO TOC rejection: 90-98% for NF and RO ED mainly is used to separate charged species	*High energy consumption: 0.6-1.2 kWh/m3 for NF; 1.5-2.5 kWh/m3 for RO; 1.5-2.6 kWh/m3 for ED* *Membrane fouling is severe without suitable pretreatment* *Retentate should be treated further*
	Adsorption	*Removing substances in solution by accumulating them on a solid phase*	Removal of organic constituents, inorganic constituents and odor compounds Removal rate depends on characteristics of adsorbates and adsorbents	*Depression of adsorptive capacity by some other compounds* *Regeneration is necessary* *Certain adsorptive capacity is lost in the regeneration process* *High media replacement costs* *In general, regenerated adsorbent is not used in reclaimed water applications because of the potential for the potential for residual constituents, not removed in the regeneration process*
	Ion exchange	*Removal of specified ionic constituents* *Domestic water softening* *Demineralization*	Only charged species could be removed	*Impacted severely by particulate and colloidal matter, solvents and organic polymers. Pretreatment is required to remove such constituents.* *Regeneration is necessary* *Brine should be managed properly* *High media replacement costs*

Table 2.8 Features of each tertiary and advanced treatments (continued)

Dissolved constituents	Distillation	*Limited to applications* • *A high degree of treatment is required* • *Contaminants cannot be removed by other methods* • *Inexpensive heat is available*	• High water qualities	• *Expensive, minimum energy required is about 2280 kJ/kg water* • *Carryover of volatile constituents found in treated reclaimed water* • *Concentrated waste stream should be managed* • *Scaling and corrosion problems, suitable controlling method is needed*
	Chemical oxidation	• *Odor, hydrogen sulfide control* • *Color, iron and manganese removal* • *Control of biofilm or biofouling* • *Oxidation of selected trace organic constituents* • *Disinfection*	• Selective oxidation • Most of Emerging contaminants could be removed	• *Expense of chemical addition* • *Incomplete mineralization* • *Potential for the formation of toxic byproducts* • *Increasing the biodegradability of some constituents* •
	Advanced oxidation	• *Oxidation of refractory organic compounds* • *Reaction rate is three to four orders of magnitude greater than other oxidants* • *Disinfection*	• Nonselective oxidation • Mineralization	• *Suitable to low COD reclaimed waters* • *H_2O_2 residual should be managed* • *Fouling of the catalyst may occur* • *Byproducts such as halogenated acetic acid, carboxylic acids* • *Scavengers problem*

Table 2.8 Features of each tertiary and advanced treatments (continued)

Dissolved constituents	Photolysis	• *Removal of trace organic constituents* • *Disinfection*	• The effectiveness depends on the characteristics of the reclaimed water, structure of the compounds, design of the reactor, dose and wavelength of the light.	• *Special reactors which are designed for UV illumination are required* • *High energy consumption especially for UV using* • *Fouling occur on the outside of the protective quartz sleeve*
	Advanced biological transformations	• *Further removal of refractory organic compounds* • *Biological activated carbon* • *Membrane biofilm reactor*	• Effective in removal of DBPs • Effective removal of refractory through specific organisms accumulation	• *Organisms growing on the carbon are sensitive to water quality* • *Carbon replacement is expensive*
Pathogens	Chlorine	• *One used most commonly throughout the world for Disinfection* •	• Excellent for bacteria removal • Poor for protozoa removal • Excellent for viruses removal	• *Forming DBPs* • *Increasing TDS concentration* • *Acid generation* • *Serious odor problems during breakpoint-chlorination* • *Long contact time(30-120min)* • *Residual chlorine needs dechlorination on certain cases*
	Chlorine dioxide	• *Effective disinfectant not influenced by pH*	• Disinfection efficiency • For bacteria and viruses, similar as chlorine • For protozoa, more effective than free chlorine • Not react with ammonia to form DBPs	• *Formation of chloroform (a suspected carcinogenic substance)*

Table 2.8 Features of each tertiary and advanced treatments (continued)

Pathogens	Ozone	• *Effective disinfectant* • *Shorter contact time than chlorine* • *Small footprint*	Disinfection efficiency • Excellent for bacteria removal • For protozoa, more effective than free chlorine • For viruses, more effective than free chlorine Not form chlorinated DBPs	• *Formation of DBPs, including aldehydes, various acids, and bromate* • *No residual effect*
	Peracetic acid	*Starting to use as reclaimed water disinfectant for safety*	• Absence of persistence residuals and byproducts • Not affected by pH, short contact time • High effectiveness as a bactericide and virucide	• *increasing organic content in the effluent due to acetic acid* • *Potential microbial regrowth* • *High cost*
	Ultraviolet radiation	• *Effective disinfectant* • *Requires no hazardous chemicals*	• More effective than chlorine in inactivating most viruses, spores and cyts • No formation of DBPs • Effective in the destruction of NDMA	• *No residual effect* • *High energy consumption* • *Special reactors which are designed for UV illumination are required* • *Fouling occur on the outside of the protective quartz sleeve*

2.4.4　Current situations

The use of recycled water is popular in countries with high water stress. Quality and economic aspects have to be taken into consideration when choosing suitable processes. Most of water reclamation technologies have biological treatment (treating sewage), a solid-liquid separation step (treating biological treated effluent) as pretreatment, which is then followed by a disinfection step as post treatment (Li et al., 2009). Table 2.10 summarizes some water reclamation researches.

Among various solid-liquid separation technologies, membrane processes are regarded as key elements of advanced wastewater reclamation and reuse schemes. They are implemented in a number of prominent schemes world-wide, including artificial groundwater recharge, indirect potable reuse, as well as industrial process water production (Wintgens et al., 2005). For the sewage, MBR is one of the common practical processes used (Jacob et al., 2012; Joss et al., 2011). As a straight combination of biological treatment processes and biomass retention by MF or UF membranes, merits of both processes are present in MBR. The product water is low in organic matters, particle matters, and bacteria content. For effluent from wastewater treatment plant (WWTP), treatment train that incorporate membrane filtration (MF, UF, NF, RO, et al.) and suitable pretreatment is capable of producing reclaimed water for a range of water reuse applications (Arnaldos et al., 2010; Lozier et al., 2010; Yangali-Quintanilla et al., 2010).

For pathogen disinfection, chlorination still remains as the most widely used technology. But recently, advanced oxidation attracts many attentions for effective control toxicity of chlorination DBPs (Cho et al., 2005; Gehr et al., 2003; Guo et al., 2012; Lim, M. Y. et al., 2009; Patil et al., 2009). Meanwhile, trace constituents and emerging contaminants can be removed to a safe level by using such advanced oxiation (Snyder et al., 2006).

Table 2.10   Summary of some water reclamation researches

Contaminants removed	Raw water	Technologies	Product water quality	Purpose	Country	References
SS, TN, TP,	*Sewage*	Conventional activated sludge (CAS)+MF/UF; MBR(MF/UF)	*SS below detection limit; Microbial pathogens were nearly totally rejected; TN=3-10mg/L (MBR); higher in case of CAS+MF/UF TP=0.1 mg/L (MBR); TP=0.2 mg/L (CAS+MF/UF)*	Irrigation	*Canada*	(Pierre et al., 2004)
Pharmaceuticals	*Sewage*	MBR+RO	*All the 15 pharmaceuticals measured in the influent municipal sewage were retained below 100 ng/L*	Potable or high quality industrial reuse	*Switzerland*	(Joss et al., 2011)
Pesticides, polycyclic aromatic hydrocarbons (PAHs), metals and micro-organisms	*Sewage*	MBR+NF/RO	*For pesticides, the RO membrane showed high retention for most of the molecules tested; NF membrane exhibited some variation in the retention of pesticides. PAHs and micro-organisms was completely rejected by RO and NF*	Indirect potable reuse	*France*	(Jacob et al., 2012)
Organics, Bacteria	*Sewage*	Upflow anaerobic sludge bed (UASB) reactor followed by flash aeration	*BOD and COD values of 28-35 and 50-58 mg/L, respectively Sulfides were removed by more than 80% Fecal coliforms were removed 2 logs*	Agriculture irrigation	*India*	(Khan et al., 2012)
SS, Pathogen	*Sewage*	O_3+Coagulation,Sedimentation+O_3+Chlorine	*Turbidity: 10 NTU No Fecal coliforms/100mL 1-3 Helminth eggs/L Reducing the formation of DBPs*	Irrigation	*Mexico*	(Campos-Reales-Pineda et al., 2008)
Organic, SS, TP, ammonium	*Sewage*	Enhanced primary treatment (CEPT)+trickling filter (TF)+UF	*95 and 88% removal of COD and ammonium were achieved TP and SS were removed completely*	Urban use	*China*	(Zhao et al., 2012)
Organics, SS	*Sewage*	Coagulation($FeCl_3$)-adsorption(powder activated carbon)-UF	*COD=7-13mg/L Turbidity<0.5NTU*	Not clear	*Algeria*	(Abdessemed et al., 2000; Abdessemed et al., 2003)

Table 2.9   Summary of some water reclamation researches (continued)

Bacteria, DOC, COD, SS	*Synthetic greywater (SGW)*	NF (AFC30, AFC40, AFC80)	*No Faecal coliforms ,Enterococcus were detected* *Removal rate of DOC was 48-92%;* *Removal rate of COD was 60-95%* *Removal rate of a-surfactants was54-90%* *Removal rates of SS, turbidity were100%*	Reuse in buildings.	*France*	(Hourlier et al., 2010)
Turbidity, TOC, COD	*Wastewater from hotel (not containing toilet flushing wastewater)*	Fine-screen + Ceramic membrane filtration (MF-0.1μm, UF-300kDa)	*Rejection rate of TOC was 53.7% (MF), 61.4% (UF)* *Rejection rate of COD was 88.7% (MF); 86.7%(UF)* *Rejection rate of turbidity was 100% (MF); 97.1% (UF)*	Toilet flushing	*South Korea*	(Ahn et al., 1998)
TN, TP, Emerging contaminants	*Municipal WWTP effluent*	Filtration using "One Step Total Effluent Polishing filter"	*TN≈2.2mg/L; TP≈0.15mg/L;* *Removal of Metoprolol was21-82%;* *Removal of Azitromycine was 9-30%;* *Removal of Carbamazepine was 9-50%;* *Removal of Clarthomycine was 9-65%;* *Removal of Lidocaine was 18-74%*	Not clear	*The Netherlands*	(Scherrenberg et al., 2010)
Pharmaceutical	*Municipal WWTP effluent*	NF+O3 O3+NF	*The overall removal rate of pharmaceutical residuals was 99%.*	Indirect potable reuse	*Sweden*	(Flyborg et al., 2010)
TN, TP	*Municipal WWTP effluent*	Enhanced coagulation + MF	*TN=0.3 mg /L* *TP=0.25 mg /L*	Not clear	*USA*	(Arnaldos et al., 2010)
DOC, TN	*Municipal WWTP effluent*	Biological Activated Carbon	*Removal rate of DOC was 37.8-45.9%* *Removal rate of TN was 51.5-54.0%*	Not clear	*Turkey*	(Kalkan et al., 2011)
Pharmaceuticals pesticides, endocrine disruptors and other organic contaminants.	*Synthetic wastewater*	NF, RO	*Removal rate of neutral compounds was about 82% and 85% for NF and RO, respectively* *Removal rate of ionic compounds was about 97% and 99% for NF and RO, respectively*	Not clear	*The Netherlands*	(Yangali-Quintanilla et al., 2010)
Organics and sulphates,	*Effluents of the paper mill*	Clarification + anaerobic and aerobic treatments + UF + RO	*TN:4-12mg/L* *TP: 0.00mg/L* *COD: 0.00mg/L* *SO4:3-5mg/L*	Reused in paper mill	*Spain*	(Ordóñez et al., 2010)

Table 2.9   Summary of some water reclamation researches (continued)

Organics, SS, Pathogen	*WWTP effluent*	MF+RO+UV	*Product water meet Title 22 Recycled Water Criteria for groundwater recharge*	Indirect potable reuse	*USA*	*(Lozier et al., 2010)*
Organics, SS, pathogen	*WWTP effluent*	Sandfiltration + peracetic acid + UV	*No Escherichia coli were detected No Total Coliforms were detected Product water fulfill Italian regulation for wastewater irrigation reuse*	Irrigation	*Italy*	*(Gori et al., 2004)*
Pathogen	*WWTP effluent*	Combination of chlorine and UV	*Totally inactivation was achieved for indicator microorganisms (E. coli or somatic coliphages) Effective inactivation of infectious Cryptosporidium spp oocysts and enteroviruses*	Urban reuse and irrigation	*Spain*	*(Montemayor et al., 2008)*
Organic, SS, TP, ammonium	*WWTP effluent*	Rapid Filtration Horizontal subsurface flow bed Rapid Filtration+Horizontal subsurface flow bed Rapid Filtration+Horizontal subsurface flow bed+ Lagooning, Chlorination+ Horizontal subsurface flow bed	*Product water from process 4 and 5 fulfill the Italian direct reuse regulations*	Irrigation and recreation	*Italy*	*(Verlicchi et al., 2012)*
Organics	*WWTP effluent*	O$_3$ + slow sand filtration (SSF) + NF	*Low DOC concentration: 0.6 ±0.2 mg/ L Low THMFP :44 ±4μg/L*	Artificial groundwater recharge	*China*	*(Linlin et al., 2011)*
Organics, bacteria, SS	*WWTP effluent*	Coagulation–flocculation +sedimentation + sandfiltration + UV–radiation Sandfiltration + UV–radiation Ultrafiltration	*Fecal coliform concentration: For Process 1: 9/100mL For process 2: 200/100mL For process 3: 0/100mL*	Irrigation	*Spain*	*(Illueca-Munoz et al., 2008)*
Organic, SS, bacteria	*WWTP effluent*	Immersed-type crossflow microfiltration (IMF)+RO	*Product water meet the requirements of both WHO drinking water standards*	Industrial application	*Malaysia*	*(Ujang et al., 2007)*

2.5   Selection target contaminants

The number and variety of contaminants that may be present in wastewater are considerable. It is impossible or impractical to study the removal of every pollutant during research. Thus, based on their occurrence in wastewater, potential risk of each contaminant, target water quality indexes are selected.

2.5.1   Common water quality indexes

Suspended Solid (SS) and Turbidity are selected to represent particulate matters. The aggregated constituents COD_{Mn} and TOC are used for organic matters characterization. Nutrients, total nitrogen (TN) and total Phosphorus (TP), should be considered for eutrophication control. Beside these indicators, color and pH are also included in the target list.

2.5.2   Pathogen indicators

Microorganisms associated with water borne disease are primarily enteric pathogens, including enteric bacteria, protozoa, and viruses. Pathogen risk is of highest concern in water reclamation and reuse. Several limitations in direct measurement of pathogens make it necessary to select suitable pathogen indicators. An ideal indicator organism should have the following characteristics (Asano et al., 2007):

1. Present in the in the intestinal tract of warm-blooded animals
2. Founded in a much higher concentrations than most pathogens in fecal material
3. Same or greater survival characteristics in the treatment processes and the environment
4. Non-pathogenic
5. Easy to detect
6. Relatively fast and inexpensive analysis

Based on comprehensive consideration of these features and targets in water reuse guidelines, total coliform, *E. coli* and bacteriophage MS2 are selected as pathogen targets in this research.

2.5.3 Target emerging contaminants

The term "emerging contaminants" encompasses a wide range of compounds that have been identified only recently and are under consideration to be regulated. Emerging contaminants (EC) includes a wide array of different compounds (as well as metabolites and transformation products- collectively referred to as degradates) including; pharmaceuticals and personal care products (PPCPs), pesticides, veterinary products, industrial compounds/by-products, food additives, as well as engineered nanomaterials (Lapworth et al., 2012). Because of the vast array of possible compounds, it is necessary to select suitable target compounds as indicator to represent the fate of other emerging contaminants during water reclamation treatment. To be an indicator, the compounds are desired to have following features:

1. Analytical methods with sufficient detection limits
2. Wildly observed in wastewater
3. Various characteristics: such as polarity, hydrophobicity, acid dissociation constant (pKa), molecular structure, and size. All of these factors affect the removal rate during biological treatment, physical, and chemical treatment.

PPCPs are selected to represent EC in this research since they are good indicator and show potential threat to aquatic ecosystems and human health (Bowman et al., 2011; Daughton et al., 1999; DeLorenzo et al., 2007; Hirsch et al., 1999; Jones, O. A. H. et al., 2001; Kidd et al., 2007; Oberlé et al., 2012; Thorpe et al., 2009; Vajda et al., 2008). Some PPCPs are already included in contaminants candidate list (CCL) 3, which means they may be regulated under the Safe Drinking Water Act (SDWA). Thus, the study on the fate of PPCPs during water reclamation processes will be beneficial to chemical risk control in reclaimed water.

2.6 Selection target processes

As discussed in section 2.4, many treatments can be used or being used in the water reclamation field. Processes are selected based on comprehensive consideration of product water quality and energy consumption, which are described in this section in details.

2.6.1 Ceramic Microfiltration membrane treatment

As mentioned in section 2.4.3, membrane filtration is regarded as the key element of advanced wastewater reclamation and reuse treatment, especially low-pressure membrane processes that have several advantages: effective removal of particulate and microbial contaminants, low energy consumption, and small footprint (Wintgens et al., 2005). Low-pressure membrane includes microfiltration (MF) membranes and ultrafiltration (UF) membranes. MF membranes have the largest pores (0.1 μm to 10 μm) and the highest permeability, so that a sufficient water flux is obtained at a low pressure. UF membranes have smaller pores (0.022 to 0.1μm) and the permeability is considerably lower than MF membranes, therefore higher pressures are needed. Low-pressure membrane is usually utilized in "semi dead-end" mode. This approach can be described by alternating raw water filtration cycles with back-wash cycles (with permeate for membrane rinsing) (Van der Bruggen et al., 2003).

In addition, membranes employed in water treatment can be classified as organic membrane and ceramic membrane. Compared to organic membrane, ceramic membrane has many advantages, such as relatively high permeability, thermal and physical stability, and antifouling potential. Besides, ceramic membrane makes it possible to incorporate other processes, such as oxidation. Several researches have reported that the incorporation of chemical treatment as a pretreatment step with ceramic membranes greatly mitigates fouling by organic matters (Karnik et al., 2005a; Kumar et al., 2008; Lehman et al., 2009; Lim, G. T. et al., 2009; Shirasaki et al., 2009a; Zhang et al., 2009) . Thus, ceramic microfiltration membrane (CM) with 0.1μm pore size is selected in this study.

2.6.1.1 Contaminants removal

Several researchers are investigating the applicability of different types of ceramic filters and their performance in removing different contaminants. Removal of particulate matters by various CM was reported by several authors to be greater than 99% (Aidan, Ahmed et al., 2007; Aidan, A. et al., 2007; Ellouze et al., 2005; Khemakhem et al., 2009).

Aiden et al.(Aidan, Ahmed et al., 2007) reported >4 log removal of *total coliform*s in membrane bioreactor, using a 0.20μm ceramic membrane. Ciora and Liu (Ciora et al., 2003) reported that >3.0 log removal of MS2 bacteriophage was attained during their study. Zhang et al.

(Zhang et al., 2009) found that the successful removal of *Escherichia coli* could be achieved using titanate nanotube membrane. Bendick et al.(Bendick et al., 2005) conducted a pilot scale investigation for approximately 12 months to evaluate the feasibility of several ceramic membranes with different pores sizes (0.05–1.4 μm) for the treatment of primary sewage effluent simulating combined and sanitary sewer overflows. All the membranes evaluated in this study were able to achieve near complete removal of fecal coliforms, *Escherichia coli*, *enterococci*, independent of the feed concentration.

Viruses generally are 0.005–0.1 μm in diameter, which correspond to the entire range of UF and the smallest pore size of MF. MF membranes alone are not expected to efficiently remove pathogenic waterborne viruses due to their large membrane pore size. Otaki et al.(Otaki et al., 1998) found that the removal ratio by ceramic MF (0.2μm) process of *E. coli* K12 phage (20-30nm) fluctuated between 40-90%, and *E. coli* C phage (hundreds of nm) had only a minor change from 98% to 100%. The removal rate was more than 40% despite the fact that the pore size of membrane was much bigger than the size of phages. It is presumably due to the accumulation of fouling matter on membrane surface. Another possible explanation is the absorption of phages on the suspended solid surface. At the same time, combination of coagulation and MF membrane process was widely investigated by researchers to enhance removal of the contaminants. Matsushita et al.(Matsushita et al., 2005) did comprehensive work using in-line coagulation-ceramic microfiltration hybrid system. Based on their research, the following results were obtained: (1) coagulant dose strongly affected virus removal. Whereas 7.4 log removal was achieved with 1.62 mg Al/L PACl dosing, only 2.8 log removal was observed with 0.54 mg Al/L; thus, the larger the coagulant dose, the greater the virus removal. (2) Pore size of the MF membrane also affected virus removal: pore sizes of 0.5 and 1.0μm showed about 1 log less removal than the 0.1μm pore-size MF membrane. (3) Coagulation time slightly affected virus removal: the longer the coagulation time, the greater the reduction in virus level.

Only several works were done regarding with removal of DBPs. Bottino et al. treated lake water using ceramic membrane composed of $\alpha\text{-}Al_2O_3$ with a mean pore size of 0.2 μm. The average retention of chloroform and dichlorobromomethane is around 56%, and the retention of dibromochloromethane and richloroethylene is 100% (Bottino et al., 2001). Lee et al. found that two ceramic tight-UF membranes with MWCO values of 1000 and 8000 are good candidates for

the removal of DBPs precursors. The removals of haloacetic acid (HAA) formation potential by the two ceramic membranes are about 80% and 60% respectively (Lee et al., 2004).

2.6.1.2   Membrane fouling

Upon filtration of wastewater, ceramic membrane is subjected to the loss of membrane permeability as a result of inorganic, organic and microbiological substances accumulation both on the membrane surface and within the membrane pores. These reduce the efficiency of membrane filtration and ultimately shorten membrane life (Ciston et al., 2008; Kim et al., 2007; Lee et al., 2009). The characteristics of foulants also influence the rejection of other substances (Ciston et al., 2009; Karnik et al., 2005a). To maintain the economic viability of a membrane process, membrane fouling has to be kept at a minimum level.

Pre-treatment prior to microfiltration may be an important option to improve ceramic membrane filtration performance. Several pretreatment methods such as adsorption, coagulation and ozonation have been studied and were found to reduce fouling. The reduction in fouling has been attributed to the modification of colloidal fraction of the organic matter by using flocculants/coagulants, to the entrapment of the organic solutes onto adsorbents by adsorption and to the organic foulant decomposition by $\cdot$OH or other radicals formed at the membrane surface through oxidants (such as ozone) decomposition (Chiu et al., 2006).

2.6.2   Ozonation

Ozone is a powerful oxidant for water and wastewater treatment. It was reported as effective process for color removal, emerging contaminants degradation, and pathogen inactivation (Beltrán, 2005; Hollender et al., 2009; Huber et al., 2003; Hunt et al., 1997; im et al., 2010; Ishida et al., 2008; Wert et al., 2011; Xu et al., 2002; Zimmermann et al., 2011). Besides, ozonation can be used as pretreatment before membrane filtration to reduce membrane fouling (Kim et al., 2008). By incorporating ozonation with CM treatment, high water quality and low energy consumption could be achieved.

2.6.2.1 Contaminants removal

Ozone is a powerful oxidant that preferentially oxidizes electron-rich moieties in carbon–carbon double bonds and aromatic alcohols. Ozone reacts with a great number of organic compounds in two different ways: by direct oxidation as molecular ozone or by indirect reaction through formation of secondary oxidants such as free radical species, in particularly the hydroxyl radicals (OH). Both ozone and hydroxyl radicals are strong oxidants (Beltrán 2005).

During bacteria inactivation by ozone, O_3 firstly attack the bacteria membrane lipid and protein. This alters permeability of membrane rather than inactivation (Komanapalli et al., 1996). Then O_3 penetrate the membrane and react with intracellular proteins and DNA, causing obvious cell viability (Cho et al., 2010; Komanapalli et al., 1996). Von Sonntag also showed that the main target for the inactivation of bacteria was the DNA and not the cell wall (von Sonntag, 1987). While O_3 decomposition product, OH, was scavenged in the cell wall, and their journey into the cell would be hindered by other cell constituents (von Sonntag, 1987). Thus, direct oxidation is the main disinfection pathway for bacteria. It was presented that more than 4 logs E. Coli inactivation could be achieved after 5 seconds for ozone dosages higher than 0.6 mg O_3/L in natural water (van der Helm et al., 2008). It should be noted that dissolved ozone is one of the important parameters to kill bacteria. As a result, ozonation seems not suitable for bacteria disinfection of high organic matter containing sewage, which will result in rapid dissolved ozone consumption. It was reported that only 2 logs fecal coliforms inactivation in the primary effluent was achieved at a transferred ozone dose as high as 30-50 mg/L (Gehr et al., 2003).

Viruses inactivation involves the destruction of protein capsid by ozone or/and OH, loses their ability to invade the host cell (Kim et al., 1980). Bacteriophage was more easily inactivated by ozone than bacterial (Hall et al., 1993). The bacteriophage f2 could be inactivated up to 5 logs at 0.09 mg O_3/L and more than 7 logs at 0.8 mgO_3/L (Kim et al., 1980).

A lot of studies have investigated the degradation of emerging contaminants PPCPs by ozonation. Nearly all antibiotics could be removed easily by ozone since they have fast-reacting functional group, such as tertiary amino groups, thio group or aniline moieties ((Dodd et al., 2006). Ozonation is an effective process to remove such chemicals, although several compounds were reported showing recalcitrant toward ozone, such as ketoprofen, ethenzamide, antipyrine,

DEET, and caffeine (Bros éus et al., 2009; Hollender et al., 2009; Huber et al., 2003; Nakada et al., 2007; Zimmermann et al., 2011).

2.6.2.2   Membrane fouling mitigation

Several researches involving ceramic membranes have been performed to demonstrate that enhanced fluxes and fouling mitigation could be achieved with pretreatment ozonation. Schlichter et al. (Schlichter et al., 2003) found that by adding ozone during microfiltration and ultrafiltration, membrane fouling for all membranes could be drastically reduced for humic acid solutions but not for bentonite solutions. Kim et al. proposed that intermittent ozonation could be an innovative and feasible pattern for incorporating ozonation and ceramic membrane (Kim et al., 2002). In addition, ozonation pretreatment effect on membrane fouling mitigation was also verified by using natural water (Karnik et al., 2005b; Kim et al., 2008; Schlichter et al., 2004) and secondary effluent (Lehman et al., 2009).

2.6.3   Coagulation

Another treatment most used to incorporate with membrane filtration is coagulation (Farahbakhsh et al., 2004; Huang et al., 2009). Because particles and colloids, as well as higher molecular substances, could be incorporated into flocs by using coagulation process as pretreatment for the CM process. This may mitigate membrane fouling and improve permeate water quality. Thus coagulation is selected as another target process.

2.6.3.1   Contaminants removal

Using coagulation as pretreatment for low membrane filtration may improve permeate water quality through enhancing the rejection of total phosphorous, viruses and high molecular weight substances.

For TP removal, it was observed that UF membrane alone can remove some phosphorus because a part of them were in colloidal form. A dosage of any kind of coagulants improved the removal significantly (Zheng et al., 2012). Genz et al. found that TP removal rate was dependent on coagulants doses. Over 80% removal of TP could be achieved by adding 2 mgFe/L (Genz et al., 2011). Zhu et al. (Zhu et al., 2005) reported a >4-log removal of viruses at pH 6.3 with 10

mgFe/L of ferric chloride and 0.22 μm pore size of polyvinylidene fluoride MF membrane. MF alone achieved a <0.5-log removal. For viruses rejection by CM was also investigated by many researchers (Shirasaki et al., 2008; Shirasaki et al., 2009a; Shirasaki et al., 2009b; Shirasaki et al., 2010). It was reported that >6-log removal of viruses was achieved by two types of 0.1μm pore size CM systems with 0.5－1.0 mgAl/L of polyaluminum chloride (Matsushita et al., 2005). In addition, removal of disinfection byproducts precursors by coagulation before membrane treatment was reported by other researcher. (Zhang et al., 2008).

2.6.3.2   Membrane fouling mitigation

The impacts of chemical coagulation on low-pressure membrane filtration were reviewed by Farahbakhsh, K. et al (Farahbakhsh et al., 2004). Under most cases, the impact of coagulation on membrane fouling has been positive(Wang et al., 2006; Wang et al., 2010; Wang et al., 2011), although some studies indicated that chemical coagulation increased the rate of membrane fouling (Schafer et al., 2001). Several mechanisms have been proposed regarding membrane fouling mitigation by coagulation (Farahbakhsh et al., 2004). One is increasing particle size, which might increase particle migration away from the membrane wal. Second, large molecular weight soluble organic matter could be rejected by membrane through forming flocs. Third, change in cake layer morphology can lower specific cake resistance.

2.6.4   Combination processes

Discussion in section 2.6.1 to 2.6.3 showed that: 1) the advantages of CM on particulate matters and bacteria rejection; 2) merit of ozonation on emerging contaminants degradation, and disinfection especially for virus; potential application in mitigating membrane fouling; 3) effectiveness of coagulation on nutrients and virus removal and on alleviating membrane fouling.

At the same time each process has disadvantages. CM membrane has membrane fouling and low rejection of dissolve organic matters and virus. On the other hand, ozone has little effect on removal of particles. Coagulation has no effect on removal of most emerging chemicals. Such shortcomings for each process are expected to be covered by combining processes together. Therefore, combination of processes based on CM, ozonation and coagulation are investigated in this research.

2.7   Innovative points in this research

As discussed above, various contaminants and treatment processes were selected to comprehensively evaluate feasibility of water reclamation. There were several innovative points, listed as follows:

1) It was the first time to treat primary effluent using only physical treatment for removal of PPCPs and pathogen.

2) Mechanisms of mitigating CMF fouling by pretreatment (O_3+coagulation/ coagulation) during treating primary effluent and secondary effluent were investigated.

3) Various processes (ozonation, coagulation, CMF) and their combinations were compared from water quality removal and energy consumption aspects.

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CHAPTER III

Removal of Contaminants by O$_3$-based Water Reclamation Processes using Semi-batch Reactor

3.1   Introduction

Ozone is not confined solely to treatment of natural waters for drinking. Ozone has been used in wastewater treatment for long time. Specific literature concerning the application of ozone in the treatment of wastewater (mainly industrial wastewater) dates back to the 1970s, when Rice and Browning (Rice et al., 1977) published a compendium of cases about ozone application. Now, ozonation is developed to be applied to municipal wastewater effluents (Paraskeva et al., 2002). Most application cases were in Japan. 200 ozonation units were established until the year of 1999 (Matsumoto et al., 1999) in Japan. There are 134 plants in Germany, 45 in United States and several in Korea until year of 2002 (Paraskeva et al., 2002). In the wastewater treatment field, ozone is applied mainly to secondary or tertiary treated effluents because the ozone demand for raw or primary treated wastewater is so large.

The main objectives of ozonation in wastewater treatment may include color removal, disinfection, and degradation of emerging contaminants. Extensive research has shown that ozone is a highly effective oxidation for treating PPCPs in secondary treated wastewater (Kim, I. H. et al., 2009; Nakada et al., 2007; Snyder et al., 2006). While there is no published research is found regarding with PPCPs degradation in raw or primary treated wastewater using ozone.

As disinfection treatment, ozone is effective against both bacteria and viruses and can also remove cysts and eggs. For bacteria disinfection, molecular ozone is found more effective than hydroxyl radicals (Zuma et al., 2009). But both molecular ozone and hydroxyl radicals could inactivate viruses even in quite low dose (Kim et al., 1980). There are already several studies

reported regarding pathogen disinfection in secondary or tertiary treated effluents, the transferred ozone doses between 2 and 15 mg/L was necessary to meet the WHO standard for irrigation (1000 *E. coli*/100ml) (Xu et al., 2002). While, the only one research published about treating primary treated wastewater directly using ozonation (Gehr et al., 2003), it showed that the transferred ozone doses needed to reach 2 log fecal coliform reduction were 30-50 mg/L, while MS2 was much easier to be disinfected.

While there are many factors might influent ozonation efficiency, such as organic matter concentration, some inorganic matters (Fe^{2+}, Mn^{2+}), pH, particles, ozone decomposition－inhibiting compounds or hydroxyl free radical scavengers et al. (Beltrán, 2005). In order to change concentration of inorganic matters or pH, certain pretreatment or chemical should be used before ozonation. It showed low feasibility in application field. Thus, we only discussed changing ozonation efficiency through removing organic matters and particles.

There is already one study reported regarding enhancing contaminants removal by removing organic matters before ozonation. Wert et al. (Wert et al., 2011) tried to improve ozonation efficiency in wastewater through enhanced coagulation pretreatment. The O_3 dose was normalized based on TOC to compare contaminants removal efficiency in treating wastewater with and without coagulation pretreatment. Although the results showed that enhanced coagulation was ineffective on improving removal efficiency of 13 PPCPs during ozonation. But the ozone consumption or ozone dose could be decreased due to less TOC left after coagulation. Thus it is still meaningful to examine pretreatment (CMF, coagulation) effect on saving ozone input dose.

Particles effect on both PPCPs (Hollender et al., 2009) and disinfection efficiency (Boyce et al., 1981) during ozonation have been discussed by many researchers. The effect on former one was observed for several chemicals with high adsorption tendency to solid particles (Zimmermann et al., 2011). The influence extent on latter one is more serious. It will cause the tailing phenomenon, which was apparent and common during ozonation treating wastewater containing particles. Two reasons were described as follows for tailing phenomenon: 1) Viruses have a demonstrated affinity for solids and exist adsorbed to clay or embedded within other solid material (Carlson et al., 1968; Schaub et al., 1975). For bacteria, association of coliform bacteria with wastewater particles has also been found recently (Loge et al., 2002). Thus the particles would significantly

protect pathogen from attacking by oxidants (Boyce et al., 1981). 2) High concentration of pollutants would suggest high reactivity with ozone (which is an indication of fast kinetic regime and ozone direct reactions) and low concentration usually means low ozone reactivity (Beltrán, 2005). It is expected to lighten tailing phenomenon through removal particles. And the most effective strategy could be to use physically filtration before ozonation.

Based on the above discussions, the research scope in this chapter was decided as follows:

1. Contaminants removal by ozonation

2. Contaminants removal by ozonation with CMF pretreatment

3. Contaminants removal by ozonation after coagulation using polyaluminium chloride (PAC) and CMF combination process

3.2   Materials and methods

3.2.1   Selected target contaminants and analyzing method

The selection of target contaminant was comprehensively discussed in Chapter 2. Totally three categories of pollutants would be studied in this chapter, which are listed in follows.

3.2.2   Common water quality indexes

Suspended Solid (SS) and turbidity are selected to represent particle matters. The aggregate constituents COD_{Mn}, DOC and TOC are used for characterization of organic matters. Beside these, color, aromatic carbon content using UV_{254} and pH are also included in the target list.

TOC, DOC were measured with a TOC analyser (TOC-5000A, Shimadzu, CO.). COD_{Mn} was analyzed using closed reflux, colorimetric method (Lenore et al., 1999). UV_{254} and color were measured by a spectrophotometer (UV-16000, Shimadzu, CO.). Turbidity was measured by a turbidity meter (2100Q01, HACH CO.).

Dissolved O_3 (DO_3) concentration was one of the important parameters for study on ozonation, which was analyzed with indigo method (Bader et al., 1981) at 600nm wavelength by a spectrophotometer (UV-16000, Shimadzu, CO., Japan).

3.2.3 Pathogen indicators

Based on comprehensive consideration about features of pathogens and targets in water reuse guidelines, total coliform, *E. coli* and bacteriophage MS2 are selected.

Total colifrom and *E. coli* were analyzed using the soft agar overlay method according to standard method (Lenore et al., 1999). In this method, high concentration of bacteria should be diluted at a suitable dilution factor in order to produce the colony count from the range of 20-200 colony forming unit (CFU) per ml. Results for *E. coli* and total coliform were reported as CFU/ml.

For bacteriophage MS2 removal study, preparation of the phage should be done before spiking MS2 in the wastewater. Procedure to prepare MS2 phage solution is summarized in Figure 3.1. The MS2 phage (NBRC 102619) and host cell *E.coli* K12 F+(A/λ) (NBRC13965) are obtained from National Institute of Technology and Evaluation (NITE) Biological Resource Center, Japan.

Preparing LB broth

• 20 g LB Broth Base (BD Science) was dissolved in 1L Milli -Q

• Autoclaved at 121℃ for 5 mins

• Cooled in air

Preparing host cells

• Add log-phase cells (*E. Coli* K12) (1mL host into 9mL)

• Incubate at 37℃ for 3-4 hours

Preparing MS2

• Add MS2 (1mL MS2 into 9mL solution)

• Incubate at 37℃ for 20-24 hours

• Centrifuge at 10,000rpm for 30 min

• Filter with 0.45μm cellulose acetate membrane filter to collect the supernatant

Figure 3.1   MS2 phage stock preparation

If wastewater sample contains certain amount suspended solid (SS), large amount viruses tended to be adsorbed onto solid (Hejkal et al., 1981), it will inhibit MS2 infection to host cell. Thus proper pretreatment was conducted to alleviate contamination to the detection of MS2 (Figure 3.2). The wastewater was filtered using 0.45μm pore size filter. The residues on the filter were extracted by beef extract. The extracted solution and filtered water were analyzed using double layer agar method with *E. coli* K12 used as the host bacteria. The result for MS2 was shown as PFU/ml.
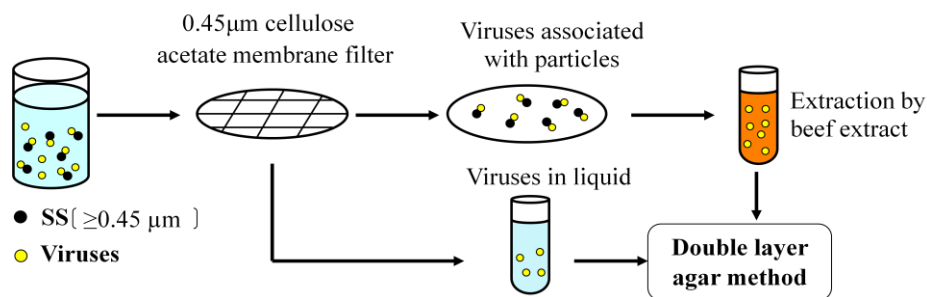
Figure 3.2   Cell culture procedure for MS2 phage

3.2.4   Target emerging contaminants

59 PPCPs were selected based on detected concentrations in water environment. The basic characteristics were listed in Table 3.1. The PPCPs consist mainly of antibiotic, analgesics and antiarrhythmic agents groups. The numbers of PPCPs in these categories are 26, 11 and 4, respectively. Anticonvulsant, ani-itch drug, antineoplastic agents, antipsychotic drug, bronchodilator et. al are also included as target PPCPs list. These chemicals are classified into category of "the others".

After collecting water samples, 1g/L ascorbic acid was added immediately to inhibit PPCPs degradation by bacteria. Besides, photodegradation was also prevented by covering sampling bottle with aluminum foil. Total PPCPs amount could be separated to two parts through filtering water sample using GF/B (1.0 μm) filter: 1) amount in liquid phase, which equaled to amount in filtered water. 2) amount in SS phase, which is assumed to equal to residues amount on GF/B filter.

For PPCPs compounds in the liquid phase quantification, 200 ml (secondary effluent-SE) or 50 ml (primary effluent-PE) of water sample was added 5g/L EDTA-2Na and 50μL 1mg/L surrogate

standard solution (surrogate for each chemical was listed in Table 3.1), followed by filtration using an Oasis HLB cartridge (Waters, 6cc/200 mg) by the concentrator (Waters, Sep-pak concentrator SPC-10) to concentrate PPCPs. Afterwards, the cartridge was dehydrated by a pneumatic pump for 2 hrs, and PPCPs were eluted from the dehydrated cartridge with 6ml methanol. The eluted solution was evaporated with N_2 gas and then dissolved with 1ml mixed solution of 0.1% formic acid and methanol. This solution of 1ml was used for PPCPs quantification by LC/MS/MS.

Table 3.11   Characteristics and surrogate for selected 58 PPCPs (NARUMIYA et al., 2009)

No.	Name of PPCPs	Surrogate	Use	Molecular Formula	Water Solubility (mg/L)	pKa	LogKow
1	Acetaminophen	Acetaminophen-d_4		$C_8H_9NO_2$	1.4E+04	9.38	0.46
2	Antipyrine	Antipyrine-d_3		$C_{11}H_{12}N_2O$	5.2E+04	1.4	0.38
3	Diclofenac	Diclofenac-d_4		$C_{14}H_{11}Cl_2N\,O_2$	2.4E+00	4.15	0.7
4	Ethenzamide	No		$C_9H_{11}NO_2$	4.5E+03	-	0.77
5	Fenoprofen	Ketoprofen-^{13}C, d_3		$C_{15}H_{14}O_3$	1.7E+02	7.3	3.9
6	Ibuprofen	Ibuprofen-d_3	Analgesics	$C_{13}H_{18}O_2$	2.1E+01	4.91	3.97
7	Indomethacin	Indomethacin-d_4		$C_{19}H_{16}ClNO_4$	9.4E-01	4.5	4.27
8	Isopropylantipyrine	No		$C_{14}H_{18}N_2O$	3.0E+06		1.94
9	Ketoprofen	Ketoprofen-^{13}C, d_3		$C_{16}H_{14}O_3$	5.1E+01	4.45	3.12
10	Mefenamic acid	Antipyrine-d_3		$C_{15}H_{15}NO_2$	2.0E+01	4.2	5.12
11	Naproxen	Ketoprofen-^{13}C, d_3		$C_{14}H_{14}O_3$	1.6E+01	4.15	3.18
12	Atenolol	Atenolol-d_7		$C_{14}H_{22}N_2O_3$	1.3E+04	9.6	0.16
13	Disopyramide	Propranolol-d_7	Antiarrhythmic	$C_{21}H_{29}N_3O$	4.5E+01	-	2.58
14	Metoprolol	Metoprolol-d_7	agents	$C_{15}H_{25}NO_3$	-	9.7	-
15	Propranolol	Propranolol-d_7		$C_{16}H_{21}NO_2$	6.2E+01	9.42	0.74
16	Ceftiofur	No		$C_{19}H_{17}N_5O_7S_3$	-		
17	Chloramphenicol	Chloramphenicol-d_5		$C_{11}H_{12}Cl_2N_2O_5$	2.5E+03	5.5	1.14
18	Ciprofloxacin	Ciprofloxacin-d_8		$C_{17}H_{18}FN_3O_3$	3.0E+04	6.09	
19	Clarithromycin	Clarithromycin-d_3		$C_{38}H_{69}NO_{13}$	3.4E-01	8.99	3.16
20	Diclazuril	Indomethacin-d_4		$C_{17}H_9Cl_3N_4O_2$	-	-	-
21	Enrofloxacin	Ciprofloxacin-d_8		$C_{19}H_{22}FN_3O_3$	3.4E+03		0.7
22	Erythromycin	Erythromycin-^{13}C,d_8		$C_{37}H_{67}NO_{13}$	1.4E+00	8.88	3.06
23	Erythromycin-H2O	Erythromycin-H2O -^{13}C,d_8		$C_{37}H_{66}NO_{12}$	1.4E+00	8.88	3.06
24	Griseofulvin	Ketoprofen-^{13}C, d_3	Antibiotic	$C_{17}H_{17}ClO_6$	8.6E+00	-	2.18
25	Levofloxacin	Levofloxacin-d_8		$C_{18}H_{20}FN_3O_4$	-	5.5, 8.0	-
26	Lincomycin	No		$C_{18}H_{34}N_2O_6S$	9.3E+02	7.6	0.29
27	Nicarbazin	Indomethacin-d_4		$C_{19}H_{18}N_6O_6$	7.3E+00	-	3.76
28	Norfloxacin	Norfloxacin-d_5		$C_{16}H_{18}FN_3O_3$	1.8E+05	6.34, 8.75	-1.03
29	Oxytetracycline	Tetracycline-d_6		$C_{22}H_{24}N_2O_9$	3.1E+02	3.27	-0.9
30	Roxithromycin	Roxithromycin-d_9		$C_{41}H_{76}N_2O_{15}$	1.9E-02	-	2.75

Table 3.10   Characteristics and surrogate for selected 58 PPCPs (NARUMIYA et al., 2009) (continued)

#	Name	Surrogate	Category	Formula		pKa	logKow
31	Sulfadimethoxine	Sulfadimethoxine-d$_4$		$C_{12}H_{14}N_4O_4S$	3.4E+02	-	1.63
32	Sulfadimidine	Sulfadimidine-$^{13}C_6$		$C_{12}H_{14}N_4O_2S$	1.5E+03	7.59	0.89
33	Sulfamerazine	Sulfamerazine-d$_4$		$C_{11}H_{12}N_4O_2S$	2.0E+02		0.14
34	Sulfamethoxazole	Sulfamethoxazole-d$_4$		$C_{10}H_{11}N_3O_3S$	6.1E+02	5.94	0.89
35	Sulfamonomethoxine	Sulfamerazine-d$_4$		$C_{11}H_{12}N_4O_3S$	4.0E+03	-	0.7
36	Sulfapyridine	Sulfapyridine-d$_4$		$C_{11}H_{11}N_3O_2S$	2.7E+02	2.7,8.3	0.35
37	Sulfathiazole	Sulfathiazole-d$_4$		$C_9H_9N_3O_2S_2$	3.7E+01	2.5,7.0	0.05
38	Thiamphenicol	Sulfathiazole-d$_4$		$C_{12}H_{15}Cl_2NO_5S$	1.2E+04	-	-0.33
39	Tiamulin	Diltiazem-d$_3$		$C_{28}H_{47}NO_4S$	7.0E-01		4.75
40	Triclosan	Triclosan-d3		$C_{12}H_7C_{13}O_2$	1.0E+01		4.76
41	Trimethoprim	Caffeine-d$_9$		$C_{14}H_{18}N_4O_3$	4.0E+02	7.12	0.91
42	Tylosin	Diltiazem-d$_3$		$C_{46}H_{77}NO_{17}$	5.0E+00	7.73	1.63
43	Carbamazepine	Carbamazepine-d$_{10}$	Anticonvulsant	$C_{15}H_{12}N_2O$	1.8E+01	-	2.45
44	Primidone	Primidone-d$_5$	Anticonvulsant	$C_{12}H_{14}N_2O_2$	5.0E+02	-	0.91
45	Crotamiton	Crotamiton-d$_7$	Anti-itch drug	$C_{13}H_{17}NO$	5.5E+02	-	2.73
46	Cyclophosphamide	Cyclophosphamide-d$_4$	Antineoplastic agents	$C_7H_{15}Cl_2N_2O_2P$	4.0E+04	-	0.63
47	Sulpiride	No	Antipsychotic drug	$C_{15}H_{23}N_3O_4S$	2.3E+03	9.12	0.57
48	Clenbuterol	Clenbuterol-d$_9$	Bronchodilator	$C_{12}H_{18}Cl_2N_2O$	3.3E+03	9.33	2
49	Theophylline	Theophylline-$^{13}C,^{5}N_2$	Bronchodilator	$C_7H_8N_4O_2$	7.4E+03	8.81	-0.02
50	Diltiazem	Diltiazem-d$_3$	Calcium channel blockers	$C_{22}H_{26}N_2O_4S$	4.7E+02	7.7	2.7
51	Bezafibrate	Bezafibrate-d$_4$	Cholesterol-lowering drug	$C_{19}H_{20}ClNO_4$	3.4E-01	3.4	4.25
52	Clofibric acid	Clofibric acid-d$_4$	Cholesterol-lowering drug	$C_{10}H_{11}ClO_3$	5.8E+02	-	2.57
53	Ifenprodil	Diltiazem-d$_3$	NMDA receptor antagonist	$C_{21}H_{27}NO_2$	2.6E+02	9.05, 9.69	3.9
54	DEET	DEET-d$_7$	Insect repellents	$C_{12}H_{17}NO$	9.1E+02		2.18
55	Furosemide	Furosemide-d$_5$	loop diuretic	$C_{12}H_{11}ClN_2O_5S$	7.3E+01	3.9	2.03
56	Pirenzepine	Caffeine-d$_9$	Selective antagonist,	$C_{19}H_{21}N_5O_2$	1.7E+01	1.8, 7.9	1.68
57	Caffeine	Caffeine-d$_9$	Acetylcholinesterase inhibitor	$C_8H_{10}N_4O_2$	2.2E+04	10.4	-0.07
58	2-QCA	2-QCA-d$_4$	The others	$C_9H_6N_2O_2$	-	-	-
59	Dipyridamol	Dipyridamol-d$_{20}$	Calcium channel blockers	$C_{24}H_{40}N_8O_4$	8.2E+00	6.3	2.74

Note:
"No": no surrogate compound was used, concentration was calculated without considering recovery
"-": no data

PPCPs on SS phase was analyzed as follows: 50μL surrogate solution (1mg/L) was added on the GF/B filter after filtration, then PPCPs on filter was extracted through ultrasonic solvent extraction (USE) using mixture of methanol and water (volume ratio=1/9) at three pH levels (pH=6, pH=11, pH=2) successively. Afterwards, the extraction solution was filtrated using GF/B

filter again to removal the particles. PPCPs amount in the filtrated water could be analyzed following the PPCPs in liquid phase measurement. Based on this PPCPs amount in the filtered water and PPCPs extraction recovery, the PPCPs amount in SS phase could be calculated. The detail information was shown in literature (Okuda et al., 2009).

3.3 Experimental setup and conditions

3.3.1 Experimental conditions

Firstly, effect on contaminants removal by ozonation treating SE and PE was investigated. Then CMF pretreatment effect on ozonation efficiency was studied. Afterwards, PAC and CMF pretreatment effect was examined. The O_3 feed rate was 0.4 and 1.5 mg O_3/L/min for SE and PE, respectively. The major characteristics of the tested wastewater and experimental conditions were listed in Table 3.2 and Table 3.3.

Table 3.12   Major characteristics of the tested wastewater and experimental conditions for ozonation (Secondary effluent case)

Run	Raw water	Pretreatment	Date	Target	Spiking	Major characteristics of wastewater				
						SS	Turbidity	pH	TOC	UV$_{254}$
						mg L^{-1}	NTU		mg L^{-1}	cm^{-1}
1	SE	No	2011.09.07	A, B	No	1.22	0.99	6.79	3.16	0.052
2	SE	No	2011.09.12	B, C	MS2	-	-	6.83	2.09	0.052
3	SE	No	2011.08.21	A, B, D	No	1.58	1.60	6.81	4.02	0.067
4	SE	CMF	2011.08.21	A, D	No	-	0.21	6.81	3.38	0.061
5	SE	No	2011.11.24	B	*E.coli* K12	1.18	1.01	7.10	3.17	0.059
6	SE	CMF	2011.11.24	B	*E.coli* K12	-	0.25	7.00	2.58	0.054
7	SE	No	2011.10.12	C	MS2	1.49	1.03	6.84	4.07	0.060
8	SE	CMF	2011.10.12	C	MS2	-	0.22	6.83	3.89	0.058
9	SE	No	2012.08.22	A, D	No	-	1.21	6.82	2.70	0.064
10	SE	PAC(25mg/L)+CMF	2012.08.22	A, D	No	-	0.17	6.83	2.35	0.049
11	SE	No	2012.08.22	C	MS2	-	-	-	-	-
12	SE	PAC(25mg/L)+CMF	2012.08.22	C	MS2	-	-	-	-	-

Table 3.13 Major characteristics of the tested wastewater and experimental conditions for O_3 (Primary effluent case)

Run	Raw water	Pretreatment	Date	Target	Spiking	Major characteristics of wastewater				
						SS	Turbidity	pH	TOC	UV_{254}
						mg L^{-1}	NTU		mg L^{-1}	cm^{-1}
13	PE	No	2011.10.01	A, B, D	No	-	44.40	7.9	27.03	0.381
14	PE	PAC(100mg/L)+Sedimentation	2011.10.01	A, B, D	No	-	12.10	7.7	14.33	0.303
15	PE	No	2011.11.08	A, D	No	44.3	46.60	7.4	28.76	0.354
16	PE	CMF	2011.11.08	A,D	No	<0.1	2.71	7.4	22.02	0.344
17	PE	No	2011.11.17	A, B, D	No	-	45.10	7.5	23.29	0.289
18	PE	CMF	2011.11.17	A, D	No	-	2.20	7.5	17.87	0.283
19	PE	No	2011.12.13	A, B	E. Coli K12	-	46.30	7.5	23.70	0.356
20	PE	CMF	2011.12.13	A, B	E. Coli K12	-	1.87	7.5	15.19	0.298
21	PE	No	2011.12.19	A, C	MS2	49.0	49.12	7.5	26.17	0.345
22	PE	CMF	2011.12.19	A, C	MS2	<0.1	3.65	7.5	19.71	0.336
23	PE	No	2012.01.09	A, B, D	No	40.19	34.4	7.1	19.9	0.215
24	PE	No	2012.01.09	C	MS2	-	-	-	-	-
25	PE	PAC(100mg/L)+Sedimentation	2012.01.09	A, B, C	MS2	8.31	3.11	7.1	16.1	0.147
26	PE	PAC(100mg/L)+CMF	2012.01.09	A, D	No	<0.1	0.29	7.2	13.5	0.133
27	PE	PAC(100mg/L)+CMF	2012.01.09	A, C	MS2	-	-	-	-	-
28	PE	PAC(100mg/L)+CMF	2012.01.09	B	E. Coli K12	-	-	-	-	-
29	PE	No	2012.08.28	A, D	No	-	36.8	6.9	36.6	0.284
30	PE	No	2012.08.28	A, C	MS2	-	-	-	-	-
31	PE	PAC(50mg/L)+CMF	2012.08.28	A, D	No	-	2.89	7.0	10.4	0.137
32	PE	PAC(50mg/L)+CMF	2012.08.28	A, C	MS2	-	-	-	-	-

Notes:
"SE" means secondary effluent; "PE" means primary effluent
"A" means common water quality items
"B" means bacteria (total coliform, *E. Coli*)
"C" means MS2
"D" means PPCPs
"-"means data was not available

3.3.2   Ozonation experimental setup

All the ozonation experiments were carried out using a cylindrical stainless reactor with an inside diameter of 30 cm, a height of 108.7 cm and an effective volume of 22L (Figure 3.3). The temperature of tested water was maintained at 20 ℃ by circulating water from water temperature controlling system into a water jacket outside the reactor. All the experiments started by feeding O_3 gas continuously into the reactor filled with tested water. During ozonation, the water was mixed by O_3 gas bubbling. The mixing was completely, which was confirmed by comparing results between using gas bubbling and mechanical agitator. After collecting samples, DO_3 was quenched by 100mg/L $Na_2S_2O_3$ for pathogen measurement, ascorbic acid for PPCPs analyzing. For common water quality items, N_2 purging was used.
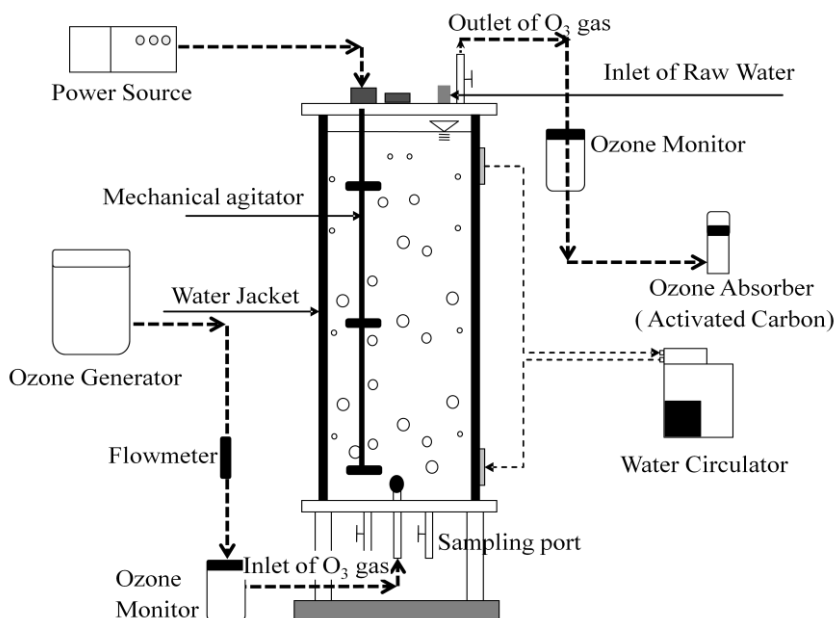
Figure 3.3   Semi-batch reactor for ozonation experiment

3.3.3   Ceramic membrane filtration experimental setup

The membrane filtration experiment was shown as Figure 3.4. The ceramic membrane (METAWATER CO., Ltd., Japan) is monolithic type, with 10 cm in length, 3 cm in diameter, 51 channels and 0.042 m^2 effective membrane surface area. The main material is Al_2O_3. Pore size is 0.1μm. The filtration experiments were operated in a constant flow rate (4.0 m/d for secondary effluent and 1.0 m/d for primary effluent) with dead-end mode. Filtration period is 30min

followed by backwashing using filtered water under 250 ml/min flux for 2 minutes. For preparing wastewater for Run 10, 12, 31, 32, 6 seconds high pressure backwashing (0.3MPa) was used instead of 250 ml/min filtration. Fifty litter permeate water was collected for ozonation. At the same time, the composited feed water sample (SE or PE) during the filtration was also collected for oxidization as the contrast test. After each experiment, membrane was successively cleaned until achieving initial condition, by using NaOH and HCl solution.
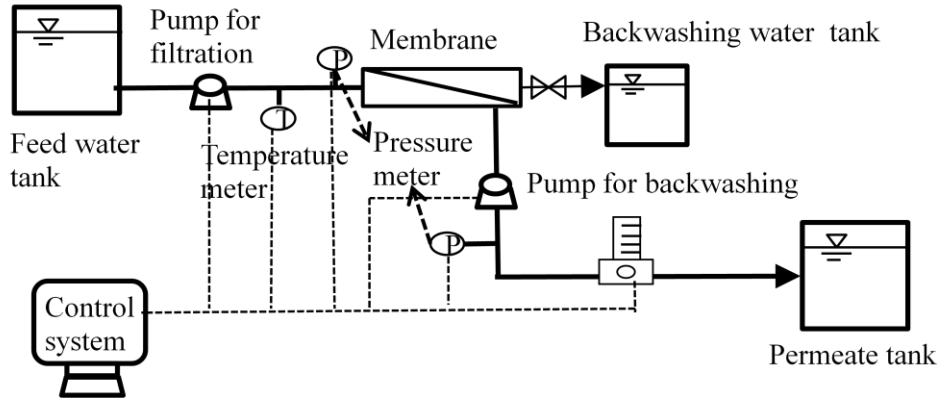
Figure 3.4　　Ceramic membrane filtration apparatus

3.4 Results and discussions

3.4.1 Specific ozone consumption calculation

Specific O_3 consumption (SOC) which is ozone consumption divided by initial TOC was adopted for the evaluation of the O_3 performance. The consumed O_3 was calculated by the following formula:

$$\text{Consumed } O_3 \text{ (mgO}_3\text{)} = \int (G_{O_3,\text{gas in}} - G_{O_3,\text{gas out}})Qdt - M_{\text{head}} - (D_{O_3} \times V)$$

Where $G_{O_3, \text{gas in}}$ is the gas ozone concentration at the inlet (mg/L), $G_{O_3, \text{gas out}}$ is the gas ozone concentration at the outlet (mg/L), Q is the gas flow rate (L/min), t is the reaction time (min), M_{head} is the ozone mass in the head space of the reactor, D_{O_3} is the dissolved ozone concentration (mg/L), and V is the water volume treated (L).

3.4.2   Common water quality items removal

3.4.2.1   Dissolved ozone

Figure 3.5 showed the result of DO_3 concentration during ozonation treating secondary effluent and primary effluent. Considering the minimum detectable concentration is 0.02 mg/L using indigo colorimetric method (Clescerl et al., 1999), the ozone in the wastewater with over 0.05 mg/L concentration was considered as detectable dissolved ozone. From this figure, the secondary effluent consumed ozone rapidly during the initial stage of ozonation until the DO_3 reached at more than 0.05 mg/L after SOC reached approximately 0.6 mg O_3/mg C. CMF (shown in green symbols) or PAC+CMF (shown in purple symbols) pretreatments did not show obvious effect on changing DO_3 result.

In primary effluent case, the mixture of oxidized water and indigo solution was filtrated using GF/B to removal SS before analyzing DO_3. Very low concentration of DO_3 was found during ozonation. Even after SOC increased to quite high dose (2.0 mg O_3/mg TOC_0), DO_3 was lower than 0.1 mg/L. And the CMF (shown in green symbols), PAC (shown in blue symbols) or PAC+CMF (shown in purple symbols) pretreatment could increase DO_3 concentration significantly. DO_3 started to appear after SOC reached approximately 0.3-0.5 mg O_3/mg C. But the DO_3 results altered a lot among these experiments. It might caused by water quality fluctuation and low DO_3 concentration.
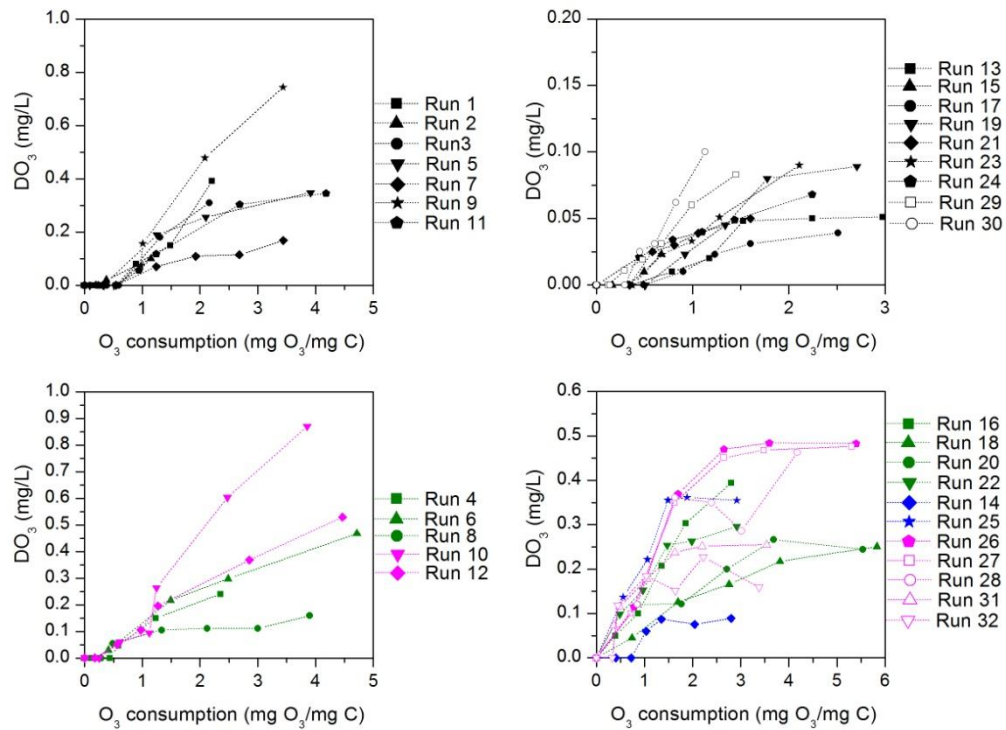
Figure 3.5   DO$_3$ changing during ozonation with SOC during ozonation (left: SE-secondary effluent; right: PE-primary effluent)

3.4.2.2 Suspended Solid

Figure 3.6 presented the change of SS during ozonation treating secondary effluent and primary effluent. For secondary effluent, the removal rate was around 25% at the SOC of 0.6 mg O$_3$/mg C. No obvious removal was observed after this point. For primary effluent, three experiments were conducted (Run 15, 21, 23) to study on SS changing by ozonation. The initial SS concentrations and removal rates were different among these experiments. Run 15 and Run 23 showed similar SS removal trend. SS started to decrease sharply after SOC reached 0.4 mg O$_3$/mg C. For Run 21, SS was not changed much by ozonation. Removal of SS by ozonation might be influenced by characteristics of wastewater.
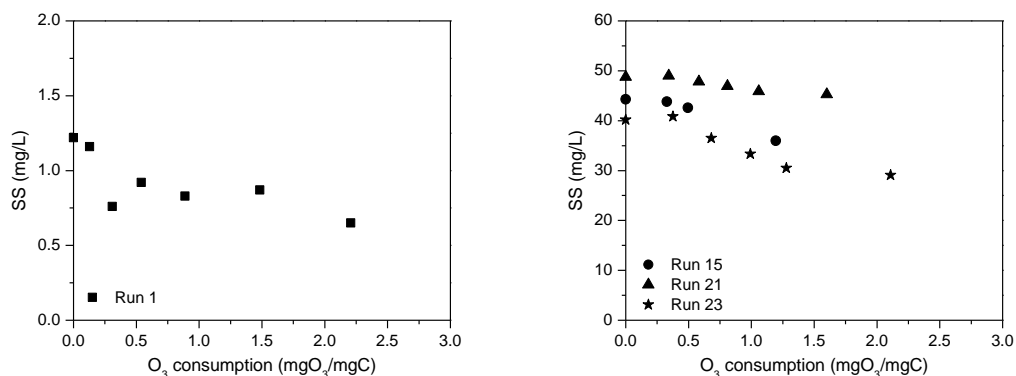
Figure 3.6   Change of SS along with SOC during ozonation (left: SE; right: PE)

3.4.2.3   TOC, COD$_{Mn}$, SUVA and Color

TOC and COD$_{Mn}$ removal by ozonation was described in Figure 3.7 and 3.8. TOC values of both secondary effluent and primary effluent did not change during ozonation, except Run 29. After SOC reached 0.6 mg O$_3$/mg C, TOC decreased by 20%. COD$_{Mn}$ in secondary effluent decreased by around 6.4% when SOC reached 0.6 mg O$_3$/mg C, followed by relative higher reducing speed. The removal rate could arrive around 23.4 % at the point of 3.4 mg O$_3$/mg C dose. Pretreatment did not change these results much. For primary effluent, lower removal rate was indentified. Increasing the ozone consumption to 1.5-3.0 mg O$_3$/mg C, the removal rate was only around 10%. No obvious effect of pretreatment on total organic matters removal by ozonation was found.

SUVA and color removal by ozonation were described in Figures 3.9 to 3.10. O$_3$ is an electrophilic and is very reactive with electron donating functional groups, and SUVA at 254 nm correlated well with aromatic carbon content. It was found that SUVA was a meaningful indicator of organic matter's reactivity toward O$_3$ (Westerhoff et al., 1999). Based on SUVA result, we could deduce that the characteristics of water changed during ozonation. The SUVA for secondary effluent and primary effluent similarly changed during ozonation (Figure 3.9). Before SOC reached 1.2-1.5 mg O$_3$/mg C, SUVA sharply reduced. The SUVA of secondary effluent and primary effluent could be reduced by 39.2-58.6% and 48.9-68.1% respectively. After this point, nearly no change was observed. Color showed the similar trend with SUVA during ozonation, but much higher removal rate than SUVA (Figure 3.10). The color of secondary

effluent and primary effluent could be reduced by 62.5-75.1% and 71.1-89.2% respectively at the SOC equal to 1.2-1.5 mg O_3/mg C. These results verified that ozonation was very effective to control color, which is one of important water quality items in water reclamation field. And the pretreatment was found little effect on enhancing removal of such items.
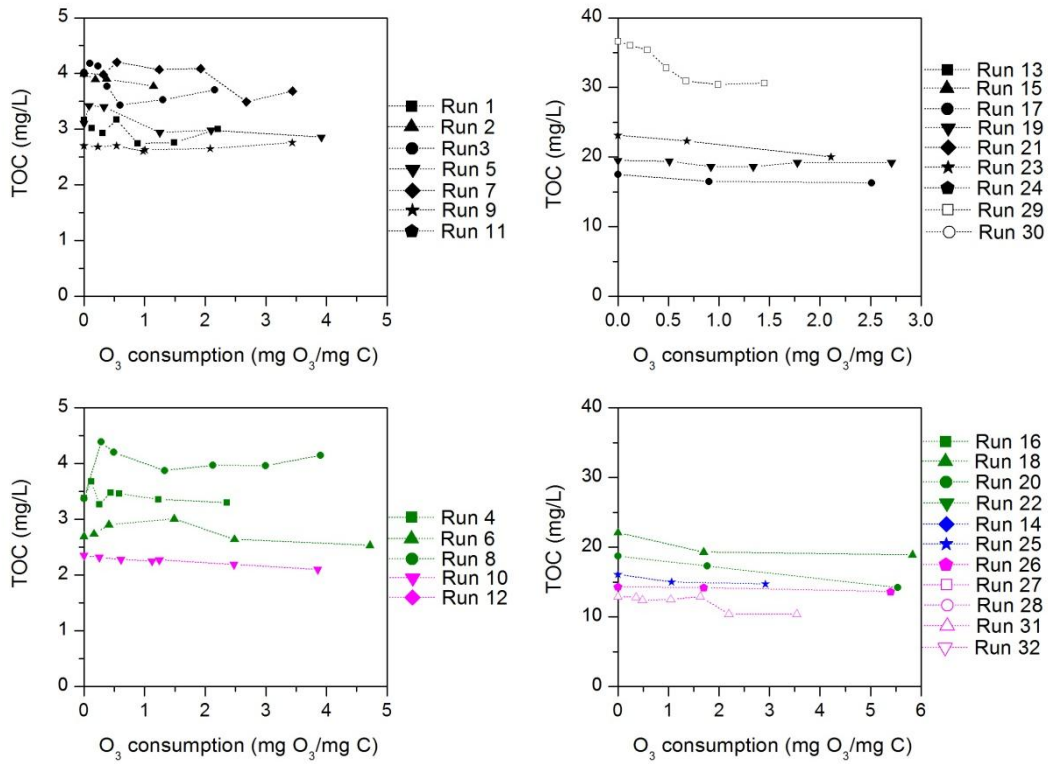
Figure 3.7   Change of TOC along with SOC (left: SE; right: PE)
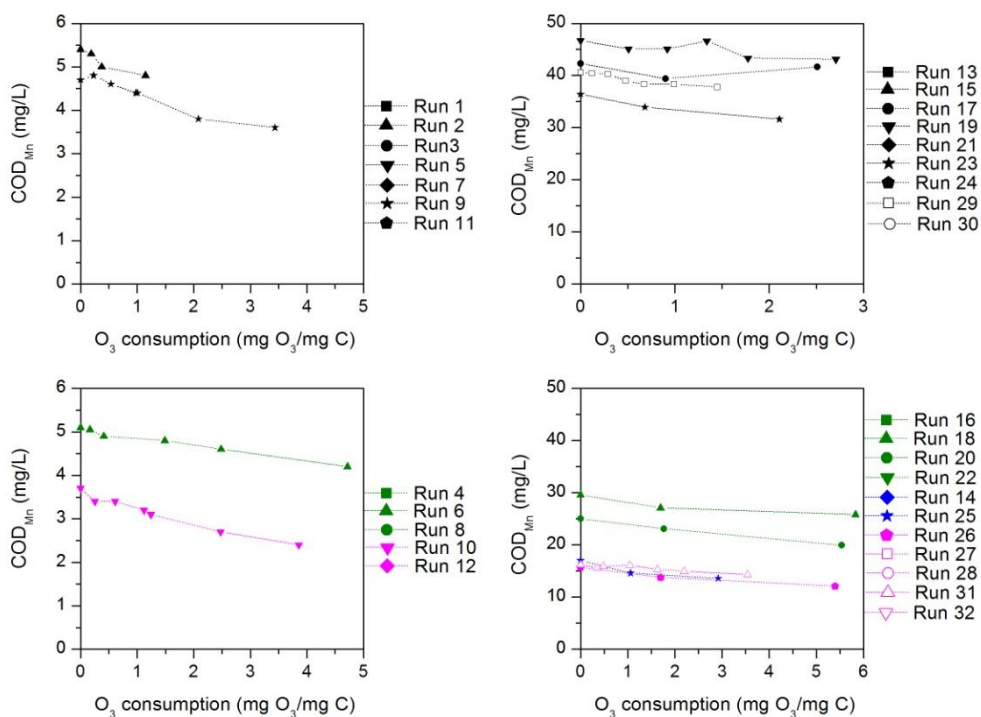
Figure 3.8　Change of COD$_{Mn}$ along with SOC during ozonation (left: SE; right: PE)
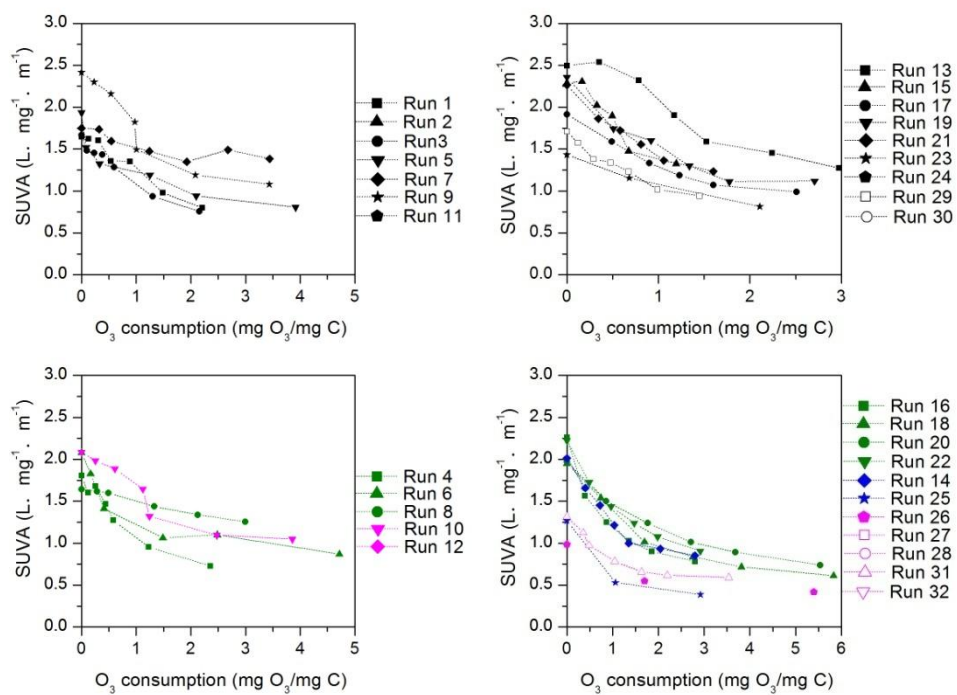
Figure 3.9　Change of SUVA along with SOC during ozonation (left: SE; right: PE)
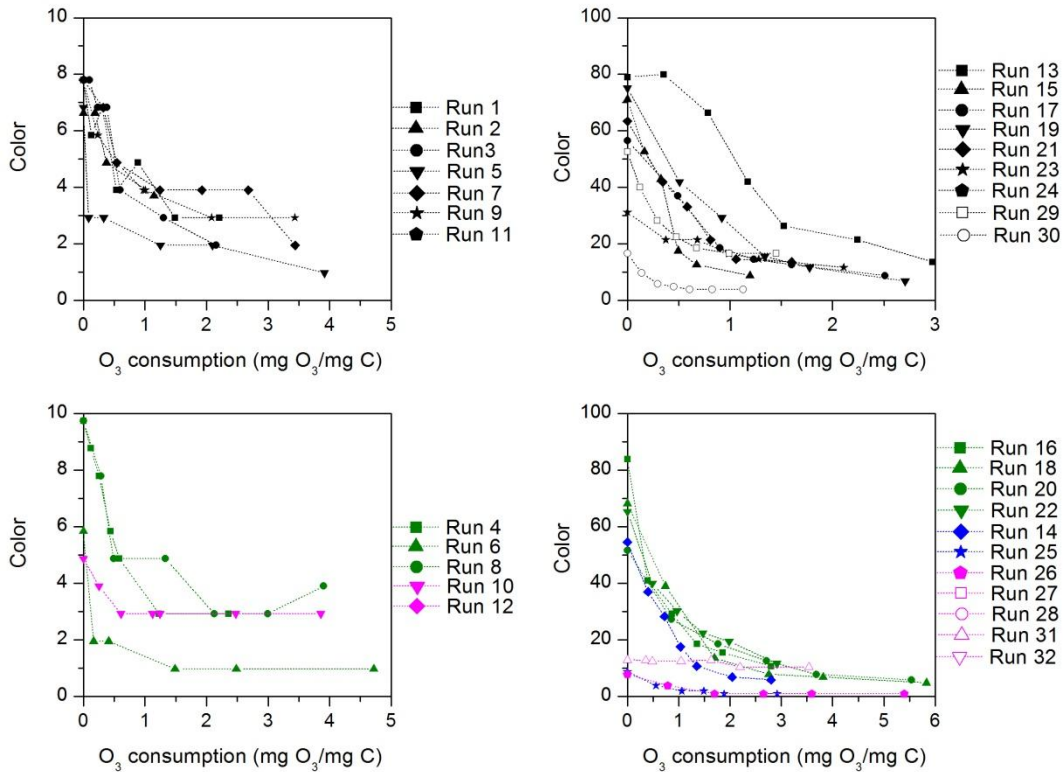
Figure 3.10   Change of color along with SOC during ozonation (left: SE; right: PE)

3.4.3   Pathogens removal

3.4.3.1   Pathogens removal by ozonation

3.4.3.1.1   Bacteria removal

Bacteria disinfection results are given in Figure 3.11 as a function of the SOC. The results showed that wastewater-original *E. coli* and total coliforms presented same inactivation speed. And the plot of wastewater-original bacterial followed a multiphasic curve, consisting of initial shoulder, rapid inactivation period and tailing-off pattern for secondary effluent. If combining bacterial removal result with DO_3 result (Figure 3.5), certain relationship among bacteria disinfection result and DO_3 concentration during ozonation could be found. Before appearing DO_3, no obvious bacteria concentration decreasing (less than 1 log removal) was found. After this point, rapid inactivation would happen.
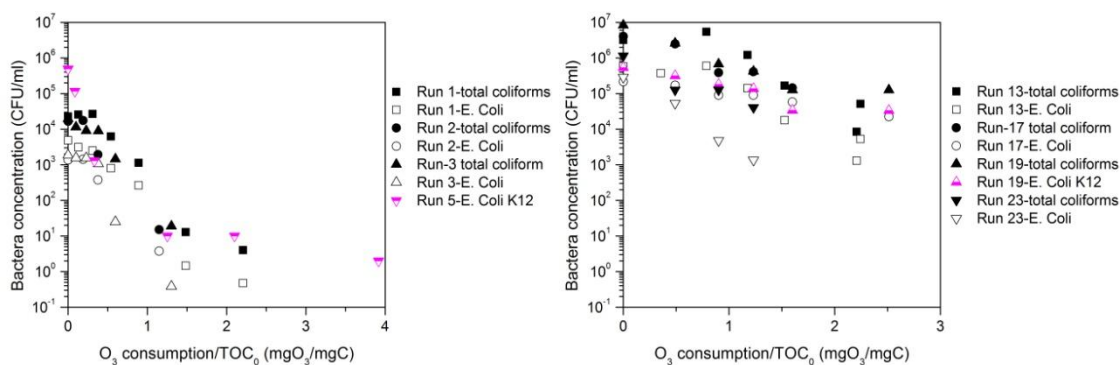
Figure 3.11   Disinfection of bacteria along with SOC during ozonation (left: SE; right: PE)

For bacteria disinfection, molecular O_3 is found more effective than hydroxyl radicals (Zuma et al., 2009). But in experiments treating secondary effluent, significant 1 log inactivation was already reached before DO_3 appeared (SOC reached 0.6 mg O_3/mg C). Similar observation was also found in earlier research (Xu et al., 2002). It could be explained by the fact that high reaction rate of bacteria with O_3 ($K_{O3}=1.0\times10^5$ $M^{-1}s^{-1}$(Hunt et al., 1997) contributing certain O_3 consumption. Afterwards, inactivation speed increased sharply. At the SOC of 1.5 mg O_3/mg C point, around 3.5 logs bacteria inactivation was observed, with less than 3 CFU/ml total coliforms and less than 1 CFU/ml *E. Coli* was left in oxidized water. After this period, no additional removal of bacteria was found with SOC increasing. In primary effluent case, no obvious inactivation was found before SOC reached 0.3 mg O_3/mg C. Increasing SOC to 2 mg O_3/mg C, inactivation rate increased to around 2.5 logs. Under this condition, total coliform and *E. coli* concentrations were still as high as 690-12600 and 137-530 CFU/ml respectively.

While for spiked *E. Coli* K12, different change trends were shown. Inactivation of *E. Coli* K12 in secondary effluent and in primary effluent results were shown as Runs 5 and 19. The spiked *E. coli* K12 could be inactivated by O_3 much faster than wastewater-original bacterial in secondary effluent (Run 5). And only rapid inactivation period and tailing-off pattern were displayed for secondary effluent. Tailing off disinfection happened after SOC reaching 1.2 mg O_3/mg C, with less than 1 CFU/ml *E. Coli* K12 left in oxidized water. The *E. Coli* K12 in primary effluent was continuously inactivated with similar speed with wastewater-original bacteria (Run 19). 3350 CFU/ml *E. Coli* K12 were still remaining in primary effluent, after the SOC increased to 2.70 mg O_3/mg C. Comparison of *E. Coli* K12 inactivation results in two kinds of wastewater, the high

removal speed in secondary effluent might caused by high initial concentration (10 times higher than wastewater-original bacteria).

3.4.3.1.2   MS2 removal

MS2 disinfection results are given in Figure 3.12 as a function of the SOC. The results showed that MS2 in secondary effluent and primary effluent presented same inactivation trend. At beginning of ozonation, MS2 concentration sharply decreased, followed by tailing off period. Tailing off phenomena happened after SOC reaching around 1.2 and 0.8 mg O_3/mg C for secondary effluent and primary effluent with 4-5 logs MS2 inactivation. At this point, several hundred MS2 left in both wastewater waters. The tail off phenomena might be caused by aggregation of MS2, or suspended solids which may produce a shielding effect from the ozone attack.
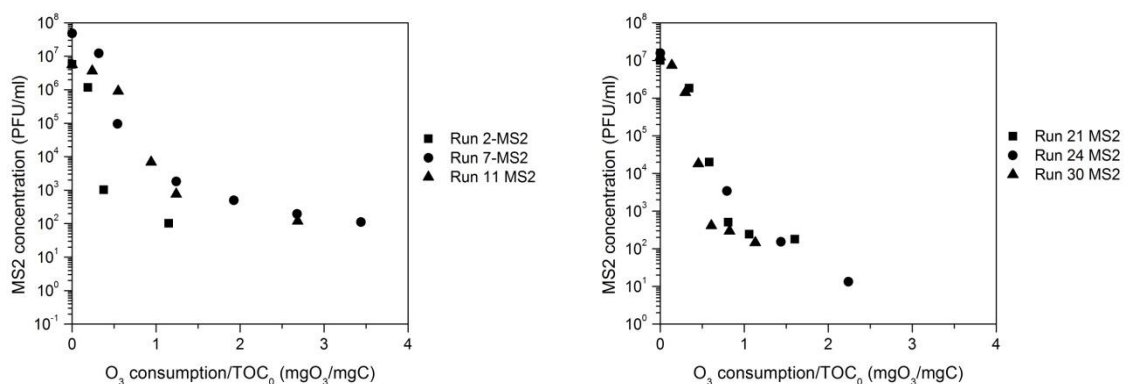
Figure 3.12   Disinfection of MS2 along with SOC (left: SE; right: PE)

3.4.3.2   CM/PAC+CM pretreatment effect

3.4.3.2.1   Bacteria removal

Bacteria disinfection during O_3 was mainly resulted not from the OH radical but from attacking by O_3 molecular (von Sonntag, 1987). And SS might protect bacteria from O_3 molecular attacking (Zimmermann et al., 2011). Thus there were two potential factors for changing inactivation efficiency by pretreatment. They were DO_3 and SS amount.

In secondary effluent case, effect of CMF pretreatment was discussed. The results were shown in Figure 3.12. In secondary effluent treatment, no enhancement by CMF pretreatment was found

(Run 5, 6). While, previous research already reported shielding effect on elimination of *E. coli* by activated sludge flocs during ozonation. Thus the result in this study might contribute to low SS (<3.0 mg/L) amount in tested water.

In primary effluent case, clear enhancement caused by CM, PAC and PAC+CM were presented (Figure 3.13). Two potential reasons might contribute the above phenomena. One is DO_3 concentration increasing during ozonation after pretreatment (Figure 3.5). The second one is removal of SS by pretreatment. The average SS concentration was around 35 mg/L. No measurable SS amount was left in filtrated water after CM and PAC+CM.
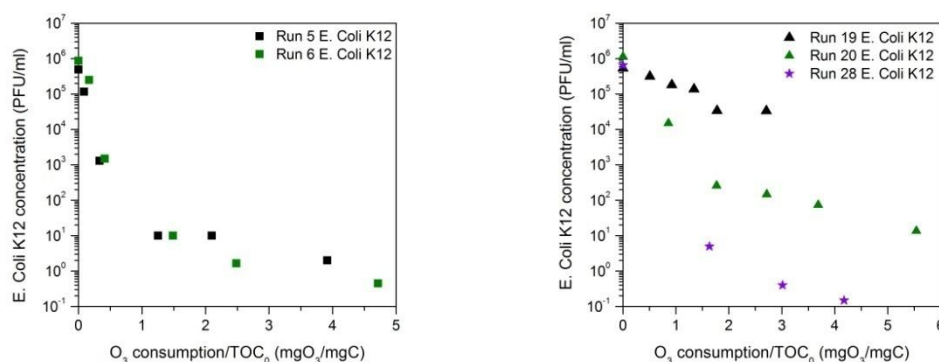
Figure 3.13   CM/PAC+CM effect on disinfection of E. Coli K12 along with SOC (left: SE; right: PE)

3.4.3.2.2   MS2 removal

For bacteriophage, both ozone or/and OH could result in attacking the protein capsid and leading to losing their ability to invade host (Kim et al., 1980). Similar with bacteria, protective effect of particles was also confirmed by previous studies, such as bentonite clay particles (Boyce et al., 1981), and organic turbidity represented by cell debris (Hoff, 1978). These indicated change of DO_3, OH radical and SS amounts by pretreatment might result in changing MS2 inactivation.

The pretreatment effect on MS2 inactivation during ozoantion was shown in Figure 3.12. In both secondary and primary effluent treatment, there were almost 2 logs difference was found for MS2 at relative higher ozone dose (SOC was larger than 1.5 mg O_3/mg C). Similar results were reported by other researchers. Ishida et al. showed 1 log higher reduction using microfiltration as pretreatment compared with normal media filtration at the same O_3 dose (Ishida et al., 2008).

For treating secondary effluent, DO_3 (Figure 3.5) and OH radical exposure assumed from DEET removal in liquid phase (Figure 3.21) did not increase after pretreatment. Thus the enhancement of MS2 removal should be caused by SS removal by pretreatment. For primary effluent treatment, improvement of MS2 inactivation by CM or PAC+CM was also found (Figure 3.12). All the DO_3, OH radical exposure in liquid phase and SS amount were changed by adding pretreatment. It was impossible to distinguish effect of each factor based on these limited results.
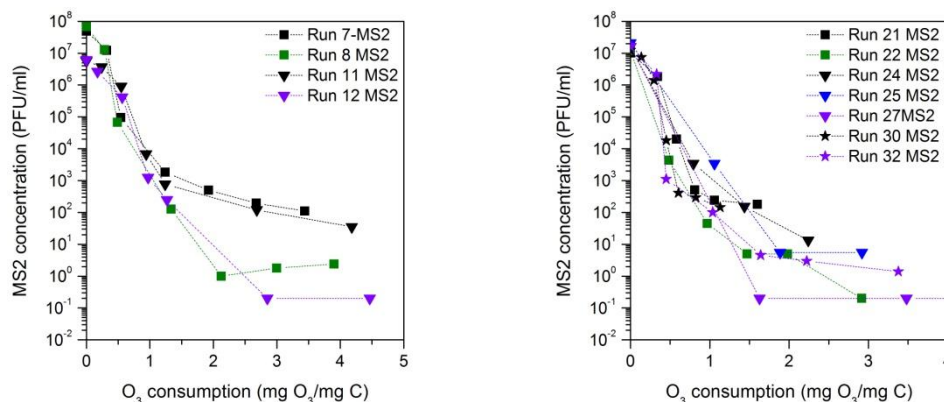
Figure 3.14   CM/PAC+CM effect on disinfection of MS2 along with SOC during ozonation (left: SE; right: PE)

3.4.4   PPCPs removal

3.4.4.1   PPCPs concentrations in wastewater

41 out of 59 PPCPs were detected in secondary (Figure 3.15) and primary effluent (Figure 3.15). Among these compounds, 13 compounds were antibiotic, 4 compounds were antiarrhythmic agents, 9 compounds were analgesics, and the others account to 15 compounds. The concentration ranged from μg L^{-1} to ng L^{-1}. And several compounds such as levofloxacin, ciprofloxacin and roxithromycin showed relative high adsorption tendency to solid. The concentration ratio in liquid and solid phase in case of secondary effluent (primary effluent) was around 10% (20%), 1% (30%) and 15% (1%) for levofloxacin, ciprofloxacin and roxithromycin respectively.
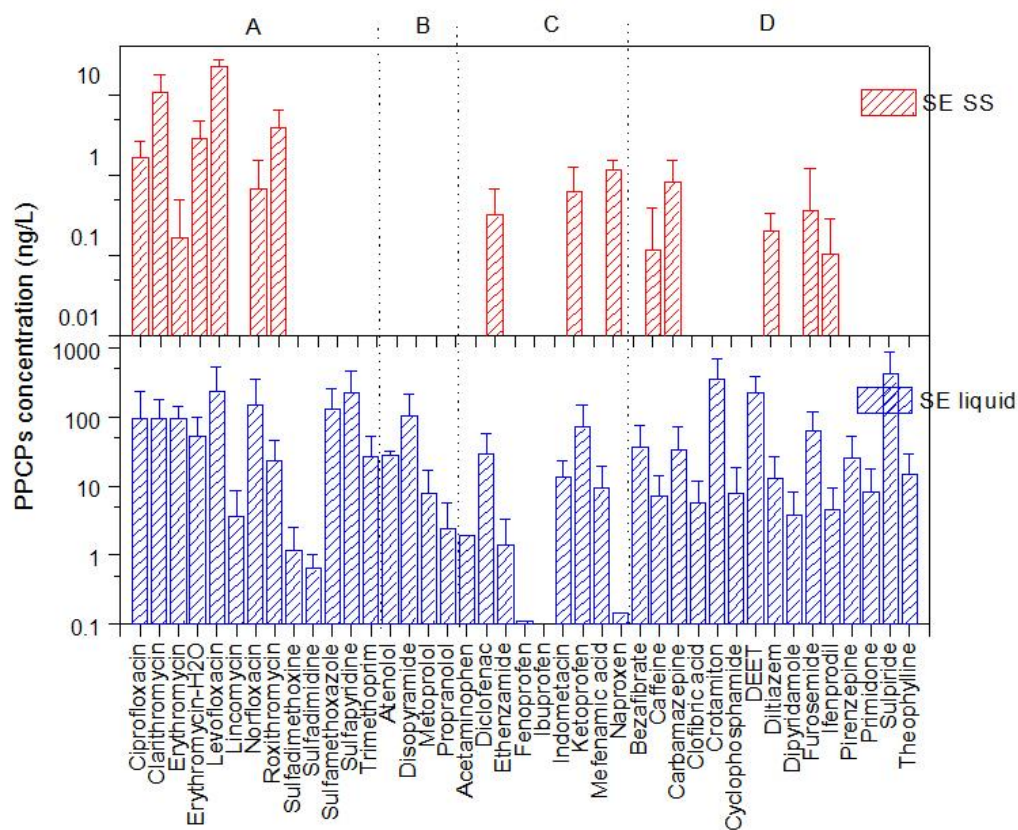
Figure 3.15   PPCPs concentration in liquid (bottom) and solid (top) phase for SE (notes: A-Antibiotic; B-Antiarrhythmic agents; C-Analgesics; D- the others)
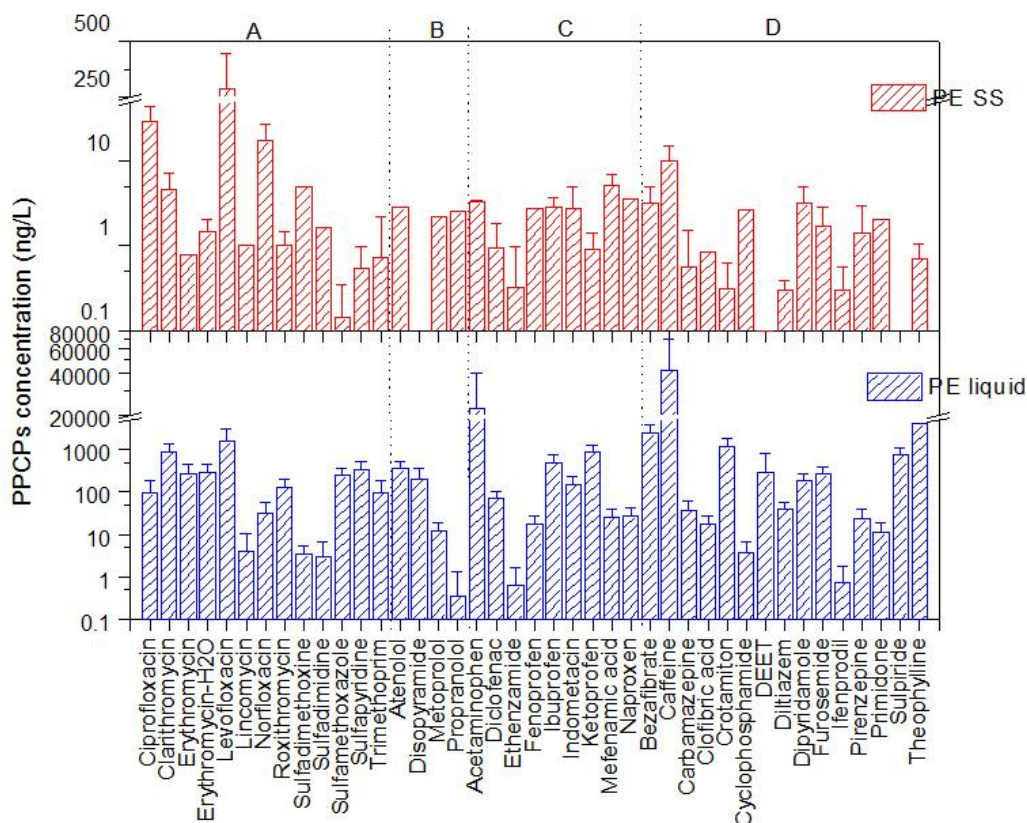
Figure 3.16   PPCPs concentration in liquid (bottom) and solid (top) phase for PE (notes: A-Antibiotic; B-Antiarrhythmic agents; C-Analgesics; D- the others)

3.4.4.2   PPCPs compounds degradability by ozonation

3.4.4.2.1   PPCPs degradability by ozonation in liquid phase

For PPCPs removal in liquid phase, removal of 29 PPCPs compounds, with higher than 2.0 ng/L concentration, by ozonation at different SOC doses were discussed. All these PPCPs compounds were divided into four categories (A-Antibiotic; B-Antiarrhythmic agents; C-Analgesics; D-the others) to discuss the degradability.

The antibiotics were eliminated significantly (over 90% removal rate) with even a relatively low ozone dosage of 0.62 and 0.29 mg O_3 /mg C for secondary effluent and primary effluent respectively (Figure 3.17). Interesting observation was DO_3 just starts to appear after this point. The high efficiency at such low ozone dosage can be attributed to the high reaction rate of each compound during ozonation. All these compounds have fast-reaction functional groups, such as

tertiary amino groups, thio group or aniline moieties, which were also proved by previous researchers (Dodd et al., 2006). Only the removal rate for ciprofloxacin was low, around 43%, at the SOC equal to 0.29 mg O_3 /mg C point. Considering reaction rate with O_3 (K_{O3}) is 1.9×10^4 for ciprofloxacin (Dodd et al., 2006), the removal rate should be much higher. And this compound show sorption affinity to solid, the concentration on solid phase (liquid phase) were 29.1 (93.8) ng/L. Meanwhile, micropollutants adsorbed on SS might be protected from ozone attack (will be discussed latter). Thus, the low removal rate was attributed to desorption of micropollutants from solid phase for lower concentration in the aqueous phase, resulted from intrinsic fast degradation.
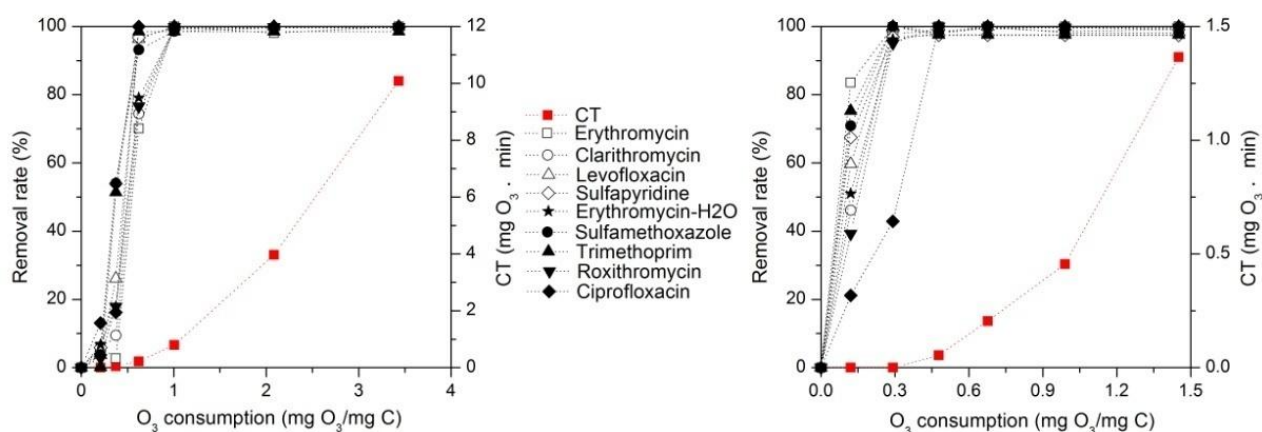
Figure 3.17   Removal of antibiotic compounds during ozonation at different SOCs (left: SE; right: PE)

For antiarrhythmic agents, the reactive sites with O_3 are activated aromatic ring and a secondary amine-moiety. The removal rate of these compounds was lower than antibiotic compounds (Figure 3.18). At the point of DO_3 just appeared, the removal rate was 42%, 34% and 51% for atenolol, disopyramide and metoprolol, respectively. It is consistent with K_{O3}. K_{O3} for antiarrhythmic compounds (10^3 M^{-1} s^{-1}) is one or two order of magnitude lower than antibiotic compound (10^4-10^5 M^{-1} s^{-1}). The disopyramide (34% removal rate) containing no secondary amine-moiety, thus showed relative lower removal compared with atenolol (42% removal rate) and metoprolol (51% removal rate).
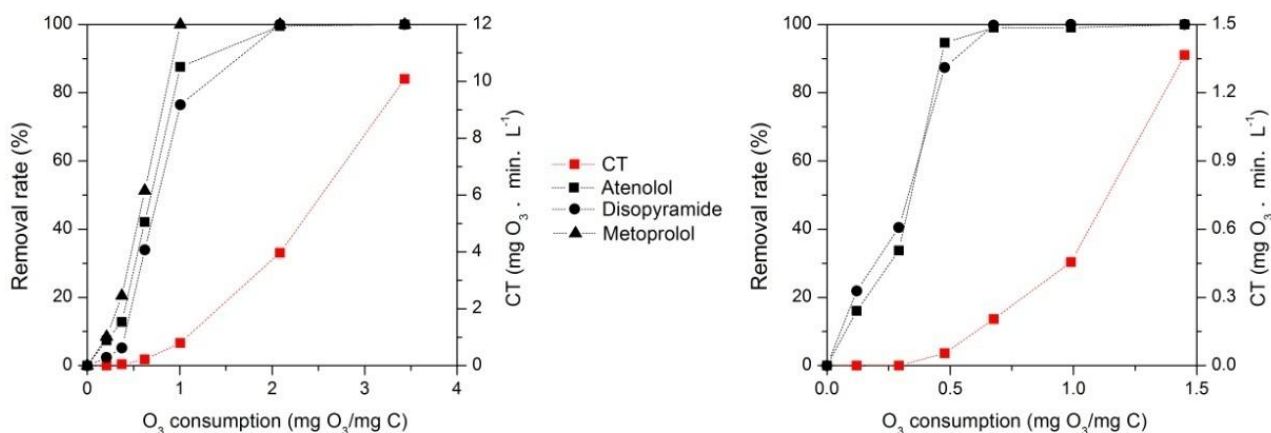
Figure 3.18   Removal of antiarrhythmic compounds during ozonation at different SOCs (left: SE; right: PE)

Ozonation performance on analgesics removal was showed in Figure 3.19. Acetaminophen, indomethacin and diclofenac (K_{O3} is $6.8 \times 10^5 \ M^{-1} \ s^{-1}$) showed quite high removal rate. It can be attributed to the main reaction site for each compound, aromatic amino group for diclofenac (Huber et al., 2003) and aromatic ring for indomethacin. ketoprofen showed low removal (around 31.9%). This caused by electron-withdrawing carboxylic groups decreasing reactivity of benzophenone with O_3.
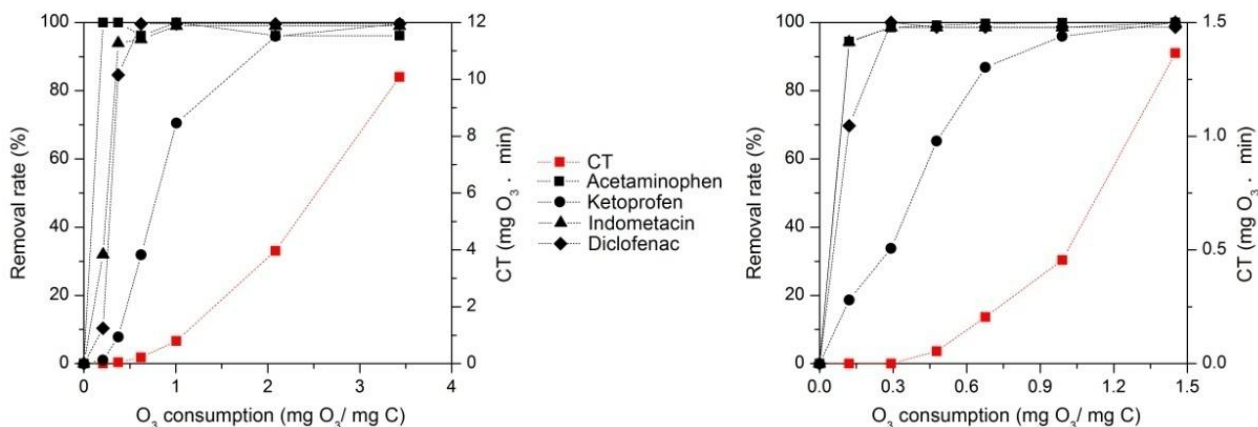
Figure 3.19   Removal of analgesics compounds during ozonation at different SOCs (left: SE; right: PE)

The other micropollutants showed quite different degradation performance for their various chemical structures (Figure 3.20). And little work has been done about oxidation these compounds during ozonation. No information was found in previous work about reaction site of

some compounds with O_3. We tried to put forward possible reaction site for each compound based on ozonation reaction mechanisms. The direct reaction of O_3 with pollutant is highly electrophilic. O_3 tended to attack to aromatic ring, carbon double bond, phenolic group, thio compounds, amines and amino acids. In addition, protonized amines and amino acid do not react with O_3 (Hoigne et al., 1983a; Hoigne et al., 1983b).

Based on these basic information and pKa value of dissociating group for each compound, we proposed that the main reaction site was aromatic ring for sulpiride, furosemide and dipyridamole. This fast-reaction site resulted in high removal for these PPCPs compounds. For diltiazem and ifenprodil, besides aromatic ring, thio group was considered as another main reason for easy degradation during ozonation.

In secondary effluent case, the removal rate of clofibric acid was around 28.7%. It might because electron-withdrawing substituents (-Cl, -O-C(CH$_3$)$_2$COOH, -COOH) decreased reactivity of aromatic ring. And similar to (Nakada et al., 2007), many compounds with an amide function such as caffeine, bezafibrate, N,N-diethyl-3-methylbenzamide (DEET) was observed persistence against O_3. The removal rate was 62.3%, 37.9%, 22.5%, respectively. The intermediate reactivity of bezafibrate is caused by the R-oxy substituent (-O-C(CH$_3$)$_2$COOH) on one of the aromatic rings (Huber et al., 2003). For caffeine, the aromatic ring containing nitrogen could be oxidized resulted in medium reaction rate (695 $M^{-1}s^{-1}$) (Broséus et al., 2009). Interesting point is the molecular structure of caffeine is same with theophylline. And theophylline could be easily degraded by O_3. The reason for low reaction rate of caffeine with O_3 might be electron-withdrawing substituents methyl substituted H in the nitrogen heterocyclic rings decreased reactivity of "C=N" in the nitrogen heterocyclic rings compared with theophylline.

While the other amide group containing compounds, such as crotamiton, carbamazepine and pirenzepine, could be completely removed at such low ozone dosage. Considering chemical structure, carbon double bond and aromatic rings were proposed as the reaction site. Such fast-reaction group resulted in high oxidation efficiency. Thus, it was deduced that compound with amide group only showed low reactivity toward O_3 under absence of electron-donating substituents. While for primary effluent treatment by ozonation, the removal rate of most compounds was similar with secondary effluent case, expect caffeine. It showed low removal rate

of 35.4% at the DO_3 just appeared point. The relative lower removal of caffeine attributed to high concentration in primary effluent.
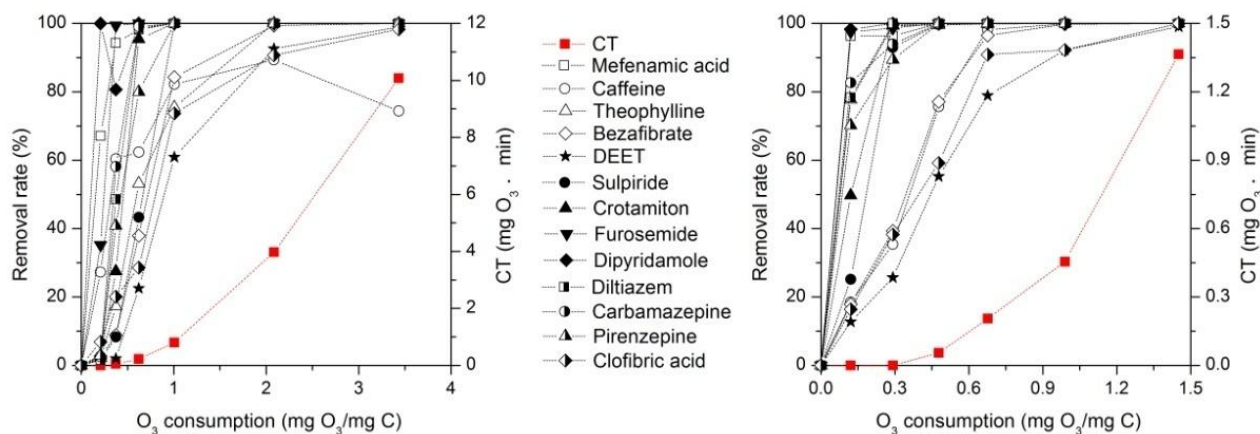
Figure 3.20   Removal of other PPCPs compounds during ozonation at different SOCs (left: SE; right: PE)

Based the above discussion, it was found that the fast-reacting substances with $K_{O3}>10^4 \ M^{-1}s^{-1}$ was effectively (>90%) removed before DO_3 appeared. Generally, these compounds contain fast-reaction functional group, such as: 1) tertiary amino groups, thio group or aniline moieties (antibiotic compounds, indomethacin, sulpiride etc.); 2) naphthalene moiety (naproxen, propranolol); 3) thio compound (diltiazem and ifenprodil). Micropollutants reacting slower with ozone ($K_{O3}<10^4 \ M^{-1}s^{-1}$), such as antiarrhythmics (except propranolol), analgesics (ketoprofen, ethenzamide, antipyrine) etc, were oxidated continuously during ozonation.

3.4.4.2.2   PPCPs degradability by ozonation in solid phase

Relative high concentration was precondition to evaluate degradability during ozonation. Thus we only discussed the compounds with over 2 ng amount in solid phase per litter wastewater.

In secondary effluent, only levofloxacin was studied due to relative high concentration in solid phase. The initial amount of levofloxacin in solid phase was 16.1 ng per litter wastewater. The amount decreased with increasing O_3 dose. The removal speed was slower than the speed in liquid phase. The pseudo-first-order reaction rate was 0.1438 and 0.2118 min^{-1} in solid phase and liquid phase, respectively. Increasing O_3 dose to 1.3 mgO_3/mgC, 2.2 ng levofloxacin were left in solid phase.

In primary effluent, degradation of eight PPCPs in solid phase was studied. They are acetaminophen, caffeine, levofloxacin, norfloxacin, ciprofloxacin, azithromycin, bezafibrate and triclocarban. The pseudo-first-order reaction rates in solid phase were compared with reaction rates in liquid phase. The result was shown in Figure 3.21. The reaction rate in liquid phase was 1.35 times as reaction rate in solid phase. The difference of the reaction rate in solid phase and in liquid phase was not so big. And only several PPCPs were detected in solid phase with much lower concentration than in liquid phase. Thus analyzing concentration of PPCPs in liquid phase was enough to evaluate ozonation performance on removal of most PPCPs.
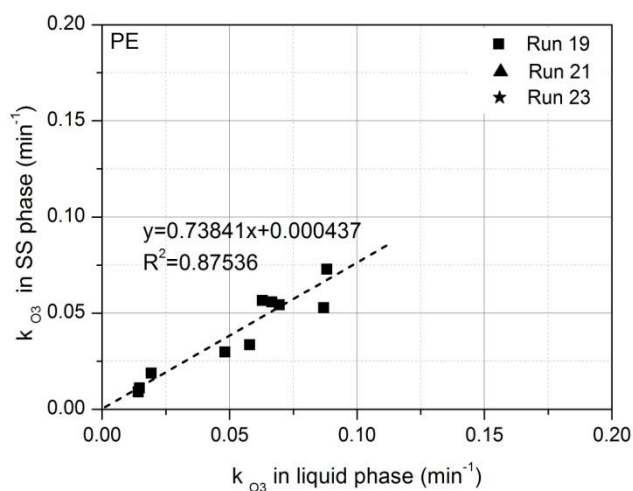
Figure 3.21   Relationship of reaction rate of 8 PPCPs during ozonation in solid phase and reaction rate in liquid phase

3.4.4.3   CM/ PAC+CM pretreatment effect

3.4.4.3.1   Pretreatment effect on PPCPs reaction rate during ozonation

Pretreatment effect on PPCPs removal during ozonation was evaluated based on pseudo-first-order reaction rate. The CMF and PAC+CMF pretreatment effects were shown in Figure 3.22. The CMF effect could be neglected due to only 2% change caused. And the reaction rate was increased by 21.5 % through taking PAC+CMF as pretreatment. The TOC value of secondary effluent was 2.75 mg/L. It decreased to 2.35 mg/L by PAC and CMF. It resulted in O_3 consumption dose per TOC was 14.5 % higher during ozonation with PAC and CMF pretreatment, resulting higher reaction rate of PPCPs.
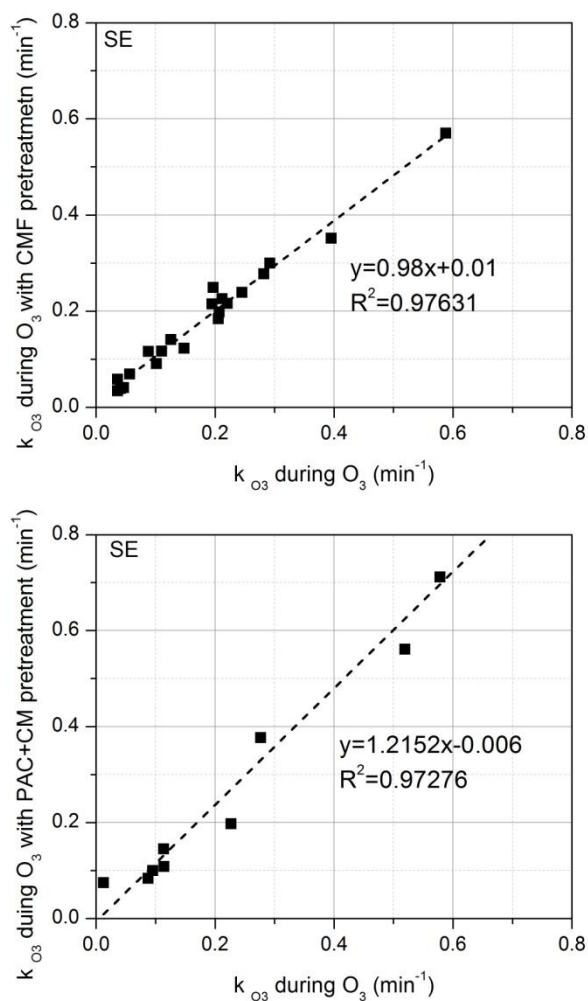
Figure 3.22   Effect of pretreatment on reaction rate of PPCPs during ozonation treating secondary effluent (top: CMF pretreatment; bottom: PAC (25 mg/L)+CMF pretreatment)

The pretreatment effect on reaction rate during ozonation treating primary effluent was shown in Figure 3.23. The reaction rate of PPCPs was increased by 1.18 and 2.94 times compared through CMF and PAC+CMF pretreatment. The TOC value was decrease by 20.8% and 64.8% by CMF and PAC+CMF pretreatment. Besides, the ratio of O_3 consumption to input O_3 was increased by 37.9% and 14.8% through CMF and PAC+CMF pretreatment, separately. Thus the O_3 consumption per TOC was increased by 172.8% and 326.1%. This could explain result of reaction rate increased by pretreatment.
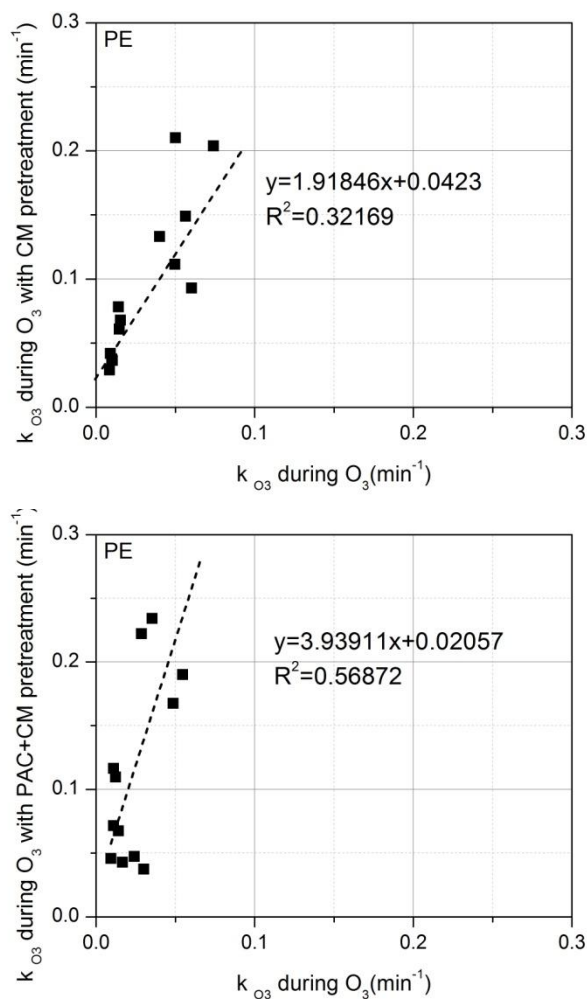
Figure 3.23   Effect of pretreatment on reaction rate of PPCPs during ozonation treating primary effluent (top: CMF pretreatment; bottom: PAC (50 mg/L) and CMF pretreatment)

3.4.4.3.2   Pretreatment effect on OH exposure formed during ozonation

Parachlorobenzoic acid (pCBA) was usually used to calculate OH exposure. The reaction rate of pCBA with molecular O_3 was ≤ 0.15 $M^{-1}s^{-1}$, the reaction rate with OH was 5×10^9 $M^{-1}s^{-1}$. Reaction rate of DEET with O_3 and OH was 5 and 5×10^9 $M^{-1}s^{-1}$ (Song, W. H. et al., 2009). Besides, Removal rate of contaminants with $K_{O3} < 10 M^{-1}s^{-1}$ was proved could be used as indicator for OH availability by previous research (Wert et al., 2009). Then we could deduce that OH exposure based on DEET removal.

The results of DEET removal were presented in Figure 3.24. The black, green, blue and violet symbol represented O_3 without any pretreatment, with CMF pretreatment, with PAC and sedimentation pretreatment, PAC and CMF pretreatment respectively. From left side figure, we could deduce that neither CMF nor PAC and CMF pretreatment could enhance removal of DEET in secondary effluent treatment. Similar result has been reported by previous research for secondary effluent treatment (Wert et al., 2011). From right side figure, improvement on removal of DEET by PAC and sedimentation, PAC and CMF pretreatment were observed in primary effluent case. But using CMF as pretreatment did not enhance DEET removal. So removing some organic matters result in DEET removal improvement. Based on these discussions, we could know that OH exposure was increased by adding PAC and sedimentation, PAC and CMF pretreatment before ozonation in primary effluent.
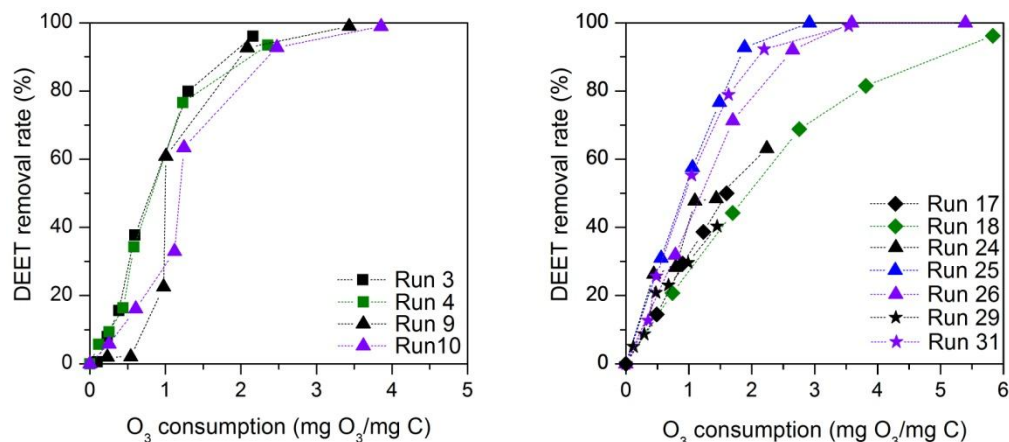
Figure 3.24   CM/PAC+CM pretreatment effect on DEET removal (left:SE; right:PE)

3.4.4.4   Comparison among different contaminants removal

SPSS statistics 17.0 software was used for correlation analysis of contaminants removal by O_3. The results were listed in Table 3.4. Pearson correlation is one common indicator to describe linear correlation between two parameters. The data of pearson correlation is in the range of 0 to 1. If the data is loser to 1, the linear relationship was stronger. The results with 0.01 level of significant (double side) showed statistical significance. From the results (table 3.4-3.5), all the contaminants removal was controlled by SOC, DO_3. It was doubtless and confirmed in previous discussions. Then correlation among different contaminants removal rates were compared. In the

secondary effluent treatment, correlations of other contaminants with SUVA were as high as 0.92, except MS2. Although the correlation in primary effluent was worse than in secondary effluent, good relationships among SUVA with other contaminants were also observed. It suggested that SUVA could be one indicator as PPCPS and pathogen removal. Then we plotted the other contaminants removal rate changing with SUVA removal rate (figure3.25-3.28).

Table 3.14　Correlation analysis of contaminants removal by ozonation with/without any pretreatment (SE)

		Concentration (mgO$_3$/mgC, mg/L)			Removal rate (%)			
		SOC	DO$_3$	SUVA	No. of PPCPs (>90% removal)	Total coliforms	E. coli	MS2
SOC	Pearson correlation	1 (1)	.821** (.810$^{**)}$)	.784** (.791$^{**)}$)	.863** (.858$^{**)}$)	.879** -	.954** (.865$^{*)}$)	.826** (.891$^{**)}$)
	N	45 (34)	45 (34)	41 (34)	14 (14)	24 -	18 (6)	18 (14)
DO$_3$	Pearson correlation		1 (1)	.844** (.746$^{**)}$)	.764** (.743$^{**)}$)	.866** -	.889** (.915$^{*)}$)	.732** (.699$^{**)}$)
	N		44 (34)	41 (34)	14 (14)	24 -	18 (6)	18 (14)
SUVA	Pearson correlation			1 (1)	.961** (.966$^{**)}$)	.926** -	.970** (.983$^{**)}$)	.709** (.901$^{*)}$)
	N			34 (27)	14 (14)	20 -	14 (6)	7 (14)
No. of PPCPs (>90% removal)	Pearson correlation				1 (1)	.955* -	.987** -	- -
	N				14 (14)	7 -	7 -	- -
Total coliforms	Pearson correlation					1 -	.967** -	.889 -
	N					24 -	18 -	4 -
E. coli	Pearson correlation						1 -	.845 -
	N						18 -	4 -
MS2	Pearson correlation							1 -
	N							18 -

Notes:
**significant correlation at 0.01 level (double side); * significant correlation at 0.05 level (double side);
- data was not available

Table 3.15   Correlation analysis of contaminants removal by ozonation with/without any pretreatment (PE)

		Concentration (mgO₃/mgC, mg/L)		Removal rate (%)				
		SOC	DO$_3$	SUVA	No. of PPCPs (>90% removal)	Total coliforms	E. coli	MS2
SOC	Pearson correlation	1 (1)	.788** (.743**)	.872** (.808**)	.856** (.709**)	.931** (.919**)	.880** (.962**)	.889** (.816**)
	N	57 (69)	57 (69)	41 (51)	44 (50)	20 (9)	21 (10)	17 (21)
DO$_3$	Pearson correlation		1 (1)	.843** (.807**)	.777** (.564$^{**)}$)	.837** (.945**)	.804** (.826**)	.876** (.877**)
	N		57 (69)	41 (44)	44 (50)	20 (9)	21 (10)	17 (21)
SUVA	Pearson correlation			1 (1)	.916** (.897**)	.866** (.843**)	.740** (.782*)	.947** (.915)
	N			41 (44)	38 (44)	19 (8)	20 (9)	6 (16)
No. of PPCPs (>90% removal)	Pearson correlation				1 (1)	.768** (.612**)	.747** (.677**)	.909** (.964**)
	N				44 (50)	16 (9)	17 (10)	10 (10)
Total coliforms	Pearson correlation					1 (1)	.861** (.949**)	- (.976*)
	N					16 (9)	20 (9)	- (4)
E. coli	Pearson correlation						1 (1)	- (.867)
	N						21 (10)	- (4)
MS2	Pearson correlation							1 (1)
	N							17 (21)

Notes:
** significant correlation at 0.01 level (double side); * significant correlation at 0.05 level (double side);
- data was not available

Figure 3.25 showed the relation between the number of PPCPs (>90% removal) and SUVA removal. Clear linear relationship was observed both in secondary effluent and primary effluent. Pretreatment showed no obvious effect on changing this relation. The number of PPCPs discussed in this part was 36 and 32 PPCPs for secondary effluent and primary effluent, respectively. The number of PPCPs with a removal efficiency of more than 90% was 32-35 under 50-60% SUVA removal rate in secondary effluent. The number of PPCPs with over 90% removal rate was 28-30 under 55-63% removal rate. Therefore, it is considered that the 60% SUVA removal should be achieved in order to satisfy high removal of a variety of PPCPs in both secondary effluent and primary effluent.

Figure 3.26 showed the relation between the *E. coli* removal and SUVA removal. After lag period from beginning to 12% and 20% SUVA removal in secondary effluent and primary effluent respectively, *E. coli* removal rate increased with SUVA removal increasing. In secondary effluent treatment, clear linear relationship was shown. The linear correlation was poor in primary effluent treatment case. The different reaction mechanisms of *E. coli* and aromatic matters with O_3 caused these phenomena. During ozonation, aromatic matters in the wastewater consumed the O_3 molecular immediately after O_3 injected. O_3 consuming speed decreased with aromatic matters amount decreasing. After the consuming speed lower than injection speed, DO_3 would appear, followed by *E. coli* inactivation. While the DO_3 concentration changed much by wastewater characteristics, correspondingly it leaded to poor correlation in primary effluent treatment. So removal of SUVA was not suitable to indicate *E. coli* inactivation during ozonation. Figure 3.27 showed *E. coli* disinfection with DO_3 concentration changing. The relationship of *E. coli* with DO_3 was better than with SUVA. And difference between without pretreatment and with pretreatment was observed in secondary effluent case under large SOC dose, it might be resulted from lightening tailing off problems through removal SS effect by pretreatment. No clear difference caused by pretreatment in primary effluent case. And it was found with 0.1mg/L DO_3 appearance, 1.5-2.5 logs of *E. Coli* could be inactivated.
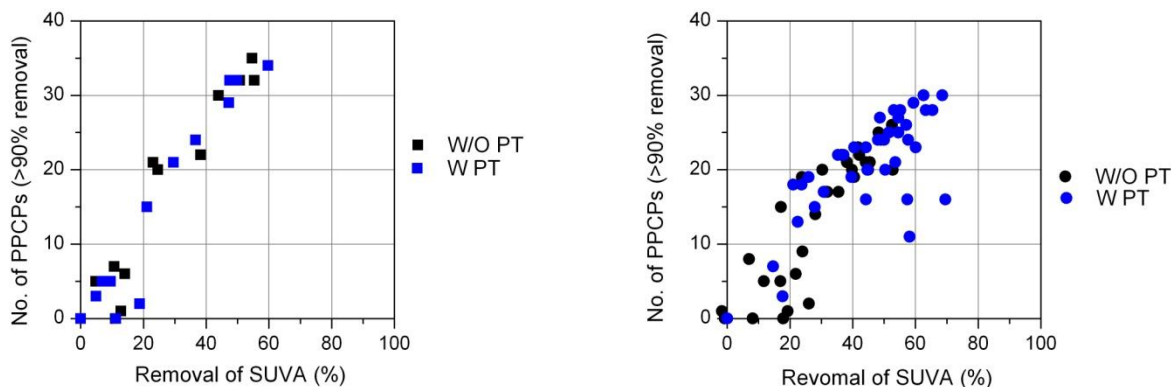
Figure 3.25   Relation between number of PPCPs (>90% removal) and the removal of SUVA during ozonation without pretreatment (W/O PT) or with pretreatment (W PT) (left:SE; right:PE)
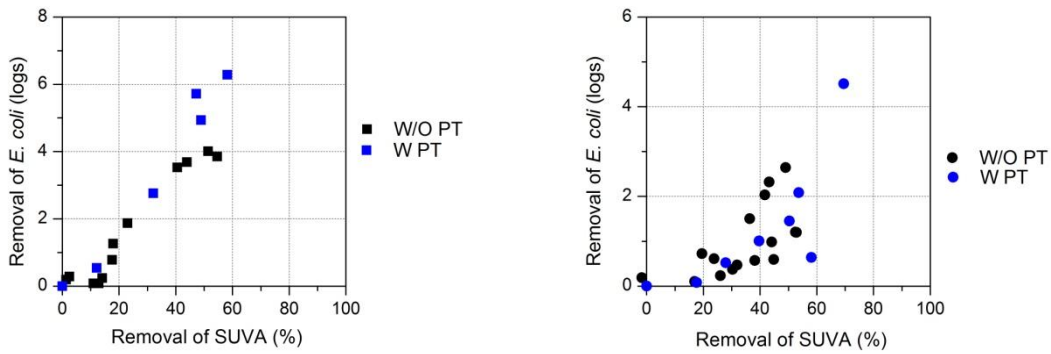
Figure 3.26   Relation between removal of *E. coli* and the removal of SUVA during ozonation without pretreatment (W/O PT) or with pretreatment (W PT) (left:SE; right:PE)
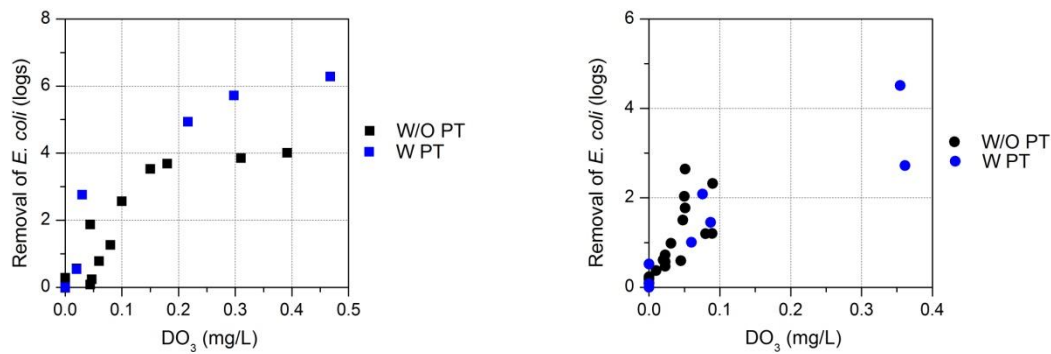
Figure 3.27   Relation between removal of *E. coli* removal with DO_3 concentration during ozonation without pretreatment (W/O PT) or with pretreatment (W PT) (left:SE; right:PE)
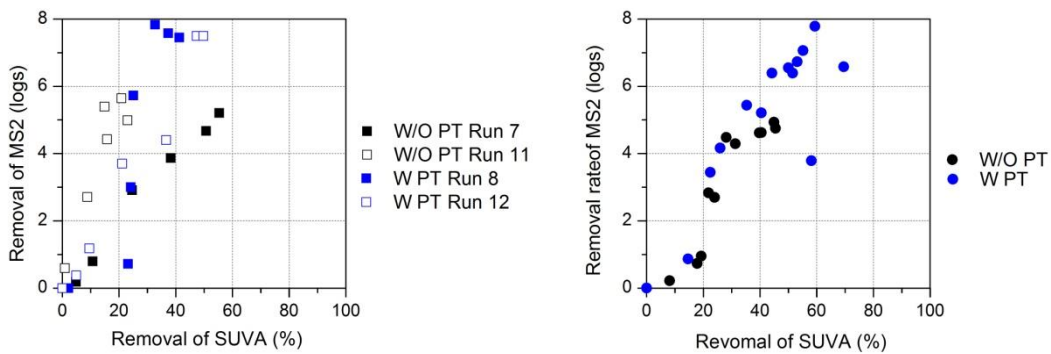
Figure 3.28   Relation between removal of MS2 and the removal of SUVA during ozonation without pretreatment (W/O PT) or with pretreatment (W PT) (left:SE; right:PE)

Figure 3.28 showed the relation between the MS2 removal and SUVA removal. Poor relationship in secondary effluent was found. In order to explore the reasons, the data points were classified to four groups. The same wastewater was used for each group. Then we found

correlation was much better in the same group. Thus we could deduce that influence of wastewater characteristics on the relation of MS2 removal with SUVA removal must be considered. In other word, SUVA was not suitable indicator to evaluate removal of MS2.

3.5 Summary

The objective of this chapter was to research the degradability of contaminants by ozonation, including common water quality items, bacteria, virus indicator MS2 and PPCPs compounds. Furthermore, the effect of CM/PAC/PAC+CM pretreatment on these contaminants degradation was studied. For these purposes, the semi-batch experiments were conducted, and the conclusions obtained are listed as follows:

1.   TOC values of both secondary effluent and primary effluent almost were not changed during ozonation. After consuming 3.0 mg O_3/mg C dose O_3, the removal rate of COD_{Mn} could arrive around 23.4 % and 10% for secondary effluent and primary effluent, respectively. The SUVA of secondary effluent and primary effluent could be reduced by 39.2-58.6% and 48.9-68.1%, respectively at 1.5 mg O_3/mg C dose. CMF, PAC+CMF pretreatment showed limited enhancement effect on removal of these common water quality items, while showed significant effect on increasing DO_3 concentration during treating primary effluent.

2.   Ozonation performances on bacteria inactivation were found different in secondary effluent and primary effluent. The bacterial disinfection followed a multiphasic curve, consisting of initial shoulder, rapid inactivation period and tailing-off pattern for secondary effluent. While bacterial in primary effluent was continuously inactivated at quite slow speed during ozonation. Around 3.5 logs bacteria inactivation could be achieved in secondary effluent at the SOC of 1.5 mg O_3/mg C point, while in primary effluent case, around 2.5 logs bacteria disinfection was attain at the same SOC dose. CMF pretreatment showed no effect on bacteria inactivation in secondary effluent. While, obvious enhancement on bacteria disinfection was observed in primary effluent due to increasing DO_3 by CMF, PAC+CMF pretreatment.

3.   Similar changing trend for MS2 in two kinds of wastewater were observed. 4-5 logs MS inactivation was achieved after SOC reaching around 1.2 and 0.8 mg O_3/mg C for secondary effluent and primary effluent respectively. CMF and PAC+CMF pretreatment showed tiny enhancement on MS2 inactivation, expect lightening tail off phenomena.

4.   41 out of 59 PPCPs were detected in wastewater. For PPCPs in liquid phase, all the antibiotics could be effectively (90% removal rate) degraded by ozonation before DO_3 appeared with SOC of 0.6 and 0.3 mg O_3/mg C for secondary effluent and primary effluent, respectively. For antiarrhythmic agents, the SOC should be doubled to effectively remove them (90% removal rate). For analgesics and other compounds, most compounds could be easily removed, except ketoprofen, caffeine, bezafibrate, DEET, clofibric acid. For PPCPs in solid phase, only levofloxacin was studied in secondary effluent due to relative high concentration in solid phase. The pseudo-first-order reaction rates were 0.1438 and 0.2118 min^{-1} in solid phase and liquid phase, respectively. In primary effluent, degradation of eight PPCPs in solid phase was studied. They were acetaminophen, caffeine, levofloxacin, norfloxacin, ciprofloxacin, azithromycin, bezafibrate and triclocarban. The reaction rate in liquid phase was 1.35 times as high as reaction rate in solid phase. This is the first time to compare reaction rate of PPCPs in liquid phase and in solid phase.

5.   CMF and PAC+CMF pretreatment were found no obvious effect on changing ozonation efficiency for degradation PPCPs during treating secondary effluent. While in primary effluent case, removal efficiency of PPCPs during ozonation was enhanced by coagulation+sedimentation and coagulation (PAC)+CMF. It was proposed that OH exposure was increased by adding PAC+sedimentation, PAC+CMF pretreatment before ozonation.

6.   Relation among different contaminants removal was calculated using SPSS statistics 17.0 software. Clear relationship of SUVA removal with number of PPCPs (>90% removal) in both wastewaters was found. SUVA showed high possibility to be used to control O_3 injection for PPCPs removal in the application field. And DO_3 concentration showed clear relation with bacteria removal during ozonation. While for MS2 removal, it showed linear

relation with removal of SUVA in primary effluent. In secondary effluent case, the relationship was affected by wastewater characteristics.

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CHAPTER IV

Performance of Ceramic Membrane Filtration-based Processes during Treating Secondary Effluent

4.1 Introduction

Among various water reclamation treatments, low-pressure membrane technology has been extensively studied, due to high removal of turbidity and bacteria, low energy consumption and small footprint (Wintgens et al., 2005). However, an inevitable problem with membrane processes is the loss of membrane productivity over time, i.e. membrane fouling. It would increase energy costs, and system downtime for maintenance (Ciston et al., 2009). Pretreatment prior to the application of membrane was one common option to increase the sustainable flux by reducing the organic matter loading on membrane. Several pretreatment methods such as adsorption, flocculation and coagulation have been studied and were found to reduce fouling (Farahbakhsh et al., 2004; Huang et al., 2009).

Recently, ceramic membrane (CM) makes it possible to incorporate various pretreatments with membrane process, including oxidation, due to mechanically superior and chemical resistance. It was found that the membrane fouling extent decreased obviously by application of coagulation before membrane (Ellouze et al., 2005; Konieczny et al., 2006; Lerch et al., 2005; Loi-Brügger et al., 2006). Ozonation pretreatment was also successfully used to reduce membrane fouling thus obviate the need to backwash or clean the membranes (Kim et al., 2008; Kim et al., 2002; Schlichter et al., 2003). And Lehman et. al. (Lehman et al., 2009) investigated application of ceramic membrane filtration (CMF) for wastewater treatment plant (WWTP) effluent treatment. It was showed that ozonation and coagulation pretreatment was quite effective to mitigate membrane fouling. There was, however, no information about mechanisms of mitigation

membrane fouling by each pretreatment. In addition, the combination process was not evaluated based on product water quality aspect.

Thus the objective of this work was to evaluate the potential of CMF with pretreatments by ozonation and coagulation for water reuse in terms of product water quality and membrane fouling mitigation aspects. Besides, mechanisms of membrane fouling during CMF with and without pretreatment were also studied to some extent.

4.2 Experimental setup and conditions

4.2.1 Ozonation pretreatment using bench scale reactor

Ozonation experiment setup in this study consists of three reactors (R1, R2 and R3) (Figure 4.1). The effective volume and reaction time of one reactor is 35 L and 5 minutes, respectively. The secondary effluent is fed into reactor from top side through magnetic drive pump (MD-15RN, IWAKI CO., LTD). The flow rate is 7 L/min. The O_3 gas is injected into the reactor through a diffuser at the bottom of the first reactor. O_3 gas is produced by an O_3 generator (FZH-12, Fuji Electric Co.). Two O_3 gas monitors (model-600, Ebara Jitsugyo Co., OZ-20, Fuji Electric Co.) are used for monitoring influent and effluent O_3 gas concentrations, respectively. O_3 gas flow rate is adjusted by a flowrate meter (SUS 316, Flow-Cell Co.). In this study, the O_3 gas flow rate is 0.6 L/min. Influent O_3 gas concentration is controlled to obtain desired O_3 dosage. The raw wastewater and oxidized water after the first reactor (reaction time=5min) and the second reactor (reaction time=10 min) was collected to study on O_3 performance on contaminants removal.

For ozonation, coagulation and CMF combination study, the oxidized water after the first or the third reactor was fed into coagulation and CMF equipment. The detail of coagulation and CMF equipments are described in the following section.
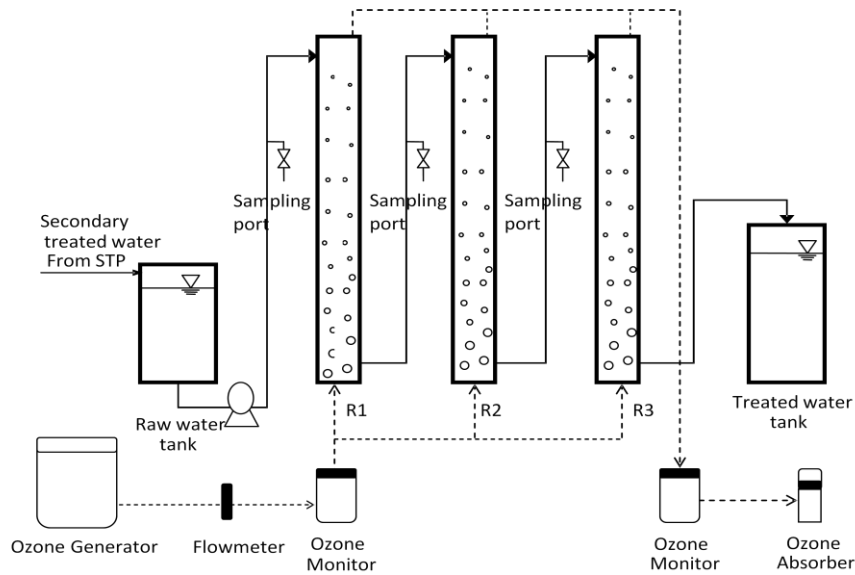
Figure 4.1   Bench scale ozonation reactor setup

4.2.2   Coagulation and CMF experimental setup

Two sets of coagulation and CMF equipments (Figure 4.2) are operated at the same time to evaluated ozonation, coagulation and CMF combination process. The coagulation was conducted using a 8L tank with mechanical agitation at 150 rpm (G=36.4 s^{-1}). The feed water flow rate for coagulation is 1 L/min. Polyaluminium chloride (PAC) was dosed from top side continuously. Then the treated water was fed in the CMF at 4m/d flow rate. The CMF was operated at dead-end mode with the same membrane used in Chapter 4. Filtration cycle was 30 minutes, followed by backwashing under 0.3 MPa. This experiment was lasted for 5 days to evaluate change of reversible and irreversible fouling through TMP recording. The CMF was operated for 20 minute filtration to remove residual filtrated water in membrane house. Afterwards, raw water and filtrated water was collected to evaluate removal of common water quality items, including bacteria, turbidity, TOC, DOC, COD$_{Mn}$, TN, TP, SUVA and color. Then rejection of virus indicator MS2 was measured through spiking MS2 stock solution in the raw water. At the end of experiment, after removing cake layer on the surface of the membrane, foulants were extracted using NaOH (pH=11) and HCl (pH=2) solution. Solution to extract foulants was analyzed amount of polysaccharide, protein, humic substances, TOC and UV$_{254}$. In order to examine

coagulation pretreatment effect on fouling control, particle size distributions (PSD) of samples before and after coagulation were also measured.
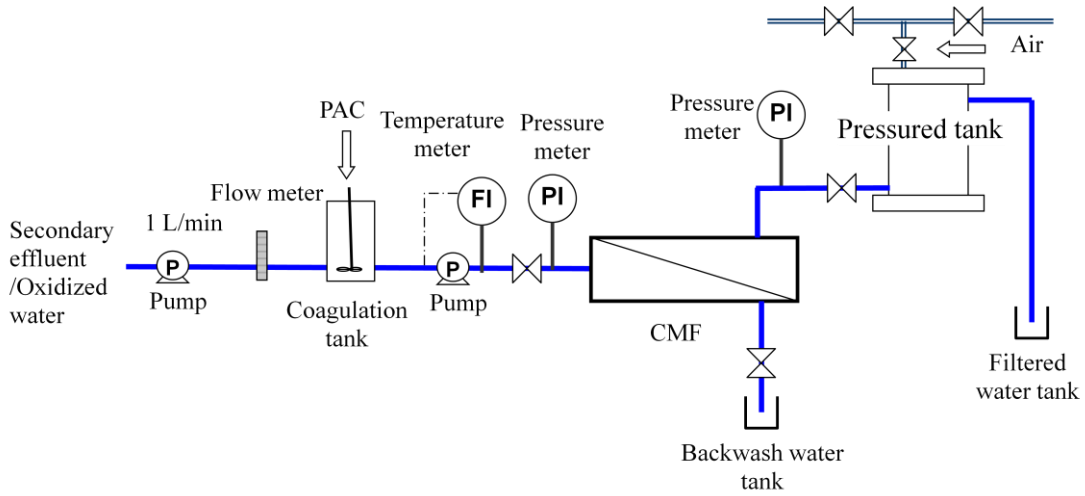
Figure 4.2   Continuous coagulation and CMF experimental setup

4.2.3   Experimental conditions

Two facility sets consisting coagulation and CMF were operated at the same time to study ozonation and/or coagulation effect on CMF. Firstly, PAC dose was optimized with high O_3 dose (6 mg/L) pretreatment. 15 minutes reaction time was selected to consume DO_3 in ozonation reactor thus prevent O_3 gas releasing from the coagulation tank. During the same time coagulation and CMF combination process performance was evaluated under different PAC doses. Then performance of coagulation with two PAC doses on CMF process was studied under lower O_3 dose (2, 4 mg/L) pretreatment. The major characteristics of the tested wastewater and experimental conditions were listed in Table 4.1.

Table 4.1   Major Characteristics of the Tested Wastewater and Experimental Conditions

Date	Operational parameters				Major characteristics of feed water to PAC+CMF				
	O$_3$		PAC	CM					
	Input O$_3$ dose	Reaction time	Dose	Flux	SS	Turbidity	pH	TOC	UV$_{254}$
	mg/L	min	mg/L	m/d	mg/L	NTU		mg/L	cm^{-1}
2012.06.12-06.18	6	15	50	4	0.4	0.76	6.65	3.05	0.024
2012.06.18-06.25	6	15	25	4	-	1.13	6.46	2.75	0.018
2012.06.18-06.25	0	-	25	4	-	1.70	6.44	2.35	0.049
2012.06.25-07.02	6	15	15	4	-	1.4	6.43	2.89	0.018
2012.06.25-07.02	0	-	35	4	0.9	1.71	6.46	2.28	0.049
2012.07.09-07.17	4	5	25	4	3.6	6.09	6.45	3.67	0.03
2012.07.09-07.17	4	5	35	4	3.6	6.09	6.45	3.67	0.03
2012.07.17-07.23	2	5	25	4	-	0.79	6.54	2.47	0.029
2012.07.17-07.23	2	5	35	4	-	0.79	6.54	2.47	0.029
2012.07.23-07.24	0	-	0	4	1.9	3.03	6.39	2.96	0.054
2012.07.23-07.28	0	-	15	4	1.9	3.03	6.39	2.96	0.054
2012.07.24-07.30	0	-	50	4	-	3.39	6.40	2.84	0.053

Notes:
"-"means data was not available

4.2.4   Analytical methods

Total organic carbon (TOC) and dissolved organic carbon (DOC) concentrations were measured with a TOC analyser (TOC-5000A, Shimadzu, CO.). COD$_{Mn}$, total nitrogen (TN), dissolve total nitrogen (DTN), total phosphorous (TP) and dissolve phosphorous (DTP) were analyzed according to standard method (Lenore et al., 1999). UV$_{254}$ and color were measured by a spectrophotometer (UV-16000, Shimadzu, CO.). Turbidity was measured by a turbidity meter (2100Q01, HACH CO.). Particle size distribution (PSD) was measured by SALD-2000 (Shimadzu, CO.). Protein and humic substances were analyzed using Lowry's method (Lowry et al., 1951) and modified Lowry' method (Frolund et al., 1995), respectively. And bovine serum albumin and humic acid were used as a standard, separately. Polysaccharide was analyzed by phenol-sulfuric acid method (Dubois et al., 1956), and the results were given as glucose equivolent. The humic subastants and certain protein matters in the solution was analyzed

through fluorescence Excitation–Emission Matrices (EEMs) method. The fluorescence spectrophotometer (F-4500, Hitachi, Ltd. Japan) was used. Emission scans were performed from 200 to 600nm at 5nm steps, with excitation wavelengths from 200 to 600nm at 5nm intervals.

4.3   Results and discussions

4.3.1   Performance of ozonation pretreatment using bench scale reactor

4.3.1.1   Specific O_3 consumption calculation

Specific O_3 consumption (SOC) which is O_3 consumption divided by initial DOC was used for evaluation of the O_3 performance. The consumed O_3 was calculated by the following formula:

$$\text{Consumed } O_3 \text{ (mgO}_3) = \frac{(G_{O_3,\text{gas in}} - G_{O_3,\text{gas out}}) \times Q_{O_3}}{Q_{\text{water}}} - D_{O_3}$$

Where $G_{O_3, \text{gas in}}$ is the gas O_3 concentration at the inlet (mg/L), $G_{O_3, \text{gas out}}$ is the gas O_3 concentration at the outlet (mg/L), Q_{O_3} is the gas flow rate (L/min), Q_{water} is the wastewater flow rate (L/min), D_{O_3} is the dissolved O_3 concentration (mg/L).

4.3.1.2 DO_3

The DO_3 result was shown in Figure 4.3. The DO_3 after first reactor (with 5 minutes reaction time) appeared after 0.60 mgO$_3$/mgC O_3 consumed. This was nearly same as results taken using semi batch O_3 reactor (Chapter 3). The DO_3 would be decomposited or consumed by contaminants in the second reactor. Thus the DO_3 for 10 minutes reaction time was lower than the result for 5 minutes. With 4 mg/L O_3 input dose, the O_3 consumption was 0.95 and 1.12 mgO$_3$/mgC, respectively, the DO_3 was 0.64 and 0.16 mg/L for 5 and 10 minutes reaction time, respectively.
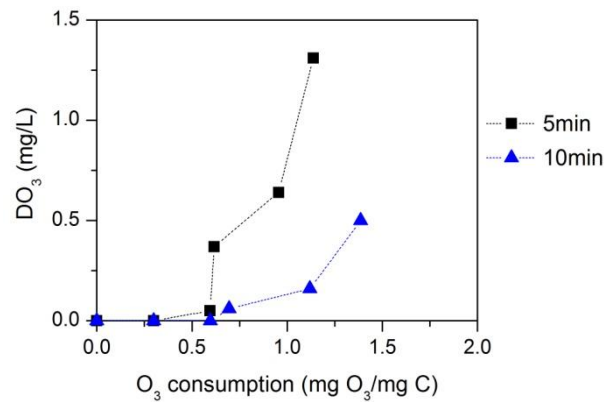
Figure 4.3   DO$_3$ results using bench scale ozonation reactor with factor of O$_3$ consumption

4.3.1.3   Removal of common water quality items

The ozonation performance on COD$_{Mn}$, TOC was described in Figure 4.4. The black and blue symbols showed the results for 5 and 10 minutes reaction time, respectively. There was no obvious difference between removals of contaminant during different reaction times. And with increasing O$_3$ consumption, removal of all these contaminants indexes was increased to certain extent. Removal of COD$_{Mn}$ was 17.6 % at point of 1.38 mgO$_3$/mgC dose. The removal rate of TOC was 10% lower than COD$_{Mn}$ at the same dose, due to incomplete mineralization during ozonation. Figure 4.5 presented removal of SUVA and color with a factor of O$_3$ consumption. The SUVA and color removal was 46.7% and 70.0% with 1.14 mg mgO$_3$/mgC O$_3$ consumption, respectively.
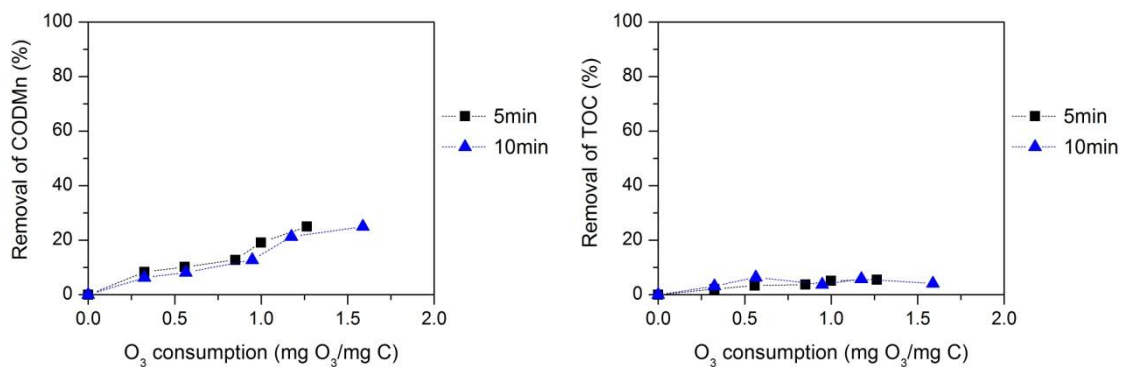
Figure 4.4   Removal of COD$_{Mn}$ and TOC using bench scale ozonation reactor with factor of O$_3$ consumption and reaction time
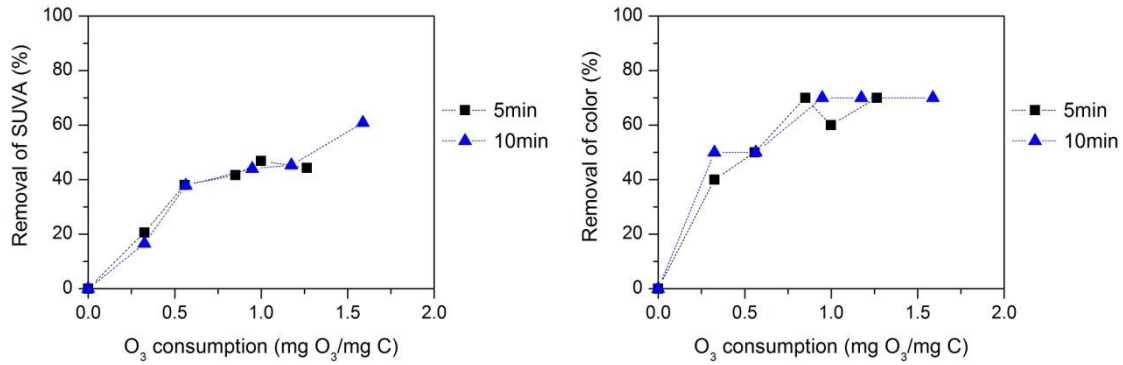
Figure 4.5   Removal of SUVA and color using bench scale ozonation reactor with factor of O_3 consumption and reaction time

4.3.1.4   Pathogen removal

Bench scale ozonation performance on bacteria was shown in Figure 4.6. There was no obvious difference between 5 and 10 minute reaction time. 2.0 logs of total coliforms and 2.7 logs of *E. coli* were inactivated with 0.56 mgO$_3$/mgC consumption. There were two reasons for such high inactivation observed without DO$_3$ appearance. Firstly, the removal could be explained by the fact that high reaction rate of bacteria with O_3 (KO$_3$=1.0×10^5 M^{-1}s^{-1}(Hunt et al., 1997)) contributing certain inactivation of bacteria. Similar observation was also found in earlier research (Xu et al., 2002). Secondary, it might be caused be incomplete mixing between the O_3 gas and wastewater. DO$_3$ might already partially appear in the O_3 reactor. It resulted in high bacteria inactivation without DO$_3$ detection. Only 80 CFU/100ml and 55 CFU/100ml total coliforms and *E. coli* were left after this period. Afterwards, the inactivation speed was much lower for tailing off phenomena. It could be explained as follows, some bacteria was associated with wastewater particles (Loge et al., 2002), the particles would significantly protect pathogen from attacking by oxidants (Boyce et al., 1981). During the ozonation, 8 and 5 CFU/100ml total coliforms and *E. coli* were left after increasing O_3 consumption to 1.00 mgO$_3$/mgC. Thus it is difficult to completely kill all bacteria through O_3.
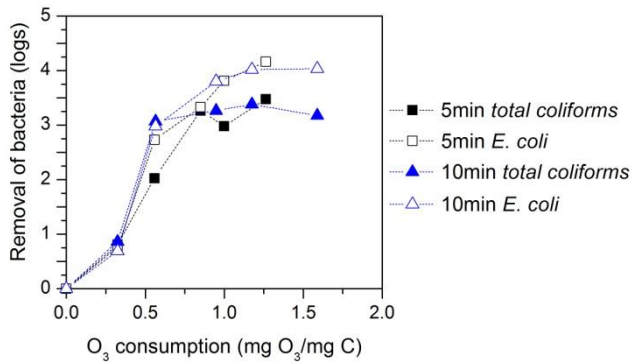
Figure 4.6   Total coliforms and *E. coli* removal using bench scale ozonation reactor with factor of O_3 consumption and reaction time

The bench scale O_3 performance on MS2 removal was shown in Figure 4.7. Same as bacteria disinfection, no significant difference was observed between results of 5 and 10 minutes reaction time. But much higher disinfection speed was observed than bacteria. 5.1 logs lost their activities after consuming 0.62 mgO_3/mgC, with 14.5 PFU/ml MS2 left in oxidized water. Afterwards, removal rate kept stable among 5.0 to 7.0 logs for tailing off phenomena.
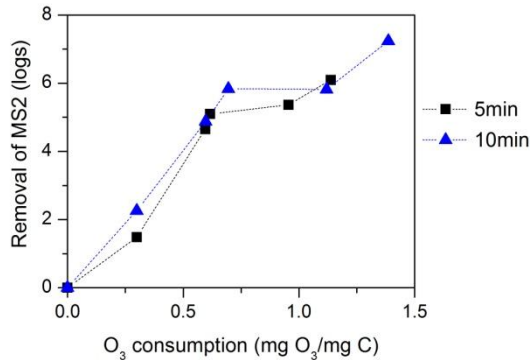
Figure 4.7   MS2 removal using bench scale ozonation reactor with factor of O_3 consumption and reaction time

4.3.1.5   PPCPs removal

36 PPCPs detected in secondary effluent were degraded by O_3. Similar results were observed for 5 minutes and 10 minutes reaction time (Figure 4.8-4.9). All these PPCPs compounds were divided into four categories (A-Antibiotic; B-Antiarrhythmic agents; C-Analgesics; D-the others) to discuss the degradability. In order to degrade most of PPCPs, SOC of 0.56 mg O_3/mg TOC_0

were needed. All the fast-reaction compounds with $KO_3 > 10^4$ $M^{-1}s^{-1}$ were effectively (with 90% removal rate) removed before DO_3 appeared. It was accord with previous finding (Chapter 3). But the removal rate of each PPCP was much higher than results gotten using semi-batch O_3 reactor. It was discussed in next section.
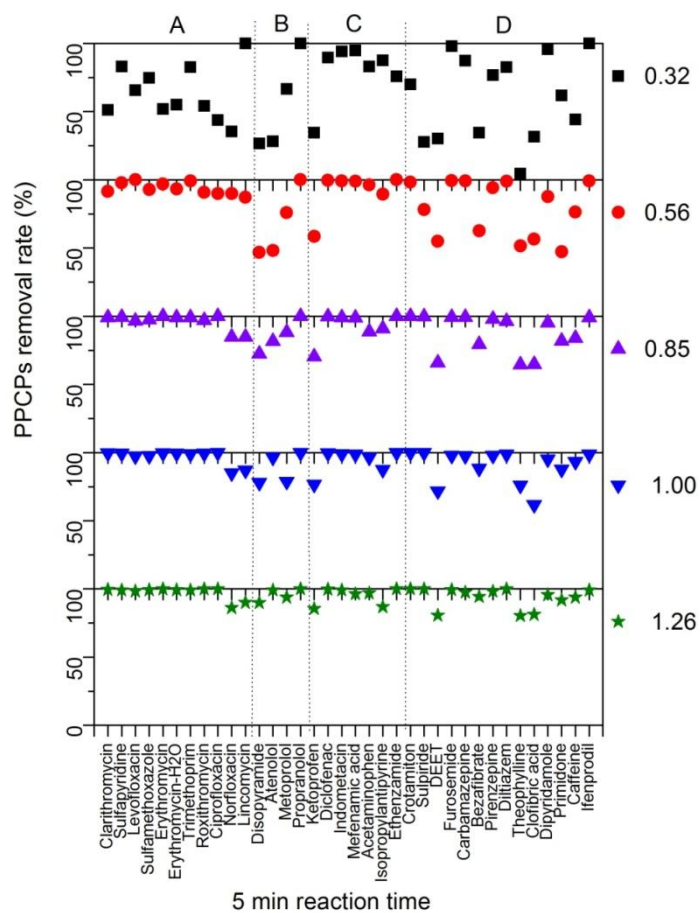
Figure 4.8   PPCPs compounds removal using bench scale ozonation reactor with factor of O_3 consumption under 5 minute reaction time (A-Antibiotic; B-Antiarrhythmic agents; C-Analgesics; D-the others)
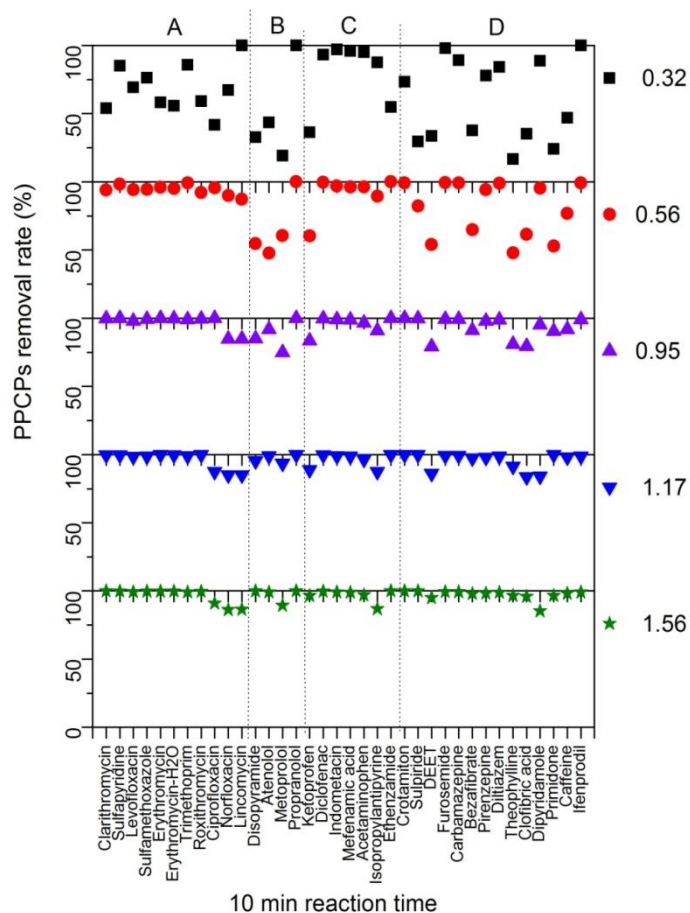
Figure 4.9   PPCPs compounds removal using bench scale ozonation reactor with factor of O_3 consumption under 10 minute reaction time (A-Antibiotic; B-Antiarrhythmic agents; C-Analgesics; D-the others)

4.3.1.6   Comparison PPCPs removal results during ozonation using semi-batch reactor and bench scale ozonation reactor

The reaction rate of antibiotics and DEET with O_3 (K_{O3}) is over $1.1\text{-}67 \times 10^5$ $M^{-1}s^{-1}$ (Huber et al., 2005) and 10 M^{-1} s^{-1} (Song, W. et al., 2009), respectively. The reaction rate of antibiotics and DEET with OH (K_{OH}) was $2.9\text{-}8.5 \times 10^9$ (Huber et al., 2005) and 5×10^9 M^{-1} s^{-1} (Song, W. et al., 2009), separately. Consideration the same level of K_{OH} with less than 1 magnitude difference and much different K_{O3}, the effect of O_3 molecular and OH on PPCPs removal could be roughly discussed based on antibiotics and DEET removal respectively. And this idea has been proved by previous work. It was showed that the percentage of degradation which resulted from OH reaction was negligible for easy reaction compound with O_3 (Hollender et al., 2009). While over

80% removal of compounds with low reaction rate with O_3, such as atrazine (K_{O3}=6.0 $M^{-1}s^{-1}$), was attributed to OH reaction (Hollender et al., 2009). Thus the ratio of antibiotic removal with DEET removal was used to evaluate reactor effect on forming OH. The removal of sulfamethoxazole was used to compare O_3 consumption calculated during ozonation using semi batch and bench scale reactor.

Removal of sulfamethoxazole during ozonation was plotted with factor of O_3 consumption as Figure 4.10. Significant right side shift of figure was observed. Although the experiments were conducted using secondary effluent collected on different day. The PPCPs degradability during ozonation was proved to be stable for wastewater sampled on different days in Chapter 3. Thus the difference should be caused by O_3 consumption calculation. This error mainly attribute to O_3 consumption calculated in semi batch reactor. The calculation method was shown in Chapter 3. We assumed gas phase in head space was perfect mixed, the O_3 concentration at outlet of reactor equaled to the concentration in head space. But the gas phase was much closer to plug flow. Certain errors would be showed for calculation O_3 mass in the head space. This caused O_3 consumption calculated was larger than real amount in using semi batch reactor case. O_3 consumption in bench scale O_3 rector was calculated after 30 minutes operation. Thus the O_3 consumption in bench scale O_3 rector would be equal to real amount.
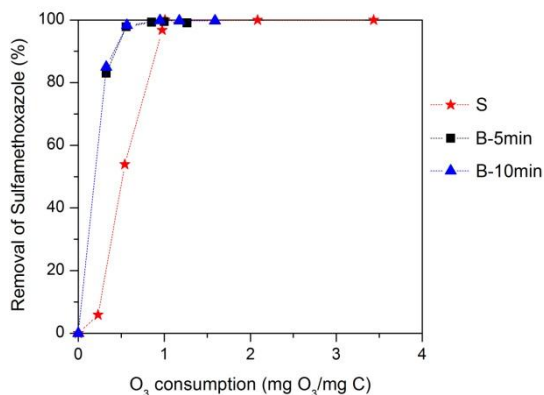
Figure 4.10   Effect of reactor on Sulfamethoxazole removal during ozonation using semi-batch reactor
(reactor described in chapter 3)

Figure 4.11 showed relationship between antibiotics removal and DEET removal during ozonation using semi batch reactor. Figure 4.12 showed the results using bench scale reactor with 5 minutes (left) and 10 minutes (right) reaction time. All the antibiotics were effectively removed

before measurable removal of DEET using semi batch reactor. For bench scale reactor, antibiotics started to be eliminated after 30% and 33% DEET removal was observed for 5 and 10 minute reaction time respectively. It should be mentioned that the exact reaction time was difficult to calculate for semi batch reactor, due to the reaction time was changed with different sampling time. But because the sampling time was 0, 1.5, 2.5, 5 minutes for the first four symbols. The reaction time was much shorter than 5 minutes in semi batch reactor.
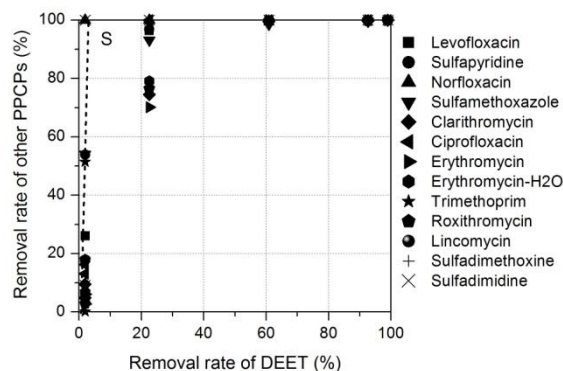
Figure 4.11   Relation of antibiotics removal and DEET removal during ozonation using semi batch reactor
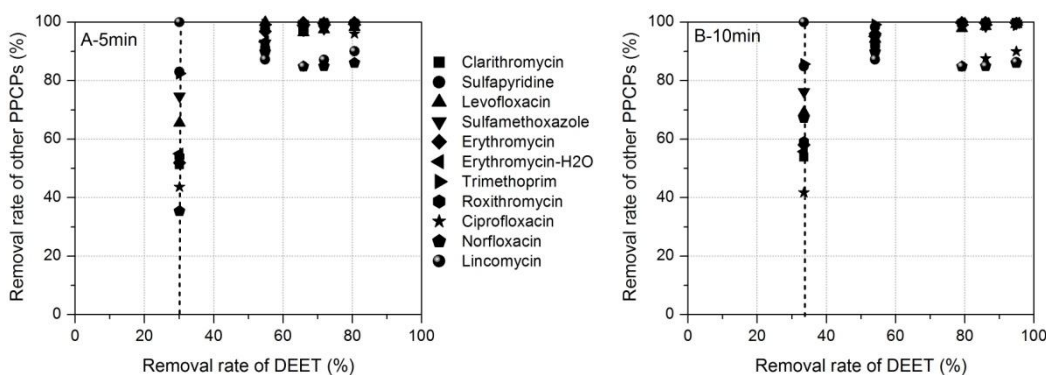
Figure 4.12   Relation of antibiotics removal and DEET removal during ozonation using Bench scale reactor (left: 5minutes reaction time; right: 10 minutes reaction time)

It was reported that significant OH forming was experienced during the first 20 second of ozonation (Buffle et al., 2006). Similar result was also presented by other researchers, it was found that over 70% of the overall OH formed during the first 30 seconds of ozonation (Wert et al., 2009). Thus it was deduced that no obvious OH amount was expected with longer than 1

minute reaction time. Due to O_3 gas was continuously fed into semi batch reactor. Thus there was always certain amount O_3 experienced less than 1 minute reaction time. It caused less OH amount formed during ozonation. Based on above discussions, different O_3 feeding pattern in semi batch and bench scale ozonation reactor was one important reason for different performance on PPCPs removal.

4.3.2 Performance of CMF-based processes

4.3.2.1 Removal of contaminants

4.3.2.1.1 Removal of common water quality items

Removal of common water quality items by ozonation, coagulation and CMF combination processes was shown in Figure 4.13. Coagulation effect was studied based on experiments adding 0, 15, 50 mg/L PAC doses. These experiments were done on adjacent days. Wastewater characteristics used was nearly same. The rejection COD_{Mn}, TOC, DOC, SUVA and color by CMF was 53.8%, 21.6%, 10.8%, 0.38% and 14.3% respectively. The removal rate increased with increasing PAC dose. The removal rate increased to 69.1%, 33.8%, 20.3% 10.0% and 42.9% under adding 50mg/L PAC before CMF.

Although experiments with ozonation pretreatment were done on different days under various wastewater qualities, there was clear changing trend appeared. Removal of organic matters (COD_{Mn}, TOC) tended to decreased by 0-30% through ozonation pretreatment. Degradation larger organic matter or particles into smaller organic matter resulted in more organic matter passed through coagulation and CMF processes, decreasing removal rate. In the other hand, ozonation pretreatment improved SUVA and color removal rate, due to ozonation could effectively degrade aromatic matters and matters with chromophoric groups. With ozonation pretreatment under 4 or 6 mg/L input dose, removal rate of SUVA and color increased to 60%-70% and 100%.
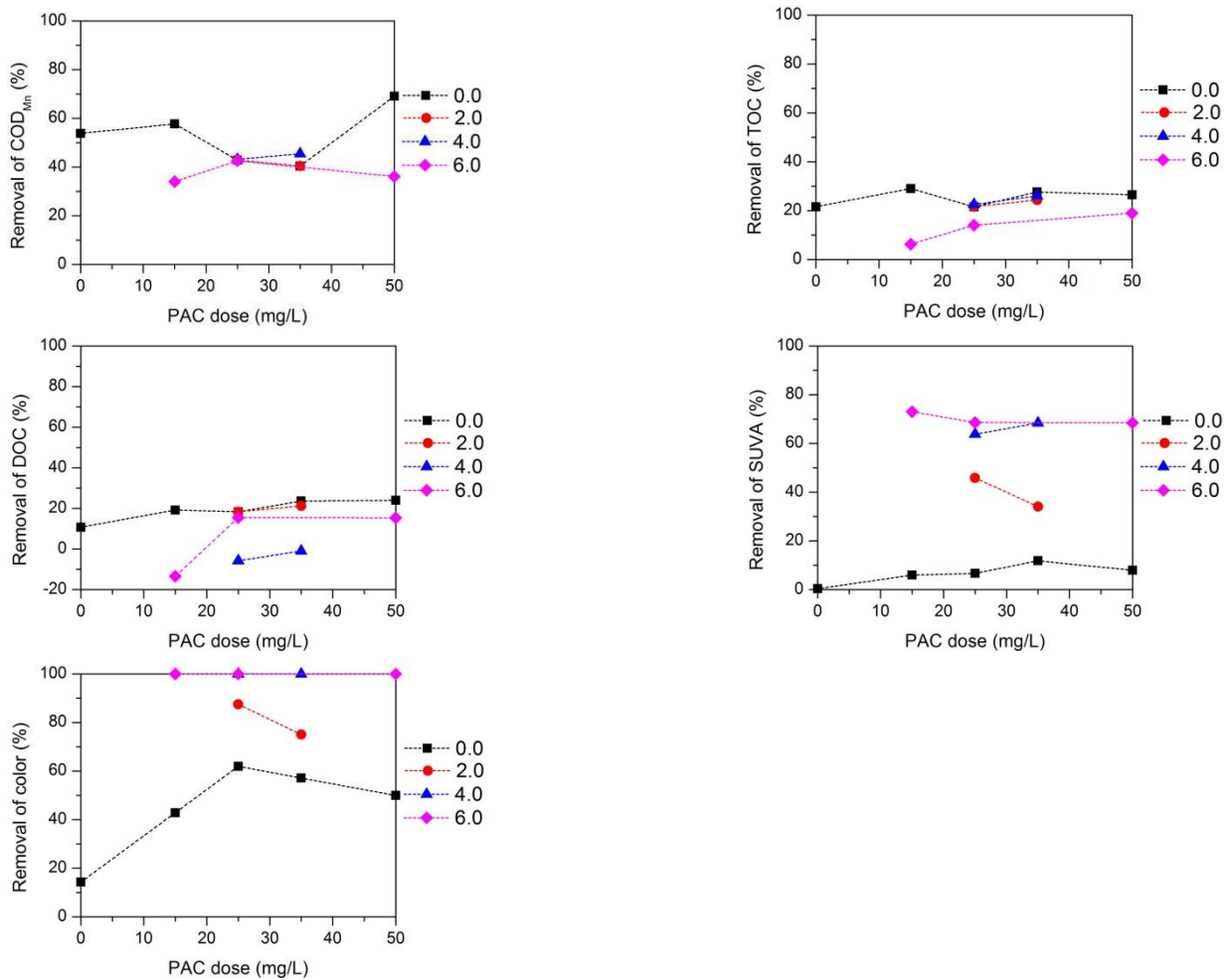
Figure 4.13   Common water quality items removal with factor of PAC dose during ozonation, coagulation and CMF combination processes (data shown in legend meant O_3 dose)

4.3.2.1.2   Removal of pathogen

The bacterial and MS2 removal by coagulation and CMF combination processes was shown in table 4.2. CMF could completely reject all the *E. coli* and total coliforms. No bacteria was detected in 100 ml filtrated water. And only 0.45 logs MS2 could be removed by CMF. The removal rate increased significantly by incorporated with coagulation pretreatment. With adding 15, 25, 35, 50mg/L PAC before CMF, no MS2 was detected in 50 ml filtrated water. The removal rate was over 8 logs. Unfortunately, ozonation pretreatment effect on MS2 removal by coagulation and CMF could not be studied for not detected MS2 in all cases. Under 2, 4, 6 mg/L input O_3 conditions, over 8 logs MS2 rejection by coagulation and CMF could be also achieved.

Considering excellent ozonation performance on MS2 inactivation (see in 4.3.1.4), MS2 removal by ozonation, coagulation and CMF combination processes was much higher than 8 logs.

Table 4.2   MS2 rejection by ozonation, PAC and CMF combination processes

O_3 Input O_3 dose	PAC Dose	CM Flux	E. coli/total coliforms	MS2 rejection by PAC and CMF part
mg/L	mg/L	m/d	CFU/100ml	logs
0	0	4	N.D.	0.45
0	15	4	N.D.	>8.14
0	25	4	N.D.	>8.57
0	35	4	N.D.	>8.26
0	50	4	N.D.	>8.09
2	25	4	N.D.	>8.16
2	35	4	N.D.	>8.34
4	25	4	N.D.	>8.09
4	35	4	N.D.	>8.13
6	15	4	N.D.	>8.23
6	25	4	N.D.	>8.30
6	50	4	N.D.	>8.38

Notes:
"N.D.": Not Detected

4.3.2.1.3   Removal of PPCPs

The number of PPCPs (>90% removal) by coagulation and CMF combination process with ozonation pretreatment was shown in Figure 4.14. The number of PPCPs discussed in this part was 36 PPCPs. The combination processes could reduce PPCPs concentration through changing operation parameters, mainly through changing O_3 dose. PAC and CMF presented quite limited removal rate. It was reasonable considering pore size was much larger than PPCPs molecular size. The number of PPCPs with a removal efficiency of more than 90% was 0-1, 28-30, 36 and 38 for adding 0, 2, 4 and 6 mg/L dose O_3, respectively.
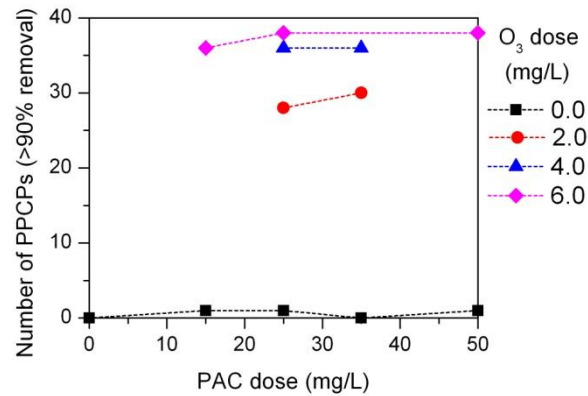
Figure 4.14   Number of PPCPs(>90% removal) by ozonation, coagulation and CMF combination processes with factor of PAC and O_3 dose (data shown in legend meant O_3 dose)

4.3.2.2   TMP change

4.3.2.2.1   Coagulation +CMF processes

Figure 4.15 showed membrane fouling was obviously mitigated by adding PAC before CMF. Without adding PAC, TMP increased to 70 kPa within 6 hours. The operation time before TMP reached 70 kPa could increase to100 hours, 135 hours and 77 hours by adding 15mg/L, 25 mg/L and 35 mg/L PAC, respectively. Increasing PAC dose to 50mg/L, the TMP increasing speed was much slower. TMP just increased from 15 kPa to 31 kPa duing 120 hours filtration.
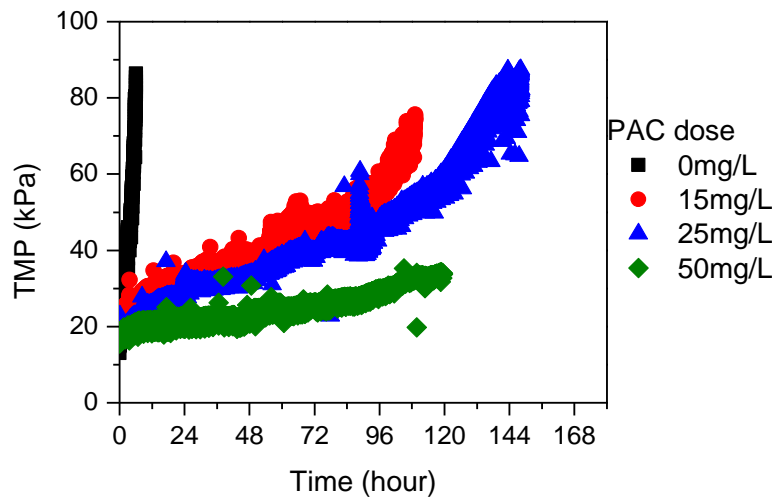
Figure 4.15   TMP changing of CMF with adding PAC

4.3.2.2.2   Ozonation+coagulation+CMF processes

With adding 6.0 mg/L of O_3, the O_3 consumption and DO_3 were in the range of 3.8 to 4.4 mg/L and 0.2 to 1.5 mg/L, respectively. The DO_3 was analyzed just after O_3 reactor. Although certain amount of DO_3 appeared, it decreased under detection limit at the CMF inlet after 8 minutes coagulation. Thus DO_3 effect on fouling mitigation was not discussed in this work. The TMP at starting point of each filtration cycle increased from 21 to 38 kPa in 136 hours with adding 15 mg/L of PAC (Figure 4.16-A). With adding 25 mg/L of PAC (Figure 4.16-B), TMP increased from 20 to 25 kPa within 136 hours. And under adding 50 mg/L of PA, TMP was not increased within 136 hours. Besides, no obvious TMP increasing during each filtration cycle with adding 25 and 50 mg/L of PAC was observed. Thus 25 mg/L was suitable PAC dose for control CMF fouling with 6mg/L O_3 pretreatment.
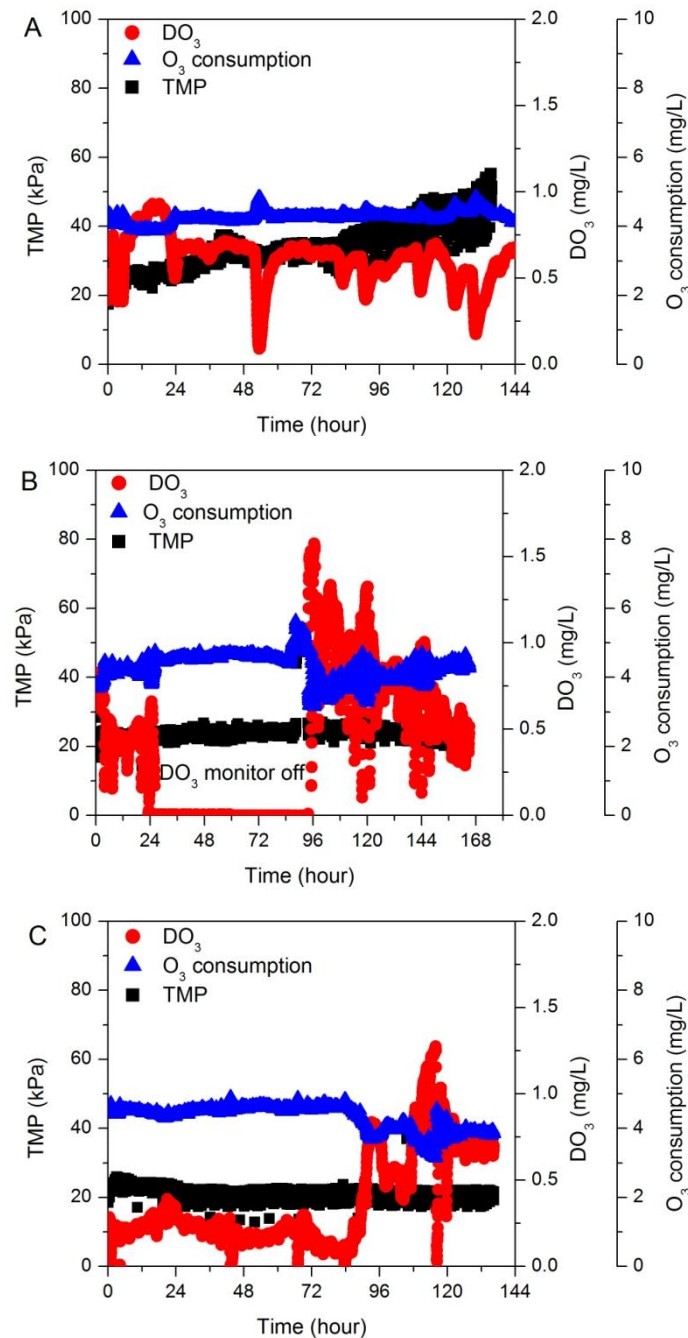
Figure 4.16   PAC dose effect on TMP changing of CMF with ozonation pretreatment (O_3 input dosage=6.0mg/L; A: PAC dose=15mg/L; B: PAC dose=25 mg/L; C: PAC dose=50 mg/L)

Figure 4.17 showed the fouling mitigation by adding PAC before CMF with ozonation pretreatment under 4 mg/L O_3 dose. During first 75 hours filtration, membrane fouling could be effectively controlled by adding 25 mg/L PAC. But afterwards, TMP sharply increased to 80 kPa

within 9 hours. In case of adding 35 mg/L of PAC, similar results were found with prolonging of effectively fouling controlling period to 96 hours. Unfortunately, we have no information about wastewater quality changing during 72 and 144 hours during filtration. But we could get some idea based on O_3 consumption and DO_3 results. The DO_3 concentration was a little higher during this period than most other timing (Figure 4.18-A). While it indicated that contaminants in wastewater might be lower during 72 and 96 hours. Thus water quality changing was not the main reason for the sharp TMP increasing. Potential other reasons was tried to be found through measuring foulants extracted from used membrane. Detail information was shown in foulants characteristic parts.
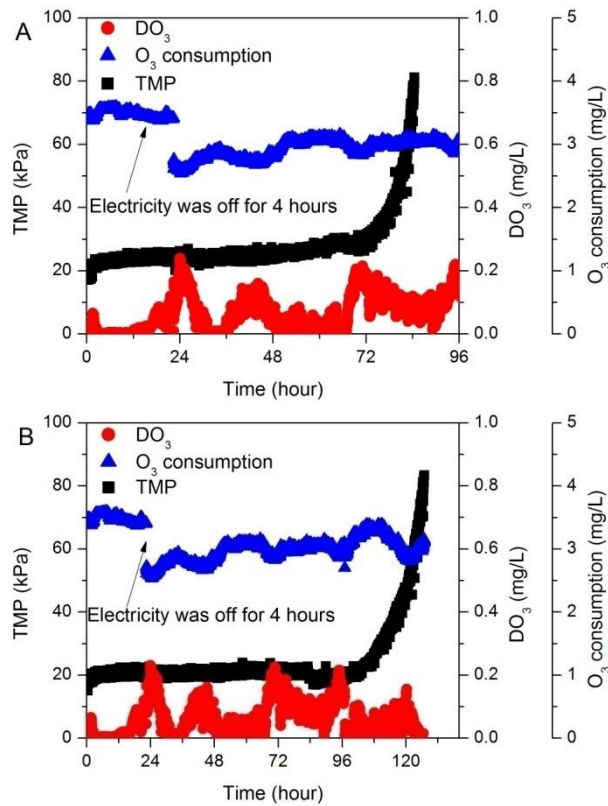
Figure 4.17   PAC dose effect on TMP changing of CMF with ozonation pretreatment (O_3 input dosage=4.0mg/L, A: PAC dose=25mg/L; B: PAC dose=35 mg/L)

Figure 4.18 showed the fouling mitigation results by adding PAC before CMF with 2 mg/L of O_3 pretreatment. TMP continuously increased with filtration time increasing with 25 and 35 mg/L of PAC adding. The TMP increasing speed with ozonation pretreatment was much higher than

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experiments without ozonation pretreatment under same PAC dose. The TMP increased to 60 kPa within 57 and 115 hours with 25 and 35 mg/L of PAC coagulation, respectively.
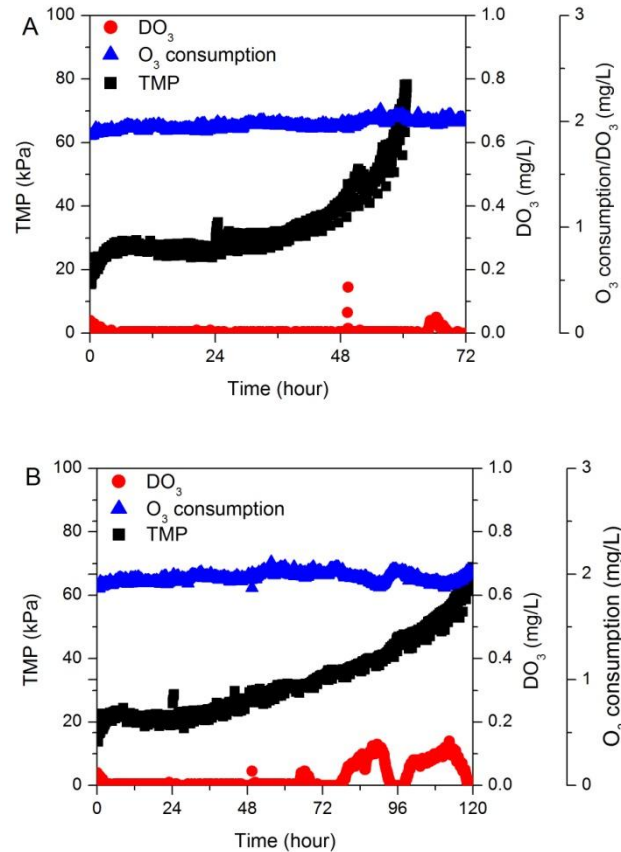
Figure 4.18   PAC dose effect on TMP changing of CMF with ozonation pretreatment (O_3 input dosage=2.0mg/L, PAC dose=25mg/L; B: PAC dose=35 mg/L)

4.3.2.3   Pretreatment effect on membrane fouling caused by particles

4.3.2.3.1   PAC pretreatment

The PSD was used to discuss pretreatment effect on membrane fouling caused by particles. The effluent from activated sludge reactor after treated by coagulation and sedimentation was used in our study. The PSD of secondary effluent tested in this research might be changed based on performance of coagulation and sedimentation used upstream. Thus the PSD on different days changed a little. Figure 4.19 showed the PSD results after coagulation with different PAC doses. In order to exclude wastewater quality effect, the PSD results using secondary effluent sampled at

the same day were plotted in one figure. The PSDs of secondary effluent and coagulated water under 15, 50 mg/L PAC were shown in Figure 4.19-A. The results of secondary effluent and coagulated water under 25 was presented in Figure 4.19-B. It was found that smaller particles were tended to form bigger one after coagulation. The size of raw wastewater was in the range of 10 to 200 μm. After coagulation the size range was changed to 20-1000 μm. And certain amount of larger flocs with size between 200-1000 μm was formed. And ratio of particles in the range of 20-100μm was found decreased, while ratio of particles in the range of 200-1000μm increased with PAC dose. According to Carman–Kozeny relationship (Carman, 1938), as the particles were smaller, the fouling formed was more serious. This could explain membrane fouling mitigation by adding 0, 15, 25, 50 mg/L PAC before CMF. Based on these results, it was deduced that Adding PAC before CMF could decrease the fouling significantly through increasing particle size.
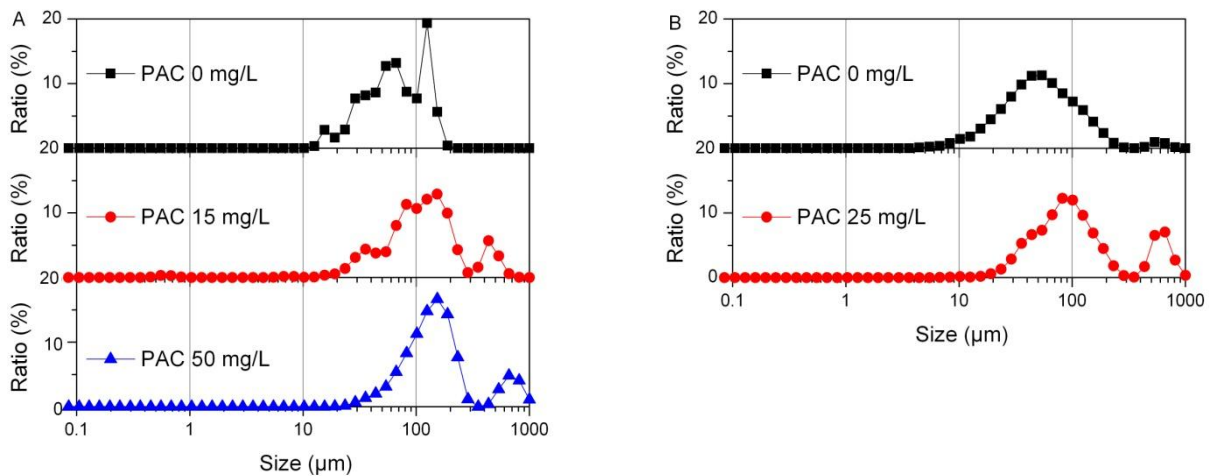
Figure 4.19   PSD changing with adding PAC

4.3.2.3.2   Ozonation and coagulation pretreatment

Results of PAC effect on PSD changing with ozonation pretreatment under 6 mg/L O_3 dose were shown in Figure 4.20. The PSD results during the experiments using the same secondary effluent were plotted in one figure. After ozonation with 6 mg/L O_3 input dose, particles size decreased a little, and increased significantly through adding PAC. Comparison the PSD results under the same PAC dose between with (Figure 4.20) and without ozonation pretreatment (Figure 4.19), the ratio with size larger than 200μm was much higher in case of oxidized water by 6 mg/L

O_3. It was found that 6mg/L of O_3 pretreatment enhanced coagulation on forming bigger size particles. This could one reason for less fouling tendency of oxidized wastewater with 6 mg/L O_3.
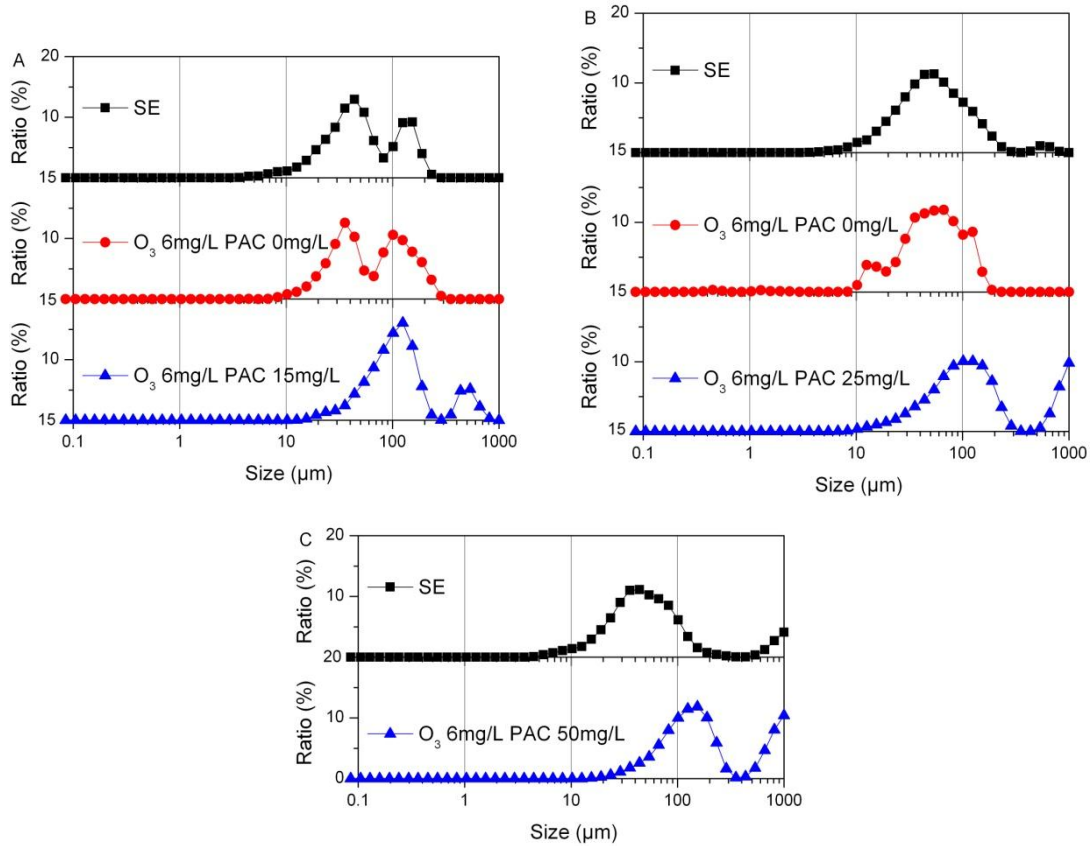
Figure 4.20   PAC effect on PSD changing with ozonation pretreatment (O_3 input dosage=6.0mg/L)

Figure 4.21 and 4.22 showed the PSD results of treated wastewater after ozonation and coagulation pretreatment under 2 and 4 mg/L input O_3 dose. These results were quite similar with the ones under condition of ozonation pretreatment with 6 mg/L O_3 dose. The PSD results were in accordance with low fouling tendency of coagulated water at the beginning of filtration (Figure 4.17, 4.18). But the TMP quickly increased to 80kPa in the latter filtration period. In order to explore the reason, membrane fouling caused by dissolve organic matter should be examined, and forming complexes among organic matter and metal irons was also discussed in the latter part.
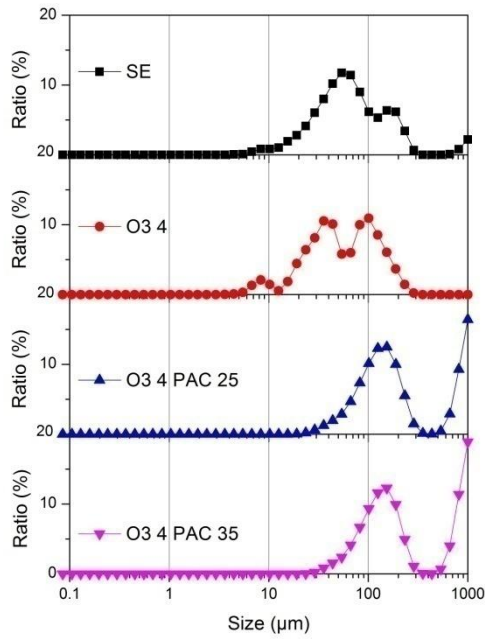
Figure 4.21   PAC effect on PSD changing with ozonation pretreatment (O$_3$ input dosage=4.0mg/L)
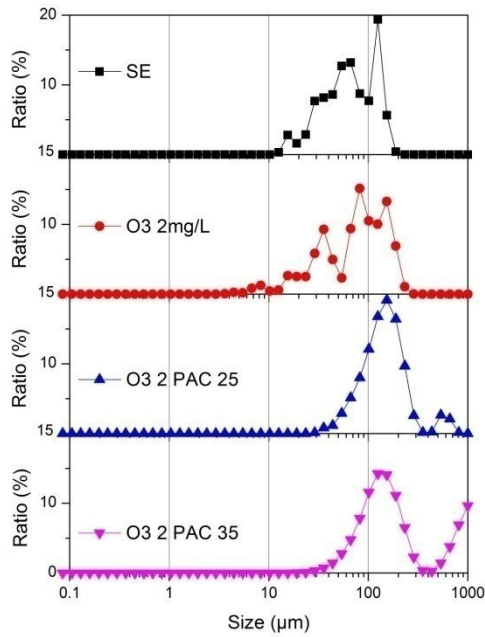
Figure 4.22   PAC effect on PSD changing with ozonation pretreatment (O$_3$ input dosage=2.0mg/L)

4.3.2.4   Pretreatment effect on membrane fouling caused by dissolved organic matters

Humic substants (Yamamura et al., 2007) and protein (Jones, K. L. et al., 2001; Rabe et al., 2011) were reported as two common organic matter contributing to membrane fouling. Thus we analyzed the removal of humic subastants and protein by CMF with/without pretreatment through fluorescence Excitation–Emission Matrices (EEMs) method.

In the EEM spectra of the secondary effluent and reclaimed water, four regions of high fluorescence intensity were observed: peak A at (Em/Ex) 300-305/220 nm; peak B at (Em/Ex) 340-350/ 220 nm, peak C at (Em/Ex) 265-370/280 nm, and peak D at (Em/Ex) 410-430/320-340 nm. Peak A is associated with tyrosine-like organic matter, peak B is attributed to tryptophan-like compounds, peak C contains phenol-like organic compounds and peak D is associated with more fulvic-like material (Chen et al., 2003; Leenheer et al., 2003).

The fluorescence intensity of four components at their peak points identified in secondary effluent and reclaimed water was shown in Table 4.3. The intensity of peak A, peak B, peak C and peak D in secondary effluent was 61.99-89.23, 106.15-157.69, 43.037-53.74 and 71.83-86.80, respectively. The intensity was decreased obviously by ozonation. With 2mg/L O_3 dose ozonation, the removal rate by ozonation was around 65.6%, 84.0%, 81.4% and 82.7% for these four components, respectively. The removal rate increased a little with future increasing O_3 dose. The removal rate was 96.1%, 92.0%, 97.1% and 87.3% respectively with 6 mg/L O_3 dose ozonation.

Table 4.3   The fluorescence intensity of four components identified in secondary effluent and treated water

O₃ dose	PAC dose	Intensity in secondary effluent				Intensity in treated water							
						After ozonation				After ozonation, coagulation and CMF			
		Peak A	Peak B	Peak C	Peak D	Peak A	Peak B	Peak C	Peak D	Peak A	Peak B	Peak C	Peak D
mg/L	mg/L	nm⁻¹	nm⁻¹	nm⁻¹	nm⁻¹	nm⁻¹	nm⁻¹	nm⁻¹	nm⁻¹	nm⁻¹	nm⁻¹	nm⁻¹	nm⁻¹
0	0	89.225	143.65	53.376	86.802	–	–	–	–	71.095	100.85	48.756	66.672
0	15	89.225	143.65	53.376	86.802	–	–	–	–	74.245	115.05	47.586	59.722
0	25	70.703	106.15	44.291	71.962	–	–	–	–	63.103	95.95	38.271	66.882
0	50	86.135	127.75	49.536	85.472	–	–	–	–	77.745	126.95	46.286	78.132
2	25	84.088	157.692	53.277	83.881	28.938	25.222	9.907	14.501	28.498	21.162	9.028	12.071
2	35	84.088	157.692	53.277	83.881	28.938	25.222	9.907	14.501	28.488	21.742	8.833	11.841
4	25	65.946	123.374	44.927	71.83	15.246	16.394	5.228	10.92	12.446	13.374	3.158	7.248
4	35	65.946	123.374	44.927	71.83	15.246	16.394	5.228	10.92	9.686	14.754	3.266	7.09
6	15	61.99	111.624	43.037	73.013	2.394	8.934	1.268	9.24	4.273	5.561	1.474	8.814
6	25	70.703	116.558	44.291	71.947	-0.01	9.158	1.045	8.179	-0.98	6.078	0.628	8.444
6	50	72.768	128.702	53.735	84.503	6.138	10.042	1.74	5.92	4.758	6.202	1.664	4.903

The removal rate of each component by coagulation and CMF combination process was shown in Figure 4.23. The removal by single CMF was 20.3%, 29.8%, 8.7% and 23.2% for peak A, peak B, peak C and peak D, respectively. The removal rate decreased to 9.7%, 0.6%, 6.6% and 8.6% respectively with 50mg/L PAC dose. Thus, larger proportion of these four components passed through coagulation and CMF combination process could be explained as fouling tendency of these compounds decreased by coagulation.
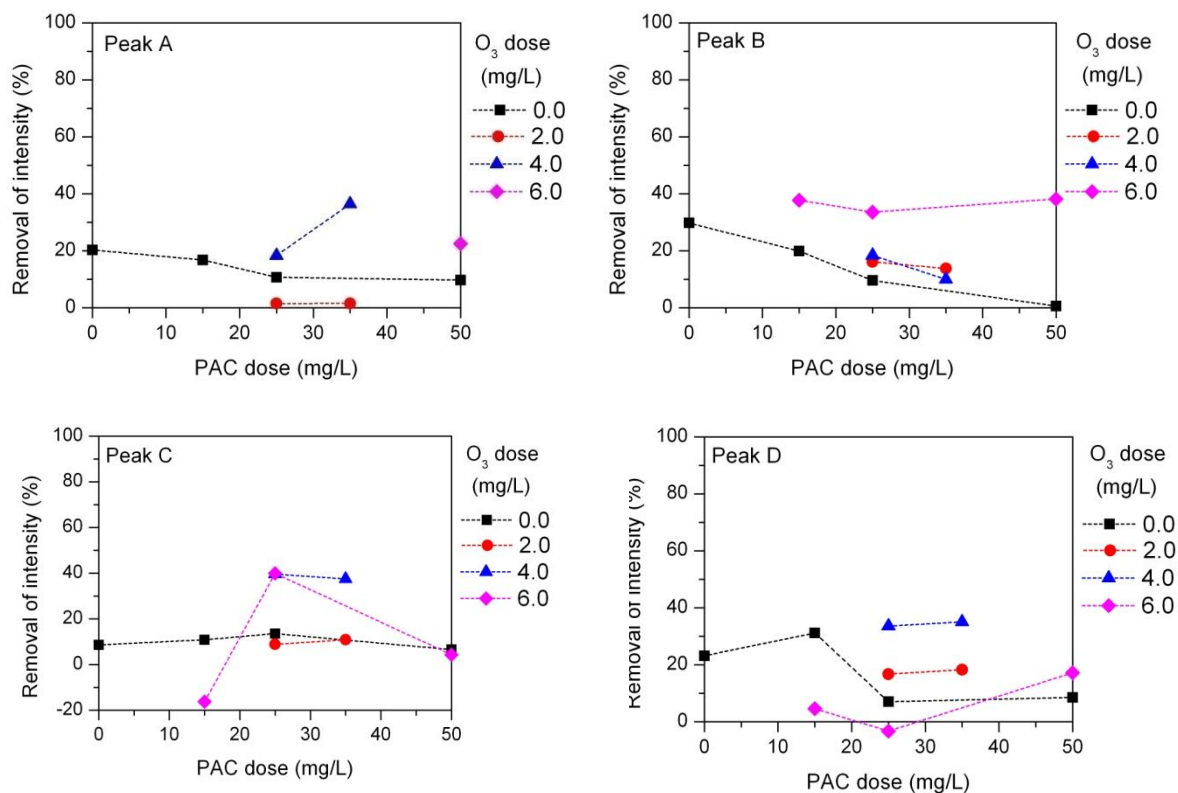
Figure 4.23   Removal rate of four components by coagulation and CMF comination process with different O_3 doses ozonation pretreatment (peak A: tyrosine-like organic matter; peak B: tryptophan-like compounds, peak C: phenol-like organic compounds; peak D: fulvic-like material)

It was interesting to find the removal of intensity was increased after ozonation pretreatment. In other word, the fouling tendency of same amount of humic substances and proteins increased by ozonation pretreatment. Around 90% of these components were degraded by ozonation with 6mg/L input dose. Although the fouling tendency increased, it was too tiny to cause more serious fouling. While for 4mg/L dose ozonation, around 80% of these components were removed. The

residual substances could cause certain membrane fouling. This could be one of the reasons for the sharply increasing TMP after 75-96 hours filtration to certain extent.

4.3.2.5   Characterization of foulants inside of CM

At the end of each experiment, foulants inside of CM were extracted using NaOH (pH=11) and HCl (pH=2) solution successively after removing cake layer on the surface of membrane. The carbon amount was obtained through the volume of the solution multiplied by TOC value in solution used to extract foulants. Then the carbon amount was divided by accumulated volume of filtrated water to get normalized amount of carbon presented in the foulants deposited on the membrane per 1 liter of wastewater filtered. The results were shown in Figure 4.24. It was found that most of organic matter in foulants was recovered by basic solution. The ratio of organic matter extracted by basic solution was over 93%. And amount of carbon in the foulants decreased significantly with increasing PAC dose. The amount of carbon in basic solution was 266.0 μg in case of directly filtration wastewater without any pretreatment. It decreased to 9.5, 3.8, 6.9 and 4.0μg by adding 15, 25, 35 and 50mg/L PAC before CMF, respectively (Figure 4.24-A). And amount of carbon in foulants with 2 and 4 mg/L O_3 pretreatments was higher than the one in foulants without O_3 pretreatments (Figure 4.24-B, C). While the amount of carbon decreased by adding 6 mg/L O_3 (Figure 4.24-D). All these results were in accord with the TMP changing results.
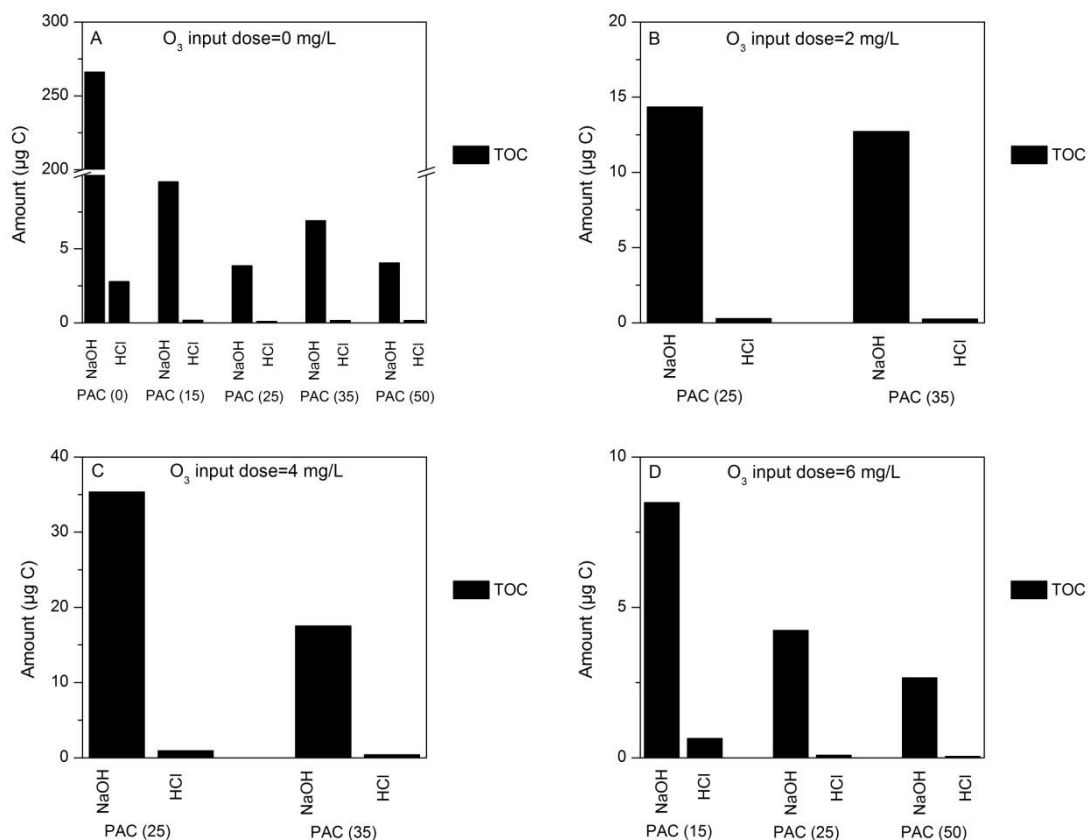
Figure 4.24   Amount of carbon presented in the foulants deposited inside of ceramic membrane per 1 liter of SE filtered.

Then we tried to get more clues from analyzing sugar, protein and humic substances amount to explain TMP changing results. The amount of sugar, protein and humic substances extracted from used membrane was normalized with accumulated volume of wastewater filtered. The normalized amount of each component under different PAC doses was shown in Figure 4.25. Similar as TOC result, basic solution nearly recovered all the organic foulants. Over 95% sugar, protein and humic substances were recovered by basic solution for most cases. The normalized amount of sugar, protein and humic substances decreased obviously with increasing PAC dose. The normalized amount was 150.1, 473.2 and 232.1 µg per 1 liter of wastewater filtered for sugar, protein and humic substances. With 15 mg/L PAC, the normalized amount sharply decreased to 4.2, 13.3 and 8.4µg per 1 liter of wastewater filtered, respectively. With adding larger dose of PAC (25, 35, 50mg/L PAC), the normalized amount decreased continuously. It meant the coagulation could mitigate membrane fouling caused by dissolve organic matters. And it was

consistent with removal of humic substances and proteins by coagulation and CMF based on EEMs analyzing (4.3.2.4).
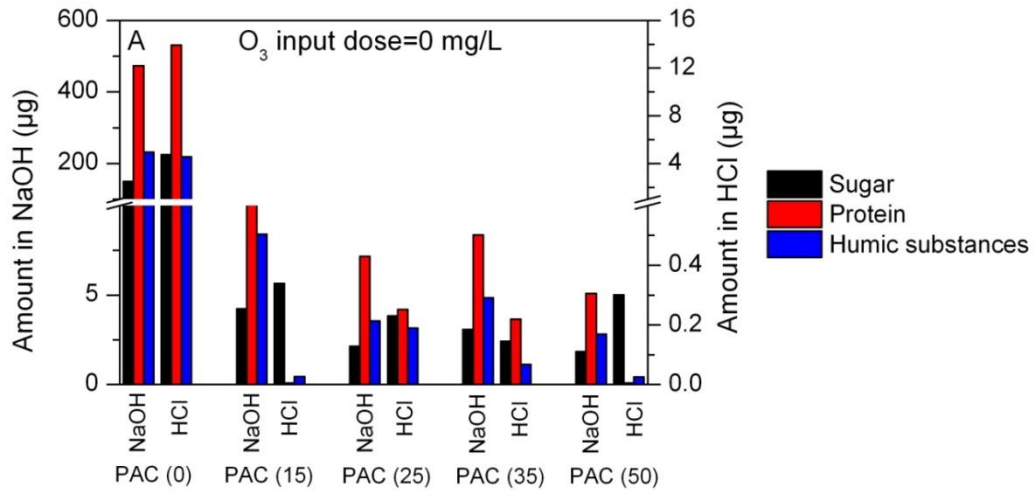
Figure 4.25   Amount of Sugar, protein and humic substances presented in the foulants deposited on the membrane per 1 liter of SE filtered (O_3 input dose=0 mg/L)

The normalized amount of sugar, protein and humic substances under same PAC dose increased with increasing O_3 dose with 2, 4mg/L O_3 dose (Figure 4.26). Considering ozonation could degrade protein and humic substances effectively based on EEMs results (4.3.2.4), it could be deduced that the fouling tendency of residual sugar, protein and humic substances increase obviously by ozonation pretreatment. Increasing fouling tendency might be caused by more complexes formed between metal ions and –COOH group in foulants, due to some carboxylic acids formed after ozonation (Beltrán, 2005). This should be confirmed through metal ions analyzing. Under the same PAC dose, the normalized amount of these three foulants was lower with 6 mg/L O_3 dose ozonation than without ozonation. It could be explained by nearly completely degradation of humic substance and protein by ozonation under 6 mg/L O_3 dose (4.3.2.4).
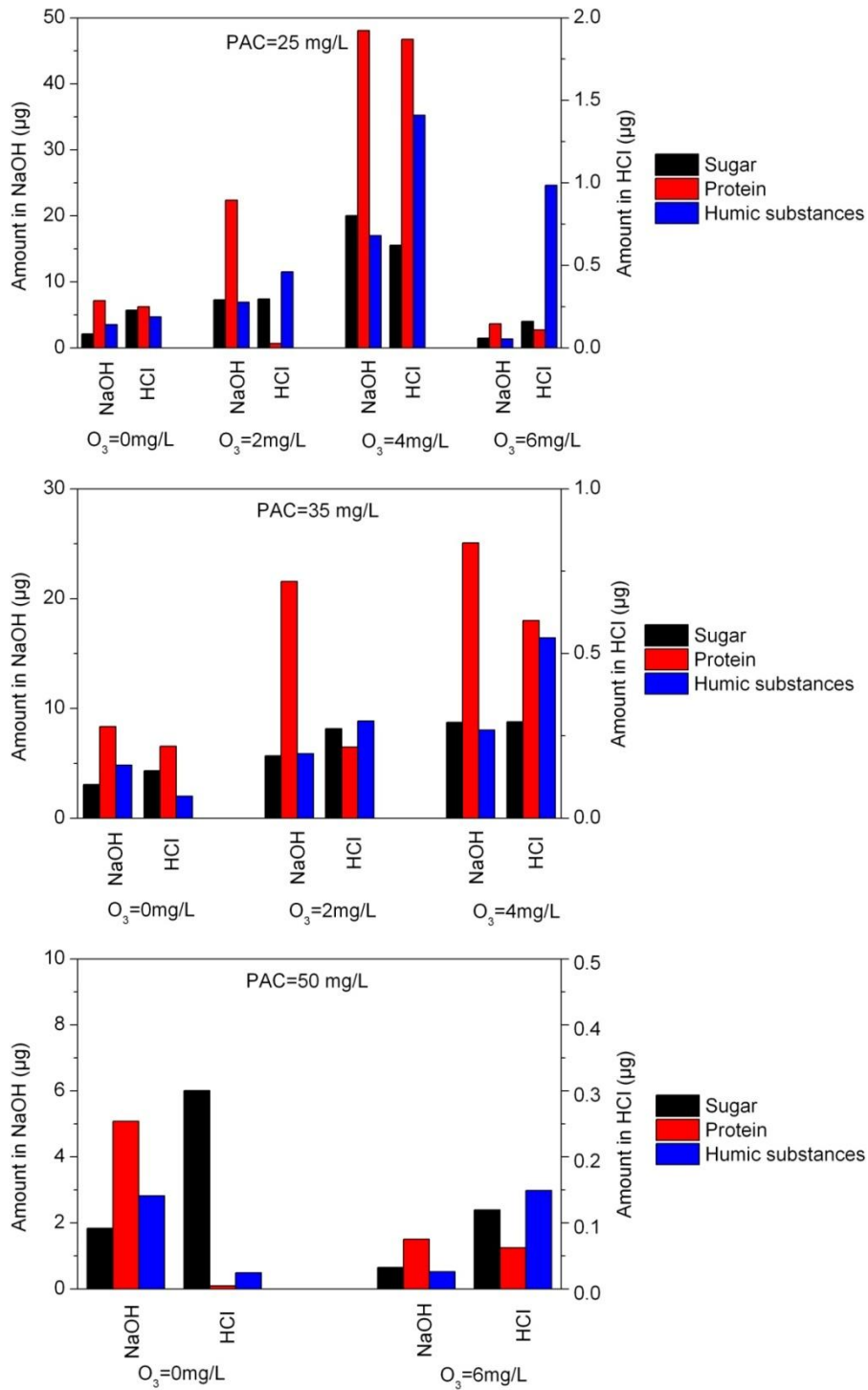
Figure 4.26   Effect of ozonation on amount of sugar, protein and humic substances presented in the foulants deposited on the membrane per 1 liter of SE filtered (PAC=25, 35, 50 mg/L)

4.4 Summary

The objectives of this chapter were to study: 1) Performance of ozonation pretreatment on contaminants removal using bench scale reactor. 2) Long term performance of ozonation, coagulation and CMF combination process from improving product water quality and mitigating membrane fouling aspects. Furthermore, fouling mechanisms for particles and dissolved foulants were discussed. The conclusions obtained are as follows:

1.   During ozoantion using bench scale reactor, 17.6 % removal of COD_{Mn} could be achieved by consuming 1.38 mgO_3/mgC dose. Under the same O_3 dose, the removal rate of TOC was 10% lower than COD_{Mn}. SUVA and color could be removed efficiently. The SUVA and color removal were 46.7% and 70.0%, respectively with 1.14 mg mg O_3/mg C of O_3 consumption.

2.   2.0 logs total coliforms and 2.7 logs *E. coli* were inactivated with 0.56 mg O_3/mg C of O_3 dose consumption before DO_3 appearance. And it is difficult to completely inactivate all bacteria through ozonation. 8 and 5 CFU/100ml total coliforms and *E. coli* were still left after increasing O_3 consumption to the dose as high as 1.00 mgO_3/mgC of O_3 dose. MS2 disinfection showed much higher speed than bacteria. 5.1 logs their inactivation was observed after consuming 0.62 mgO_3/mgC of O_3 dose, with 14.5 PFU/ml MS2 left in oxidized water.

3.   The removal rate of each PPCP was much higher than results obtained using semi-batch ozonation reactor. SOC of 0.56 mg O_3/mg C were needed to degrade most PPCPs using bench scale ozonation reactor. There are two reasons for the difference. One was O_3 consumption calculated for experiments using semi-batch ozonation reactor was larger than real data. The second was less OH amount formed during ozonation using semi-batch reactor due to different O_3 gas feeding patterns.

4.   The rejection of COD_{Mn}, TOC, DOC, SUVA and color by CMF was 53.8%, 21.6%, 10.8%, 0.38% and 14.3% respectively. The removal rate increased with increasing

PAC dose. The removal rate increased to 69.1%, 33.8%, 20.3% 10.0% and 42.9% under 50mg/L PAC dose before CMF. Ozonation pretreatment decreased removal of organic matters and (COD_{Mn}, TOC) by 0-30%. In other hand, ozonation pretreatment increased removal rate of SUVA and color to 60%-70% and 100%. CMF alone could completely reject *E. coli* and total coliforms, while only 0.45 logs MS2. The removal rate increased significantly to over 8 logs by adding coagulation before CMF. The ozonation, coagulation and CMF combination process could effectively eliminate PPCPs residuals with adjusting input O_3 dose.

5.　　　Without adding PAC before CMF, TMP increased to 70 kPa within 6 hours. Coagulation taking PAC as coagulant effectively mitigated membrane fouling. TMP just increased from 15 kPa to 31 kPa duing 120 hours filtration under 50 mg/L PAC. Ozonation with 6 mg/L input dose improved coagulation effect. Obvious membrane fouling control was achieved under 25 mg/L PAC with 6 mg/L O_3 pretreatment. While 2 and 4 mg/L O_3 pretreatments showed negative influence on coagulation effect for mitigating membrane fouling.

6.　　　Increasing particle sizes was proposed as reason for mitigating membrane fouling caused by particles through coagulation pretreatment. Ozonation pretreatment could enhance forming larger size (200-1000 μm) particles during coagulation. Besides, the effect of coagulation on changing fouling caused by dissolved organic matters was studied based on EEMs analyzing. The removal rate by CMF was 20.3%, 29.8%, 8.7% and 23.2% for tyrosine-like organic matter, tryptophan-like compounds, phenol-like organic compounds and fulvic-like materials, respectively. The removal rate decreased with adding PAC before CMF. With adding 50mg/L dose of PAC, the removal rate decreased to 9.7%, 0.6%, 6.6% and 8.6%, respectively. While removal rate by coagulation and CMF part was increased by ozonatio with 2, 4 mg/L O_3 dose.

7.　　　The foulants inside of CM was characterized through analyzing amount of sugar, protein and humic substances. Without adding PAC, the normalized amount was 150.1, 473.2

and 232.1 μg per 1 liter of wastewater filtered for sugar, protein and humic substances, respectively. With 15 mg/L PAC, the normalized amount sharply decreased to 4.2, 13.3 and 8.4μg, respectively. The normalized amount did not obvious changed with larger PAC dose. While fouling tendency of sugar, protein and humic substances was increased by ozonation. And forming complexes among metal ions and organic foulants was proposed as the reason. But membrane fouling was not aggravated by ozonation under 6 mg/L O_3 dose due to nearly completely degradation of humic substance and protein.

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CHAPTER V

Performance of Ceramic Membrane-based Process during Treating

Primary Effluent

5.1 Introduction

A lots of studies have already been done to treat sewage using MBR for water reclamation (Jacob et al., 2012; Joss et al., 2011; Pierre et al., 2004). And few studies about sewage treatment using chemical technologies have also been reported. Mondala et al. presented potential reuse primary effluent in fermentation processes using ozonation treatment (Mondala et al., 2011). Ravazzini directly filtrated sewage using UF treatment (Ravazzini et al., 2005). Ozonation and coagulation processes were also tried in this field (Campos-Reales-Pineda et al., 2008; Zhao et al., 2012). Abdessemed et al. conducted coagulation and UF combination process to evaluate product water quality based on common water quality items (Abdessemed et al., 2000; Abdessemed et al., 2003). But there was no published studies related with treating primary effluent using ceramic membrane filtration. And neither emerging contaminants, pathogen removal by membrane filtration, nor fouling mitigation issue have been found until now.

Thus it is important to evaluate performance of ozonation, coagulation and CMF processes in primary effluent treatment from product water quality and membrane fouling mitigation aspects. The research work in this chapter could be divided into two parts. During the first part research, several pretreatment was conducted for several hours to mitigate CMF fouling, such as ozonation, ozonation and coagulation, coagulation. Suitable pretreatment was selected based on these researches. The second part research was followed to examine performance of the selected combination process during several days operation. In the second part research, firstly, removal of common water quality items, virus indicator MS2 was studied to discuss the product water

safety. Then operation stability of this combination process was examined based on transmembrane pressure (TMP) development. Last, study on fouling mechanism was done through analyzing characteristics of particles, dissolved organic matters, foulants extracted from used membrane.

5.2   Experimental setup and conditions

5.2.1   Experimental setup for short term evaluation

The schematic diagram of short term evaluation experimental setup was shown in Figure 5.1. It contains three parts, ozonation reactor, coagulation tank, CMF part. Several combination processes, including CMF, PAC+CMF, ozonation+CMF, ozonation+PAC+CMF, could be conducted using this equipment.
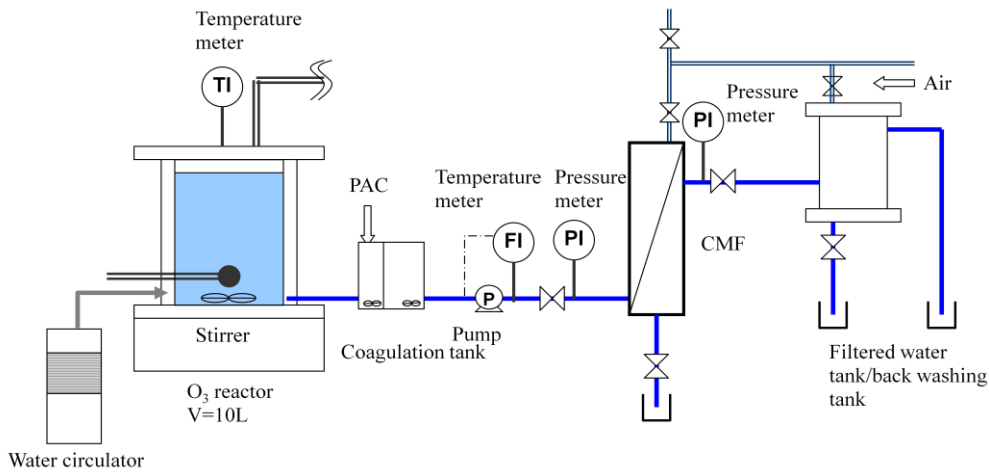
Figure 5.1   Experimental set up for short term evaluation of ozonation, coagulation and CMF combination process

The effective volume of the ozonation reactor was 10 L. Ozone gas was continuously fed into the reactor through a diffuser at the bottom of the reactor. In this study, the ozone feed rate was 1.0 L/min. After certain ozone dose was attained, O_3 feed in gas was stopped, followed with coagulation or directed feeding the oxidized water into CMF module. The coagulation was conducted in two steps, rapid mixing at 600rpm (G=161s^{-1}) and slow mixing at 300rpm (G=38 s^{-1}) using small tank with 146 ml and 292 ml of effective volume, respectively. Polyaluminium chloride (PAC) was dosed from top side continuously. Then the treated water was feed in the

CMF at 1m/d flow rate. The membrane was operated at constant flow rate with dead-end mode. The ceramic membrane (METAWATER CO. Ltd.) is monolithic type, with 0.042 m^2 effective membrane surface. The main material is Al_2O_3. Pore size is 0.1μm. The flux was 1 - 2m/d, and filtration period was 10 - 40 min., followed by backwashing under 0.3 MPa. During filtration, pressures before and after membrane filtration unit and temperature of wastewater were recorded. The feed water and filtrated water were collected to study the removal of common water quality items. At the end of each experiment, membrane was successively cleaned by NaOH and HCl until initial condition was attained.

5.2.2   Experimental set up for long term evaluation

Figure 5.2 showed equipment for long term evaluation experiment. Only coagulation and CMF combination process was studied in this part. The coagulation was conducted using a 8L tank with mechanical agitation at 150 rpm (G=36.4 s^{-1}). The feed water flow rate for coagulation is 1 L/min. Polyaluminium chloride (PAC) was dosed from top side continuously. Then the treated water was feed in the CMF at 1m/d flow rate. The CMF was also operated at dead-end mode with the same membrane as former experiments. Filtration cycle was 30 minutes, followed by backwashing under 0.3 MPa.
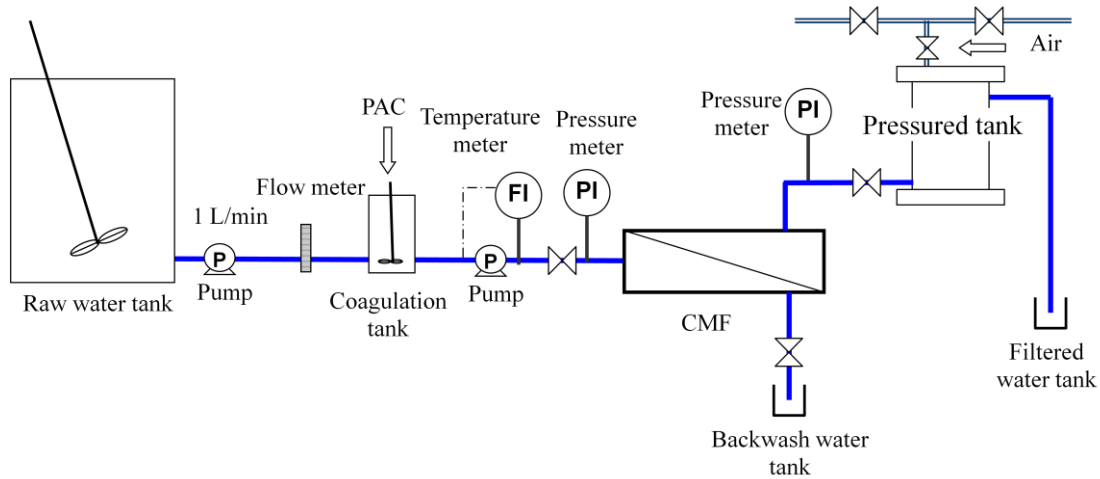
Figure 5.2   Long term evaluation experimental set up

This experiment was lasted for 5 days to evaluate reversible and irreversible fouling changing through TMP recording. After 20 minutes, raw water and filtrated water was collected to evaluate

removal of common water quality items, including bacteria, turbidity, TOC, DOC, COD_{Mn}, TN, TP, SUVA and color. After 1 hour filtration, rejection of virus indicator MS2 was measured followed by spiking MS2 stock solution in the raw water. At the end of experiment, after removing cake layer on the surface of membrane, foulants were extracted using NaOH (pH=11) and HCl (pH=2) solution. Amount of TOC, polysaccharide, protein and humic acid in extracting solution was analyzed to investigate coagulation pretreatment effect on fouling caused by dissolved organic matters. Particle size distributions (PSD) before and after coagulation were measured to examine coagulation pretreatment effect on fouling caused by particles.

5.2.3 Analytical methods

Total organic carbon (TOC) and dissolved organic carbon (DOC) concentrations were measured with a TOC analyser (TOC-5000A, Shimadzu, CO.). COD_{Mn}, total nitrogen (TN), dissolve total nitrogen (DTN), total phosphorous (TP), and dissolve phosphorous (DTP) were analyzed according to standard method (Lenore et al., 1999). UV_{254} and color were measured by a spectrophotometer (UV-16000, Shimadzu, CO.). Turbidity was measured by a turbidity meter (2100Q01, HACH CO.). Particle size distribution (PSD) was measured by SALD-2000 (Shimadzu, CO.). Protein and humic substances were analyzed using Lowry's method (Lowry et al., 1951) and modified Lowry' method (Frolund et al., 1995), respectively. And bovine serum albumin and humic acid were used as a standard, separately. Polysaccharide was analyzed by phenol-sulfuric acid method (Dubois et al., 1956), and the results were given as glucose equivolent. The humic subastants and certain protein matters in the solution was analyzed through fluorescence Excitation–Emission Matrices (EEMs) method. The fluorescence spectrophotometer (F-4500, Hitachi, Ltd. Japan) was used. Emission scans were performed from 200 to 600nm at 5nm steps, with excitation wavelengths from 200 to 600nm at 5nm intervals.

5.3   Results and discussions

5.3.1   Short term evaluation of ozonation, PAC effect on CMF

5.3.1.1   TMP change during CMF

5.3.1.1.1   Effect of flux

CMF was operated at different flux to find out critical flux. Critical flux has been defined as the permeate flux of a membrane system under which little of no fouling is observed. Exceeding critical flux resulted in rapidly increasing membrane fouling (Choi, 2005; Field et al., 1995). This concept might be used for improving operation of the membrane system through proposal suitable flux. The result was shown in Figure 5.3. In order to keep same amount wastewater passed through CMF, the filtration period was decided as 40, 20, 12.5, 10 minutes for experiments under 0.5, 1.0, 1.5, 2.0 m/d flux, respectively. Except operation under 0.5 m/d flux, TMP increased so sharply that CMF was stopped within one hour due to exceed pressure limitation (100kPa).
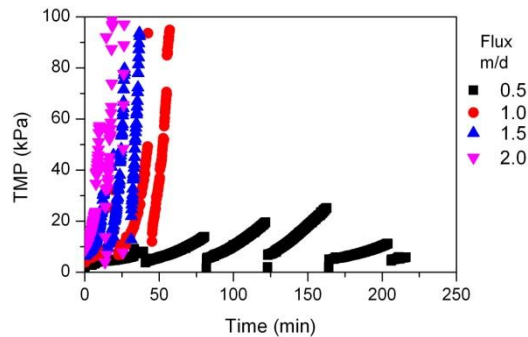
Figure 5.3   Effect of flux (0.5, 1.0, 1.5, 2.0 m/d) on TMP change with filtration time

Total fouling can be divided into reversible and irreversible subdivisions (Kimura et al., 2007). Normally backwashing was used to distinguish these two terms. The recovered and unrecovered part of flux was considered to be due to reversible fouling and irreversible fouling separately. From reversible fouling, we can only get the preliminary information about filtration feasibility. But irreversible fouling was more important factor, due to chemical cleaning was needed to recover the irreversible fouling. It resulted in high cost, secondary pollution by chemicals and

low operation stability. Thus, TMP changes caused by both reversible and irreversible fouling were considered in short term evaluation experiments.

In order to keep relative same potential foulants passing through CM, the accumulated filtered water volume during same period was kept at same level. Thus the flux and filtration period were decided as follows: 1.0 m/d for 10 minutes, 1.5 m/d for 6.7 minutes, 2.0 m/d for 5 minutes. The TMP result was shown in Figure 5.4. The TMP change caused by irreversible fouling increased with increasing flux. That indicated that high flux operation would worsen cleanability of foulants. The reason was high pressure caused by high flux would result in more compact foulants on the membrane surface. The TMP trend of operation under 1.0m/d slightly increased during filtration. It justified that operation under 1.0 m/d was acceptable for the following experiments, due to the slight fouling happened was hoped to be controlled by proper pretreatment or chemical cleaning. In our study, therefore, all the experiments in the following parts to treat primary effluent were conducted under 1.0 m/d.
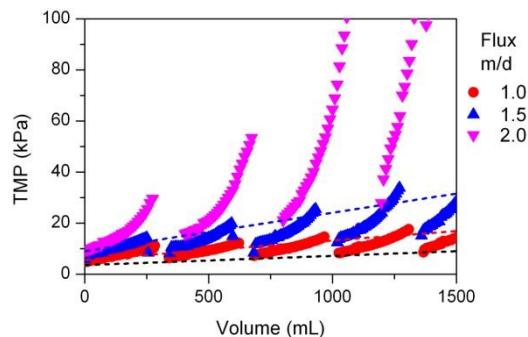
Figure 5.4   Effect of flux (1.0, 1.5, 2.0 m/d) on TMP change with accumulated volume of filtrated water

5.3.1.1.2   Effect of filtration period

Besides flux, filtration period was another important parameter. We studied the filtration period effect on irreversible fouling. The result was presented in Figure 5.5. Two filtration periods 10 and 30 minutes were examined. Although reversible fouling increased seriously for the longer filtration periods, there was no obvious difference on the irreversible fouling development. It suggested that filtration period in the 10-30 minutes range showed limited effect on the cleanability of the foulants.
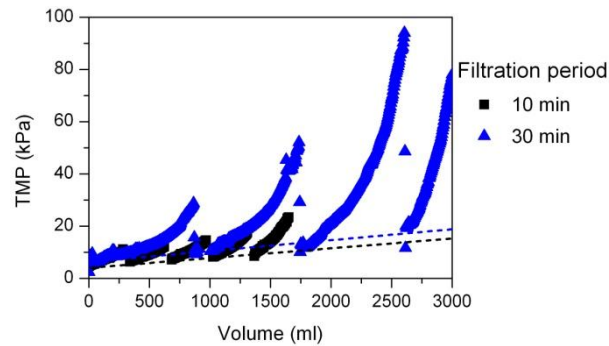
Figure 5.5 Effect of filtration period (10, 30 min) on TMP changing with accumulated volume of filtrated water

5.3.1.2 Effect of coagulation pretreatment on TMP change

The coagulation pretreatment effect on membrane fouling mitigation with factor of PAC doses was described in Figure 5.6. Adding PAC before CMF showed advantage for both reversible and irreversible fouling controlling. In one filtration cycle, the TMP increased caused by reversible fouling was around 80, 30, 12, 7, 5 and 3 kPa with PAC dose of 0, 5, 25, 50, 100 and 150 mg/L, respectively. The TMP resulted from irreversible fouling without PAC adding increased by 10kPa within 60 minutes. The TMP was increased by 5 kPa within 200 minutes under 5, 25, 50 mg/L PAC. There was no further improvement by coagulation with PAC dose of 100 and 150 mg/L during 80 minutes filtration. This result indicated that PAC with range of 25 to 100 mg/L might be suitable for both reversible and irreversible fouling controlling.
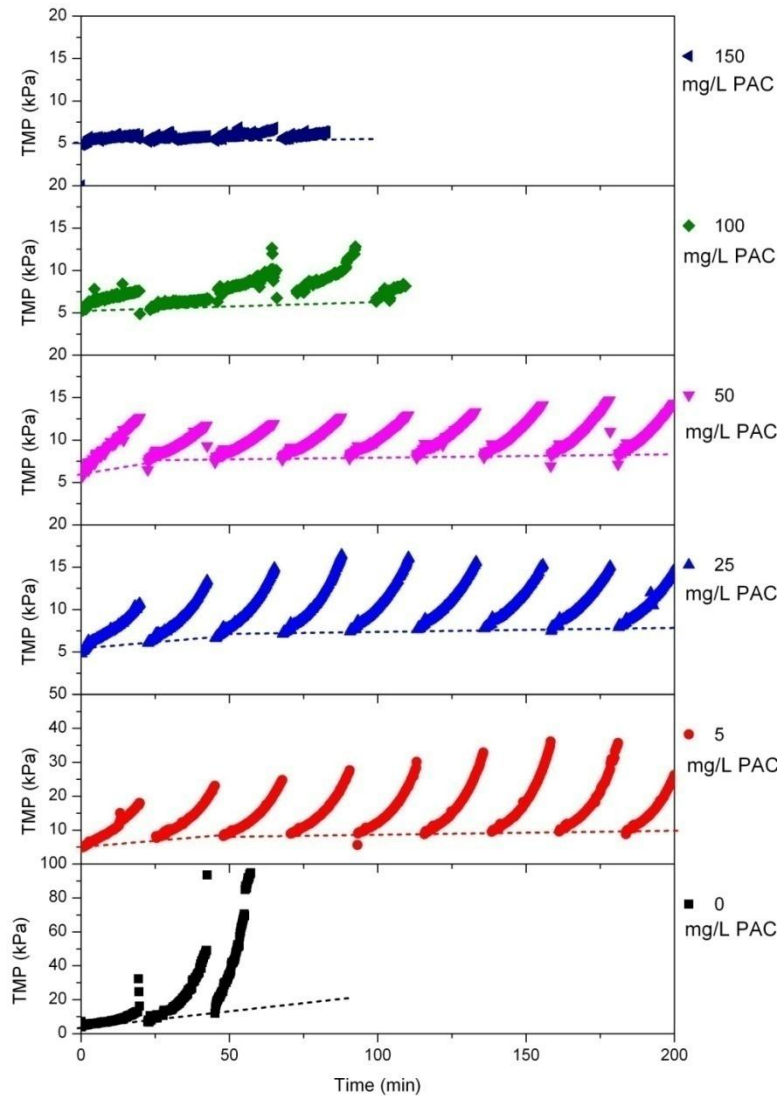
Figure 5.6   Effect of PAC doses (0, 5, 25, 50, 100, 150 mg/L) on TMP change

5.3.1.3   Effect of ozonation pretreatment on TMP change

The TMP change with adding different doses of O_3 before CMF was presented in Figure 5.7. Only slight effect on TMP increasing trend caused by reversible and irreversible fouling was found. With adding low dose of O_3 (0.12 mgO_3/mgC), the reversible fouling increased more sharply. With larger doses, the reversible fouling increasing speed decreased with increasing O_3 dose.
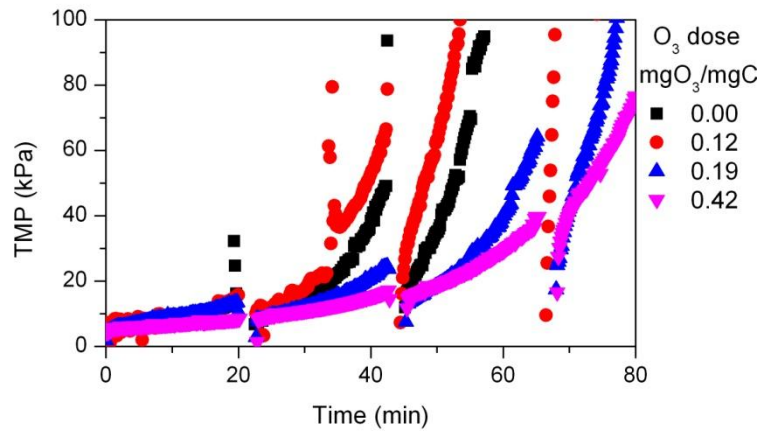
Figure 5.7   Effect of ozonation with different O_3 doses (0.00, 0.12, 0.19, 0.42 mgO$_3$/mgC) on TMP change

In order to examine the reasons for ozonation pretreatment effect on CMF fouling, PSDs of raw wastewater and oxidized wastewater were shown in Figure 5.8. Ozonation with 0.12 mg O_3/mg C dose O_3 decreased the ratio of particles with size range of 1 to 100 μm. Through increasing O_3 doses, the ratio of the particle with size below 1.0 μm started to decrease. And the ratio of particles with size between 100 and 1000 μm started to increase. Comparison between TMP and PSD changes, it was deduced that the fouling tendency could be reduced through increasing ratio of larger particles with size between 100 and 1000 μm.
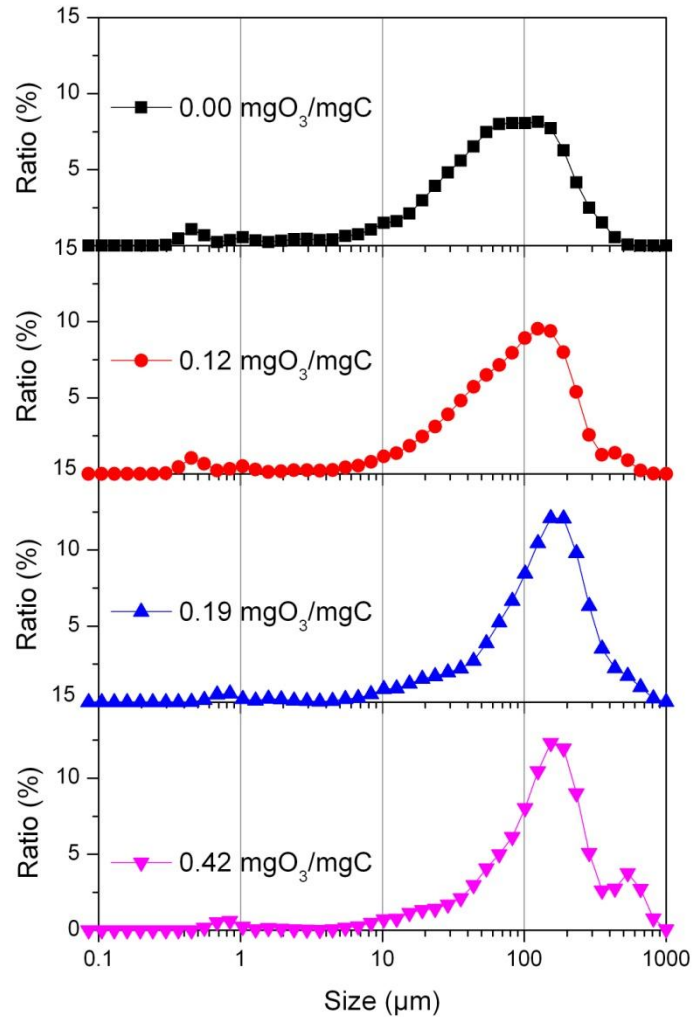
Figure 5.8   Effect of O_3 doses (0.00, 0.13, 0.22, 0.48 mgO$_3$/mgC) on PSD

5.3.1.4   Assistant effects of ozonation on coagulation for fouling mitigation

Results of TMP change for ozonation, coagulation and CMF combination processes with factor of PAC and O_3 doses were shown in Figure 5.9. Under condition of 50 mg/L PAC, adding 0.12 and 0.19 mg O_3/mg C dose O_3 could enhance the coagulation effect on both reversible and irreversible fouling control. While under condition of 100 mg/L PAC, adding 0.12 and 0.19 mg O_3/mg C dose O_3 slightly increased the irreversible fouling tendency with perfect reversible fouling controlling. These phenomena could be caused by ozonation effect on particles and dissolve organic matters. After adding O_3, reaction between O_3 and organic matters adsorbed to

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the particle surface altered the particle stability. This alteration could result in enhancement of coagulation through microflocculation. Thus the reversible fouling was lightened. At the same time, the flocs size would be increased by increasing PAC dose. Higher porosity of the foulants on the surface of the membrane was expected with higher PAC dosages. Consequently, the reversible fouling tendency was less in the case of 100 mg/L PAC case. At the same time, ozonatin would be expected to convert the larger organic matters into smaller ones. Thus it is easier for smaller organic matter to pass through the foulants and to be adsorbed on the membrane as irreversible foulants. These results indicated that ozonation pretreatment showed negative effect on assistant fouling controlling by coagulation under high PAC dose.
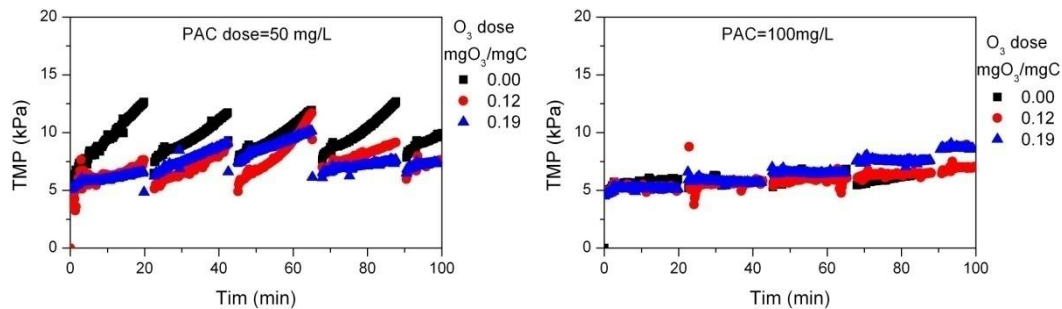
Figure 5.9   Assistant effect of ozonation on coagulation about TMP change (left: PAC dose=50 mg/L; right: PAC dose=100 mg/L)

5.3.1.5   Effect of flux on TMP changing during PAC+CMF process

Based on studies discussed above, coagulation was found as the most effective pretreatment for membrane fouling control. Thus only coagulation and CMF combination process was selected for further study. Before study on coagulation and CMF process, suitable flow rate for coagulation and CMF combination process was examined. Figure 5.10 showed the TMP change during coagulation (PAC dose=50mg /L) and CMF process at three flow rates. Ceramic membrane filtration under 1.0 m/d could be continuously operated. While TMP during filtration under 1.5 and 2.0 m/d increased to 100kPa within 2 filtration cycles. Thus 1.0 m/d was decided for further studies.
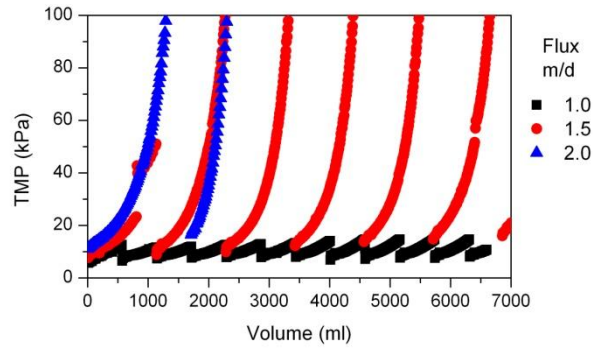
Figure 5.10   Effect of flux on TMP change during PAC (50mg/L)+CMF process

5.3.1.6   Removal of common water quality items

COD_{Mn} and dissolved COD_{Mn} ($DCOD_{Mn}$) were shown in figure 5.11. The COD_{Mn} and $DCOD_{Mn}$ removal rate by CMF was around 50% and 30% respectively, and increased slightly by adding PAC. Adding 0.12 mg O_3/mg C dose O_3 before coagulation and CMF did not affect the results obviously. But the removal rate decreased a little through adding 0.19 mg O_3/mg C dose O_3. The TOC and DOC rejection rates by CMF were 60% and 40% separately (Figure 5.12). The effect of coagulation and ozonation on removal of TOC and DOC was similar to effect on COD_{Mn} and $DCOD_{Mn}$.
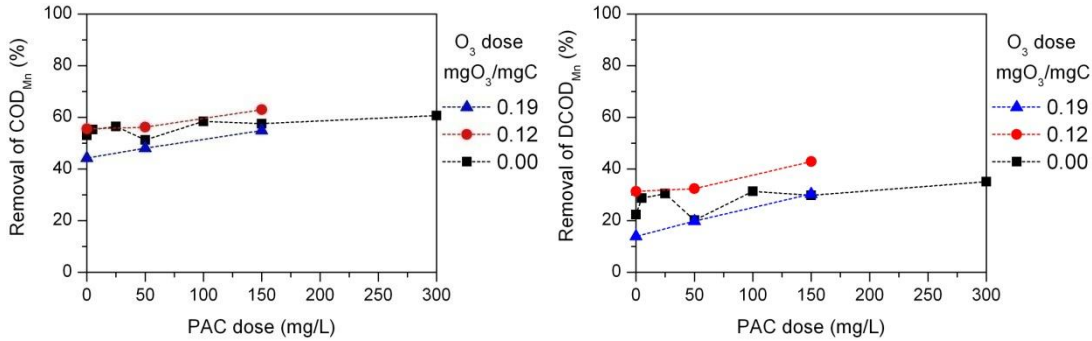
Figure 5.11   Removal of COD_{Mn} (left) and $DCOD_{Mn}$ (right) during O_3+PAC+CMF process
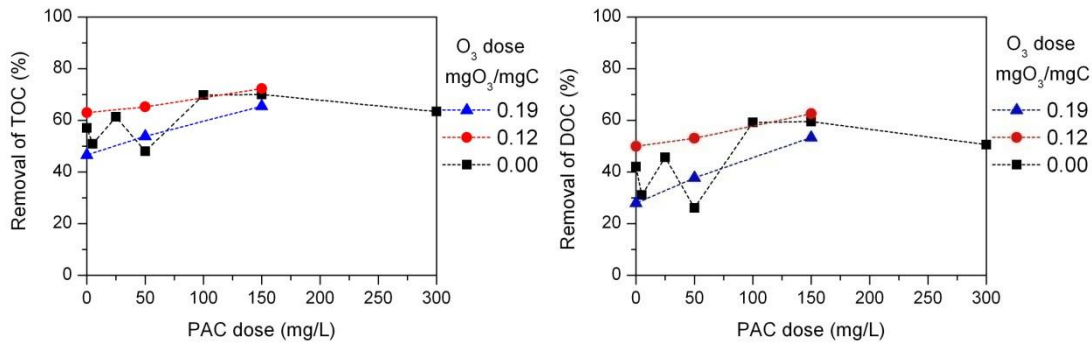
Figure 5.12   Removal of TOC (left) and DOC (right) during O_3+PAC+CMF process

Removal of SUVA and color by ozonation, coagulation and CMF combination process was shown in Figure 5.13. The removal rate of SUVA by CMF was -18.7%. With adding different doses of PAC, the removal rate fluctuated among -75.4% and 3.3%. Negative SUVA removal (Figure 5.13) indicated that aromatic matters/double bonds matters could pass through the membrane more easily than other organic matters. Thus foulants might be less aromaticity. It was accord with common finding that polysaccharide and protein might cause higher fouling tendency that other matters. The removal rate of color by CMF was 37.5%. The removal rate increased with increasing PAC dose. 74.6% removal of color could be achieved by coagulation (300mg/L PAC) and CMF combination process. Ozonation pretreatment further increased the removal rate to 86.8% under condition of 0.19 mg O_3/mg C dose of O_3 and 150 mg/L dose of PAC.
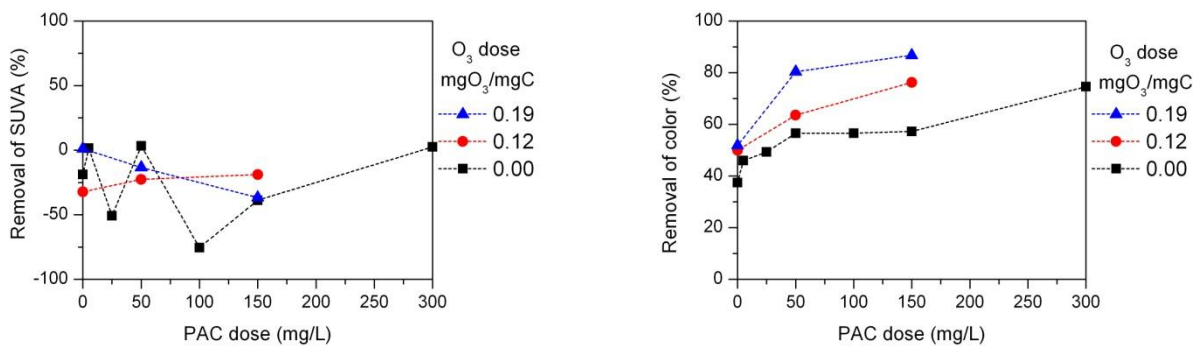
Figure 5.13   Removal of SUVA (left) and color (right) during O_3+PAC+CMF process (data shown in legend meant O_3 dose)
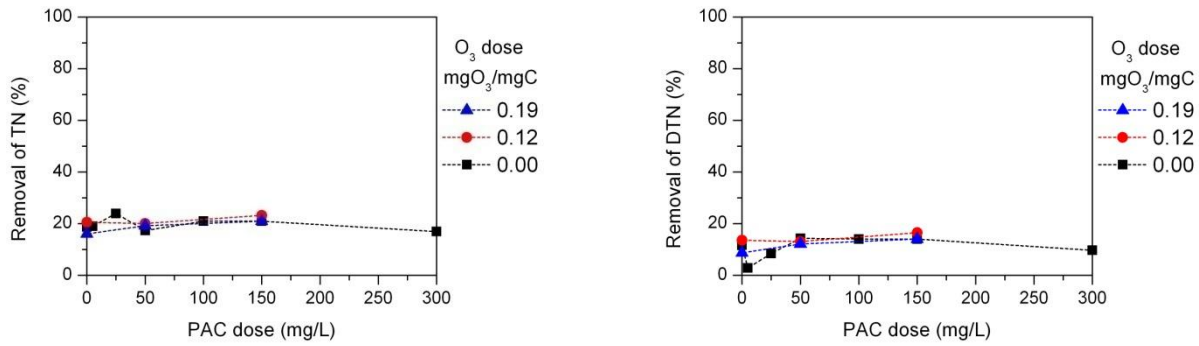
Figure 5.14   Removal of TN (left) and DTN (right) during O3+PAC+CMF process (data shown in legend meant O$_3$ dose)
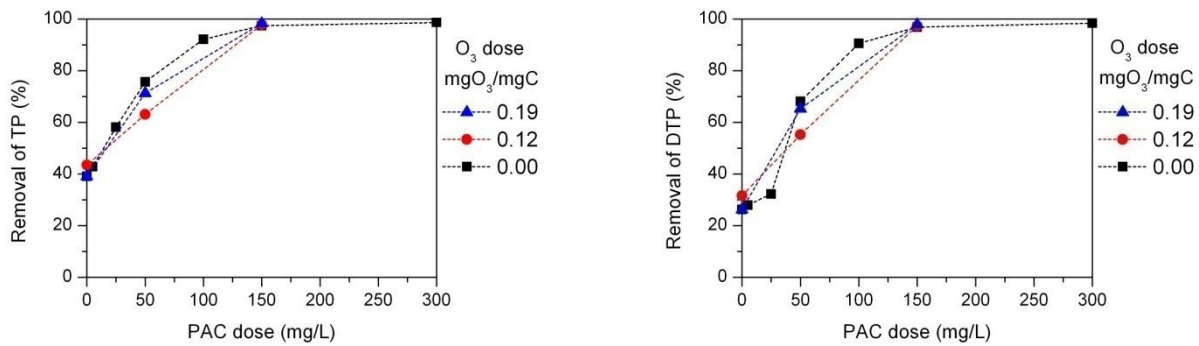
Figure 5.15   Removal of TP (left) and DTP (right) during O3+PAC+CMF process (data shown in legend meant O$_3$ dose)

The nutrients rejection showed in Figure 5.14 and 5.15. Only 18.8% TN and 11.7% DTN could be rejected by CMF. No obvious enhancement by ozonation and coagulation pretreatment was observed. On the contrary, TP and DTP removal rate by CMF was much higher than TN and DTN. The removal rate of TP and DTP by CMF was 39.1% and 26.3%, respectively. And the removal rate increased significantly by adding PAC before CMF, With 100 mg/L PAC, the removal rate could attain over 90%. And ozonation pretreatment did not affected removal rate of TP and DTP.

5.3.2   Long term performance of PAC + CMF process

Based on short term experiments, It was found that coagulation was necessary to mitigate membrane fouling, and showed advantages on TP removal. On the contrary, ozonation was ineffective for controlling fouling, even showed slightly negative effect incorporated with

coagulation under high PAC dose. Furthermore, ozonation pretreatment showed limited effect on removal of common water quality items, except slightly negative effect on organic matter (COD_{Mn}, TOC) removal. Thus coagulation and CMF combination process seemed suitable for primary effluent treatment. In this part, long term experiment was conducted to evaluate the operation stability of this combination process.

5.3.2.1   Removal of contaminants

5.3.2.1.1   Removal of common water quality items

Removal of the common water quality items by coagulation and CMF combination process with factor of PAC doses were shown in Figure 5.16. Similar results with the ones during short term experiment were obtained. The rejection rates of COD, TOC and color by CMF were 50%, 60% and 42%, respectively. Adding PAC before the CMF increased removal rate of such items. Under condition of 75mg/L PAC, the removal rates were increased to 58.8%, 61.7% and 81.6% for COD, TOC and color, respectively. For the nutrients removal, phosphorous was effectively rejected by CMF with combined with coagulation. The removal rate of TP and DTP by coagulation (75mg/L PAC) and CMF was 86.9% and 87.6%, respectively. And the removal of SUVA was negative, except in the case of adding 25 mg/L PAC.
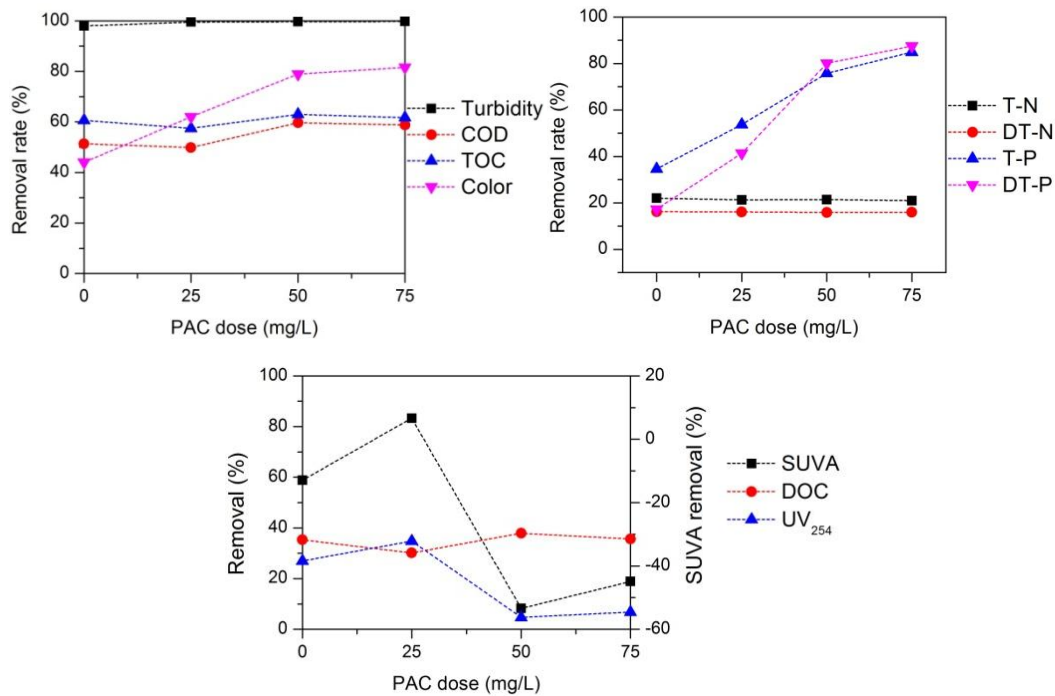
Figure 5.16   Effect of PAC dose on removal of common water quality items during PAC+CMF process

5.3.2.1.2   Removal of pathogen

The MS2 removal by combination process was shown in Figure 5.17. The rejection by CMF was around 0.2 logs, and the rejection changed with adding PAC. Obvious enhancement on removal by PAC was observed with adding 150 mg/L PAC dose. During coagulation, it was shown that PAC could act by bridging, leading to forming larger size particles and neutralizing charge (Gregory et al., 2001; Wang et al., 2002). Based on results of zeta potential, at lower than 100 mg/L of PAC dose, no significant neutralization was happened. But PSD was obviously changed by adding PAC with lower than 100 mg/L dose (Figure 5.19). In the range of 100 to 150 mg/L PAC, zeta potential increased rapidly from -21.4 to -15.9 mV with further forming more large size particles and significant removal of MS2. It indicated that during coagulation, firstly the PAC was adsorbed among particles acting as bridge to form larger size particles, followed by excess PAC was adsorbed on the surface of particles or flocs resulted in neutralizing charge, at the same time MS2 would be linked to flocs through charge attraction.
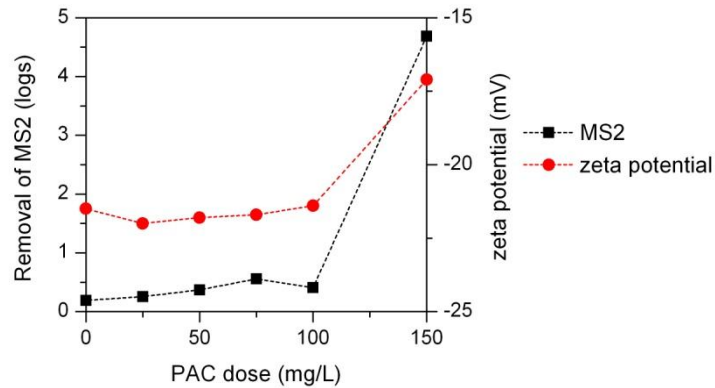
Figure 5.17   Effect of PAC dose on MS2 removal and zeta potential change during PAC+CMF process

5.3.2.1.3   Removal of PPCPs

The number of PPCPs (>90% removal) was taken as indicator to discuss effect of coagulation and CMF combination process on removal of PPCPs. The number of PPCPs discussed in this part was 32 PPCPs. The combination processes could not effectively remove PPCPs. It was reasonable considering pore size was much larger than PPCPs molecular size.

5.3.2.2   Effect of PAC dose on TMP change

Coagulation and CMF combination process was operated for more than 120 hours to check the long time performance on the fouling development. The CMF was operated for 30 min at 1 m/d flux, followed by high pressure backwashing (0.3MPa). Thus the TMP was expected to increase during 30 min filtration period, then decreased to certain level by removing reversible fouling through the high pressure backwashing. Correspondingly, TMP fluctuated in the range of maximum and minimum value during one filtration cycle. Thus the TMP symbols were distributed in the wide band shown in Figure 5.18. The bottom of the band indicated TMP changing caused by irreversible fouling with filtration time. The difference of top and bottom of this band described TMP changing attributed to reversible fouling.

The CMF without PAC adding, the TMP increased sharply to the limitation 100 kPa (87 kPa at 20 °C) in 1.5 hours. Afterwards, the filtration period was changed from 30 min to 5 min, CMF stop due to exceeding limit of TMP within 4 hours. With adding 25 mg/L PAC, CMF could be operated continuously for 120 hours with TMP increasing from 10 kPa to 31 kPa. This indicated

that PAC dose was not enough for fouling control during long term running. And the TMP caused by reversible fouling fluctuated a lot with change of turbidity concentration in the raw water. This was another evidence for insufficient PAC dose for long time filtration. Increased PAC dose to 50 or 75 mg/L, long term stable filtration could be achieved. And TMP did not change much with turbidity fluctuation of raw water. Thus 50 mg/L was the optimal PAC dose for membrane fouling control.
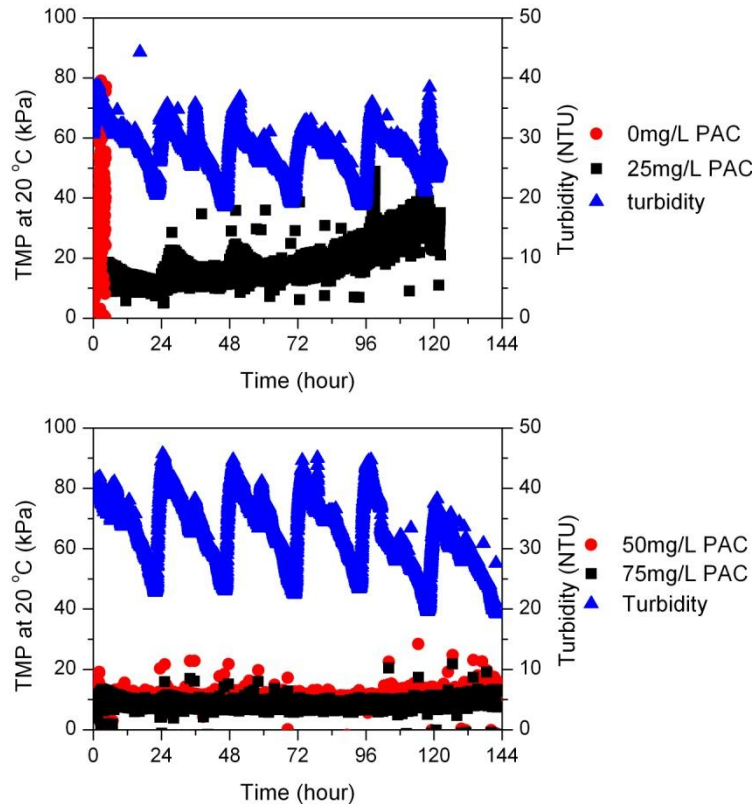
Figure 5.18   Long time performance of PAC+CMF process (PAC dose =0, 25, 50, 75 mg/L)

5.3.2.3   Pretreatment effect on membrane fouling caused by particles

PSD was analyzed to discuss coagulation effect on fouling caused by particles. The result was shown in Figure 5.19. Adding 25 mg/L PAC mainly changed the medium particle size in the range of 1.0 to 10 μm into particles with size between 10 to 100 μm. The particles were smaller, the fouling formed was more serious according to Carman–Kozeny relationship (Carman, 1938). Thus adding 25 mg/L PAC decreased the fouling significantly (Figure 5.18). But small size particles (<1.0μm) were still existed after PAC of 25 mg/L treatment. Such particles were

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expected to pass through cake layer to reach membrane surface to form fouling. Consequently certain level fouling was formed during filtration. Increasing PAC dose to 50 or 75 mg/L, all the particles were changed to ones with size larger than 10 μm. And comparison with TMP changing result (Figure 5.18), it was deduced that the particles with size larger than 10 μm did not contribute to irreversible fouling much.
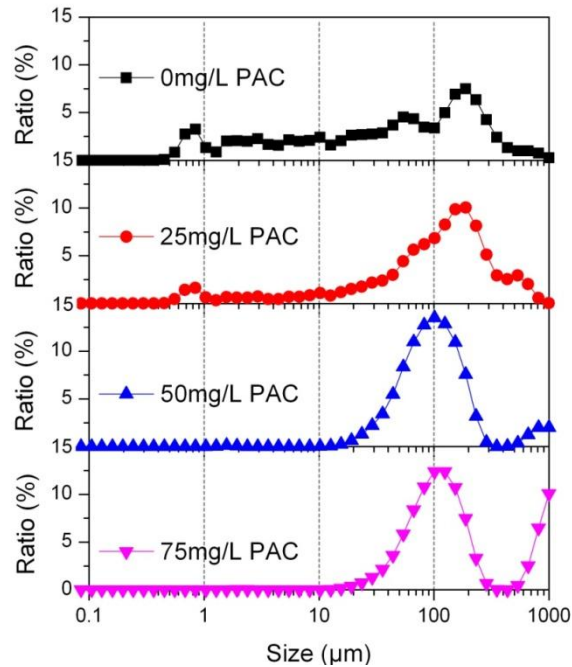
Figure 5.19   PAC dose effect on Particle Size Distribution (PAC dose =0, 25, 50, 75 mg/L)

5.3.2.4   Pretreatment effect on membrane fouling caused by dissolved organic matters

In the EEM spectra of the primary effluent and reclaimed water, four regions of high fluorescence intensity were observed: peak A at (Em/Ex) 300-305/220 nm; peak B at (Em/Ex) 340-350/ 220 nm, peak C at (Em/Ex) 265-370/280 nm, and peak D at (Em/Ex) 410-430/320-340 nm. Peak A is associated with tyrosine-like organic matter, peak B is attributed to tryptophan-like compounds, peak C contains phenol-like organic compounds and peak D is associated with more fulvic-like material (Chen et al., 2003; Leenheer et al., 2003).

The fluorescence intensity of four peak identified in primary effluent and reclaimed water was shown in Table 5.4. The intensity of peak A, peak B, peak C and peak D in primary effluent was 1289.1-1372.1, 1179.3-1216.7, 356.6-339.9 and 213.8-220.7, respectively. The removal rate by

coagulation and CMF was 8.1%, 15.7%, 7.2% and 5.3% for peak A, peak B, peak C and peak D, respectively. The removal rate slightly decreased with adding PAC before CMF. With adding 75mg/L dose of PAC, the removal rate decreased to 1.0%, 12.0%, 8.1% and 5.3% for peak A, peak B, peak C and peak D, respectively. The removal rate by coagulation and CMF in case of treating primary effluent was much lower than the one in case of treating secondary effluent (Figure 4.23). The reasons were discussed in the latter parts of this Chapter.

Table 5.4   The fluorescence intensity of four components identified in primary effluent and treated water

PAC dose	Intensity in primary effluent				Intensity in treated water			
	Peak A	Peak B	Peak C	Peak D	Peak A	Peak B	Peak C	Peak D
mg/L	nm^{-1}	nm^{-1}	nm^{-1}	nm^{-1}	nm^{-1}	nm^{-1}	nm^{-1}	nm^{-1}
0	1372.1	1179.3	339.9	213.8	1269.0	999.6	315.7	202.5
25	1372.1	1179.3	339.9	213.8	1295.0	1042.0	323.6	219.1
50	1289.1	1216.7	356.6	220.7	1239.0	1060.0	326.5	214.8
75	1289.1	1216.7	356.6	224.5	1284.0	1077.0	328.0	214.8

5.3.2.5   Characterization of foulants inside of CM

At the end of experiment, after removing cake layer on the surface of the membrane, foulants were extracted using NaOH (pH=11) and HCl (pH=2) solution, successively. The carbon amount was obtained through the volume of the solution multiplied by TOC value in solution used to extract foulants. Then the carbon amount was divided by accumulated volume of filtrated water to get normalized amount of carbon presented in the foulants deposited on the membrane per 1 liter of wastewater filtered. The results were shown in Figure 5.20. 96% to 97% of organic matter could be extracted by basic solution. The amount of carbon was 2221.8 μg, 28.6μg, 56.6μg and 36.0 μg for the experiments with coagulation under 0, 25, 50 and 75 mg/L PAC dose, respectively. The experiments with adding 0 and 25 mg/L, 50 and 75 mg/L dose PAC were done using the same primary effluent as feed water, respectively. Comparison the TOC result within experiments using same wastewater, it was found amounts of organic foulants decreased with increasing PAC dose. This was in accord with the results of TMP change.
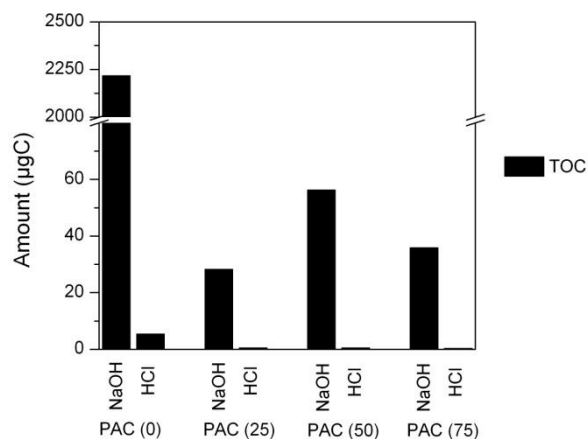
Figure 5.20   Amount of carbon presented in the foulants deposited inside of ceramic membrane per 1 liter of PE filtered.

Then we tried to get more clues from analyzing amount of sugar, protein and humic substances to explain results of TMP change. The amount of sugar, protein and humic substances extracted from used membrane was normalized with accumulated volume of wastewater filtered. The normalized amount of each component under different PAC doses was shown in Figure 5.21. Similar as TOC result, basic solution early recovered all the foulants. The recovery rate of sugar, protein and humic acid by basic solution was 88.5-95.4%, 99.8-100.0% and 98.9-99.7%, respectively. The sugar recovery rate was 5% to 10% lower than other foulants. In order to find the reasons for the phenomena, the fouling mechanisms should be understood firstly, which is listed in the following paragraph.

Hydrophobic interaction was reported as the explanations for humic acid to membrane (Yamamura et al., 2007). Protein molecules adsorbing on the membranes surfaces was controlled by a number of interaction mechanisms namely ionic, entropic, hydrophobic, van der Waals, specific/affinity etc. (Jones, K. L. et al., 2001; Rabe et al., 2011). There was little work was done to identify how sugar induced fouling. But there were several studies showing that sugar would form complexes with metals to contribute to fouling (Decho, 1999; Donati et al., 2004; Grant et al., 1973). Besides these, hydrogen bond was another force resulting in fouling. –COOH, –OH and –NH$_2$ were common functional groups with forming hydrogen bond tendency. And it was reported that only when pKa value was larger than pH of the solution, the functional group was protonated. And protonated functional groups contributed to the formation of a strong hydrogen

bond (vanderVegte et al., 1997). In previous studies estimated that carboxyl groups have pKa values between 3 and 6 (Vezenov et al., 1997). And hydroxyl groups have pKa values between 9 and 13 (Ahimou et al., 2002). The pKa value for $-NH_2$ was estimated at 7 (vanderVegte et al., 1997). Thus $-OH$ could form strong hydrogen bond, and $-NH_2$ could form soft hydrogen bond in the wastewater with pH in the range of 6.5 to 7.4. In addition, both biopolymers could interpenetrate each other forming a network structure due to ionic bonds or multiple hydrogen bonds (Susanto et al., 2008; Velings et al., 1994).
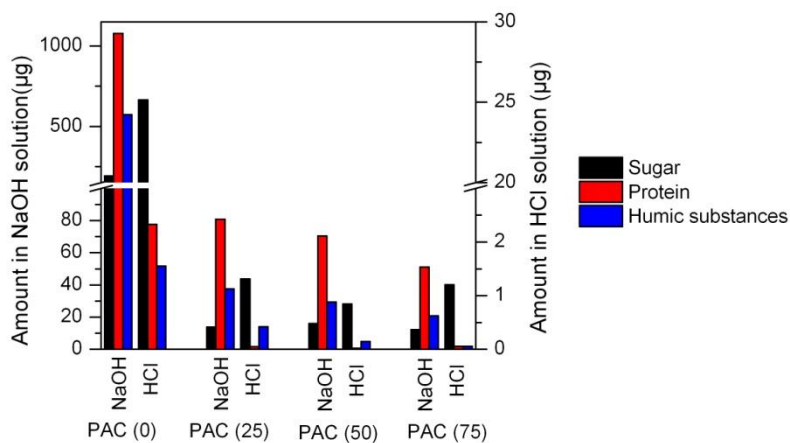
Figure 5.21   Amount of sugar, protein and humic substances presented in the foulants deposited on the membrane per 1 liter of PE filtered

Based on the above information, we could deduce that alkaline solution might result in protein hydrolysis or destroy hydrogen bond of protein and sugar with other foulants or ceramic membrane. And basic condition made it easy to dissolve humic substances for ionizing the functional groups (Ghosh et al., 1980). Using acid solution, 10% of total amount sugar and 1% of total amount humic acid could be removed from membrane. And it has been reported that a large portion of organic matter desorbed from the fouled membrane by acid resulted fouling through forming complexes with metals (Kabsch-Korbutowicz et al., 1999). It was suggested that destroying the bonds between metals and organic matters caused foulants recovering by acid solution.

From Figure 5.21, it was found that the normalized amount of sugar, protein and humic substances decreased obviously with increasing PAC dose. The normalized amount was 218.3, 1079.4 and 575.2 µg per 1 liter of wastewater filtered for sugar, protein and humic substances.

With 25 mg/L PAC, the normalized amount sharply decreased to 15.2, 80.8 and 38.0μg per 1 liter of wastewater filtered, respectively. The normalized amount did not obvious changed with larger PAC dose (50, 75mg/L PAC).

5.3.2.6 Comparison of foulants inside of CM during treating secondary effluent and primary effluent

In order to clearly show the difference between foulants inside of CM during treating secondary effluent and primary effluent, the amount of each substance in the foulants should be converted into TOC value. The relationship between concentrations of sugar, protein and humic substances and TOC were shown in Figure 5.22.
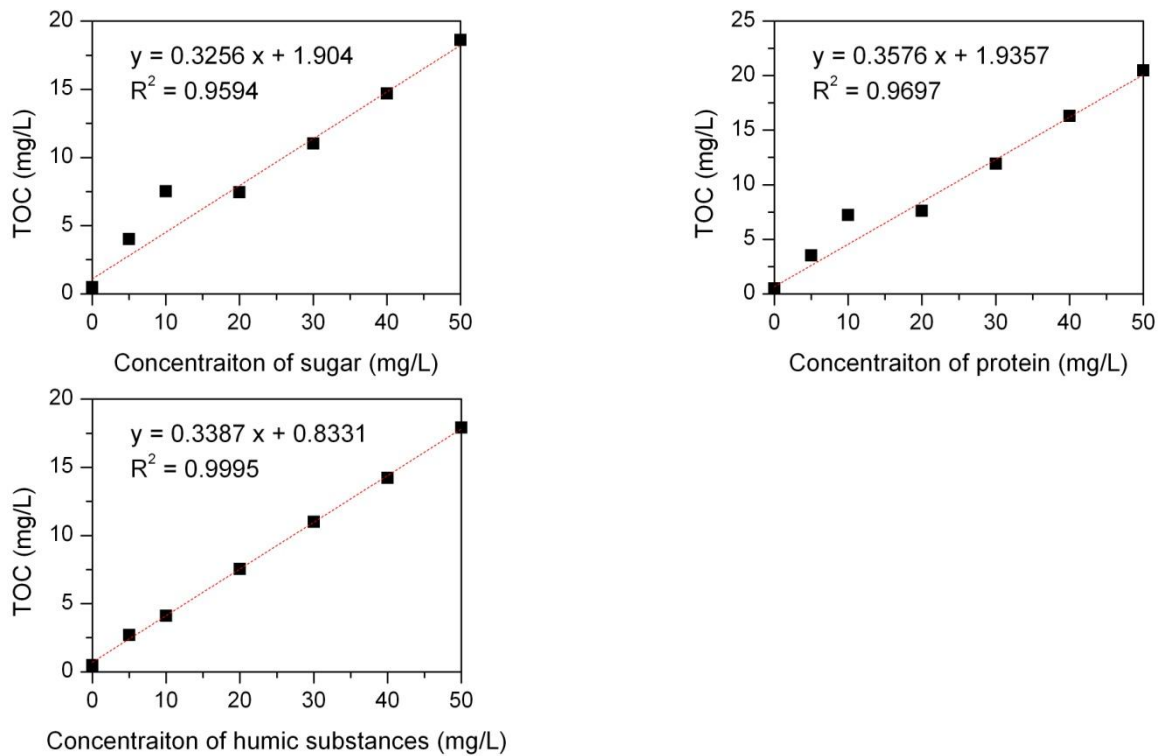
Figure 5.22   Relationship of concentration of each substance (sugar, protein and humic substances) withTOC

Based on the standard curves shown in Figure 5.22, the TOC values of sugar, protein and humic substances presented in the foulants deposited on the ceramic membrane per 1 liter were calculated. And the difference between the TOC of extraction solution and calculated TOC of sugar, protein and humic substances represented the TOC of other organic matters in foulants

(except sugar, protein and humic substances). The results were shown in Figure 5.23. In case of secondary effluent, the TOC amount was 38.7, 146.1, 71.0 and 13.0 μg for sugar, protein, humic substances and other organic matters, respectively. During treating primary effluent, the TOC amount was 73.0, 387.9, 195.6 and 1565.2 μg, respectively. The ratio of other organic matters with total foulants was 4.8% and 70.4% in case of secondary effluent and primary effluent case, respectively. That meant there were a lots unknown organic matters caused CM fouling. Thus more efforts should be done to characterize the foulants in CM during treating primary effluent.
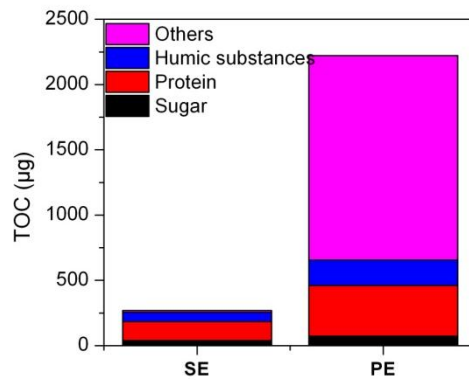
Figure 5.23   TOC value of sugar, protein, humic substances and others organic matters (except sugar, protein and humic substances) presented in the foulants deposited on the membrane per 1 liter of SE/PE filtered (PAC dose=0mg/L)

Then coagulation effect on mitigating fouling was compared during treating these two wastewaters (Figure 5.24). No significant difference was found. In both case, the TOC amount of each substance in the foulants was decreased with adding 25mg/L dose PAC. Further increasing PAC dose, the TOC amount of each substance was not obviously decreased. While interesting point was found in the results in primary effluent case. The decreasing speed of other organic matters amount was much higher than others. The amount ratio of organic matters with total foulants was 70.4% in case of without adding PAC. The ratio decreased to 12.2% after adding 25mg/L PAC, and further decreased to 4.7% after adding 75mg/L PAC. This meant the fouling caused by other organic matters was much easier to be controlled by adding PAC than fouling resulted from sugar, protein and humic substances.
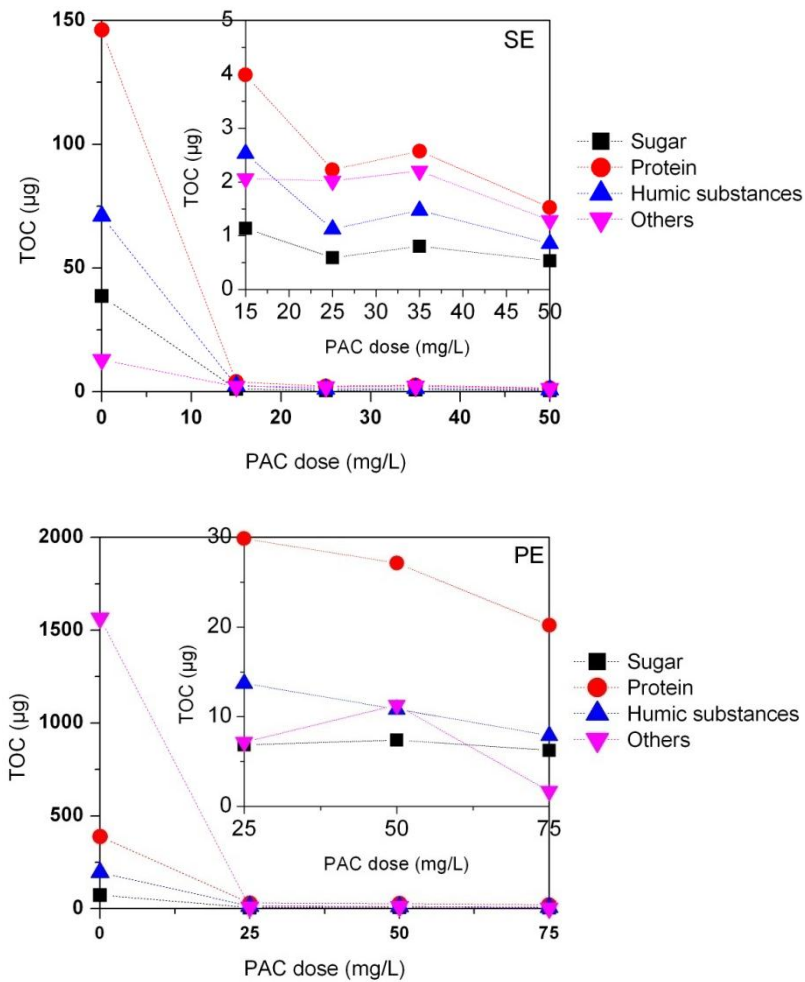
Figure 5.24   PAC dose effect on TOC amount of sugar, protein, humic substances and other organic matters (except sugar, protein and humic substances) presented in the foulants deposited on the membrane per 1 liter of SE/PE filtered

Based on the above discussion, it was found there was relative large amount of organic matters except sugar, protein and humic substances in primary effluent could result in CM fouling. But the membrane fouling caused by these potential organic foulants could be easily alleviated by coagulation with PAC as coagulant.

5.4 Summary

The objective of this chapter was to research the performance of ozonation, coagulation and CMF combination processes treating primary effluent. The conclusions obtained are as follows:

1.	Through short term experiment, ozonation was found not effective for controlling fouling. While coagulation was found necessary to mitigate membrane fouling, and showed advantages on removal of TP. Thus coagulation and CMF combination process was selected as candidate reclamation process for treating primary effluent.

2.	The rejection rates of COD, TOC and color by CMF were 50%, 60% and 42%, respectively. Adding PAC before the CMF increased removal rate of such items. Under condition of adding 75mg/L dose PAC, the removal rates were increased to 58.8%, 61.7% and 81.6% for COD, TOC and color, respectively. For the nutrients removal, phosphorous was effectively rejected by CMF with combined with coagulation. The removal rate of TP and DTP by coagulation (75mg/L PAC) and CMF was 86.9% and 87.6%, respectively. For MS2, the removal of MS2 by CMF was around 0.2 logs. Significant removal enhance by PAC was observed with large PAC dose (150 mg/L) with obvious zeta potential increase. It was deduced that removal of MS2 just happened after PAC dose was high enough to neutralize charge. For PPCPs, no obvious removal was found due to larger pore size compared with molecular size of PPCPs.

3.	The CMF without PAC adding, the TMP increased sharply to the limitation in 4 hours. Coagulation pretreatment could effectively mitigate membrane fouling. And 50mg/L PAC was found as the optimal PAC dose for membrane fouling control. Under this condition, no obvious increasing TMP was found during 144 hours operation.

4.	Increasing particle sizes was proposed as reason for mitigating membrane fouling caused by particles by coagulation pretreatment, which was investigated based on PSD measurement. Besides, changing fouling tendency of dissolved organic matters by coagulation was another reason. It was studied through analyzing EEMs. The removal rate by coagulation and CMF was 8.1%, 15.7%, 7.2% and 5.3% for tyrosine-like organic matter, tryptophan-like compounds, phenol-like organic compounds and fulvic-like materials, respectively. The removal rate slightly decreased with adding PAC before CMF. With adding

75mg/L dose of PAC, the removal rate decreased to 1.0%, 12.0%, 8.1% and 5.3%, respectively.

5. The foulants inside of CM was characterized through analyzing amount of sugar, protein and humic substances. Without adding PAC, the normalized amount was 218.3, 1079.4 and 575.2 μg per 1 liter of wastewater filtered for sugar, protein and humic substances, respectively. With 25 mg/L PAC, the normalized amount sharply decreased to 15.2, 80.8 and 38.0μg, respectively. The normalized amount did not obvious changed with larger PAC dose.

6. Based on calculating the TOC amount of each potential foulant (sugar, protein and humic substances) in the foulants deposited on membrane, fouling caused by other organic matters was discussed. It was found that relative large amount of organic matters in primary effluent resulted in ceramic membrane fouling. But the membrane fouling caused by these potential organic foulants could be easily alleviated by coagulation with PAC as coagulant.

5.5　References

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CHAPTER VI

Discussion on the Feasibility of Cascaded Water Use with Water Reclamation System

6.1 Introduction

Nowadays, the water scarcity and water pollution widely happened. As a consequence, many water reuse projects were established. The USA was by far the largest producer, with a volume of reused water estimated at close to 6.5 million cubic meters per day (Bixio et al., 2005). The number must be much larger than this now because these data were summarized in 2005. With the exception of South Africa, large amount of reclaimed water are used for non-potable use, such as agricultural and landscape irrigation. Small scale applications are mostly for urban, recreational and environmental uses. In our study, crop irrigation was decided as main usage. Besides, urban usage, such as recreational impoundment, municipal irrigation, fire fighting and toilet flushing was also discussed.

There is a high potential for human exposure to reclaimed water through food (crop irrigation), direct contact or ingest (urban usage). The contaminants in the reclaimed water showing potential risks were divided into microorganisms and chemical constituents. Microorganisms associated with water borne disease are primarily enteric pathogens, including enteric bacteria, protozoa, and viruses. Pathogen risk is the most common concern in water reclamation and reuse. Here we mainly discussed the removal of virus taking MS2 as an indicator and removal of enteric bacteria taking total coliforms as an indicator. For chemical contaminants, although there is no reported disease happened due to exposure to chemical contaminants in reclaimed water. Removal of chemical contaminants should be taken into consideration due to ecological risk related to some chemicals especially pharmaceuticals and personal care products (PPCPs) (Kawakami, 2010;

Kim, J. W. et al., 2009; Nassef et al., 2009; Nassef et al., 2010a; Nassef et al., 2010b; Oberlé et al., 2012; Porte et al., 2009; Schnell et al., 2009). Then PPCPs was also selected as target contaminants in our study.

In addition, energy consumption is another important factor to consider the feasibility of process. Thus the objective of this chapter was to propose technical rout for various usages based on comprehensive consideration of both reduction risk and saving energy.

6.2   Evaluation methods

6.2.1   Energy calculation methods

6.2.1.1   Ozonation

In this study, we have assumed that the conditions are the same as ones used in previous research (Munoz et al., 2007). The energy consumption in this ozonaiton system was described as follows. One oxygen-fed ozone generator with a capacity of 1 kg O_3/h was used. The gas-to-liquid transfer efficiency was 75%. The energy included power consumption for producing O_3, pumping and residual O_3 destruction. And costs by oxygen and cooling water were also converted to energy consumption. Energy requirements per kg O_3 production was 15.85 kWh. Among this, 12.8 kWh was used for O_3 generator. Power consumption was 2.2, 1.55 and 0.1 kWh for main pump, recirculation pump and O_3 destructor, respectively. And 8.3 kg O_2 was needed for 1 kg O_3 producing. The energy consumption for producing O_2 per kg O_3 was 8.28 kWh. This value included electricity for process, cooling water and infrastructure for air separation plant. Thus the total power consumption was 21.08 kWh/kg O_3.

Considering maximum O_3 consumption needed for treating secondary effluent was 4.5 mgO_3/L (Chapter 4), this ozonation system could supply O_3 to treat 3720 m^3/d. Thus the capacity of water reclamation for treating secondary effluent was decided as 3600 m^3/d.

6.2.1.2   Coagulation

There are two parts should be taken into consideration, power for mixing and energy cost to produce coagulant PAC. The energy consumption during mixing in coagulation tank was calculated based on the formula (Camp et al., 1943) as follows:

$$Energy = G^2 \times \mu \times T$$

Where, Energy is energy consumption during mixing (Wh/m^3); G is velocity gradient (s^{-1}); μ is dynamic viscosity of wastewater (1.005×10^{-3} Pa s at 20 °C); T is coagulation time (h).

In our study, the G was 36.39 s^{-1}. The coagulation period was 8 minute. Thus the energy for mixing was 1.8×10^{-2} kWh/m^3.

The power cost for coagulant was described as follows: The CO_2 mission during producing PAC was 0.405 kg CO_2/kg (LCA 実務入門編集委員会, 1998). And the converting ratio between CO_2 mission and energy consumption was 0.555 kg CO_2/kg (LCA 実務入門編集委員会, 1998). Thus the energy intensity of PAC was assumed 0.7297 kWh/kg.

6.2.1.3 Ceramic membrane filtration

The energy in CMF system is mainly consumed by feed water pump, air compressor (for backwashing) and chemicals for cleaning membrane. The capacity was assumed as 3600m^3/d according to ozonation systems. Then equipments were selected as follows (Table 6.1).

Table 6.1 Basic information about feed water pump and air compressor selected (中国市政工程西南设计院, 1986)

	Type	Flow rate	Pressure	Power	comments
Feed water pump	200F-34A	327 m^3/h	0.27 MPa	70 kW	Assumed to continuously running
Air compressor	L5.5-55/4.5	55 m^3/min	0.45 MPa	34 kW	The air compressor was operated for 10 second every 30 minutes

The energy consumption during filtration in CMF part was calculated as follows (the energy consumption was multiplied by 1.5 of safety factor):

$$Energy\ (kWh/m^3) = 1.5 \times (\frac{70kW \times 1h}{3600m^3/h \times 1h} + \frac{34kW \times 10 \sec onds/60/60}{3600m^3/h \times (30/60)h}) = 1.5 \times (1.9444 \times 10^{-2} + 5.24 \times 10^{-5}) = 0.0292\ kWh/m^3$$

During filtration, chemical enhanced backwashing (CEB) using H_2SO_4 was done to recover permeability of CMF. According to our experience of off-line membrane washing, 0.5 ml H_2SO_4 was needed for membrane with surface membrane of 0.042m^2. Thus in case of 3600 m^3/d treatment plant, the H_2SO_4 amount required was 20.2 kg per CEB. And neutralization using NaOH solution should be done before discharging the solution after cleaning membrane. The

NaOH amount was calculated based on stoichiometric chemistry. The amount of NaOH was 68.7 kg NaOH (24% wt). The energy consumption for production H_2SO_4 and NaOH was 0.157 and 0.405 kWh/kg (LCA 実務入門編集委員会, 1998). Thus energy consumption per CEB= $(0.157 \times 20.2 + 0.405 \times 68.7)/3600 = 8.6 \times 10^{-3}$ kWh/(CEB m^3)

6.2.2   Quantitative Microbial Risk Analyses (QMRA)

Quantitative Microbial Risk Analyses (QMRA) was used to characterize and estimate potential adverse health effects associated with exposure of virus to human. In our study norovirus was selected as virus model due to its high risk. Norovirus have been identified as the cause of many outbreaks (Desai et al., 2012; Mesquita et al., 2012; Souza et al., 2012).

The first step was to set up exposure scenarios. Five exposure scenarios aimed to various reuse applications were decided in this study, including recreational impoundment (scenario 1), municipal irrigation (scenario 2), fire fighting (scenario 3), toilet flushing (scenario 4) and crop irrigation (scenario 5) (Table 6.2).

The second step was calculating risks using disability adjusted life years (DALYs). DALYs have been used extensively to assess disease burdens. It could be calculated using formula (NRMMC et al., 2006) listed as follows:

DALY per year=$P_{infs} \times P_{ill/inf} \times$ DALY per case $\times$ susceptibility   (1)

Where, P_{infs} is risk of infection (probability of infection per event). It could be calculated using dose-response relationship (Teunis et al., 2008) listed in Table 6.3. $P_{ill/inf}$ (Probability of illness conditional on infection) was reported as 0.68 (Teunis et al., 2008). The DALY loss per case of norovirus was 9×10^{-4} (Kemmeren et al., 2006). Susceptibility was 1 based on the conservative assumption that everyone is susceptible to illness.

The third step was getting acceptable concentration in reclaimed water. In our study, the tolerable level of risk is defined as $<10^{-6}$ DALY per years, as high as level of health protection is required for drinking-water (NRMMC et al., 2006). Acceptable norovirus concentration in reclaimed water could be calculated through substituting the $<10^{-6}$ DALY per years into equation (1).

Table 6.2   Exposure scenarios used in the risk assessment

	Purposes	Risk groups receptor	Exposure frequency	Amount of water ingested in a single exposure, mL	Reduction in the environment	References
Scenario 1	Recreational impoundment	Swimmer	40	100	No virus reduction	(Tanaka et al., 1998)
Scenario 2	Municipal irrigation	People involved	50	1	No virus reduction	(NRMMC et al., 2006)
Scenario 3	Fire fighting	Firefighters	50	20	No virus reduction	(NRMMC et al., 2006)
Scenario 4	Toilet flushing	Residents involved	1100	0.01	No virus reduction	(NRMMC et al., 2006)
Scenario 5	Crop irrigation	Consumer	140	1	Stop irrigation 2 weeks before harvest; 2 logs virus reduction was achieved by die-off during delivering to consumer; 1 log virus was removed by washing before eating	(NRMMC et al., 2006; WHO, 2006)

Table 6.3   Dose-response relationship of norovirus

Pathogen	Dose unit	Dose-response relationship	Dose-response parameter values	Probability of illness conditional on infection	Parameters values reference
Norovirus	genomes	$P_{infs}=1-_2F1(\alpha, (\mu(1-a))/a, \alpha+\beta, (-a)/(1-a))$	A=0.04; β=0.055; a=0.0001	$P_{ill/inf}$=0.68	(Teunis et al., 2008)

Last step was calculating log removal of norovirus required for each scenario using equation (2).

The removal required = Log10 (Conc$_w$/Conc$_{arw}$)　　　　(2)

Where, Conc$_w$ means concentration in wastewater; Conc$_{arw}$ means acceptable concentration in reclaimed water

The concentration of norovirus in wastewater was cited from Japanese government report (Report about norovirus survey in sewer in Japan, 2010). The average concentration of norovirus G in the period of September-October and November- March was 5×10^4 and 1×10^6 copies/L, respectively. The concentration in primary effluent and secondary effluent equals to concentration in sewer divided by removal rate during primary and secondary treatment, separately. 0-0.5 logs removal during primary treatment and 1.0-3.0 logs removal during secondary treatment were reported in previous work (NRMMC et al., 2006). Based on the above information, the log removal of norovirus required for each scenario was calculated (Figure 6.1).
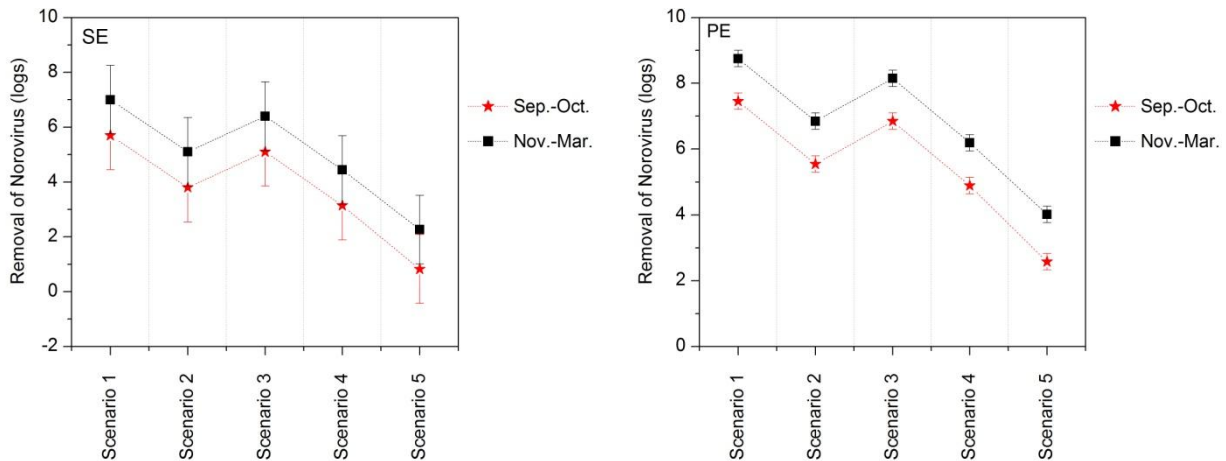
Figure 6.1　　Log removal of norovirus required for each scenario (up: SE; down:PE)

6.2.3　Ecological risk of PPCPs calculation

Ecological risk of PPCPs was evaluated based on Hazard Quotient (HQ). The HQ approach compares environmental concentrations of a contaminant with a measured effect or no-effect level in test organisms. It is determined by the ratio of "predicted environmental concentration (PEC)" to "predicted no effect concentration (PNEC)". The concentration in wastewater or reclaimed water was used instead of PEC. The PNEC is calculated by dividing No Observed

Effect Concentration (NOEC) with assessment factor (100). The NOEC obtained from algae growth inhibition test using *Pseudokirchneriella subcapitata* (Kawakami, 2010)was listed in table 6.4.

Table 6.4   NOEC for selected 58 PPCPs

No.	Name of PPCPs	Use	Molecular Formula	Water Solubility (mg/L)	pKa	LogKow	NOEC (mg/L)
1	Acetaminophen		$C_8H_9NO_2$	1.4E+04	9.38	0.46	N.D.
2	Antipyrine		$C_{11}H_{12}N_2O$	5.2E+04	1.4	0.38	N.D.
3	Diclofenac		$C_{14}H_{11}C_{12}N\ O_2$	2.4E+00	4.15	0.7	6.25
4	Ethenzamide		$C_9H_{11}NO_2$	4.5E+03	-	0.77	-
5	Fenoprofen		$C_{15}H_{14}O_3$	1.7E+02	7.3	3.9	6.25
6	Ibuprofen	Analgesics	$C_{13}H_{18}O_2$	2.1E+01	4.91	3.97	12.5
7	Indomethacin		$C_{19}H_{16}ClNO_4$	9.4E-01	4.5	4.27	50
8	Isopropylantipyrine		$C_{14}H_{18}N_2O$	3.0E+06		1.94	1.56
9	Ketoprofen		$C_{16}H_{14}O_3$	5.1E+01	4.45	3.12	0.0156
10	Mefenamic acid		$C_{15}H_{15}NO_2$	2.0E+01	4.2	5.12	5.00
11	Naproxen		$C_{14}H_{14}O_3$	1.6E+01	4.15	3.18	6.25
12	Atenolol		$C_{14}H_{22}N_2O_3$	1.3E+04	9.6	0.16	6.25
13	Disopyramide	Antiarrhythmic	$C_{21}H_{29}N_3O$	4.5E+01	-	2.58	6.25
14	Metoprolol	agents	$C_{15}H_{25}NO_3$	-	9.7	-	0.313
15	Propranolol		$C_{16}H_{21}NO_2$	6.2E+01	9.42	0.74	0.25
16	Ceftiofur		$C_{19}H_{17}N_5O_7S_3$	-			12.5
17	Chloramphenicol		$C_{11}H_{12}Cl_2N_2O_5$	2.5E+03	5.5	1.14	0.125
18	Ciprofloxacin		$C_{17}H_{18}FN_3O_3$	3.0E+04	6.09		2.5
19	Clarithromycin		$C_{38}H_{69}NO_{13}$	3.4E-01	8.99	3.16	0.0156
20	Diclazuril		$C_{17}H_9Cl_3N_4O_2$	-	-	-	-
21	Enrofloxacin		$C_{19}H_{22}FN_3O_3$	3.4E+03		0.7	0.0156
22	Erythromycin		$C_{37}H_{67}NO_{13}$	1.4E+00	8.88	3.06	0.0313
23	Erythromycin-H2O		$C_{37}H_{66}NO_{12}$	1.4E+00	8.88	3.06	0.0313
24	Griseofulvin		$C_{17}H_{17}ClO_6$	8.6E+00	-	2.18	-
25	Levofloxacin		$C_{18}H_{20}FN_3O_4$	-	5.5, 8.0	-	0.625
26	Lincomycin		$C_{18}H_{34}N_2O_6S$	9.3E+02	7.6	0.29	0.00781
27	Nicarbazin		$C_{19}H_{18}N_6O_6$	7.3E+00	-	3.76	0.156
28	Norfloxacin	Antibiotic	$C_{16}H_{18}FN_3O_3$	1.8E+05	6.34, 8.75	-1.03	3.13
29	Oxytetracycline		$C_{22}H_{24}N_2O_9$	3.1E+02	3.27	-0.9	0.156
30	Roxithromycin		$C_{41}H_{76}N_2O_{15}$	1.9E-02	-	2.75	-
31	Sulfadimethoxine		$C_{12}H_{14}N_4O_4S$	3.4E+02	-	1.63	0.625
32	Sulfadimidine		$C_{12}H_{14}N_4O_2S$	1.5E+03	7.59	0.89	-
33	Sulfamerazine		$C_{11}H_{12}N_4O_2S$	2.0E+02		0.14	0.0781
34	Sulfamethoxazole		$C_{10}H_{11}N_3O_3S$	6.1E+02	5.94	0.89	0.156
35	Sulfamonomethoxine		$C_{11}H_{12}N_4O_3S$	4.0E+03	-	0.7	0.156
36	Sulfapyridine		$C_{11}H_{11}N_3O_2S$	2.7E+02	2.7,8.3	0.35	-
37	Sulfathiazole		$C_9H_9N_3O_2S_2$	3.7E+01	2.5,7.0	0.05	0.781
38	Thiamphenicol		$C_{12}H_{15}Cl_2NO_5S$	1.2E+04	-	-0.33	0.195
39	Tiamulin		$C_{28}H_{47}NO_4S$	7.0E-01		4.75	-
40	Triclosan		$C_{12}H_7C_{13}O_2$	1.0E+01		4.76	0.000625
41	Trimethoprim		$C_{14}H_{18}N_4O_3$	4.0E+02	7.12	0.91	6.25

Table 6.4   NOEC for selected 58 PPCPs (continued)

42	Tylosin	Antibiotic	$C_{46}H_{77}NO_{17}$	5.0E+00	7.73	1.63	0.0625
43	Carbamazepine	Anticonvulsant	$C_{15}H_{12}N_2O$	1.8E+01	-	2.45	6.25
44	Primidone	Anticonvulsant	$C_{12}H_{14}N_2O_2$	5.0E+02	-	0.91	-
45	Crotamiton	Anti-itch drug	$C_{13}H_{17}NO$	5.5E+02	-	2.73	6.25
46	Cyclophosphamide	Antineoplastic agents	$C_7H_{15}Cl_2N_2O_2P$	4.0E+04	-	0.63	50.0
47	Sulpiride	Antipsychotic drug	$C_{15}H_{23}N_3O_4S$	2.3E+03	9.12	0.57	12.5
48	Clenbuterol	Bronchodilator	$C_{12}H_{18}Cl_2N_2O$	3.3E+03	9.33	2	0.156
49	Theophylline	Bronchodilator	$C_7H_8N_4O_2$	7.4E+03	8.81	-0.02	50.0
50	Diltiazem	Calcium channel blockers	$C_{22}H_{26}N_2O_4S$	4.7E+02	7.7	2.7	0.625
51	Bezafibrate	Cholesterol-lowering drug	$C_{19}H_{20}ClNO_4$	3.4E-01	3.4	4.25	25.0
52	Clofibric acid	Cholesterol-lowering drug	$C_{10}H_{11}ClO_3$	5.8E+02	-	2.57	25.0
53	Ifenprodil	NMDA receptor antagonist	$C_{21}H_{27}NO_2$	2.6E+02	9.05, 9.69	3.9	0.0391
54	DEET	Insect repellents	$C_{12}H_{17}NO$	9.1E+02		2.18	50.0
55	Furosemide	loop diuretic	$C_{12}H_{11}ClN_2O_5S$	7.3E+01	3.9	2.03	25.0
56	Pirenzepine	Selective antagonist,	$C_{19}H_{21}N_5O_2$	1.7E+01	1.8, 7.9	1.68	25.0
57	Caffeine	Acetylcholinesterase inhibitor	$C_8H_{10}N_4O_2$	2.2E+04	10.4	-0.07	25.0
58	2-QCA	The others	$C_9H_6N_2O_2$	-	-	-	-
59	Dipyridamole	Calcium channel blockers	$C_{24}H_{40}N_8O_4$	8.2E+00	6.3	2.74	-

Note:
 "-": no data

6.2.4   Water quality requirement for each scenario

Besides virus and PPCPs, bacteria in wastewater should be also removed, especially the enteric bacteria. These bacteria can infect human and cause typhoid and diarrhea. The WHO guideline for water reuse in agriculture requires that *E. coli* does not exceed 10^3/100ml and 10^5/100 ml for unrestricted irrigation and restricted irrigation, respectively (WHO, 2006). In EPA guideline, fecal colifroms should be less than 200 fecal coli/100ml for restricted irrigation and environmental reuse, and no fecal coliforms should be detected in 100ml reclaimed water for urban usage (EPA, 2004). In the California Title 22 criteria, concentration of total coliforms is also decided for various usage. For restrict irrigation including municipal irrigation and restricted urban reuse, the concentration of total colifroms should be less than 23 /100 ml. And the concentration should be less than 2.2/100ml for unrestricted urban reuse (CDHS, 2008). The guideline in Japan requires that *E. coli* dosed not exceed 1000/100ml for urban and impoundments reuse (MLITT, 2005).

In addition, turbidity and color as the common water quality item should be removed to certain extend according to the application purpose of reclaimed water. Based on water reuse regulations established, the contaminants removal target for each scenario in our study was decided (Table 6.5)

Table 6.5   Contaminants removal target for each scenario

		Scenario 1 Recreational impoundment	Scenario 2 Municipal irrigation	Scenario 3 Fire fighting	Scenario 4 Toilet flushing	Scenario 5 Crop irrigation
Virus	Logs removal	8.25 (SE); 9.00 (PE)	6.35 (SE); 7.09 (PE)	7.65 (SE); 8.40 (PE)	5.69 (SE); 6.44 (PE)	3.52 (SE); 4.27 (PE)
Ecological risk related with PPCPs	Removal rate (%)	90%	90%	90%	90%	90%
Total colifroms	CFU/100ml	≤ 2.2	≤ 23	≤ 2.2	≤ 2.2	$\leq 10^3$
Turbidity	NTU	≤ 2	≤ 2	≤ 2	≤ 2	≤ 2
Color	-	≤ 10	≤ 2	≤ 2	≤ 2	-

Note: SE: secondary effluent;
PE: primary effluent
-: decided by consumer

6.3   Results and discussions

6.3.1   Energy required to remove contaminants by each process

6.3.1.1   Energy calculation for each process

For secondary effluent, CMF-based processes (CMF, PAC+CMF, ozonation+PAC+CMF) were studied using continuous experiments. The operational parameters and energy consumption were shown in Table 6.5. Energy consumption in ceramic membrane filtration part without any pretreatment was 0.07 kWh/m^3. With adding coagulation pretreatment, the power required was decreased to 0.03 kWh/m^3. The chemical enhanced backwashing (CEB) period increased from 0.21 days to 19.8 days. Adding ozonation before coagulation and CMF, CEB period increased to 90 days, but the energy consumption by ceramic membrane filtration did not reduced obviously. It resulted from low power requirement for chemical enhance backwashing (0.0086 kWh/m^3). And the total energy consumption did not decreased obviously by adding pretreatments due to additional energy needed in pretreatment part. For using ozonation pretreatment, the total energy consumption even increased due to high energy needed in ozonation part. But operational stability was improved by pretreatment. In addition, removal of contaminants was expected to be enhanced by ozonation. Thus comprehensive evaluation was necessary to decide whether pretreatment was needed or not.

For the ozonation-based processes (ozonation, CMF+ozonation and PAC+CMF+ozonation), 22 L semi batch reactor was used for ozonation. We converted O$_3$ consumption needed in batch

reactor to O_3 dose required in continuous reactor through assuming gas transfer efficiency was 75%. Then the energy consumption was calculated. In Table 6.5, only power requirement in coagulation and ceramic membrane filtration part was listed. The energy consumption in ozonation unit was discussed in the latter part.

For primary effluent, the ozonation had been proved ineffective on mitigating fouling (Chapter 5). Thus only coagulation pretreatment was incorporated with ceramic membrane filtration process. Without pretreatment, energy consumption for ceramic membrane was 0.26 kWh/m^3. Power requirement in membrane filtration part decreased to 0.117-0.118 kWh/m^3 by adding coagulation as pretreatment. The CEB period increased from 0.06 to 10-60 days. And the total energy consumption including coagulation and membrane filtration was lower than 0.26 kWh/m^3. It indicated that pretreatment was necessary for treating primary effluent using ceramic membrane process. The pretreatment effect on contaminants removal was discussed in latter part. For ozonation-based experiments, the energy requirement calculation method was same as in secondary effluent case and was also shown in latter part.

Table 6.6   Operational parameters of each combination processes (secondary effluent case)

1st treatment	2nd treatment	3st treatment	O_3 input dose mg/L	O_3 reactor	PAC dose mg/L	CM flux m/d	CEB interval days	Energy kWh/m³ O_3	PAC	CMF	total
CM	-	-	-	-	-	4.0	0.21	0	0	0.070	0.070
PAC	CM	-	-	-	15	4.0	4.2	0	0.029	0.031	0.060
		-	-	-	25	4.0	3.0	0	0.037	0.032	0.068
		-	-	-	35	4.0	9.1	0	0.044	0.030	0.074
		-	-	-	50	4.0	19.8	0	0.054	0.030	0.084
O_3	PAC	CM	2	Bench scale	25	4.0	2.0	0.042	0.036	0.034	0.112
			2		35	4.0	5.0	0.042	0.044	0.031	0.117
			4		25	4.0	3.0	0.084	0.036	0.032	0.153
			4		35	4.0	5.0	0.084	0.044	0.031	0.159
			6		15	4.0	20	0.126	0.029	0.030	0.185
			6		25	4.0	90	0.126	0.036	0.029	0.192
			6		50	4.0	90	0.126	0.054	0.029	0.210
O_3	-	-	O_3 consumption divided by 75%	Lab scale	-	4.0	-	D	0	0	D
CM	O_3	-			-	4.0	0.21	D	0	0.070	D
PAC	CM	O_3			25	4.0	3.0	D	0.037	0.032	D

Notes: "-" no data
"D" depending on operation parameters

Table 6.7   Operational parameters of each combination processes (primary effluent case)

1st treatment	2nd treatment	3st treatment	O$_3$ input dose mg/L	O$_3$ reactor	PAC dose mg/L	CM flux m/d	CEB interval days	Energy kWh/m^3 O$_3$	PAC	CMF	total
CM	-	-	-	-	-	1.0	0.06	0	0	0.260	0.260
		-	-	-	25	1.0	10	0	0.036	0.118	0.154
PAC	CM	-	-	-	50	1.0	60	0	0.054	0.117	0.171
		-	-	-	75	1.0	60	0	0.073	0.117	0.190
O$_3$	-	-	O$_3$ consumption divided by 75%	Lab scale	-	-	-	D	0	0	D
CM	O$_3$	-			-	1.0	0.06	D	0	0.260	D
PAC	CM	O$_3$			50	1.0	60	D	0.054	0.117	D

Notes: "-" no data

"D" depending on operation parameters

6.3.1.2   Energy required for virus removal

Figure 6.2 showed the energy requirements for MS2 removal in ceramic membrane filtration-based (CMF-based) experiments. And the virus removal targets for various water reuse scenario was also shown in this figure. The virus removal targets for each scenario during disease epidemic period were higher than during unepidemic period (discussed in calculation methods part). Here we used the removal target during disease epidemic period to ensure safety of reclaimed water. And in our study, we assumed the removal of MS2 equal to removal of norovirus.

For secondary effluent, MS2 rejection by ceramic membrane was around 0.45 logs. The rejection increased to over 8.0 logs with coagulation pretreatment. The product water satisfied virus removal for all the scenarios except scenario 1 (recreational impoundment). CMF incorporated with ozonation and coagulation pretreatment, could achieve more than 12 logs removal. It could produce reclaimed water to meet requirement in all scenarios.

For primary effluent, ceramic membrane rejected 0.28 logs MS2. The removal only increased to less than 0.6 logs by adding coagulation pretreatment with 25, 50 and 75 mg/L PAC dose. The product water from coagulation and CMF combination process could not meet requirement for any scenario. Further process, such as ozonation, was needed.
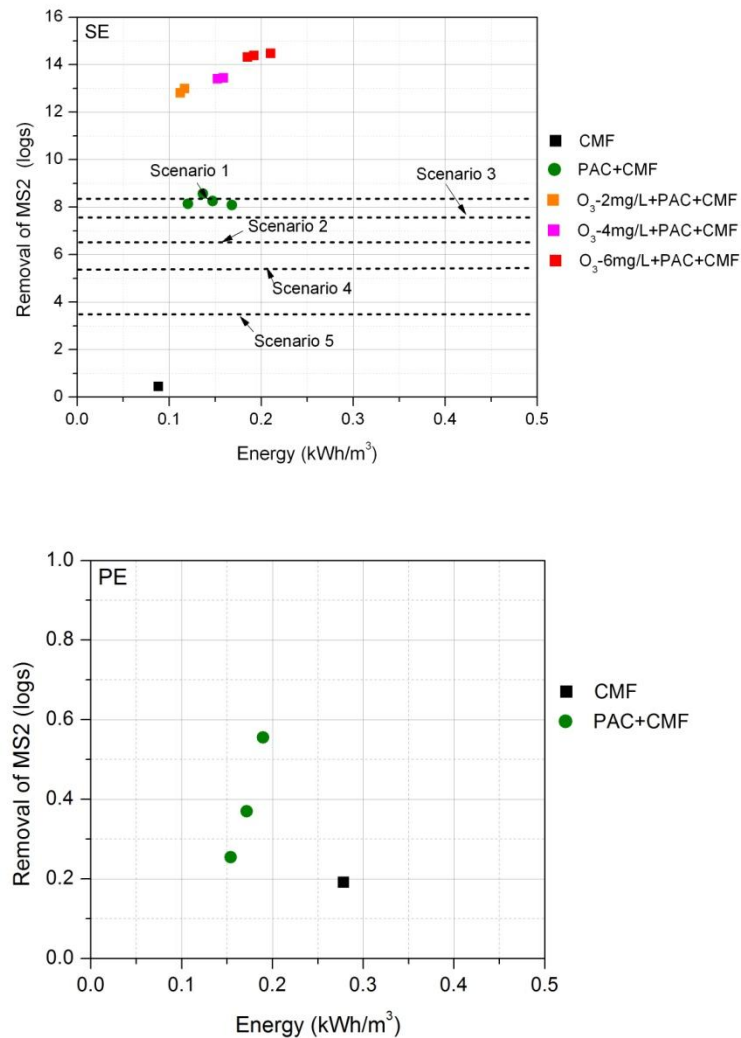
Figure 6.2   Evaluation feasibility of CMF- based process for 5 scenarios from virus removal aspect (top: SE; bottom: PE)

For secondary effluent, although CMF-based technologies (CMF incorporated with ozonation and/or coagulation pretreatment) could produce high enough quality reclaimed water, ozonation-based processes (ozonation with CMF and/or coagulation pretreatment) was also studied in our research to propose feasible process based on both product water quality and energy consumption evaluation. The MS2 removals by ozonation-based processes were plotted in Figure 6.3. Ozonation could only meet virus removal requirement for scenario 5 (crop irrigation) with over 0.08 kWh/m^3 energy consumption. Ozonation combined with CMF pretreatment could produce

reclaimed water for scenario 4 (toilet flushing), 3 (fire fighting), 2 (municipal irrigation) and 1 (recreational impoundment) usage. The power requirement was 0.15, 0.25, 0.17 and 2.7-3.6 kWh/m^3, respectively. The energy consumption could be reduced to 0.9 kWh/m^3 by using coagulation, CMF and ozonation combination process to produce reclaimed water satisfied requirements for all the scenarios.
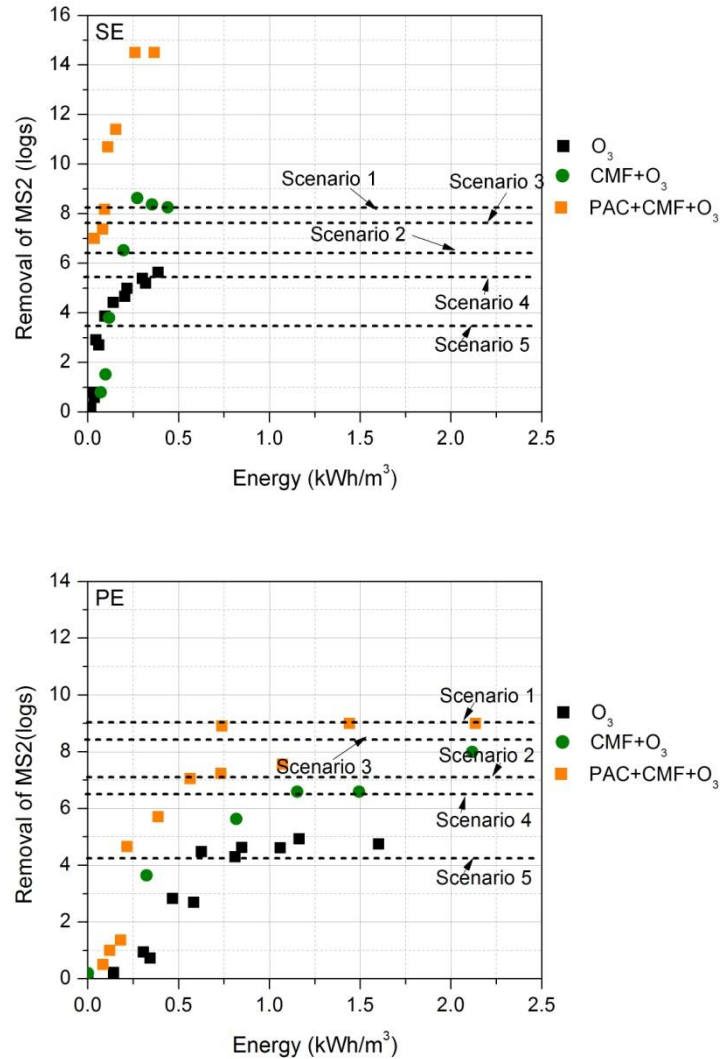
Figure 6.3   Evaluation feasibility of O$_3$-based process for 5 scenarios from virus risk removal aspect (top: SE; bottom: PE)

In case of treating primary effluent, ozonation could produce reclaimed water for scenario 5 usage with 0.7 kWh/m^3 energy consumption. With CMF the energy was reduced to 0.5 kWh/m^3.

The energy requirement could be further decreased to 0.25 kWh/m^3 by adding coagulation and CMF before ozonation. And, the product water from CMF and ozonation combination process could be used in scenario 4 and 2. The power requirement was in the range of 1.3-2.2 kWh/m^3. Adding coagulation before CMF and ozonation combination process could reduce the energy consumption to 0.6-1.5 kWh/m^3 for scenario 4 and 2.

Based on above discussion, each process with suitable operational parameters could produce reclaimed water to meet virus removal target.

6.3.1.3   Energy required for removing ecological toxicity related with PPCPs

Figure 6.4 presented the energy required for ∑HQ related with PPCPs (sum of PPCPs detected in wastewater) by CMF-based processes. For secondary effluent, ceramic membrane with/without coagulation pretreatment could remove <20% of ∑HQ with 0.06-0.08 kWh/m^{3}energy consumption. The removal was mainly caused by removal PPCPs in solid phase, such as triclosan. With ozonation pretreatment, nearly 100% of ∑HQ was removed with 0.12-0.25 kWh/m^3. This corroborated the results that PPCPs were mainly removal by ozonation. In case of primary effluent, only CMF with/without coagulation was studied. Thus only 9%-22% removal of ∑HQ was observed with 0.15-0.28 kWh/m^3.
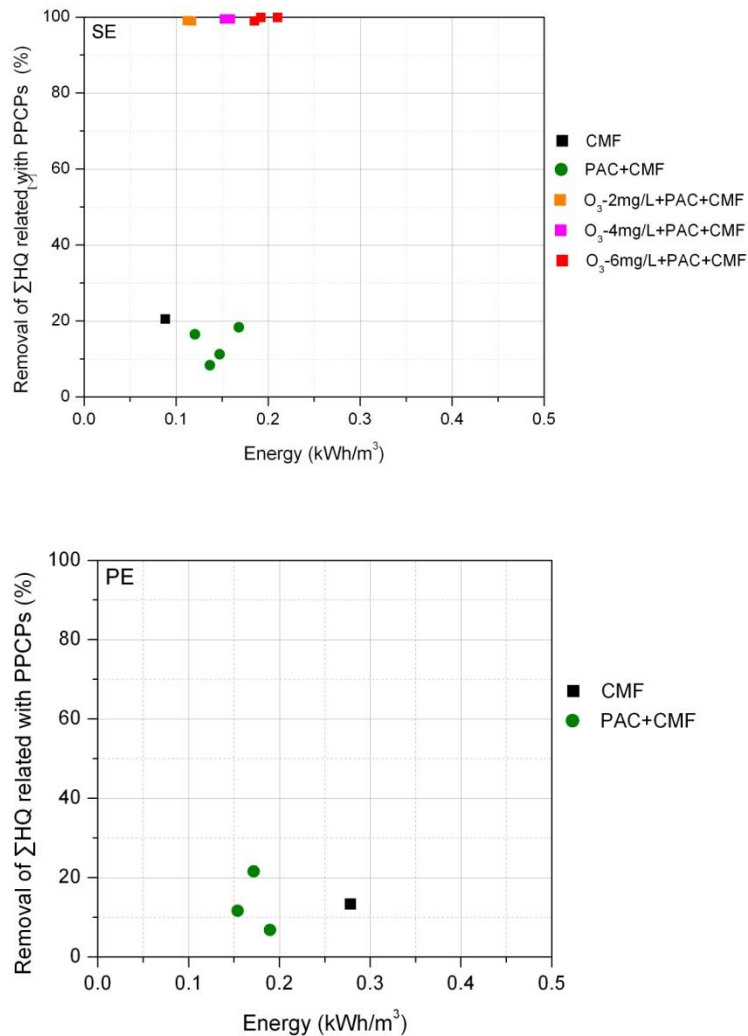
Figure 6.4   Evaluation feasibility of CMF-based processes from removal of ΣHQ related with PPCPs aspect (top: SE; bottom: PE)

Figure 6.5 showed the removal of ecological risk related with PPCPs during ozonation based processes. For treating secondary effluent, ozonation could reduce ecological risk obviously. Over 90% removal could be achieved with energy consumption of 0.03-0.05 kWh/m^3. Adding ceramic membrane with/without coagulation pretreatment, the power required for removing 90% ecological risk was increased to 0.09-0.12 kWh/m^3. It could be explained as follows. Based on discussion in previous chapters, PPCPs was mainly removed by ozonation, and coagulation and ceramic membrane showed little effect. Although ozone consumption to meet same PPCPs

removal rate saved by pretreatment due to decreasing amount of organic matter. Energy consumed in pretreatment part was found much higher than energy saved in ozonation part by pretreatment. In case of primary effluent, no significant difference was found between energy required in ozonation with and without pretreatment. In order to remove 90% ecological risk, 0.25-0.50 kWh/m^{3}was needed. It was resulted from that energy consumed by pretreatment almost equaled to energy saved in ozonation part by pretreatment.
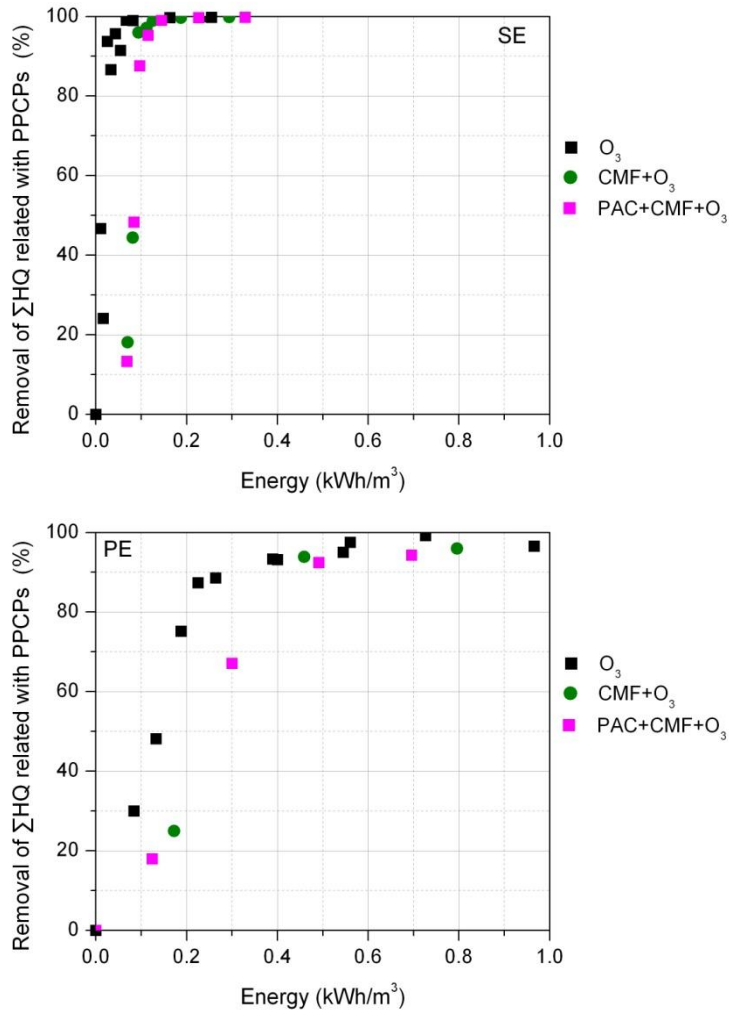
Figure 6.5   Evaluation feasibility of ozonation-based processes from removal of $\sum$HQ related with PPCPs aspect (top: SE; bottom: PE)

6.3.2 Technical rout for cascade water use based on safety and energy calculation

Based on above discussion, ozonation is effective for removing MS2 but could not achieve bacteria removal target. CMF showed excellent performance to reject bacteria. And taking coagulation as pretreatment could effectively mitigate membrane fouling. Thus coagulation and CMF with post ozonation is selected as reclamation process to treat primary effluent. And the produced water could only meet requirement of scenario 5. The detail operation parameters and product water quality are described in Figure 6.6. The energy consumption is 0.390 kWh/m^3. It was much lower than energy consumed by membrane bioreactor (MBR), which is generally used now. It was reported that the typical energy consumption for MBR was in the range of 0.7-1.6 kWh/m^3 with extreme vaules up to 2.2-2.5 kWh/m^3 (Ruel, 2012). It indicated that coagulation, CMF and ozonation showed high potential to be used in directly treating primary effluent for irrigation usage.

For secondary effluent, ozonation and combination process among coagulation, CMF and ozonation could achieve contaminants removal for certain usage. Ozonation could produce reclaimed water for scenario 4 (toilet flushing) and scenario 5 (crop irrigation). The energy consumed in reclamation process was 0.387 and 0.139 kWh/m^3, respectively. Considering power required during biological wastewater treatment is 0.43-1.09 kWh/m^3 (Serre et al., 2003), the total energy consumption in treating sewage for scenario 4 and 5 usage could be 0.817-1.477 and 0.569-1.229 kWh/m^3. In the following discussion, only power required in reclamation process was mentioned. Coagulation, CMF and ozonation could be used as treatment for scenario 1 (recreational impoundment) with 0.109 kWh/m^3 power consumption. The energy consumption decreased to 0.082 and 0.092 kWh/m^3 for producing reclaimed water for scenario 2 (municipal irrigation), 4 (toilet flushing), 5 (crop irrigation) usage and scenario 3 (fire fighting) usage. The ozonation, coagulation and CMF could produce high quality level water, which can meet requirement of all usages mentioned in 5 scenarios. The energy consumption was 0.112-0.192 kWh/m^3. It is much lower than using ozonation process. And it is a little higher than power required in coagulation, CMF and post ozonation combination process. Thus coagulation, CMF and post ozonation showed potential possibility to be used in water reclamation field instead of ozonation, coagulation and CMF.

Primary effluent

PAC+CM+O₃

Scenario 5
E: 0.390 kWh/m³
PAC: 50mg/L
O₃ : 10.88 mg/L
MS2 : 5.7 logs
B: not detected
∑HQ : 97.9%
Color: 10
Turbidity:<1.0

Biological wastewater treatment (Energy consumption=0.43-1.09 kWh/m³ (Serre, M. 2003)

O₃

Scenario 4
E: 0.387 kWh/m³
T E: 0.817-1.477 kWh/m³
O₃: 3.44 mg/L
MS2: 5.64 logs
B: ~40CFU/100mL
∑HQ : ~100%
Color: ~2.0
Turbidity:~0.66

Scenario 5
E: 0.139 kWh/m³
T E: 0.569-1.229 kWh/m³
O₃:1.23 mg/L
MS2: 4.42logs
B: ~188CFU/100mL
∑HQ : ~100%
Color: ~3.9
Turbidity:~1.2

PAC+CMF+O₃

Scenario 1
E: 0.109 kWh/m³
T E: 0.539-1.119 kWh/m³
O₃: 0.97 mg/L
MS2: 10.7 logs
B: not detected
∑HQ : 89.6-95.3%
Color: ~3.0
Turbidity:<0.3

Scenario 2, 4, 5
E: 0.082kWh/m³
T E: 0.512-1.172 kWh/m³
O₃:0.174 mg/L
MS2 : 7.37logs
B: not detected
∑HQ : ~48.3%
Color: 3.9-4.9
Turbidity:<0.3

Scenario 3
E: 0.092kWh/m³
T E: 0.522-1.182 kWh/m³
O₃:0.565mg/L
MS2 : 8.18logs
B: not detected
∑HQ : ~87.6%
Color: ~3.0
Turbidity:<0.3

O₃ + PAC+CMF

Scenario 1, 2, 3, 4, 5
E: 0.112-0.192 kWh/m³
T E: 0.542-1.202 kWh/m³
O₃: 1.85-2.0 mg/L
MS2: >12.81 logs
B: not detected
∑HQ : 99.0-100%
Color: ~2.0
Turbidity:<0.3

Notes:
E =energy consumption in reclamation process
T E = total energy consumption in secondary treatment and reclamation process
PAC =PAC dose
O₃ =O₃ consumption
MS2 =MS2 removal:
B = Total coliforms concentraiton/100ml
∑HQ = removal of total hazard quotient related with PPCPs
Turbidity (unit=NTU)

Figure 6.6   Technical rout for cascade water usage

6.4 Summary

The objective of this chapter was to evaluate the feasibility of combination process based on ozonation, coagulation and CMF in water reclamation field. For these purposes, the risk and energy evaluation was conducted, and the conclusions obtained are as follows:

1.　　In the case of treating secondary effluent, energy consumption in CMF part was 0.07 kWh/m^3. The energy consumption could be decreased to 0.03 kWh/m^3 by adding coagulation or ozonation+coagulation pretreatment. But the total energy consumed by the coagulation and CMF combination process was same as the energy consumed by CMF. And the power required for ozonation, coagulation and CMF combination process was as high as 0.120-0.211 kWh/m^3 due to high power required in ozonation part.

2.　　In the case of treating primary effluent, energy consumption in CMF process was 0.260 kWh/m^3. Coagulation pretreatment could obviously save power required. The total energy consumption by coagulation and CMF combination process was decreased to 0.154-0.190 kWh/m^3.

3.　　Technical rout for various usages was proposed based on consideration of contaminants removal and energy consumption. For treating primary effluent, coagulation, CMF and post ozonation was suitable process to reuse water in scenario 1 (crop irrigation) usage. The energy consumption was 0.390 kWh/m^3, much lower than power required by MBR. Thus coagulation, CMF and post ozonation showed potential to treat primary effluent as crop irrigation usage.

4.　　In case of secondary effluent, several processes with suitable parameters could produce reclaimed water to meet requirement in various usages. Among these technologies, coagulation, CMF and ozonation showed advantages for low energy consumption (0.082-0.109 kWh/m^3). It was lower than power required in ozonation, coagulation and CMF combination process (0.112-0.192 kWh/m3). Thus CMF and post ozonation showed potential

to replace ozonation, coagulation and CMF combination process in secondary effluent reclamation field.

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CHAPTER VII

Discussion and Recommendations

7.1 Conclussions

There have been a lot of researches on water reclamation from sewage using ozonation, membrane filtration processes. Nevertheless, little work has been reported about combination processes based on ozonation and CMF to produce reclaimed water. Moreover, no research work was found about comprehensive study on such combination processes from both product water quality and saving energy aspects. Thus comprehensive study of water reclamation from sewage was conducted in our research. Target contaminants include PPCPs, virus, bacteria, nutrients and some common water quality items. Various processes including ozonation-based (ozonation, CMF+ozonation, PAC+CMF+ozonation) and CMF-based (CMF, PAC+CMF, ozonaton+PAC+CMF) were examined to treat secondary effluent and primary effluent from municipal wastewater treatment plant.

In Chapter 3, ozonation effect on PPCPs degradation and pathogen disinfection was studied. And we try to enhance the removal of contaminants by various pretreatments, such as CMF, coagulation and CMF combination process. In Chapter 4, CMF-based processes treating secondary effluent with several pretreatments were examined. Both removal of contaminants and mitigation membrane fouling were studied. In Chapter 5, short term experiments were done firstly to select suitable water reclamation process candidate for treating primary effluent. Afterwards, long term experiments were done about the candidate process from product water quality and mitigation fouling aspect. In Chapter 6, risk and energy evaluation of each combination processes were studied. Quantitative microbial risk analyses (QMRA) was used to characterize and estimate potential adverse health effects associated with exposure of virus to human. Risk caused by bacteria was examined based on water reuse guidelines established. For

PPCPs, ecological risk based on hazard quotient (HQ) was used to consider risk reduction by reclamation processes. Then the energy consumption for each process was calculated. Moreover, five water reuse scenarios were established according to previous works. Finally, suitable technology was proposed for each reuse scenarios based considerations of risk reduction and energy cost.

Then the main results from each Chapter were summarized as follows:

The objective of Chapter 3 was to research the degradability of contaminants by ozonation with or without pretreatments, including common water quality items, bacteria, virus indicator MS2 and PPCPs. For these purposes, the semi-batch experiments were conducted, and the conclusions obtained are as follows:

1.   Ozonation performances on bacteria inactivation were found different in treating secondary effluent and primary effluent. With 1.5 mg O_3/mg C consumption, around 3.5 logs and 2.5 logs bacteria inactivation could be achieved in the two wastewaters, respectively. CMF pretreatment showed no effect on bacteria inactivation in secondary effluent. But obvious enhancement on bacteria disinfection was observed in primary effluent case due to increasing DO_3.

2.   Similar change trend for MS2 in two kinds of wastewater were observed. 4-5 logs MS inactivation was achieved after SOC reaching around 1.2 and 0.8 mg O_3/mg C for secondary effluent and primary effluent respectively. CMF and PAC+CMF pretreatment showed tiny effect on MS2 inactivation enhancement, except lightening tail off phenomena.

3.   41 out of 59 PPCPs were detected in wastewater. The degradability in secondary effluent and primary effluent was similar. For PPCPs in liquid phase, all the antibiotics could be effectively (90% removal rate) degraded by ozonation before DO_3 appeared. It was a little harder to remove antiarrhythmic agents. For analgesics and other compounds, most compounds could be easily removed, except ketoprofen, caffeine, bezafibrate, DEET,

clofibric acid. The pseudo-first-order reaction rate was used to compare degradation of PPCPs in liquid phase and solid phase. The reaction rate in liquid phase was 1.35 times as high as reaction rate in solid phase. And this is the first time to compare reaction rate of PPCPs in liquid phase and in solid phase.

4.   Considering normalized ozone consumption with initial TOC, CMF and PAC+CMF pretreatment were found no obvious effect on improving ozonation efficiency for degradation PPCPs in secondary effluent treatment. While enhancement by PAC+sedimentation and PAC+CMF was observed in treating primary effluent. Based on DEET removal results, it was deduced that the reason of enhancement was caused by increasing OH exposure by adding PAC and sedimentation, PAC and CMF pretreatment. Considering same input ozone dose, CMF and PAC+CMF pretreatment could increase reaction rate of each PPCPs in both wastewaters. It caused by the O_3 consumption per TOC was increased by these pretreatment than in raw wastewater.

5.   Relation among different contaminants removal was calculated using SPSS statistics 17.0 software. Clear relationship of SUVA removal with PPCPs removal in both wastewaters was found. SUVA showed high possibility to be used to control O_3 injection for removal of PPCPs in the application field. Bacteria removal was increased with increasing DO_3. While for MS2 removal, it showed clear linear relation with SUVA removal only in primary effluent not in secondary effluent.

The objectives of Chapter 4 were to study performance of CMF-based processes for treating secondary effluent from improving product water quality and mitigating membrane fouling aspects. The conclusions obtained are as follows:

1.   The rejection COD_{Mn}, TOC, DOC, SUVA and color by CMF was 53.8%, 21.6%, 10.8%, 0.38% and 14.3% respectively. The removal rate increased with increasing PAC dose. Ozonation pretreatment decreased removal of organic matters (COD_{Mn}, TOC) by 0-30%. In the other hand, ozonation pretreatment increased removal rate of SUVA and color to 60%-70%

and 100%. CMF could completely reject all the E. coli and total coliforms. And only 0.45 logs MS2 could be removed by CMF. The removal rate increased significantly to over 8 logs by adding coagulation or ozonation+coagulation before CMF. The ozonation, coagulation and CMF combination process could effectively eliminate PPCPs residuals. The removal happened mainly in ozonation part.

2.   Coagulation taking PAC as coagulant effectively mitigated membrane fouling. Ozonation with 6 mg/L input dose O_3 improved coagulation effect through forming larger particles. Obvious membrane fouling controlling was observed under 25 mg/L PAC with ozonation with 6 mg/L O_3 dose. While ozonation with 2 and 4 mg/L dose O_3 pretreatments showed negative effect on coagulation enhancement for membrane fouling mitigation.

3.   Increasing particle size and alleviating fouling tendency of sugar, protein and humic substances were found as reasons for mitigating membrane fouling by coagulation. Ozonation pretreatment could enhance forming larger size particles during coagulation. While fouling tendency of sugar, protein and humic substances was increased by ozonation under 2 and 4 mg/L O_3 dose. But ozonation pretreatment under 6 mg/L O_3 dose could effectively decreased the amount of protein and humic substances to mitigate membrane fouling.

The objective of Chapter 5 was to research the performance of CMF-based processes treating primary effluent. The conclusions obtained are as follows:

1.   Through short term experiment, ozonation was found ineffective to control fouling. And coagulation was found necessary to mitigate membrane fouling, and show advantages on removal of phosphorous. Thus coagulation and CMF was selected as suitable water reclamation process candidate for treating primary effluent.

2.   The rejection rates of COD, TOC and color by CMF were 50%, 60% and 42%, respectively. Adding PAC before the CMF increased removal rate of such items. For the nutrients removal, phosphorous was effectively rejected by CMF with combined with

coagulation. For MS2, the removal of MS2 by CMF was around 0.2 logs. Significant removal enhance by PAC was observed with large PAC dose (150 mg/L) with obvious zeta potential increase. It was deduced that removal of MS2 just happened after PAC dose was high enough to neutralize charge. For PPCPs, no obvious removal was found due to larger pore size compared with molecular size of PPCPs.

3.   During long term operation of coagulation and CMF combination process, 50mg/L PAC was found effective to control membrane fouling development. Coagulation pretreatment could mitigate membrane fouling significantly through changing PSD of particles. Coagulation pretreatment was also shown certain effect on organic matter fouling mitigation. Besides, it was found that relative large amount of organic matters other than sugar, protein and humic substances in primary effluent resulted in ceramic membrane fouling. But the membrane fouling caused by these potential organic foulants could be easily alleviated by coagulation with PAC as coagulant.

The objective of Chapter 6 was to evaluate feasibility of combination process based on ozonation, coagulation and ceramic membrane filtration in water reclamation field based on risk and energy evaluation, and the conclusions obtained are listed as follows:

1.   Technical rout for various usages was proposed based on contaminants removal and energy evaluation. For treating primary effluent, coagulation, ceramic membrane filtration and post ozonation was suitable process to produce water for scenario 1 (crop irrigation) usage. The energy consumption was 0.390 kWh/m^3, much lower than power required by MBR. Thus coagulation, ceramic membrane filtration and post ozonation showed potential to treat primary effluent as crop irrigation usage.

2.   In secondary effluent case, several processes with suitable parameters could produce reclaimed water to meet requirement in various usages. Among these technologies, coagulation, ceramic membrane filtration and ozonation showed advantages for low energy consumption (0.082-0.109 kWh/m^3). It was lower than power required in ozonation,

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coagulation and ceramic membrane filtration combination process (0.112-0.192 kWh/m^3). Thus ceramic membrane filtration and post ozonation showed potential to replace ozonation, coagulation and ceramic membrane filtration combination process in secondary effluent reclamation field.

7.2 Recommendations for future research

1. The risk of chemicals from reclaimed water was evaluated through simple adding ecological toxicity of each PPCP detected together. Synergistic and/or antagonism effect among different chemicals should be considered in evaluation total risk of mixture of many chemicals. Many other chemicals besides PPCPs presented in wastewater and reclaimed water might also contribute to toxicity. In addition, the ecological toxicity of each PPCP was obtained based on acute toxicity. Thus comprehensive risk testing of reclaimed water should be done with considering risk of various chemicals and interaction among chemicals. And evaluation risk from reclaimed water based on chronic toxicity was also necessary to ensure reclaimed water safety.

2. The reclamation process was proposed based on experiments treating wastewater from only one municipal wastewater treatment in our research. It is needed to examine feasibility of proposed reclamation process for treating other wastewaters. And stability evaluation of the process during much longer time operation should be also done.