Applicability of UV-based and O_3-based Processes for the Reduction of Pharmaceuticals and Personal Care Products (PPCPs)

2008

ILHO KIM

Applicability of UV-based and O_3-based Processes for the Reduction of Pharmaceuticals and Personal Care Products (PPCPs)

(PPCPs の除去のための紫外線、オゾンおよび促進酸化処理の適用性に関する研究)

ILHO KIM

A Dissertation submitted in partial fulfillment of
the requirements for the degree of
Doctor of Engineering
Department of Urban and Environmental Engineering
Graduate School of Engineering

Kyoto University
Kyoto, Japan
September 2008

ABSTRACT

Pharmaceuticals and personal care products (PPCPs) are a group of various chemicals, used for the bodies of humans and domestic animals and plants. Many PPCPs are highly bioactive and most are polar when present in the environment, usually occur at no more than trace concentrations. On the other hand, there has also been a growing interest in water reuse according to the lack of water resources and the advanced technologies for water treatment such as membrane treatment and advanced oxidation processes (AOPs). In Japan, the amount of reclaimed water in 2005 was about 200 million m^3, which corresponds to just 1.4% of total effluent from wastewater treatment plant. Wastewater can be reclaimed and piped to individual households for uses such as toilet flushing, garden watering and washing of cars and outdoor surfaces. Therefore, the water reuse of wastewater treatment plant discharges can lead to an exposure of user to potential harmful constituents such as PPCPs. In the future, high quality treated water after conventional wastewater treatment will be needed for water reuse. According to the above background, the applicability of physicochemical processes such as UV-based processes (UV and UV/H_2O_2 processes) and O_3-based processes (O_3, O_3/H_2O_2 and O_3/UV processes) for the removal of PPCPs in secondary effluent was investigated in this study.

Firstly, degradation characteristics of the 30 PPCPs detected often in the aquatic environment by UV-based processes were examined. Two types of UV lamps with different wavelength each other (UV/Lamp1 - 254nm, UV/Lamp2 - 254/185nm) were used for UV alone process. UV/Lamp2 was more effective for the PPCPs degradation than UV/Lamp1 maybe due to the contribution of OH radicals formed from the photolysis of H_2O molecular by the wavelength of 185nm. Photochemistry in the vacuum-ultraviolet (VUV) spectral domain (140~200nm) is of high applicatory interest in environmental techniques for the oxidative treatment of water. However, limited information on the application of the VUV spectral domain is still available. This study provided research data on the degradation of PPCPs, emerging contaminants and demonstrated the availability of the VUV spectral domain in the area of wastewater treatment.

For UV/Lamp1 process, UV dose required for degrading 90% of initial concentration of each PPCP ranged from 38 mJ/cm^2 to 5,644 mJ/cm^2, indicating that for several PPCPs, very high UV dose will be needed for the effective removal. This means that considerable energy will be consumed for the effective PPCPs removal by UV/Lamp1 alone process. Contrarily,

for UV/Lamp1/H_2O_2 process, most of PPCPs were degraded by more than 90% at UV dose of 691 mJ/cm^2, showing that the addition of H_2O_2 during UV process can reduce the energy consumption.

Based on the results, the removal performance of UV/Lamp1 and UV/Lamp1/H_2O_2 processes for the PPCPs present in real secondary effluent was investigated using bench scale plant. Among the 38 PPCPs detected in secondary effluent, only 18 PPCPs were removed by more than 90% despite UV dose of 2,768 mJ/cm^2, which was the highest UV dose introduced for UV/Lamp1 alone process. In contrast with UV/lamp1 process, UV dose of 923 mJ/cm^2 was required for the 90% removal of all the PPCPs when initial H_2O_2 concentration in tested water was 6.2 mg/L during UV/Lamp1 process. Energy consumption is a very critical point in designing water treatment facilities. This study showed that the combination of H_2O_2 with UV process contributed to the decrease of operating cost as well as the significant improvement of the PPCPs removal.

Secondly, the removal potential of 30 PPCPs detected in aquatic environment with O_3, O_3/UV and O_3/H_2O_2 processes was investigated through batch experiments. Rate constants of the 30 PPCPs increased with the increase of O_3 feed rate. However, the degradations of the 30 PPCPs to the amount of O_3 consumed were more efficient at O_3 feed rate of 0.3 mg/L/min than 0.6 mg/L/min probably due to the promoted reaction of O_3 molecules with OH radicals by the supply of excess O_3. The combination of UV or H_2O_2 with O_3 process could improve the degradation rates of the PPCPs significantly, resulting in the reduction of required O_3 dose. Consequently, it was considered that most of the PPCPs can be degraded easily by O_3-based processes. On the other hand, most of the PPCPs were degraded by more than 90% at O_3 consumptions of 6.3 mg/L and 4.5 mg/L for O_3 and O_3/UV processes, respectively, when using tested water prepared by pure water spiked with the 30 PPCPs (initial H_2O_2 concentration : 13.4~144.0 μg/L). However, O_3 consumptions increased by 8.9 mg/L and 7.7 mg/L for O_3 and O_3/UV processes when the PPCPs were spiked into biologically treated water. For O_3 process, the addition of H_2O_2 promoted the degradation rates of almost all the PPCPs, whereas, it was found that the addition of excess H_2O_2 could cause a scavenging effect of OH radicals resulting in the decrease of PPCPs degradation rates.

The removal performance of O_3 and O_3/UV processes for PPCPs in secondary effluent was investigated using bench scale plant. Among the 37 PPCPs, only 24 PPCPs including carbamazepine, crotamiton and diclofenac were removed by more than 90% even at O_3 dose of 2 mg/L during O_3 process. However, an increased O_3 dose (6 mg/L) could lead to the 90%

removal for all the PPCPs except primidone (87%). Consequently, it is considered that O_3 dose of 6 mg/L can ensure the efficient removal of the investigated PPCPs for O_3 alone process. For O_3/UV process, most of PPCPs showed the removal efficiency of more than 90% by the combination of UV_{65W} with O_3 dose of 4 mg/L. An electrical energy of 1.09 kWh/m^3 was needed for the effective PPCPs removal by O_3/UV process. This was compared with for O_3 alone process (0.09 kWh/m^3). As a consequence, a considerable electrical energy was required due to the application of UV lamps for O_3/UV process.

Finally, the applicability as technologies for the reclamation of secondary effluent of O_3, UV/H_2O_2 and O_3/UV processes was discussed. UV/H_2O_2 and O_3/UV processes can be used as treatment options for various water reuses such as urban reuse, agricultural reuse, recreational reuse and potable reuse, with their superior disinfection effectiveness, decrease effect of ecological risk and no bromate formation potential as well as an effective PPCPs removal. In addition, an effective disinfection (4~5 log inactivation of total coliform) is expected when the investigated processes are applied for the effective removal of PPCPs in secondary effluent for water reuse. Therefore, the application of these processes for water reuse can bring the minimization or omission of the disinfection process. On the other hand, the formation potential of bromate is likely to be high at O_3 dose of 6 mg/L that showed the effective PPCPs removal during O_3 process. The combination of UV or H_2O_2 with O_3 process is recommended to suppress bromate formation for direct and indirect potable reuses. UV/H_2O_2 process can be also a treatment option in terms of bromate suppression.

These studies were performed mainly for investigating the reactivity of limited kinds of PPCPs with UV, O_3 or OH radicals. This study focused on the effective removal of various PPCPs in real secondary effluent with UV- and O_3-based processes. Moreover, appropriate process for water reuse of secondary effluent was proposed based on the energy consumption, the formation potential of disinfection by products (DBPs), disinfection effectiveness and decrease effect for ecological risk. Applicability of UV/H_2O_2, O_3 and O_3/UV processes for water reuse was confirmed through this study.

TABALE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

CHAPTER I

INTRODUCTION

1.1 Research background

The precautionary principle with regard to wastewater treatment implies an efficient removal of all potential harmful constituents. In recent years, there has been a growing concern regarding the occurrence of pharmaceuticals and personal care products (PPCPs) in the aquatic environment (Heberer *et al.*, 2002; Smital *et al.*, 2004). The PPCPs have been detected in samples from the aquatic environment such as river water, ground water and drinking water and the main source of them has been known as the effluent from wastewater treatment plants (Halling-Sørensen *et al.*, 1998; Kanda *et al.*, 2003). There are also several investigations showing that PPCPs are not eliminated during wastewater treatment and also not biodegraded in the environment (Ternes, 1998; Daughton *et al.*, 1999; Nakada *et al.*, 2006; Okuda *et al.*, 2007).

On the other hand, there has also been a growing interest in water reuse according to the lack of water resources and the advanced technologies for water treatment such as membrane treatment and advanced oxidation processes (AOPs). It has been reported that the majority of states in U.S. have regulations regarding water reuse and reclaimed water use on a volume basis is growing at an estimated 15 percent per year (U.S EPA, 2004). In Japan, the amount of reclaimed water in 2005 was about 200 million ton, which corresponds to only 1.4% of total effluent from all the municipal wastewater treatment plants (The Ministry of Land, Infrastructure and Transport of Japan, 2005).

Wastewater can be reclaimed and piped to individual households for uses such as toilet flushing, garden watering and washing of cars and outdoor surfaces. U.S.EPA suggests advanced water treatment facilities such as MBR and UV treatment in the guidelines for water

reuse for ensuring the safety from chemical constituents, whereas the guideline of Japan has not treated with it yet. At the present, the concentration of residual chlorine is being regulated by the Japanese guideline on the use of the reclaimed water for the microbiological safety of the reclaimed water. However, disinfection with chlorine does not lead to a general removal of PPCPs (Huber *et al*., 2005). Therefore, the water reuse of wastewater treatment plant discharges can lead to an exposure of user to potential harmful constituents such as PPCPs. In the future, high quality treated water after conventional wastewater treatment will be needed for water reuse.

UV treatment, which is very popular for disinfection of potable water, lacks knowledge on applicability for the PPCPs removal in wastewater treatment system. Contrarily, recently several studies have demonstrated that O_3 and AOPs are very effective for the oxidation of PPCPs in water treatment process (Huber *et al.*, 2003; Ternes *et al.*, 2003; Rosenfeldt *et al.*, 2006; Balcioglu *et al.*, 2003). These processes are very promising for the removal of potential harmful constituents, microorganisms and viruses that may present in the reclaimed water. However, up to now, most of the studies on PPCPs degradation using these processes have been done to confirm the reactivity of PPCPs with O_3, UV and OH radicals. In the future, in applying physicochemical processes such as UV-based processes (UV and UV/H_2O_2 processes) and O_3-based processes (O_3, O_3/H_2O_2 and O_3/UV processes) for water reuse, it will be also necessary to take into consideration a required energy consumption and decrease effect of ecological risk as well as an effective PPCPs removal by the processes.

1.2 Research objectives

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

1) To study the degradation characteristics of PPCPs by UV-based and O_3-based processes,

2) To investigate the removal performance of UV-based and O_3-based processes for PPCPs in secondary effluent using a bench scale plant,

and 3) To discuss the applicability of the investigated processes as water reuse technologies.

1.3 Research structure

This dissertation consists of seven chapters. Fig. 1-1 shows the schematic diagram of research structure. Introduction of each chapter is as follows;

In Chapter I, a research background, research objectives and research structure were described. In Chapter II, literature review was performed to obtain the knowledge on the PPCPs as an emerging contaminant, the world trend for water reuse and the potential of physicochemical processes such as UV-based and O_3-based processes for PPCPs removal.

In Chapter III, photodegradability of PPCPs with 2 types of UV lamps that emit at the wavelengths of 254 nm and 254 nm/185 nm, respectively, and the effect of H_2O_2 addition during UV process on the PPCPs degradation were studied in a laboratory scale plant. Tested waters spiked with 30 PPCPs, which were selected on the basis of consumption and environmental relevance, were used for batch UV treatment experiments. Degradation rate constants of the 30 PPCPs by UV and UV/H_2O_2 treatment were calculated, and UV doses required for the 90% removal of the 30 PPCPs in secondary effluent during UV and UV/H_2O_2 processes were estimated.

In Chapter IV, removal characteristics of the 30 PPCPs by O_3, O_3/UV and O_3/H_2O_2 processes were examined in the laboratory scale plant. Tested waters spiked with the 30 PPCPs were used for semi-batch O_3 process experiments. Degradation rate constants of the 30 PPCPs by O_3, O_3/UV and O_3/H_2O_2 treatment were calculated. O_3 doses required for the 90% removal of the 30 PPCPs in secondary effluent during O_3 and O_3/UV processes were estimated. In Chapter V and VI, the operating factors such as UV dose, H_2O_2 addition, O_3 dose and UV combination for the removal of PPCPs by UV and O_3 processes were investigated in a bench scale plant. Electrical energy and operating costs required for the effective removal of PPCPs in secondary effluent were also estimated for each process.

In Chapter VII, the applicability of UV/H_2O_2, O_3 and O_3/UV processes as technologies for wastewater reuse considering the removal of PPCPs was discussed, based on energy consumption, disinfection effectiveness, the formation potential of by-products and decrease effectiveness of ecological risk as well as the removal effectiveness of PPCPs.

In Chapter VIII, conclusions from this research and recommendations for further study were summarized.

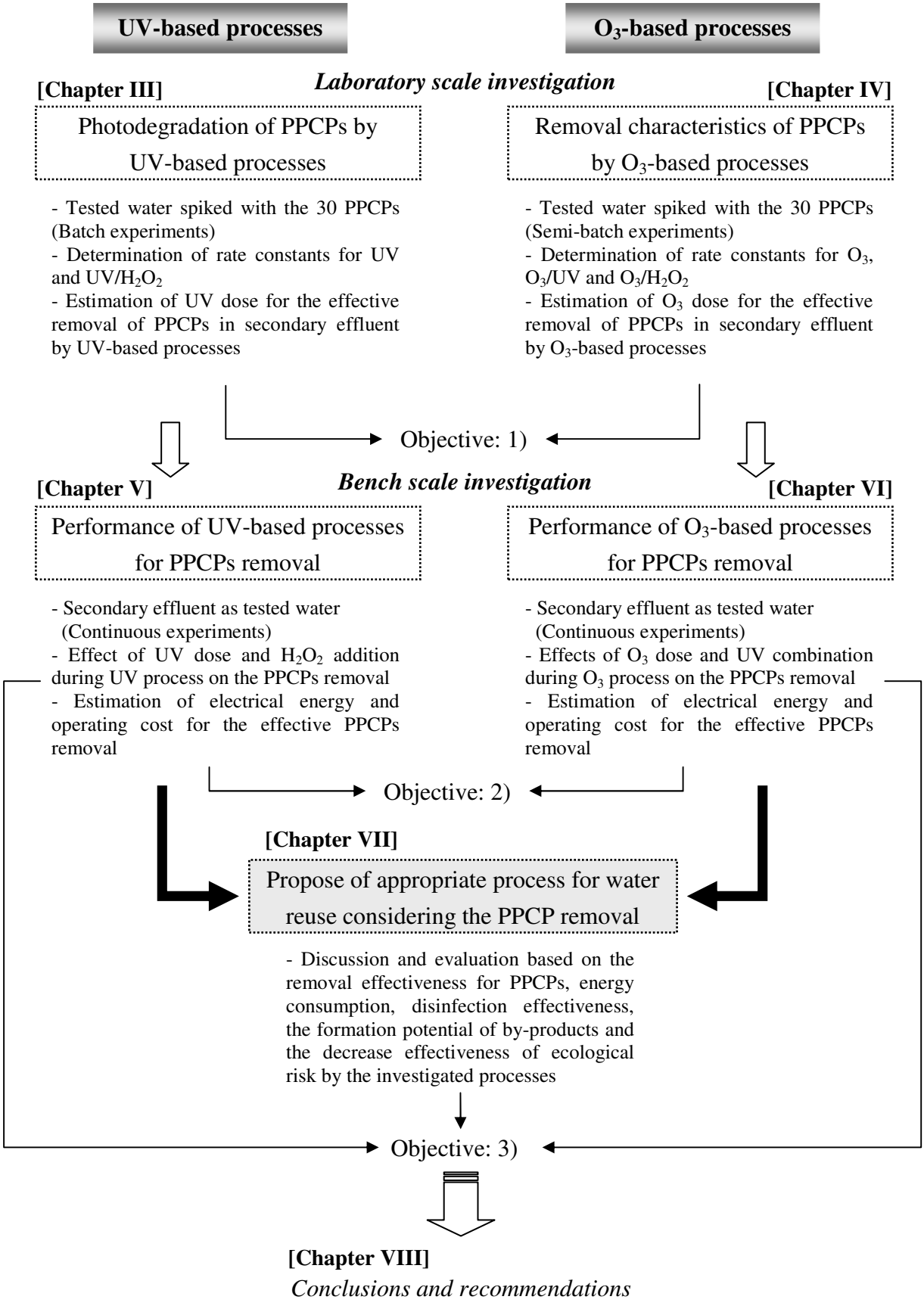


Fig. 1-1 Schematic diagram of research structure

1.4 References

Balcioglu I.A., Otker M., 2003, Treatment of pharmaceutical wastewater containing antibiotics by O_3 and O_3/H_2O_2 processes, *Chemosphere* 50, 85-95

Daughton C.G., Ternes T.A., 1999, Pharmaceuticals and Personal Care Products in the Environment: Agents of Subtle change?, *Environmental Health Perspectives* 107, 907-938

Halling-Sørensen B., Nielsen S.N., Lanzky P.F., Ingerslev F., Lutzhoft H.C.H., Jorgensen S.E., 1998, Occurrence, fate and effects of pharmaceutical substances in the environment- A review, *Chemosphere* 36, 357-393

Heberer T., 2002, Occurrence, fate and removal of pharmaceutical residues in the aquatic environment: a review of recent research data, *Toxicol. Lett.* 131, 5-17

Huber M.M., Canonica S., Park G.Y., von Gunten U., 2003, Oxidation of pharmaceuticals during ozonation and advanced oxidation processes, *Envir. Sci. & Tech.* 37, 1016-1024

Huber M.M, Korhonen S., Ternes T.A., von Gunten Urs, 2005, Oxidation of pharmaceuticals during water treatment with chlorine dioxide, *Water Res*. 39, 3607-3617

Kanda R., Griffin P., James H.A., Fothergill J., 2003, Pharmaceutical and personal care products in sewage treatment works, *J. Environ. Monit.* 5, 823-830

Nakada N., Tanishima T., Shinohara H., Kiri K., Takada H., 2006, Pharmaceutical chemicals and endocrine disrupters in municipal wastewater in Tokyo and their removal during activated sludge treatment, *Water Res.* 40, 3297-3303

Okuda T., Kobayashi Y., Nagao R., Yamashita N., Tanaka H., Tanaka S., Fuji S., Konishi C., Houwa I., 2007, Removal efficiency of 66 pharmaceuticals during wastewater treatment process in Japan, *Water Sci. & Tech.* 57, 65-71

Rosenfeldt E.J., Linden K.G., Canonica S., von Gunten U., 2006, Comparison of the efficiency of ·OH radical formation during ozonation and the advanced oxidation processes O_3/H_2O_2 and UV/H_2O_2, *Water Res.* 40, 3695-3704

Smital T., Luckenbach T., Sauerborn R., Hamdoun A.M., Vega R. L., Epel D., 2004, Emerging contaminants-pesticides, PPCPs, microbial degradation products and natural substances as inhibitors of multixenobiotic defense in aquatic organisms, *Mutation Research* 552, 101-117

Ternes T.A., 1998, Occurrence of drugs in German sewage treatment plants and rivers, *Water*

Res. 32, 3245-3260

Ternes T.A., Stuber J., Herrmann N., McDowell D., Ried A., Kampmann M., Teiser B., 2003, Ozonation: A tool for removal of pharmaceuticals, contrast media and musk fragrances from wastewater?, *Water Res*. 37, 1976-1982

The Ministry of Land, Infrastructure and Transport of Japan, 2005, Manual for water reuse of treated water in sewage treatment plant

U.S.EPA, 2004, Guidelines for Water Reuse, EPA/625/R-04/108

CHAPTER II

LITERATURE REVIEW

2.1 Introduction of PPCPs

2.1.1 PPCPs and related knowledge

2.1.1.1 Definition of PPCPs

"Not only is drug discovery important to the medical health of humankind, it is also an important component of our economic health." "New chemical entities (NCEs) as therapeutics for human disease may become the "oil and gas" of the 21st century." "As the world's population increases and health problems expand accordingly, the need to discover new therapeutics will become even more pressing." These were quoted from "Medicinal chemistry" written by Nogrady *et al* (2005) and, thus, the number of pharmaceuticals used by human is expected to increase continuously in the future, although the large number of pharmaceutical ingredients (>3,000) are registered now (Richardson *et al.*, 2005).

Pharmaceuticals and personal care products (PPCPs) are a group of various chemicals, used for the bodies of humans and domestic animals and plants. PPCPs consist of all drugs including the new genre of biologics, diagnostic agents, nutraceuticals, and other consumer chemicals such as fragrances and sun-screen agents (See Table 2-1). Many PPCPs are highly bioactive and most are polar when present in the environment, usually occur at no more than trace concentrations. PPCPs used in large amounts over the world have recently become a new environmental concern (Daughton *et al*., 1999; Ferrari *et al*, 2003) because of their high production level and their pharmacokinetical behavior during normal therapeutic use. One more reason is that a variety of PPCPs belonging to antibiotics, analgesics, lipids regulator agents, β-blockers and antiepileptics and so on have been detected in the aquatic environment.

Table 2-1 Some chemical classified as PPCPs (Esplugas *et al*., 2007)

PPCPs class	Compound detected	Use/origin
Analgesics/non-steroidal anti-inflammatories (NSAIDs)	Acetaminophen (analgesic), diclofenac, ibuprofen, ketoprofen, naproxen, Phenazone, indomethacine	NSAIDs are the most used and abused drugs in the world today. All NSAIDs have analgesic, antipyretic and anti-inflammatory effect
Antibiotics/antimicrobials	Sulfonamides,fluoroquinolones, trimetoprim, hlortetracycline, erythromycin, lincomycin, oxytetracycline, tetracycline, roxithromycin, tylosin	Antibiotics/antimicrobials are vital medicines for the treatment of bacterial infections in both humans and animals
Antiepileptics	Carbamazepine	Antiepileptics are commonly used in medicine to stop, prevent, or control seizures (convulsions, partial seizures, generalized tonic-clonic seizures, etc.)
Antihypertensives	Bisoprolol, metoprolol, propranolol	Antihypertensives are used to reduce the blood pressure in the arteries. It is difficult to prevent the hypertension, because a high blood pressure does not usually give signs or symptoms
Antineoplastics	Cyclophosphamide, ifosfamide	Antineoplastics are commonly used in the treatment of various solid tumors, lymphomas, leukemias and in some autoimmune disorders such as rheumatoid arthritis
Antiseptics	Triclosan	Antiseptics are chemical agents that slow or stop the growth of microorganisms (germs) on external surfaces of the body and help prevent infections. Antiseptics should be distinguished from antibiotics that destroy microorganisms inside the body, and from disinfectants, which destroy microorganisms found on inanimate (non-living) objects
Contraceptives	7α-Ethynylestradiol	Oral contraceptives are chemicals taken by mouth to inhibit normal fertility by acting on the hormonal system
Sympathomimetics (bronchodilators)	Albuterol	Bronchodilators are medicines that help open the bronchial tubes (airways) of the lungs, allowing more air to flow through them
Lipid regulators	Clofibrate, bezafibrate	Lipid regulators may be used to lower cholesterol and triglyceride (fat-like substances) levels in the blood
Musks fragrances (synthetic)	Nitromusks, galaxoline, tonalide, polycyclic musks, reduced metabolites of nitromusks	Synthetic musk fragrances are commonly used in perfumery
Anti-anxiety/hypnotic agents	Diazepam	Anti-anxiety/hypnotic agents are used to relieve anxiety, nervousness, and tension associated with anxiety disorders
Sun screen agents	Benzophenone, octylmethoxycinnamate, methylbenzylidene camphor	Sun screen agents provide the protection against the harmful effects of the ultraviolet radiation coming from the sun
X-ray contrast agents	Diatrizoate, iopamidol, iopromide, iomepol	Radiocontrast agents (or simply contrast agents) are compounds used to improve the visibility of internal bodily structures in an X-ray image

Although the concentrations are generally at trace levels (ng/L to low μg/L) in the aquatic environment, it can be sufficient to induce toxic effects because all drug molecules are designed to interact with biological structures (e.g., biomembranes, the cell nucleus), biomolecules (e.g., lipoproteins, enzymes, nucleic acids) and other small molecules on their way “from the gums to the receptor” (Nogrady *et al*., 2005).

On the other hand, Daughton (2004) has suggested that there may be as many as 6

million PPCP substances commercially available worldwide and that the use of pharmaceuticals is increasing by 3%-4% by weight per annum. With increasing urbanization and associated commercial activities, and an increasing concern with personal care and health, the significance of PPCPs as a societal lifestyle cause of water pollution is likely to impose an increased risk.

2.1.1.2 Research trends of PPCPs

In U.S. many studies on the fate and transport of PPCPs in the aquatic environment, assessment of potential ecological effects and potential human health effects and so on have been done since 1990s. Especially, in *STAR* project started in 2001, studies on the occurrence and the fate of PPCPs in groundwater, drinking water, sewage treatment facilities and coastal waters, and effects of some PPCPs such as fluoroquinolone antibacterial agents in aquatic ecosystems have been investigated very widely and this project will also continue until 2010. Apart from the *STAR* project, U.S. EPA is carrying out a wide range of research for PPCPs management in the environment and in particular, PPCPs are considered in a research on the persistent contaminants from wastewater discharges during drinking water treatment.

For Europe, 3 big projects on PPCPs called *REMPHARMAWATER*, *ERAVMIS* and *POSEIDON*, respectively, were done between 2000 and 2004. *REMPHARMAWATER* project was performed mainly for assessing the presence of PPCPs in wastewaters and sludges of municipal sewage treatment plants (STPs), the ecotoxicity of PPCPs found in STP effluents with respect to living organisms such as algae and invertebrates and fish, and the possibility of removing the PPCPs in STP effluents by means of integrated biological processes or AOP techniques. The objective of *ERAVMIS* project was to develop approaches for assessing the environmental impact of veterinary medicines released to the environment through the spreading of manure, slurry and sludge. Finally, for *POSEIDON* project, to develop a strategy to assess and improve the removal of PPCPs in wastewater and drinking water and, to perform environmental risk assessments (ERAs) for selected PPCPs were main objectives. The above three studies provided the first data to enable the assessment of the presence and effects of PPCPs in the environment at the European level. They also proposed solutions for PPCPs removal from wastewater (e.g. AOPs or sunlight). Furthermore, they have

demonstrated that microbial populations appear to change due to exposure to antibiotics.

At the present in Europe, *KNAPPE* (Knowledge and Need Assessment on Pharmaceutical Products in Environmental Waters) project is in progress aiming at identification of the relevant priority actions to be taken in order to reduce presence, impacts and risk of pharmaceutical products in environmental waters. Regulatory approaches and prevention action will be also likely to be implemented.

2.1.1.3 Methods for PPCPs determination

About 3,000 different compounds are used as constituents of medicinal products in human and veterinary medicine and, therefore, it appears to be nearly impossible to develop analytical methods for all the PPCPs. Actually, analytical methods have only been developed for a very small subset of compounds (~150) in environmental matrices (Richardson *et al*., 2005). Several methods have been developed for the determination of PPCPs in the lower ng/L range using solid phase extraction (SPE), derivatization, detection and confirmation by GC/MS (gas chromatography / mass spectrometry), GC/MS/MS, HPLC/MS (high-performance liquid chromatography coupled to mass spectrometry) and particularly tandem mass spectrometry (HPLC/MS/MS) and a wide range of PPCPs can be determined down to the lower ng/L range.

Ternes *et al* (2001) have reported that a multi-analytical method which consists of SPE using 500mg RP-C18 (Merck), followed by methylation of carboxylic groups with diazomethane, acetylation of phenolic hydroxyl groups with acetanhydride / triethylamine (1:1, v/v) and determination by GC/MS was applied for the quantification of acidic drugs (e.g. antiphlogistics, lipid regulators), and their recoveries frequently exceeded 80% and standard deviations varied between 5% and 26%. Kanda *et al* (2003) have used GC/MS for the determination of musks, aspirin, clofibric acid, ibuprofen and triclosan in sewage treatment works, and the LOD (Limit of detection) of below 10 ng/L for each PPCP determined by GC/MS was attained. They have also carried out LC/MS analysis for fluvoxamine quantification and the LOD of 24ng/L was obtained.

Many PPCPs have been detected in aqueous samples with LC/MS/MS, predominantly in the positive ion mode with ESI. A multicompound LC ESI-MS/MS method was developed by

Vanderford *et al* (2003), which enabled the determination of 27 compounds, including various pharmaceuticals, pesticides, steroids and personal care products. Hirsch *et al* (1998) determined the concentration of 18 antibiotics such as penicillins, tetracyclines, sulfonamides and macrolide antibiotics with LC/MS/MS. In the study, lyophilizaiton and SPE for pretreatment processes were also compared and, recoveries using SPE had a tendency to be slightly lower than for the lyophilization procedure. When using the freeze-drying enrichment step, LOQs (Limits of quantification) of the antibiotics were 50 ng/L for the tetracyclines and 20 ng/L for all others, and the results were largely independent of the kind of water matrices. Okuda *et al* (2007) also have reported on the removal efficiency of 66 pharmaceuticals during wastewater treatment based on PPCPs quatification method with SPE-LC/MS/MS. In the study, they mentioned that limit of quantification for 66 pharmaceuticals ranged from 11 ng/L to 140 ng/L.

2.1.1.4 Ecological effects of PPCPs

Recently, PPCPs were identified as an emerging class of potential pollutants for the aquatic environment. In addition, Halling-Sørensen *et al* (1998) have reported that PPCPs may pose an environmental threat, as they have been designed to have a physiological effect on humans or animals, and an additional concern regarding the environmental impact of PPCPs is the fact that many of these compounds have been designed to be lipophilic and biologically persistent in order for them to pass through membranes and to remain active until their curing function has been performed.

Potential risks associated with releases of PPCPs into the aquatic environment have become an increasingly important issue for environmental regulators and the pharmaceuticals industry (Jørgensen *et al*., 2000). Exposure of aquatic wildlife to human pharmaceuticals is most likely to occur from sewage treatment plants. Ferrari *et al* (2003) have investigated ecotoxicological impact of carbamazepine, clofibric acid and diclofenac found in treated wastewaters using bacteria, algae, invertebrates and fish. In their study, the risk was estimated by the PEC (predicted environmental concentration)/PNEC (predicted no-effect concentrations) ratio and the MEC (measured environmental concentration)/PNEC ratio. The result demonstrated that carbamazepine seemed the most dangerous tested compound for the

aquatic environments. They also suggested that among different keys for the hazard and risk assessment of pharmaceuticals, chronic effect studies seem to be highly adequate and the use of appropriate removal technologies in STPs should be an adequate approach for limiting aquatic risk.

A study has been done to examine the cytotoxic and oxidative effects of PPCPs such as caffeine, ibuprofen, naproxen, oxytetracycline, novobiocin, carbamazepine gemfibrozil, bezafibrate, trimethoprim, sulfamethoxazole and sulfapyridine and other wastewater-related products such as estradiol-17β, nonylphenol and cholesterol with primary cultures of rainbow trout hepatocytes (Gagne *et al*., 2006). Primary cultures of rainbow trout hepatocytes were exposed to various drugs identified in the municipal effluent for 48h at 15°C. They suggested that the basic redox properties of PPCPs could influence oxidative metabolism in liver cells and lead to oxidative damage, indicating that the PPCPs have the potential to produce a toxic response in aquatic organisms.

On the other hand, chronic aquatic toxicity tests have been adopted in the most recent draft of environmental risk assessment guidance document for human pharmaceuticals produced by the European Medicines Agency (EMEA, 2005) in support of Directive 2001/83/EC (EC, 2001). In contrast to acute toxicity tests, which often use mortality as the only measured effect, chronic tests usually include additional measures of effect such as growth or reproduction (Crane *et al*., 2006). Little is known about chronic effect of most pharmaceuticals, although an increasing amount of information is becoming available on the effects of antimicrobial substances. Several authors have measured alterations in microbial assemblages after exposure to antibiotics at concentrations similar to those found in hospital wastewaters (Al-Ahmad *et al*., 1999; Kummerer *et al*., 2000). Ash *et al* (2002) found evidence of resistance to imipenem and the beta-lactams ampicillin, cefotaxime and ceftazidime in bacteria cultured from water samples taken from UV streams.

However, it does not seem to be clear to decide whether PPCPs pose a significant threat to the aquatic environment. The most practical current solution to this problem will be to test the acute and chronic toxicity of a range of model substances, representative of the range of modes of action of human pharmaceuticals, on a representative range of aquatic organisms.

2.1.2 Sources and degradation of PPCPs in the aquatic environment

In contrast to other pollutants, PPCPs are present in the environment directly because of their frequent use by individuals dispersed throughout the community or concentrated in medical centers and hospitals (Halling-Sørensen *et al*., 1998). Disposal of unused PPCPs can also be a route to the environment either through disposal to sewer via the toilet or drain, or to landfill in domestic refuse or as special waste by waste contractors. Other sources of PPCPs will be landfill leachates, manufacturing residues and agriculture applying large amounts of PPCPs as veterinary drugs and feed additives in livestock breeding (Heberer, 2002).

On the other hand, PPCPs have been detected in samples from all aquatic environment such as sewage effluent, river water, ground water and drinking water. It has been reported that many PPCPs occurred in ground water and drinking water samples from water works using bank filtration, artificial ground water recharge or downstream from STPs (Heberer *et al*., 1997). Daughton *et al.* (1999) have reported that most of PPCPs were disposed or discharged into the aquatic environment via sewage treatment plants and wet-weather runoff. Many of the pharmaceuticals applied in human medical care are not completely eliminated in the human body. They are excreted by the state only slightly transformed or even unchanged and mostly conjugated to polar molecules. These conjugates can easily be cleaved during sewage treatment and the original PPCPs will then be released into the aquatic environment mostly by effluents from STPs (Heberer, 2002). There are several investigations showed that PPCPs are not eliminated during wastewater treatment and also not biodegraded in the environment (Ternes, 1998; Daughton *et al*., 1999; Nakada *et al*., 2006; Okuda *et al*., 2007).

Antiphlogistics, betablockers, lipid regulators, antibiotics, antiepileptics, estrogens and iodinated X-ray contrast media as well as personal care products such as musk fragrances are discharged into receiving waters due to their incomplete removal in municipal sewage treatment plants. Obviously, the currently applied wastewater treatment techniques are inappropriate to remove significantly those trace pollutants. Therefore, more enhanced technologies such as ozonation, advanced oxidation processes (AOPs) or membrane filtration may be crucial for the future. In drinking water treatment, it has already been shown that ozonation and AOPs are very effective in oxidizing pharmaceuticals (Zwiener *et al*., 2000; Ternes *et al*., 2002).

2.1.3 Position of this research

From literature review of this section, it can be known that a variety of PPCPs may be present in the aquatic environment. In addition, PPCPs can affect water quality and potentially impact drinking water supplies, ecosystem and human health if they are continuously introduced into the environment and are prevalent at low concentrations. Hence, it is necessary to treat the effluents containing PPCPs adequately before discharging them from STPs, a main source of PPCPs. These PPCPs are not completely removed by conventional activated sludge treatment. Very little information is still available because of the use of a great variety of PPCPs although there are several studies on the PPCPs removal with physicochemical processes such as O_3, UV, AOPs, chlorination, activated carbon adsorption and membrane treatment. Therefore, the removal potential of UV-based (UV and UV/H_2O_2) and O_3-based (O_3, O_3/H_2O_2 and O_3/UV) processes for the 30 PPCPs, which were selected based on consumption and environmental relevance, was examined in Chapter III and IV of this dissertation.

2.2 Circumstances for water demand and reuse

2.2.1 Overview of water reuse

The demand for water will increase with the dramatic increase of the world urban population by the year 2020 (See Fig. 2-1). However, available water resources have been already limited in many areas of the world and, therefore, water reuse and reclamation will be necessary for extending available water resources. In addition, there has also been a growing interest in water reuse according to the advanced technologies for water treatment such as membrane treatment and advanced oxidation processes (AOPs).

Water reuse is a relatively new market, though growing rapidly, and already supplying just under 0.2% of total water abstraction. With a forecast annual growth rate of 14%, it is predicted to outstrip desalination by 2020 (Pearce, 2008). Wastewater treatment normally consists of a biological treatment stage, known as conventional activated sludge and

clarification process. If followed by filtration, e.g. by a sand filter, the treatment is known as tertiary treatment. Historically, 70% of reused wastewater has only been treated to a secondary or tertiary standard, which would only be suitable for agricultural use in less developed parts of the world (Pearce, 2008). To be considered for reintroduction to the drinking water supply chain, and for most industrial uses, wastewater normally requires a further level of treatment.

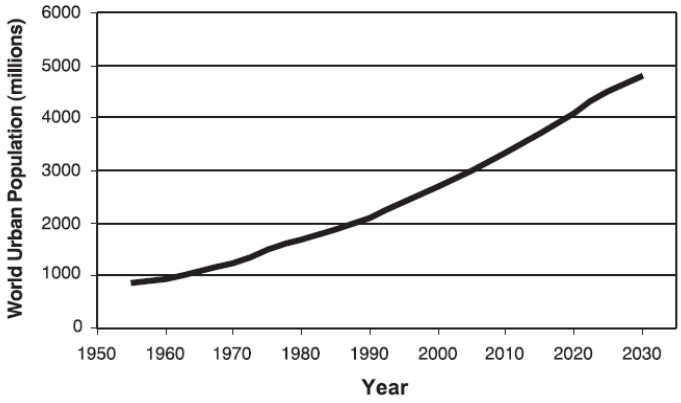


Fig. 2-1 Estimated and Projected Urban Population in the World (U.S. EPA, 2004)

2.2.2 Technologies for water reuse

U.S. EPA suggests wastewater treatment processes, reclaimed water quality, monitoring, and setback distances for various types of water reuse. Suggested guidelines include the following categories: urban reuse, restricted access area irrigation, agricultural reuse, recreational impoundments and landscape impoundments, construction uses, industrial reuse, environmental reuse, groundwater recharge and indirect potable reuse. Fig. 2-2 and 2-3 show the types of reuse occurring in California and Florida, respectively, accounting for the majority of the water reuse in the U.S.

On the other hand, one of the most critical objectives in water reuse is to ensure that public health protection is not threatened by the use of reclaimed water. Public health protection can be achieved by (1) reducing or eliminating concentrations of pathogenic bacteria, parasites, and enteric viruses in the reclaimed water, (2) controlling chemical constituents in reclaimed water, and/ or (3) limiting public exposure (contact, inhalation, ingestion) to reclaimed water. The most commonly used disinfectant for eliminating pathogens is chlorine. O_3 and UV are also promising disinfection alternatives used at

wastewater treatment plants. However, U.S. EPA suggests disinfection effectiveness and reliability, capital costs, operating and maintenance costs, and potential adverse effects when evaluating such disinfection alternatives.

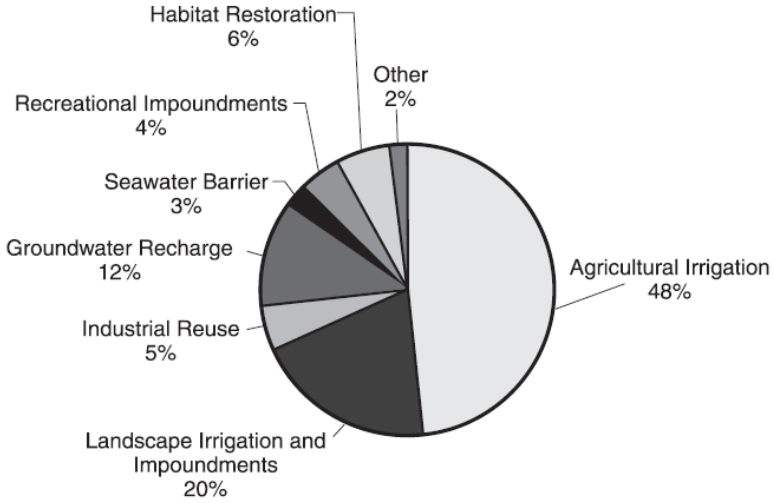


Fig. 2-2 California water reuse by type (Total 358 mgd) (U.S. EPA, 2004)

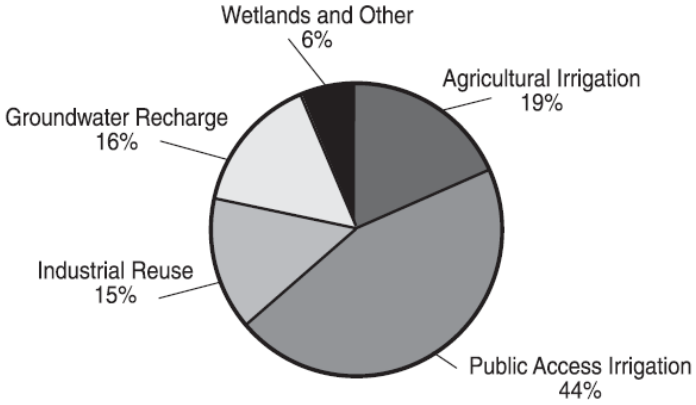


Fig. 2-3 Florida water reuse by type (Total 584 mgd) (U.S. EPA, 2004)

The chemical constituents potentially present in municipal wastewater are a major concern when reclaimed water is used for potable reuse. Several studies (Purdom *et al.,* 1994; Harries *et al.,* 1997) demonstrated that chemicals in wastewater effluent caused male fish to exhibit female characteristics, resulting in a great concern with respect to water reuse. Therefore, advanced wastewater treatment beyond traditional secondary treatment should be applied especially if high quality reclaimed water such as for urban landscaping, food crops eaten raw, contact recreation, many industrial applications and so on is needed. Advanced wastewater treatments include filtration, UV treatment, coagulation-sedimentation, carbon

adsorption and membrane processes.

Stackelberg *et al.* (2004) conducted a study on the persistence of pharmaceutical compounds and other organic wastewater contaminants using a conventional drinking water treatment plant consisting of flocculation-sedimentation-GAC (granular activated carbon) filtration process. In their study, 34 out of 106 organic contaminants were detected in more than 10% of the 24 water samples collected at a drinking water treatment facility. The 34 compounds included prescription and non-prescription drugs and their metabolites, fragrance compounds, cosmetic compounds and a solvent. Consequently, they suggested the 34 compounds removal through conventional water treatment processes. There are several studies using nanofiltration and/or ultrafiltration membranes for PPCPs retention (Nghiem *et al*., 2005; Yoon *et al*., 2006). Retention of trace organics by membranes highly depends on the compound's physicochemical properties, the solution chemistry and the membrane retention behavior still poorly understood.

Low PPCPs removal in wastewater treatment process has been already reported by several researchers (Nakada *et al*., 2006; Okuda *et al*., 2007). In addition, potential risks of PPCPs into the aquatic environment have become an increasingly important issue for environmental regulators and the pharmaceuticals industry as mentioned above. Therefore, the issue on PPCPs as an emerging contaminant is also likely to grow in succession in the area of water reuse.

2.2.3 Position of this research

In the literature review mentioned above, it can be found that much more attentions will be paid on the reuse of secondary effluent of municipal wastewater in the future because of the shortage of water resources. With respect to the increase of water reuse, it will also become very important to consider the health assessment of pathogenic microorganisms, chemical constituents and endocrine disrupters for the reuse of secondary effluent. Chlorination is the most widely used for the disinfection of pathogenic microorganisms. Whereas, filtration, UV treatment, coagulation-sedimentation, carbon adsorption and membrane processes are suggested for the removal of chemical constituents in the guidelines for water reuse (U.S. EPA, 2004). However, as discussed above, it is thought that the removal

of PPCPs by the suggested processes will not be so effective.

Therefore, in this study the removal efficiency of O_3-based processes (O_3 and O_3/UV) and UV-based processes (UV and UV/H_2O_2) for PPCPs present originally in secondary effluent was investigated in order to evaluate the applicability as processes for water reuse. On the other hand, energy-saving treatment processes are recommended for the reduction of operating cost. It is very difficult to compare processes from different papers because the cost analyses are often based on different assumptions and, consequently, they can lead to very different operating costs. However, comparison of the operating cost associated with different processes is a subject of major importance. Therefore, this study estimated the electrical energy and operating costs required for the effective PPCPs removal by 4 processes (UV, UV/H_2O_2, O_3 and O_3/UV) using the same secondary effluent and the same assumptions. The results were described in Chapter V.

2.3 Removal of PPCPs by UV-based and O_3-based processes

2.3.1 UV-based processes

Ultraviolet (UV) is an effective disinfectant in water and is used widely for this purpose in many countries. The portion of the UV radiation band that is most effective for inactivating microorganisms is between about 220 and 320 nm. UV disinfection is generally more effective than chlorine for inactivation of most viruses, spores and cysts. However, UV does not show a good oxidation power of organic compounds when it is used alone. UV/H_2O_2 process, one of UV-based processes, has been shown to degrade 99.9% of various contaminants including benzene (Weir *et al*., 1987), trichloroethene (Weir and Sundstrom, 1993), pesticides (Beltran *et al*., 1993) and acetone (Stefan *et al*., 1996) although the rates of parent compound transformation differ widely.

UV/H_2O_2 process used UV radiation to cleave the O-O bond in H_2O_2 and generate the OH radical (Glaze *et al*., 1987). The OH radical can then be scavenged by an organic compound to oxidize the organic, recombine with other hydroxyl species to reform H_2O_2 or initiate a radical chain degradation of H_2O_2 in the series of reactions shown below (Glaze *et al*., 1987):

$$H_2O_2 \xrightarrow{h\nu} \cdot OH + \cdot OH \quad (1)$$

$$\cdot OH + H_2O_2 \longrightarrow H_2O + HO_2 \cdot \quad (2)$$

$$HO_2 \cdot + H_2O_2 \longrightarrow H_2O + O_2 + \cdot OH \quad (3)$$

$$2HO_2 \cdot \longrightarrow H_2O_2 + O_2 \quad (4)$$

OH radicals commonly attack organic molecules by abstracting a hydrogen atom frome the molecule (Clarke and Knowles, 1982). There are several studies on the degradation of PPCPs by UV and/or UV/H_2O_2 processes. Table 2.2 shows the results of UV-based processes used to degrade PPCPs in aqueous samples and sewage effluents. As known in Table 2.2, UV process was combined with H_2O_2, TiO_2 or Fenton due to its poor removal potential for PPCPs. On the other hand, most of these studies were carried out at laboratory scale, and only a few PPCPs have been investigated on the degradation by UV, UV/H_2O_2 or UV/TiO_2 processes. As mentioned before, PPCPs are a various group of chemicals and tens of PPCPs have been detected in the aquatic environment. This means that much more studies on the PPCPs removal are necessary to be done.

2.3.2 O_3-based processes

The structure of O_3 has been described as a resonance hybrid of the four canonical forms. Table 2.3 shows some important properties of O_3. The main reasons for the use of O_3 are disinfection and oxidation such as taste and odor control, decolorization, elimination of micropollutants and so on. Similar to other disinfectants such as chlorine or chlorine dioxide for water treatment, O_3 is unstable in water, and undergoes reactions with some water matrix components. However, the O_3 is decomposed, forming OH radicals which are the strongest oxidants in water (Staehelin *et al*., 1985). While disinfection occurs dominantly through O_3, oxidation processes may occur through both oxidants, O_3 and OH radicals (Langlais *et al*., 1991). O_3 reacts with a large number of inorganic and organic compounds. The fact that rate constants for the reaction with O_3 range over several orders of magnitude demonstrates that O_3 is a very selective oxidant. With respect to organic compounds, O_3 is particularly reactive toward phenols, amines, compounds exhibiting C=C double bonds, and activated aromatic compounds.

Table 2-2 Results of PPCPs degradation by UV-based processes

Year	Compound	Type of Water	Process	Operational conditions	Results	References
2002	Carbadox, sulfadimethoxine, sulfachlorpyridazine, sulfamerazine, sulfamethazine, sulfathiazol, trimethoprim)	Distilled, Deionized water, River water	UV	Low pressure lamp (254 nm); C_0 = 20 and 50 mg L^{-1}; T=20°C; pH 7.5; Tr = 30 min	Normal UV dose (30 mJ cm^{-2}) used in water treatment plants were not enough to remove antibiotics. By using UV dose of 3.0 J cm^{-2}, antibiotic removals between 50% and 80% were reached	Adams *et al*. (2002)
2003	Clofibric acid	Aqueous solution	UV/H_2O_2	Low pressure lamp (17W, 254 nm); C_0 = 1.0 mmol L^{-1}; C_{H2O2} = 1.0 mol L^{-1}; pH 5; Tr=60min	Almost complete removal of clofibric acid in 60 min with small mineralization	Andreozzi *et al*. (2003)
2004	Carbamazepine	Doubly distilled water	UV/H_2O_2	Low pressure lamp (254 nm); C_0 =20μmol L^{-1}; C_{H2O2} = 5.0 mmol L^{-1}; pH 5; Tr = 4 min	100% removal of carbamazepine in 4 min of treatment with a 35% removal of TOC. Intermediates formed in the oxidation were more toxic than the original pharmaceutical	Vogna *et al*. (2004)
2004	Diclofenac	Doubly distilled water	UV/H_2O_2	Low pressure lamp (17W, 254 nm); I_0 = 2.7μEinstein s^{-1}; C_0 = 1.0μmol L^{-1}; C_{H2O2} = 0.1 or 1.0 mol L^{-1}; pH 7.0	100% removal of diclofenac with a complete release of chlorine by using H_2O_2/UV. Almost 40% of chlorine formed chlorate ions	Vogna *et al*. (2004_
2005	Clofibric acid, carbamazepine, iomeprol	Ultrapure water	Photocatalysis	TiO_2 in suspension; solar simulator (1kW Xe lamp)	Efficient removal degree was reached by using photocatalysis	Doll and Frimmel (2005)
2005	Antibiotic (amoxiline)	Aqueous solution	UV/H_2O_2	Low pressure lamp (254 W); C_0 = 0.5 mmol L^{-1}	The kinetic constant for the direct attack depends strongly in the pH of the solutions. UV/H_2O_2 was used to evaluate the constant for the OH radical attack to the amoxicillin molecule at pH 5.5. Kinetic constant obtained $k_{OH,AM}$ = 3.93 nmol L^{-1} s^{-1}	Andreozzi *et al*. (2005)
2006	Antibiotic (metronidazol)	Deionized water	UV photo-Fenton UV/H_2O_2	Low pressure lamp; UV= 0–600 mJ cm^{-2}; C_{H2O2} = 25 – 50 mg L^{-1}; C_0 =6μmol L^{-1}; pH (UV) = 6 pH (photo-Fenton) = 3.5	UV provides small degradation compared to UV/H_2O_2. Photo-Fenton gives 20% higher removal than Fenton	Shemer *et al*. (2006)
2007	Herbicide of metsulfuron-methyl (MM)	Distilled water	Photocatalysis	TiO_2 was dosed at a rate of 1.5gL^{-1}; C_0 =10mgL^{-1}	The system had a high removal rate of over 90%	Areerachakul *et al*. (2007)
2007	Sulfonylurea herbicide	Milli Q water	Photocalatalysis	Light source HPK 125W Philips (365 nm); C_0 = 25, 15, 10 and 5mgL^{-1}	The degradation rate was strongly affected by the TiO_2 amount and the light flux. More than 20 intermediates were unambiguously identified	Sleiman *et al*. (2007)

Table 2-3 Selected properties of O_3

Molecular weight	48.0g/mol	Diffusion coefficient	$1.7 \times 10^{-9} m^2/s$
Melting point	-193˚C	UV absorption	ε(258nm)=3,000/M/cm
Boiling point	-112˚C	Instant odor threshold	$40 \mu g/m^3$
Henry constant(20˚C)	100atm/M	Permissible exposure limit (averaged over 8h workshift)	0.1ppm($200 \mu g/m^3$)

O_3-based AOPs are applied to oxidize O_3-resistant compounds too, such as pesticides and chlorinated solvents such as tri- and tetrachloroethene, by OH radicals. OH radical is a powerful and non-selective oxidant. It reacts very fast with various inorganic and organic components of the water matrix. Therefore, OH radicals can also contribute to the oxidation of micropollutants. However, their efficiency is most often limited by the scavenging effect of the water matrix. In O_3-based AOPs, the formation of OH radicals during O_3 process is accelerated by increasing the pH of the water, by dosing H_2O_2, or by the application of UV irradiation. This can ensure a faster oxidation of compounds that do not exhibit an appreciable reactivity with O_3 directly.

However, it has to be emphasized that the application of AOPs does not increase the overall oxidation capacity of O_3 process. The main advantage of O_3-based AOPs is a shorter reaction time which allows the application of higher O_3 dose without causing excess O_3 concentrations at the outlet of a reactor (von Gunten, 2003). There are relatively many studies on the degradation of PPCPs by O_3-based processes. Table 2.4 shows the results of O_3-based processes used to degrade PPCPs in aqueous samples and sewage effluents. As known in Table 2.4, removals higher than 90% were reached for several PPCPs such as anti-inflammatories, antiepileptics and antibiotics. O_3 process was the oxidation process most studied which gives a good expectative to be applied with success although some PPCPs seem to be a little more recalcitrant to the oxidation (clofibric acid and X-ray contrast agents).

Table 2-4 Results of PPCPs degradation by O_3-based processes

Year	Compound	Type of Water	Process	Operational conditions	Results	References
2003	Clofibric acid	Aqueous solution	Ozonation	Tr = 60 min; pH 2.0–6.0; C_0 = 1.0–1.5 mmol L^{-1}; C_{O3} aqueous = 1.0×10^{-5} mol L^{-1}	100% removal of clofibric acid was reached in 20 min with 34% mineralization. 49% mineralization was reached in 60 min. No halogenocompounds were detected in the oxidation products	Andreozzi *et al.* (2003)
2003	Bezafibrate, carbamazepine, diazepan, diclofenac, 17β-ethinylestradiol, ibuprofen, iopromide, sulfametoxazol and roxithromycin	Milli Q, river and lake water	Ozonation	C_{O3} = 0.1; 0.2; 0.5; 1.0 and 2.0mg L^{-1}; C_0 = 0.5μmol L^{-1}; natural water properties: pH 7.2–7.9; COD= 0.8–3.7 mg L^{-1}; alcalinity = 0.7–5.8 mol L^{-1} HCO_3^-	Ozone doses ranging from 0.2 up 0.5 mg L^{-1} were observed with 97% removal of all compounds. Removal of bezafibrate was lower	Huber *et al.* (2003)
2003	Iodinated X-ray contrast media antibiotics, betablockers, antiphlogistics, lipid regulator metabolites, antiepileptics and estrogens	DWTP effluent	Ozonation	C_{O3} = 5, 10, 15 mg L^{-1}; effluent properties: pH 7.2; DOC=23mgL^{-1}; COD=30mgL^{-1}; SST = 4.5 mg L^{-1}	Ozone doses ranging from 5 up to 15mg L^{-1} were necessary for complete removal of these compounds. The only exceptions were iodinated X-ray contrast media which were removed 13–89% with ozone doses from 10 to 15 mg L^{-1}, respectively	Ternes *et al.* (2003)
2004	Diclofenac	Distilled water	Ozonation	pH 5.0; 5.5 and 6.0; scavenger = *tert*-butyl alcohol; C_0 = 0.1 mmol L^{-1}; C_{O3} Aqueous = 0.1 mmol L^{-1}	100% of chlorine release was observed and 32% mineralization	Vogna *et al.* (2004)
2005	Antibiotic (amoxicillin)	Aqueous solution	Ozonation	C_0 = 0.5 mmol L^{-1}; C_{O3} = 0.16 mmol L^{-1}; pH 2.5–5.0	Low mineralization and some by-products were identified	Andreozzi *et al.* (2005)
2006	Antibiotic (clarithromycin)	Milli Q water	Ozonation	C_0 = 0.1 mmol L^{-1}; C_{O3} = 10 μmol L^{-1}; T=20 ◦C	Biological activity of clarithromycin was reduced after ozonation	Lange *et al.* (2006)
2007	Benzafibrate (lipid regulator)	Distilled water	Ozonation	C_{O3} = 1μmol L^{-1}; C_0 = 0.2μmol L^{-1}; pH 6 to 8	The complete BZF abatement is achieved. However, only a small part of the substrate is mineralized	Dantas *et al.* (2007)
2007	Pharmaceutical and personal careproducts	Groundwater	Ozonation	C_0 = 4 and 400μmol L^{-1}; C_{O3} = 20 mg L^{-1}	No significant influence of ozone pre-treatment was observed on PPCPs elimination except for carbamazepine	Carballa *et al.* (2007)
2007	Ibuprofen, bezafibrate, amoxicillin, sulfamethoxazole	Pure water	Ozonation	C_0 =10μmol L^{-1}	In the ozone-Membrane Filtration hybrid experiments, the pre-ozonation was able to reduce the membrane fouling	Oh *et al.* (2007)

2.3.3 Position of this research

As known above, up to now, most of studies on the removal potential of O_3, UV and AOPs for PPCPs have been performed using laboratory scale investigation. However, considering tens of PPCPs detected in the aquatic environment, more practical approaches such as the expansion of target PPCPs and the magnification of experimental setup are also necessary for efficient PPCPs control. In this study, bench scale continuous O_3-based and UV-based processes were operated for the removal of various PPCPs present originally in secondary effluent. Moreover, the practical approaches should include an integrated discussion on the disinfection effectiveness, decrease effect of ecological risk and the formation potential of by products as well as the PPCPs removal effectiveness and a saving of operating cost. In Chapter VI, the integrated discussion on the applicability of O_3-based and UV-based processes into technologies for water reuse was done based on the results from this study and previous researches.

2.4 Summary

Chapter II made a literature review on PPCPs and their removal processes such as UV treatment, O_3 and advanced oxidation processes (AOPs). The findings from this literature review were as follows;

1) Very little information on the removal characteristics of PPCPs is still available although there are several studies on the PPCPs removal with physicochemical processes such as O_3, UV, AOPs, chlorination, activated carbon adsorption and membrane treatment.

2) Therefore, considering a variety of PPCPs detected in the aquatic environment, more practical approaches such as the expansion of target PPCPs and the magnification of experimental setup are also necessary for efficient PPCPs control.

2.5 References

Adams C., Wang Y., Loftin K., Meyer M.T., 2002, Removal of antibiotics from surface and distilled water in conventional water treatment processes, *J. Environ. Eng.* 128, 253–260

Al-Ahmad A., Daschner F.D., Kummerer K., 1999 Bidegradability of cefotiam, ciprofloxacin, meropenem, penicillin G and sulfanethoxazole and inhibition of wastewater bacteria, *Arch Environ Contam Toxicol* 37, 158-163

Andreozzi R., Caprio V., Marotta R., Radovnikovic A., 2003, Ozonation and H_2O_2/UV treatment of clofibric acid in water: a kinetic investigation, *J. Hazard. Mater.* 103, 233–246

Andreozzi R., Canterino M., Marotta R., Paxeus N., 2005, Antibiotic removal from wastewaters: the ozonation of amoxicillin, *J. Hazard. Mater.* 122, 243–250

Areerachakul N., Vigneswaran S., Ngo H.H., Kandasamy J., 2007, Granular activated carbon (GAC) adsorption–photocatalysis hybrid system in the removal of herbicide from water, *Sep. Purif. Technol.* 55, 206–211

Ash R.J., Mauck B., Morgan M., 2002 Antibiotic resistance of gram-negative bacteria in rivers, United States, *Emerg Infect Dis* 8, 713-717

Beltran F.J., Ovejero G., Acedo B., 1993, Oxidation of atrazine in water by ultraviolet radiation combined with hydrogen peroxide, *Water Res.* 27, 1013-1021

Cahill J.D., Furlong E.T., Burkhardt M.R., Kolpin D. and Anderson L.G., 2004 Determination of pharmaceutical compounds in surface- and ground-water samples by solid-phase extraction and high-performance liquid chromatography-electrospray ionization mass spectrometry, *Journal of chromatography A* 1041, 171-180

Carballa M., Manterola G., Larrea L., Ternes T., Omil F., Lema J.M., 2007, Influence of ozone pre-treatment on sludge anaerobic digestion: Removal of pharmaceutical and personal care products, *Chemosphere* 67, 1444–1452

Clarke N. and Knowles G., 1982, High purity water using H_2O_2 and UV radiation, *Effluent and Water Treatment Journal* 22, 335-341

Crane M., Watts C. and Boucard T., 2006 Chronic aquatic environmental risks from exposure to human pharmaceuticals, *Science of the Total Environment* 367, 23-41

Dantas R.F., Canterino M., Marotta R., Sans C., Esplugas S., Andreozzi R., 2007, Bezafibrate removal by means of ozonation: primary intermediates, kinetics, and toxicity assessment, *Water Res.* 41, 2525–2532

Daughton C.G. and Ternes T.A., 1999 Pharmaceuticals and Personal Care Products in the Environment: Agents of Subtle change?, *Environmental Health Perspectives* 107, 907-938

Daughton C.G., 2004, Non-regulated water contaminants: emerging research, *Environmental Impact Assessment Review* 24, 711-732

Doll T.E., Frimmel F.H., 2005, Photocatalytic degradation of carbamazepine, clofibric acid and iomeprol with P25 and hombikat UV100 in presence of natural organic matter (NOM) and of other organic water constituents, *Water Res.* 39, 403–411

EC, 2001 Directive 2001/83/EC of the European parliament and of the council of 6 November 2001 on the community code relating to medicinal products for human use. Brussels, Belgium: European Union

EMEA, 2005 Guideline on the environmental risk assessment of medicinal products for human use. Committee for medicinal products for human use (CHMP). London, UK: European Medicines Agency; CHMP/SWP/4447/00 draft

Esplugas S., Bila D.M., Krause L.G.T., Dezotti M., 2007, Ozonation and advanced oxidation technologies to remove endocrine disrupting chemicals (EDCs) and pharmaceuticals and personal care products (PPCPs) in water effluents, *Journal of Hazardous Materials* 149, 631-642

Ferrari B., Paxeus N., Giudice R.L., Pollio A. And Garric J., 2003 Ecotoxicological impact of pharmaceuticals found in treated wastewaters: study of carbamazepine, clofibric acid, and diclofenac, *Ecotoxicology and Environmental Safety* 55, 359-370

Gagne F., Blasise C. and Andre C., 2006 Occurrence of pharmaceutical products in a municipal effluent and toxicity to rainbow trout (*Oncorhynchus mykiss*) hepatocytes, *Ecotoxicology and Environmental Safety* 64, 329-336

Glaze W.H., Kang J.W., Chapin D.H., 1987, The chemistry of water treatment processes involving ozone, hydrogen peroxide and ultraviolet radiation, *Ozone Sci. Engin.* 9, 335-352

Halling-Sørensen, B., Nielsen S.N., Lanzky P.F., Ingerslev F., Lutzhoft H.C.H., Jorgensen S.E., 1998 Occurrence, fate and effects of pharmaceutical substances in the environment- A review, *Chemosphere* 36, 357-393

Harries J.E., Sheahan D.A., Jobling S., Mattiessen P., Neall P., Routledge E.J., Rycroft R., Sumpter J.P., and Tylor T., 1997, Estrogenic Activity in Five United King-dom Rivers Detected by Measurement of Vitellogenesis in Caged Male Trout, *Environ Toxicol Chem.* 16, 534542

Heberer T., Stan H.J., 1997 Determination of clofibric acid and N-(phenylsulfonyl)-sarcosine in sewage, river and drinking water, Int. *J. Environ. Anal. Chem.* 67, 113-124

Heberer T., 2002 Occurrence, fate and removal of pharmaceutical residues in the aquatic environment: a review of recent research data, *Toxicol. Lett.* 131, 5-17

Hirsch R., Ternes T.A., Haberer K., Mehlich A., Ballwanz F. and Kartz K.-L., 1998 Determination of antibiotics in different water compartments via liquid chromatography–electrospray tandem mass spectrometry, *J. Chromatogr. A* 815 , 213

Huber M., Canonica S., Park G.Y., 2003, Oxidation of pharmaceuticals during ozonation and advanced oxidation processes, *Environ. Sci. Technol.* 37, 1016–1024

Jørgensen S.E., Halling-Sørensen B., 2000, Drugs in the environment, *Chemosphere* 40, 691-699

Kanda R., Griffin P., James H.A. and Fothergill J., 2003 Pharmaceutical and personal care products in sewage treatment works, *J. Environ. Monit.* 5, 823-830

Kummerer K., Al-Ahmad A., Mersch-Sundermann V., 2000 Biodegradability of some antibiotics, elimination of the genotoxicity and affection of wastewater bacteria in a simple test, *Chemosphere* 40, 701-710

Lange F., Cornelissen S., Kubac D., Sein M.M., von Sonntag J., Hannich C.B., Golloch A., Heipieper H.J., Moder M., von Sonntag C., 2006, Degradation of macrolide antibiotics by ozone: a mechanistic case study with clarithomycin, *Chemosphere* 65, 17–23

Langlais B., Reckhow D.A., Brink D.R., 1991, Ozone in water treatment, Application and engineering, Chelsea: Lewis

Nakada N., Tanishima T., Shinohara H., Kiri K. and Takada H., 2006 Pharmaceutical chemicals and endocrine disrupters in municipal wastewater in Tokyo and their removal during activated sludge treatment, *Water Res.* 40, 3297-3303

Nghiem L.D., Schafer A.I., Elimelech M., 2005, Pharmaceutical retention mechanisms by nanofiltration membranes, *Environ. Sci. Technol.* 39, 7698-7705

Nogrady T. and Weaver D.F., 2005 Medicinal chemistry; A molecular and biochemistry approach third edition, Oxford university press

Oh B.S., Jang H.Y., Hwang T.M., Kang J.W., 2007, Role of ozone for reducing fouling due to pharmaceuticals in MF (microfiltration) process, *J. Membr. Sci.* 289, 178–186

Okuda T., Kobayashi Y., Nagao R., Yamashita N., Tanaka H., Tanaka S., Fuji S., Konishi C., Houwa I., 2007 Removal efficiency of 66 pharmaceuticals during wastewater treatment process in Japan, *Micropol & Ecohazard 2007*, 213-219

Pearce G.K., 2008, UF/MF pre-treatment to RO in seawater and wastewater reuse applications: a comparison of energy costs, *Desalination* 222, 66–73

Purdom C.E., Hardiman P.A., Bye V.J., Eno C.N., Tyler C.R., and Sumpter J.P., 1994, Estrogenic Effects from Sewage Treatment Works, *Chem Ecol* 8, 275-285.

Richardson S.D. and Ternes T.A., 2005 Water analysis: Emerging contanminants and current issues, *Analytical chemistry* 77, 3807-3838

Shemer H., Kunukcu Y.K., Linden K.G., 2006, Degradation of the pharmaceutical metronidazole via UV, Fenton and photo-Fenton processes, *Chemosphere* 63, 269–276

Sleiman M., Conchon P., Ferronato C., Chovelon J.M., 2007, Iososulfuron degradation by TiO_2 photocatalysis: kinetic and reactional pathway investigations, *Appl. Catal. B: Environ.* 71, 279–290

Stackelberg P.E., Furlong E.T., Meyer M.T., Zaugg S.D., Henderson A.K., Reissman D.B., 2004, Persistence of pharmaceuticals compounds and other organic wastewater contaminants in a conventional drinking-water-treatment plant, *Science of the Total Environment* 329, 99-113

Staehelin J., Hoigne J., 1985, Decomposition of ozone in water in the presence of organic solutes acting as promoters and inhibitors of radical chain reactions. *Environ Sci Technol* 19, 1206−1213

Stefan M.I., Hoy A.R., Bolton J.R., 1996, Kinetics and mechanism of the degradation and mineralization of acetone in dilute aqueous solution sensitized by the UV photolysis of hydrogen peroxide, *Environ. Sci. Technol.* 30, 2382-2390

Ternes T.A., 1998 Occurrence of drugs in German sewage treatment plants and rivers, *Water Res.* 32, 3245-3260

Ternes T.A., 2001 Analytical methods for the determination of pharmaceuticals in aqueous environmental samples, *trends in analytical chemistry* 20, 419-434

Ternes Th.A., Meisenheimer M., McDowell D., Sacher F., Brauch H-J., Haist-Gulde B., Gudrun P.G., Wilme U., Zulei-Seibert N., 2002, Removal of pharmaceuticals during

drinking water treatment. *Environ. Sci. Technol.* 36, 3855-3863

Ternes T.A., Stuber J., Herrmann N., McDowell D., Ried A., Kampann M., Teiser B., 2003, Ozonation: a tool for removal of pharmaceuticals, contrast media and musk fragrances from wastewater? *Water Res.* 37, 1976–1982

Vanderford J., Pearson R.A., Rexing D.J. and Snyder S.A., 2003 Analysis of endocrine disruptors, pharmaceuticals and personal care products in water using liquid chromatography/tandem mass spectrometry. *Anal. Chem.* 75, 6265-6274.

Vogna D., Marotta R., Andreozzi R., Napolitano A., D'ischia M., 2004, Kinetic and chemical assessment of the UV/H_2O_2 treatment of antiepileptic drug carbamazepine, *Chemosphere* 54, 497–505

Vogna D., Marotta R., Napolitano A., 2004, Advanced oxidation of the pharmaceutical drug diclofenac with UV/H_2O_2 and ozone, *Water Res.* 38, 414–422

von Gunten U., 2003, Ozonation of drinking water: Part I. Oxidation kinetics and product formation, *Water Res.* 37, 1443-1467

Weir B.A., Sundstrom D.W., Klei H.G., 1987, Destruction of benzene by ultraviolet light-catalyzed oxidation with hydrogen peroxide, *Haz. Waste & Haz. Mater.* 4, 165-175

Weir B.A., Sundstrom D.W., 1993, Destruction of trichloroethylene by UV light-catalyzed oxidation with hydrogen peroxide, *Chemosphere* 27, 1279-1291

Yoon Y., Westerhoff P., Snyder S.A., Wert E.C., 2006, Nanofiltration and ultrafiltration of endocrine disrupting compounds pharmaceuticals and personal care products, *Journal of Membrane Science* 270, 88-100

Zwiener C., Frimmel F.H., 2000, Oxidative treatment of pharmaceuticals in water. *Water Res.* 34, 1881−188

CHAPTER III

PHOTODEGRADATION OF PHARMACEUTICALS AND PERSONAL CARE PRODUCTS BY UV AND THE EFFECT OF H_2O_2 ADDITION

3.1 Introduction

There are a great variety of pharmaceuticals and personal care products (PPCPs) for human and veterinary health in the medical field. Among these PPCPs, it has been reported that tens of PPCPs including antibiotic clarithromycin and anti-inflammatory agent diclofenac were detected in the range of ng/L to μg/L order from the effluent of sewage treatment plant and river water (Thomas, 2002; Tvrtko *et al*., 2004; Nakada *et al*., 2007; Okuda *et al*., 2008). However, much more PPCPs may exist in the aquatic environment, because it is estimated that the number of PPCPs being used in the medical field exceeds 3,000 (Richardson *et al*., 2005). Therefore, limitation of PPCPs reduction in water treatment plants could cause their contamination in the water environment, resulting in recent emerging concerns of the safety of drinking water, wastewater reclaimed and reuse, and aquatic ecosystems.

UV treatment, which is becoming popular for disinfection of potable water, lacks knowledge on applicability for the PPCPs removal in wastewater treatment system. However, recently many studies on the removal of various organic materials such as *N*-nitrosodimethylamine (NDMA), pharmaceuticals, hydrocarbons and water soluble fraction of crude oil with UV treatment have been done because UV treatment does not form byproducts. Moreover, it has been known to an effective process for degrading organic matters especially when it is combined with O_3 or H_2O_2 (Ziolli *et al*., 2003; Blatchley III *et al*., 2007; Mascolo *et al*., 2007; Plumlee *et al*., 2008; Canonica *et al*., 2008). NDMA, one of

several *N*-nitrosamines classified as human carcinogens, is a disinfection byproduct formed from the chlorination and chloramination of drinking water and wastewater. It has been reported that UV treatment of NDMA resulted in removals of 43% - 66% in advanced processes consisting of disinfection by chlorination, microfiltration, RO (reverse osmosis) and an ultraviolet-hydrogen peroxide advanced oxidation system (Plumlee *et al*., 2008). This study suggested that UV irradiation in combination with RO treatment and, in some cases, blending will allow operators to reliably maintain the residual NDMA below the 10 ng/L Califonia drinking water notification level.

There is some information on the removal of PPCPs in real sewage water using UV treatment (Andreozzi *et al*., 2003; Doll *et al*., 2003; Lopez *et al*., 2003). Lopez *et al*. (2003) have studied on the UV and UV/H_2O_2 degradations of pharmaceutical intermediates in aqueous solution. They found that two pharmaceutical intermediates (5-methyl-1,3,4-thiadiazole-2-methylthio and 5-methyl-1,3,4-thiadiazole-2thiol) degradation by photo-oxidation was always faster than degradation by direct photodegradation, and that during direct photodegradation, a lower substrate initial concentration led to a faster and more efficient degradation. Vogna *et al*. (2004a) have conducted a study on diclofenac oxidation with UV/H_2O_2 and ozone, and showed that both ozonation and UV/H_2O_2 systems proved to be effective in inducing diclofenac degradation. In other study, they reported that UV/H_2O_2 process could degrade carbamazepine very effectively, while UV alone process was not effective for reducing carbamazepine concentration (Vogna *et al*., 2004b). A study on the potential effectiveness of UV and UV/AOP (Advanced Oxidation Process) as drinking water remediation technologies for PhACs (Pharmaceutically Active Compounds) found most commonly in surface waters has been done (Pereira *et al*, 2007). In the study, for 6 PhACs such as carbamazepine, naproxen, clofibric acid, iohexol, ciprofloxacin and ketoprofen, their removal from surface water during UV and UV/H_2O_2 treatments was evaluated using fundamental photodegradation parameters in laboratory-grade water for all targeted PhACs. The model developed in their study predicted the experimental UV removals.

Canonica *et al.* (2008) evaluated the extent of degradation of four selected pharmaceuticals such as 17α-ethinylestradiol (EE2), diclofenac, sulfamethoxazole and iopromide in UV drinking water treatment for disinfection purposes. At the UV-C (254 nm)

drinking water disinfection fluence of 400J/m^2, the degree of depletion of the select pharmaceuticals at pH 7.0 in pure water was 0.4% for EE2, 27% for diclofenac, 15% for sulfamethoxazole, and 15% for iopromide.

Several studies on PPCPs degradation in UV and UV/H_2O_2 processes have been carried out as described above. However, limited PPCPs have been investigated in those studies, despite a great variety of PPCPs in the aquatic environment. The aim of this research is to examine the photodegradation characteristics of PPCPs detected often in the aquatic environment with UV treatment. Moreover, the effectiveness of H_2O_2 addition for PPCPs degradation during UV treatment was investigated. Finally, UV doses required for the effective removal of each PPCP were estimated. This information is useful for expecting the removal potential of UV process for various PPCPs in water and wastewater treatment plant.

The structure of this chapter is indicated in Fig. 3-1.

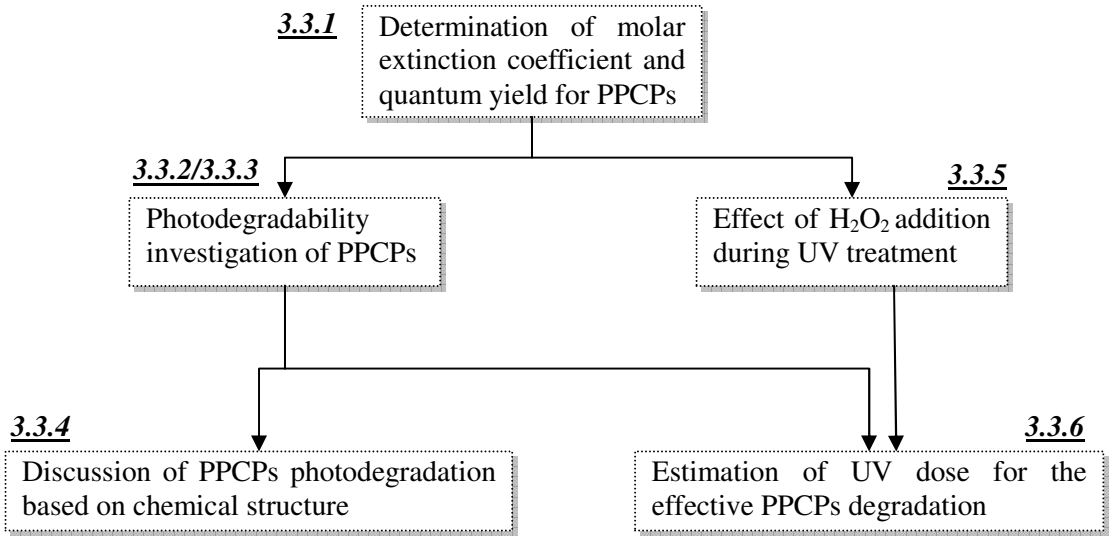


Fig. 3-1 Structure of this chapter

3.2 Materials and methods

3.2.1 Selected PPCPs

A list of 30 PPCPs was selected for this study based on consumption and environmental relevance. The name and use of the selected PPCPs are shown in Table 3-1. The PPCPs consist mainly of analgesics, antiarrhythmia agents, antibiotics and bronchiodilators. Anti-itch

drugs, anticonvulsants, antineoplastic agents, insect repellents, carbadox (antiparasitic agent) intermediates and NMDA (*N-methyl d-aspartate*) receptor antagonists are also included. Most of the PPCPs have been detected in the river water and/or effluent from sewage treatment plants in Japan (Okuda *et al*., 2008). Twenty-eight of the PPCPs were obtained from Wako, Japan; levofloxacin (Fluka) and ceftiofur (Hayasijyunyaku, Japan) were the exceptions. The concentrations of stock solutions of the PPCPs ranged from about 100-1,000 mg/L and were prepared with methanol or acetone due to their low solubility in water and stored at 4°C. The molecular weights, octanol-water partition coefficients (log *Kow*) and *pKa*s of the PPCPs ranged from about 151.165 (acetaminophen) to 747.964 (clarithromycin), -1.30 (tetracycline) to 5.12 (mefenamic acid), and 1.40 (antipyrine) to 9.42 (propranolol), respectively.

Table 3-1 Selected 30 PPCPs

No.	Name of PPCPs	Use	Molecular Formula	Molecular weight	Log Kow	pKa	Water solubility (mg/L, @25℃)
1	Acetaminophen	Analgesic	$C_8H_9NO_2$	151.165	0.46	9.38	14,000
2	Antipyrine		$C_{11}H_{12}N_2O$	188.230	0.38	1.40	51,900
3	Diclofenac		$C_{14}H_{11}Cl_2NO_2$	296.153	4.51	4.15	2.37
4	Ethenzamide		$C_9H_{11}NO_2$	165.192	0.77	-	-
5	Fenoprofen		$C_{15}H_{14}O_3$	242.274	3.90	7.30	-
6	Indomethacin		$C_{19}H_{16}ClNO_4$	357.793	4.27	4.50	0.937
7	Isopropylantipyrine		$C_{14}H_{18}N_2O$	230.311	1.94	-	3,000,000
8	Ketoprofen		$C_{16}H_{14}O_3$	254.285	3.12	4.45	51
9	Mefenamic acid		$C_{15}H_{15}NO_2$	241.290	5.12	4.20	20
10	Naproxen		$C_{14}H_{14}O_3$	230.263	3.18	4.15	15.9
11	Disopyramide	Antiarrhythmic agents	$C_{21}H_{29}N_3O$	339.483	2.58	-	44.9
12	Metoprolol		$C_{15}H_{25}NO_3$	267.369	-	-	-
13	Propranolol		$C_{16}H_{21}NO_2$	259.349	3.48	9.42	61.7
14	Ceftiofur	Antibiotics	$C_{19}H_{17}N_5O_7S_3$	523.553	-	-	-
15	Chlorotetracycline		$C_{22}H_{23}ClN_2O_8$	478.885	-0.62	3.30	630
16	Clarithromycin		$C_{38}H_{69}NO_{13}$	747.964	3.16	8.99	0.342
17	Oxytetracycline		$C_{22}H_{24}N_2O_9$	460.439	-0.90	3.27	313
18	Sulfadimethoxine		$C_{12}H_{14}N_4O_4S$	310.328	1.63	-	343
19	Sulfadimidin		$C_{12}H_{14}N_4O_2S$	278.330	0.89	7.59	1,500
20	Sulfamethoxazole		$C_{10}H_{11}N_3O_3S$	253.276	0.89	-	610
21	Sulfamonomethoxine		$C_{11}H_{12}N_4O_3S$	280.302	0.70	-	4,030
22	Tetracycline		$C_{22}H_{24}N_2O_8$	444.440	-1.30	3.30	231
23	Carbamazepine	Anticonvulsant	$C_{15}H_{12}N_2O$	236.274	2.45	-	17.7
24	Crotamiton	Anti-itch drug	$C_{13}H_{17}NO$	203.285	2.73	-	-
25	Cyclophosphamide	Antineoplastic agents	$C_7H_{15}Cl_2N_2O_2P$	261.089	0.63	-	40,000
26	Clenbuterol	Bronchodilator	$C_{12}H_{18}Cl_2N_2O$	277.195	2.00	-	-
27	Theophylline		$C_7H_8N_4O_2$	180.167	-0.02	8.81	7,360
28	2-QCA	Carbadox(Antiparasitic agents) intermediate	$C_9H_6N_2O_2$	174.159	-	-	-
29	DEET	Insect repellents	$C_{12}H_{17}NO$	191.274	2.18	-	912
30	Ifenprodil	NMDA receptor antagonist	$C_{21}H_{27}NO_2$	325.452	3.90	-	-

- : No data

3.2.2 Water used in the experiments

Test water was prepared by spiking the stock solutions of the 30 PPCPs into pure water (PW) purchased from Nisso Shoji Co., Ltd and biologically treated water (TW), respectively. Secondary effluent of sewage treatment plant was used for TW. TOC concentration of PW was below 50 μg/L, and the pH and DOC concentration of TW ranged 6.7 to 7.0 and 3.9 mg/L to 4.0 mg/L, respectively.

3.2.3 Preparation of tested water

In order to prepare the test water for UV and UV/H_2O_2 treatments, 2.2 ml of each stock solution was added to a 300 mL flask. Afterwards, the methanol and acetone used as solvents in the stock solutions were volatilized by an N_2 gas purger with a flow rate of about 3-4L N_2 gas/min at 37°C to prevent them from absorbing UV energy and deteriorating the removal of the PPCPs during UV treatments. After this procedure, only the PPCPs remained adhered to the flask. The 30 PPCPs adhered to the flask were dissolved by adding an appropriate amount of PW to the flask and agitating with a magnetic stirrer. This solution was continuously agitated for at least 12 hours to allow the PPCPs to be sufficiently dissolved in the PW. After agitation, the solution was filtered with a 0.45 μm membrane filter to remove undissolved PPCP particles. The filtrate was adjusted to a final volume of 1 L with PW. Finally, 22 L of test water for each experiment was prepared by mixing the 1L solution with 21 L of PW or TW. For tested water spiked the 30 PPCPs into PW, the pH was adjusted to 7.0 with phosphate buffer solution of 1M manufactured by K_2HPO_4 and NaH_2PO_4 solution before experiments. TW used for preparing tested water was filtered by GF/C filter (Whatman) before use. The pH adjustment of tested water prepared by TW was not done. The initial concentrations of the 30 PPCPs in tested water ranged from 5 μg/L (clenbuterol) to 119 μg/L (propranolol).

3.2.4 Experimental setup and conditions

UV treatment was carried out using a cylindrical stainless reactor with an interior

diameter of 30 cm and a height of 108.7 cm (See Fig. 3-2). The test water was agitated continuously at a speed of 300 rpm with an agitator on top of the reactor during treatment experiments. A UV lamp was introduced into the reactor and kept separated from the tested water by UV sleeve. The temperature of the test water was maintained at 20°C by circulating water into a water jacket outside the reactor using a water circulator.

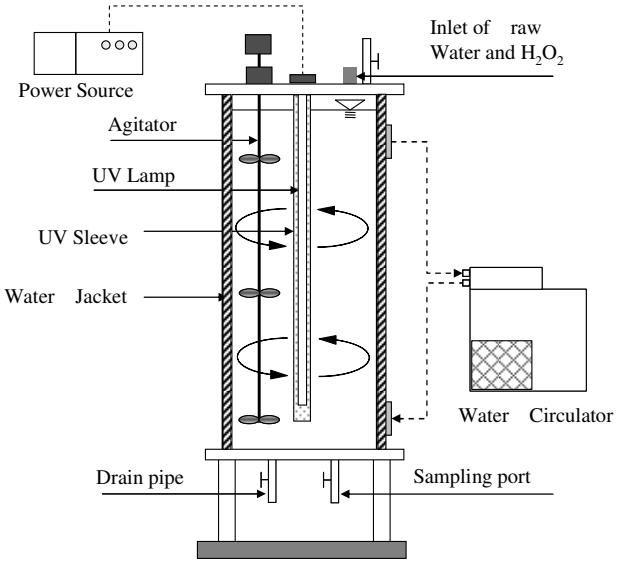


Fig. 3-2 Batch reactor for UV and UV/H_2O_2 experiments

An 8W low-pressure mercury lamp emitting at 254 nm (UV/Lamp1) was used, and the UV intensity was 0.384 mW/cm^2. Additionally, the removal potential of a 10W low-pressure mercury lamp emitting at 254 and 185 nm (UV/Lamp2) for PPCPs was also ivestigated. The UV intensity of UV/Lamp2 was 0.388 mW/cm^2. A UV lamp emitting at 254 nm is widely used for water disinfection because it is very effective for destroying DNA in microorganism. Generally, UV emitted at wavelengths of less than 200 nm photolyzes H_2O molecular, and as a resulte, OH radicals and hydrogen ions form. The OH radicals can contribute to the oxidation of organic materials (Han *et al*., 2004).

In order to investigate the removal potential of the 30 PPCPs, firstly, treatment experiments using UV/Lamp1 and UV/Lamp2 were done for tested waters spiked with the 30 PPCPs into PW. Secondly, the effect of H_2O_2 addition on the PPCPs degradation during UV treatment was investigated only for UV/Lamp1. Initial H_2O_2 concentration in tested water was 4.9 mg/L during UV/H_2O_2 treatment. Moreover, UV alone and UV/H_2O_2 treatment

experiments using UV/Lamp1 were carried out using tested waters spiked the 30 PPCPs into TW. For the UV/H_2O_2 treatment, initial H_2O_2 concentration was 6.1 mg/L. In these experiments, the contribution of OH radicals originated from the photodegradation of added H_2O_2 to the photocatalysis degradation of the 30 PPCPs was also compared with that of direct photodegradation. Degradation of the 30 PPCPs by H_2O_2 was investigated in a preliminary experiment. No significant variation in the concentration of the 30 PPCPs was observed.

Experimental conditions are summarized in Table 3-2

Table 3-2 Experimental conditions

Tested water	UV alone treatment	UV/H_2O_2 treatment
PW(pure water) + 30 PPCPs	UV/Lamp1 (254nm), UV/Lamp2 (254/185nm)	UV/Lamp1 + H_2O_2 4.9 mg/L
TW(biologically treated water) + 30 PPCPs	UV/Lamp1 (254nm), UV/Lamp2 (254/185nm)	UV/Lamp1 + H_2O_2 6.1 mg/L

3.2.5 Analytical methods

3.2.5.1 Measurement of PPCPs by LC/MS/MS

Concentrations of the 30 PPCPs were measured simultaneously using an LC/MS/MS. An HPLC Alliance Waters2695 separation module was used for the LC and a Quattro micro API Tandem mass spectrometer was used for the MS/MS. The control of the LC/MS/MS system and treatment of the data acquired during the operation of LC/MS/MS were managed with MassLynxTM Software (Waters). For simultaneous quantification of the 30 PPCPs, a gradient elution analysis method by varying the polarity of mobile phase with time was adopted. Samples taken from the experiments using tested water spiked 30 PPCPs into PW were introduced directly to LC/MS/MS for PPCP quantification. Table 3-3 shows the measurement conditions of LC/MS/MS in details.

The limit of detection (LOD) and limit of quantification (LOQ) for simultaneous analysis of the 30 PPCPs were determined by measuring solutions with a concentration in the 0 μg/L to 100 μg/L range for individual PPCPs with LC/MS/MS. From values measured three times for each solution, the average value and standard deviation value for each PPCP were calculated

and then used for acquiring a variation coefficient, which is defined as the ratio of standard deviation value as compared to the average value. Based on the standard deviation (σ) of the solution with the lowest concentration and a variation coefficient of less than 20%, the LOD (3σ) and LOQ (10σ) were calculated. The LOQ ranged from 0.033 μg/L (oxytetracycline) to 1.775 μg/L (acetaminophen) and the LOD ranged from 0.010 μg/L (oxytetracycline) to 0.533 μg/L (acetaminophen). LOQ values were used for calculating the degradation rate of each PPCP in this study. Table 3-4 shows parent ion, product ion, cone voltage, collision energy, LOD and LOQ for each PPCP.

Table 3-3 Measurement condition of LC/MS/MS for PPCPs analysis

<HPLC：Waters 2659>				
- Column：Waters SunFire C18 2.1mm×150mm,5μm				
- Column Temp.：20℃				
- Flow rate：0.2ml/min				
- Injection volume：10μl				
- Mobile Phase：A Water、B Methanol、C 1% Formic acid				
- Gradient：	Time(min)	A(%)	B(%)	C(%)
	0	70	20	10
	15	0	90	10
	20	70	20	10
<MS/MS：Quattro micro API>				
- Ionization：Electrospray Ionization(ESI) Positive				
- Spray Voltage：3.5kV				
- Capillary Temp.：350℃ - Source Temp.：120℃				

Table 3-4 Parent ion, product ion, cone voltage, collision energy, LOD and LOQ for each PPCP for LC/MS/MS analysis

No.	PPCP	Parent ion (*m/z*)	Product ion (*m/z*)	Cone voltage (V)	Collision energy (V)	LOD (μg/L)	LOQ (μg/L)
1	2-QCA	175.0	128.9	20	15	0.101	0.337
2	Acetaminophen	152.0	109.8	25	16	0.533	1.775
3	Antipyrine	189.1	76.7	30	35	0.179	0.597
4	Carbamazepine	237.1	194.0	25	20	0.390	1.299
5	Cetiofur	524.0	241.0	25	15	0.071	0.238
6	Chlorotetracycline	479.3	462.0	25	15	0.072	0.239
7	Clarithromycin	748.9	157.9	30	20	0.024	0.081
8	Clenbuterol	277.0	202.9	20	15	0.023	0.075
9	Crotamiton	204.1	68.7	30	20	0.046	0.152
10	Cycolphosphamide	261.0	139.8	25	20	0.122	0.407
11	DEET	192.1	118.8	25	15	0.065	0.216
12	Diclofenac	296.1	214.9	20	20	0.115	0.384
13	Disopyramide	340.2	239.0	20	15	0.014	0.047
14	Ethenzamide	166.0	148.9	15	10	0.031	0.102
15	Fenoprofen	243.1	196.9	15	10	0.474	1.579
16	Ifenprodil	326.2	308.1	30	20	0.010	0.032
17	Indomethacine	358.0	138.9	25	20	0.131	0.437
18	Isopropylantipyrine	231.1	184.9	20	15	0.073	0.243
19	Ketoprofen	255.1	209.0	25	15	0.056	0.188
20	Mefenamic acid	242.1	224.0	25	20	0.199	0.662
21	Metoprolol	268.2	115.9	30	20	0.092	0.306
22	Naproxen	231.1	188.9	35	20	0.145	0.485
23	Oxytetracycline	461.1	425.9	20	20	0.022	0.074
24	Propranolol	260.2	115.9	30	20	0.010	0.033
25	Sulfadimethoxine	311.0	155.9	30	20	0.128	0.427
26	Sulfadimizine	279.0	185.9	25	15	0.053	0.175
27	Sulfamethoxazole	254.0	155.9	25	15	0.119	0.396
28	Sulfamonomethoxine	281.0	155.9	25	15	0.069	0.229
29	Tetracycline	445.1	409.9	20	20	0.022	0.074
30	Theophylline	181.0	123.8	30	20	0.137	0.458

3.2.5.2 Pretreatment procedure of sample for LC/MS/MS analysis

Samples taken from the experiments using tested water spiked 30 PPCPs into TW were introduced to LC/MS/MS after pretreatment using solid phase extraction (OasisHLBcartridge 1cc/10mg P/N186000383, Waters). Firstly, a sample of 9ml taken from sampling port in outlet of each reactor was filtered with GF/B (pore size: 1.0μm) and then, EDTA and standard solution of 1ml with 90 μg/L concentrations of the 30 PPCPs were added to the filtrate. Afterwards, PPCPs in the filtrate were concentrated in Oasis HLB cartridge by the concentrator (Waters, Sep-Pak concentrator SPC-10). Oasis HLB cartridge conditioned in advance with 3ml methanol and 6ml distilled water was used for the concentration. After concentrating, the cartridge was dehydrated by pneumatic pump for 1 hr in order to avoid the

remaining of water in the cartridge, and PPCPs were eluted from the dehydrated cartridge with 2ml methanol. The eluted solution was volumed up to 10ml by a solution (Water:1% Formic acid = 7:1). This solution of 10ml was used for PPCPs quantification with LC/MS/MS.

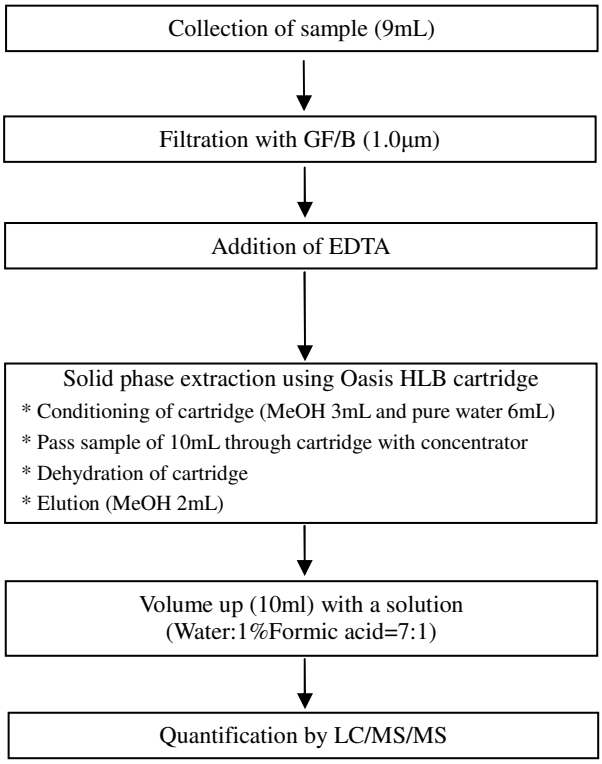


Fig. 3-3 Pretreatment procedure for LC/MS/MS measurement (For samples in TW)

3.2.5.3 Recovery rates for 30 PPCPs in TW

Table 3-5 shows recovery rates of each PPCP for LC/MS/MS analysis of the 30 PPCPs. Except for 2-QCA, acetaminophen, theophylline and mefenamic acid, good recovery rates of the 26 PPCPs were obtained (85% (ceftiofur) ~ 118% (carbamazepine)). The recovery rate of each PPCP was investigated by adding standard solution with 90 μg/L concentrations for the individual PPCPs into secondary effluent (n=3). The recovery rate was calculated by equation as follows;

$$Recovery\ rate\ (\%) = \ (Xa - X) / \alpha \times 100$$

Xa : Measured concentration of a PPCP in sample added standard solution

X : Measured concentration of a PPCP in sample

α : Added PPCP concentration

Table 3-5 Recovery rates of the 30 PPCPs for LC/MS/MS measurement (n=3)

No.	PPCP	Recovery rate(%)	No.	PPCP	Recovery rate(%)
1	2-QCA	48	16	Ifenprodil	107
2	Acetaminophen	38	17	Indomethacin	99
3	Antipyrine	101	18	Isopropylantipyrine	103
4	Carbamazepine	118	19	Ketoprofen	109
5	Ceftiofur	85	20	Mefenamic acid	138
6	Chlorotetracycline	86	21	Metoprolol	102
7	Clarithromycin	86	22	Naproxen	104
8	Clenbuterol	103	23	Oxytetracyline	94
9	Crotamiton	106	24	Propranolol	107
10	Cyclophosphamide	99	25	Sulfadimethoxine	102
11	DEET	105	26	Sulfadimizine	113
12	Diclofenac	104	27	Sulfamethoxazole	103
13	Disopyramide	106	28	Sulfamonomethoxine	112
14	Ethenzamide	102	29	Tetracycline	89
15	Fenoprofen	101	30	Theophylline	66

3.3 Results and discussion

3.3.1 Determination of molar extinction coefficient and quantum yield

Generally, degradation rate of an organic material by photodegradation is affected by UV energy absorption and quantum yield of the organic material. UV energy absorption by an organic material is expressed as molar extinction coefficient, which is a measure of how strongly the organic material absorbs light at a given wavelength. Quantum yield represents the ratio of the total numbers of molecules of the compound degraded to the total number of photons absorbed by the solution due to the presence of compound. Therefore, the quantum yield is less than 1.0. Here, photodegradation is defined as a chemical reaction in which a chemical compound is broken down by photons. Photocatalysis is defined as the acceleration of a photoreaction in the presence of a catalyst such as H_2O_2.

3.3.1.1 Measurement of molar extinction coefficient for the 30 PPCPs

Molar extinction coefficients of the 30 PPCPs investigated in this study at a wavelength of 254 nm were shown in Table 3-6. The values were calculated from UV absorbance measured with tested solution of each PPCP with a concentration of 10 mg/L. UV

absorbances of clenbuterol and ceftiofur were measured at a concentration of 1 mg/L and for metoprolol and cyclophosphamide, tested solutions of 100 mg/L and 1,000 mg/L concentrations were used, respectively, due to their very low UV absorbances. The molar extinction coefficient of clarithromycin could not be measured because tested solution showed a very unstable UV absorbance at 254 nm. As shown from Table 3-6, molar extinction coefficients ranged from 9 /M/cm (cyclophosphamide) to 19,799 /M/cm (oxytetracycline). Molar extinction coefficients of 7 PPCPs such as oxytetracycline, chlorotetracycline, ketoprofen, indomethacin, ceftiofur, sulfamonomethoxine and theophylline were quite high more than 10,000 /M/cm.

Table 3-6 Molar extinction coefficient and quantum yield for the investigated PPCPs

PPCPs	Molar extinction coefficient (ε, /M/cm) @254nm	Quantum yeild (ϕ)	PPCPs	Molar extinction coefficient (ε, /M/cm) @254nm	Quantum yeild (ϕ)
Oxytetracycline	19,799	0.0037	Mefenamic acid	4,633	0.0019
Chlorotetracycline	18,868	0.0038	Acetaminophen	4,218	0.0043
Ketoprofen	15,155	0.0724	Tetracycline	4,108	0.0098
Indomethacin	14,848	0.0016	Naproxen	3,961	0.0061
Ceftiofur	14,660	0.0208	2-QCA	3,623	0.0015
Sulfadimethoxine	14,399	0.0045	Diclofenac	3,465	0.1131
Theophyline	12,889	0.0002	Disopyramide	3,055	0.0342
Sulfamonomethoxine	9,558	0.0172	DEET	1,205	0.0035
Sulfadimidine	9,519	0.0040	Propranolol	856	0.0248
Clenbuterol	7,484	0.0044	Fenoprofen	800	0.1348
Sulfamethoxazole	7,345	0.0229	Ethenzamide	743	0.0059
Isopropylantipyrine	7,255	0.0148	Ifenprodil	391	0.1241
Antipyrine	6,626	0.0223	Metoprolol	235	0.0458
Carbamazepine	6,072	0.0015	Cyclophosphamide	9	0.4242
Crotamiton	4,777	0.0030	Clarithromycin	No data	No data

On the contrary, 6 PPCPs such as propranolol, fenoprofen, ethenzaimde, ifenprodil, metoprolol and cyclophosphamide showed very low molar extinction coefficients of below 1,000 /M/cm. Especially, the molar extinction coefficient of cyclophosphamide was considerably low compared to other PPCPs, implying that its photodegradation rate during

UV treatment can be very slow. On the other hand, tetracycline exhibited much lower molar extinction coefficient (4,108 /M/cm) than those of oxytetracycline (19,799 /M/cm) and chlorotetracycline (18,868 /M/cm) despite their similar chemical structures. This is compared with sulfonamides antibiotics such as sulfadimethoxine, sulfamonomethoxine, sulfadimidine and sulfamethoxazole showing similar molar extinction coefficients (7,345 /M/cm - 14,399 /M/cm). Molar extinction coefficients of ketoprofen and carbamazepine were 15,155 /M/cm and 6,072 /M/cm, respectively and these values agreed very well with 15,450 /M/cm and 6,070 /M/cm for ketoprofen and carbamazepine reported by Pereira *et al* (2007). The value of carbamazepine was also consistent very well with that (6,025 /M/cm) measured by Vogna *et al* (2004a). While, molar extinction coefficient of naproxen (3,961 /M/cm) obtained in this study was rather low due to unclear reason, comparing to 4,900 /M/cm reported by Vogna *et al* (2004a).

3.3.1.2 Calculation of quantum yield for the 30 PPCPs

Direct photodegradation rate of an organic compound *i* in the presence of other (*N-1*) substances that absorb UV radiation at a given wavelength depends on several factors such as UV intensity, I_0, molar extinction coefficient, ε_i, reactor optical light path, L, quantum yields, ϕ_i, and concentrations, C_i. The photodegradation rate is given by equation (1) (Beltran *et al.*, 1993):

$$-\frac{dC_i}{dt} = I_0 \phi_i f_i [1 - \exp(-2.3L \sum_{j=1}^{N} \varepsilon_j C_j)] \qquad (1)$$

where f_i, the fraction of total absorbed light which is absorbed by compound *i*, is experessed as follows:

$$f_i = \varepsilon_i C_i / \sum_{j=1}^{N} \varepsilon_j C_j \qquad (2)$$

Assuming that intermediate compounds do not absorb important fractions of UV radiation, f_i is 1. It is essential to know the quantum yield of an organic compound in order to predict the photodegradation rate of the organic compound. There are several ways to determine the quantum yield. One of them is to carry out experiments on the direct photodegradation of the organic compound under the following condition.

$$2.3L\sum \varepsilon_i C_i < 0.1 \qquad (3)$$

Under the conditions, equation (1) can be simplified as follows:

$$-\frac{dC_i}{dt} = 2.3LI_0\phi_i\varepsilon_i C_i \qquad (4)$$

Integrating equation (4), equation (5) is obtained.

$$Log\frac{C_i}{C_{i,0}} = -LI_0\phi_i\varepsilon_i t \qquad (5)$$

Therefore, quantum yield of an organic compound can be obtained if I_0 and ε_i values are availble. On the other hand, H_2O_2 degradation arises from the absorption of incident radiation at 254 nm. The contribution of other incident radiations in H_2O_2 degradation is very negligible (Nicole *et al.*, 1990). Fig. 3-4 shows the degradation of H_2O_2 with UV lamp (254 nm) used in this study. It can be known that H_2O_2 concentration decreased linearly with reaction time.

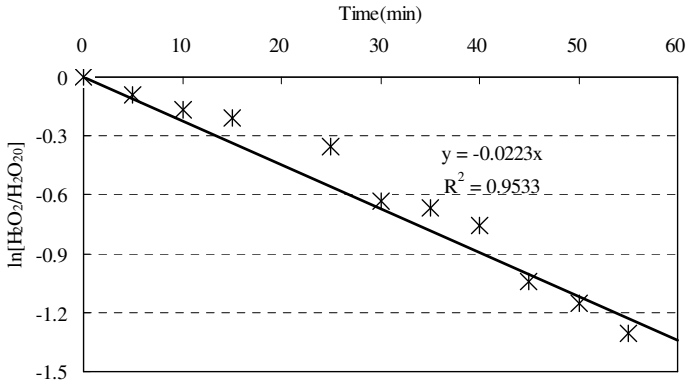


Fig. 3-4 Degradation of H_2O_2 at UV 254 nm

The photodegradation rate of H_2O_2 can be described by an apparent first-order kinetic equation (6) (Nicole *et al.*, 1990):

$$-\frac{d[H_2O_2]}{dt} = -\frac{2.3\varepsilon L\phi}{V} rI_0[H_2O_2] \qquad (6)$$

H_2O_2: H_2O_2 concentration (M) I_0: UV intensity (Einstein/sec)

ϕ: Quantum yield (1mol/photon) ε: Molar extinction coefficient of H_2O_2 (18.6 /M/cm)

L: Reactor optical light path (12.5cm) V: Volume of reactor (22L)

r: Reflexion coefficient values (1.75 for stainless steel wall)

Integrating equation (6), the following eaquation (7) can be obtained:

$$\ln[\frac{H_2O_2}{H_2O_{2,0}}] = -\frac{2.3\varepsilon L\phi}{V} rI_0 t \qquad (7)$$

On the other hand, I_0 can be obtained in equation (7). As a resulte, I_0 of the UV lamp (254 nm) used in this study was 1.9 E-04Einstein/L/sec. Substituting the I_0 of the UV lamp and ε of each PPCP to equation (5), quantum yield (ϕ) of each PPCP can be calculated.

Table 3-6 also shows quantum yield of each PPCP calculated from equation (5). Quantum yield for each PPCP ranged from 0.0002 (theophylline) to 0.4242 (cyclophosphamide). Quantum yield of theophylline was 0.0002, the lowest value among the quantum yields, whereas its molar extinction coefficient was so high (12,889 /M/cm). Quantum yields of oxytetracycline (0.0037), chlorotetracycline (0.0038) and indomethacine (0.0016) are not so high. On the contrarily, quantum yields of propranolol, fenoprofen, ifenprodil, metoprolol and cyclophophamide (0.0248 - 0.4242) are comparatively higher than the other PPCPs. These molecular extinction coefficients and quantum yields were used for discussing the photodegradability of the 30 PPCPs during UV and UV/H_2O_2 treatments.

3.3.2 Photodegradability of PPCPs in PW with UV

3.3.2.1 Determination of first-order rate constants of PPCPs for UV/Lamp1 and UV/Lamp2

Fig. 3-5 and Fig. 3-6 illustrate the variations of logarithmic relative residual concentrations of the 30 PPCPs spiked into pure water (PW) for ten minute treatments with UV/Lamp1 and UV/Lamp2, respectively. When the tested water was irradiated with UV/Lamp1 and UV/Lamp2, the logarithmic relative residual concentrations of the 30 PPCPs decreased linearly with the time as shown in Fig. 3-5 and Fig. 3-6.

Generally, when organic compounds absorbing UV are simultaneously present in water, assuming that UV absorbances by other organic compounds or intermediates formed during UV irradiation are negligible, the concentration decrease versus time of an organic material by UV photodegradation can be expressed as the following equation (8) (Lopez *et al*., 2003):

$$Log\frac{C}{C_0} = -LI_{0,254}\phi_{254}\varepsilon_{254}t = -k_{UV/Lamp1\_PW}t \qquad (8)$$

C_0: Initial concentration of an organic material (M)

C: Concentration of an organic material (M)

$I_{0,254}$: UV intensity of UV/Lamp1 (Einstein/sec)

ϕ_{254}: Quantum yield of photodegradation for UV/Lamp1 (mol/photon)

ε_{254}: Molar extinction coefficient of an organic compound for UV/Lamp1 (/M/cm)

L: Reactor optical light path (cm)

$k_{UV/Lamp1\_PW}$: First-order rate constant for UV/Lamp1 (/sec)

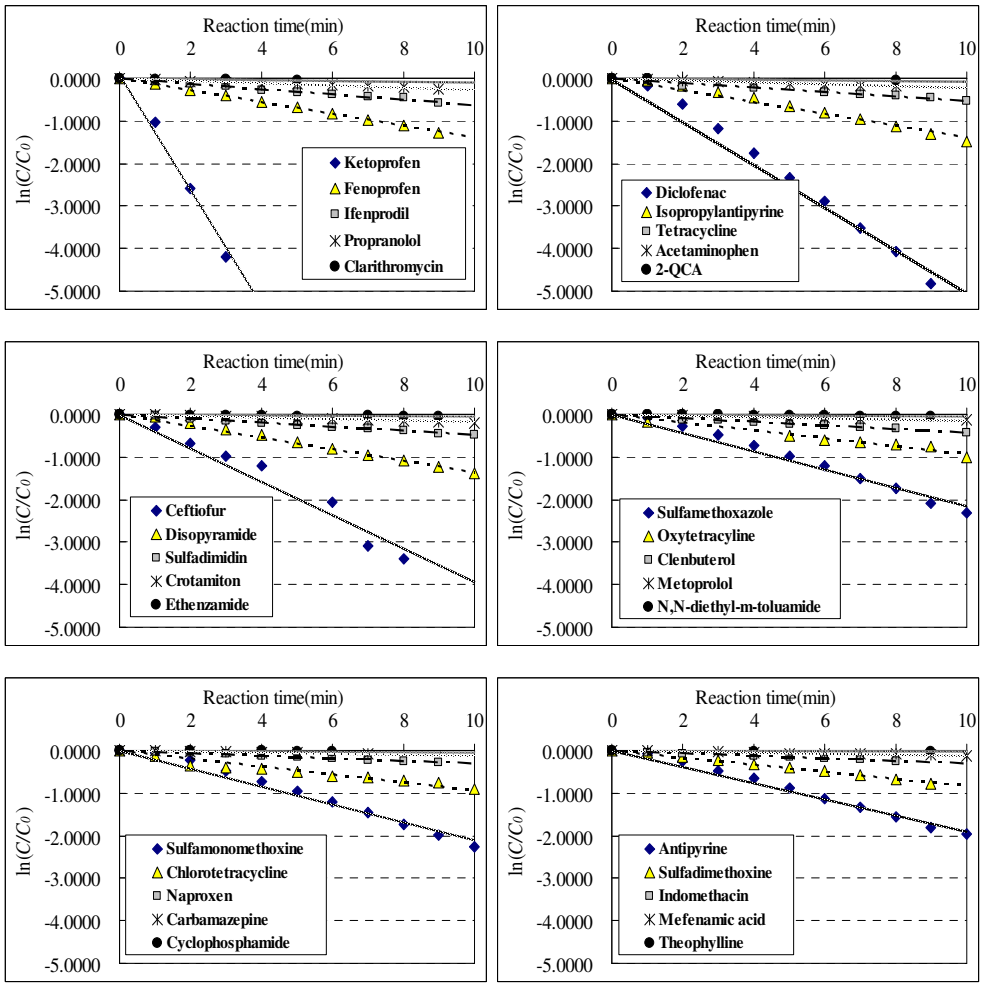


Fig. 3-5 Logarithmic relative residual concentrations of the 30 PPCPs spiked into PW during UV/Lamp1 treatment

Concerning UV/Lamp2, OH radicals generated from the photodegradation of H_2O with a wavelength of 185 nm as well as UV direct photodegradation with wavelengths 254 and 185

nm will involve the degradation of organic materials. Therefore, decreases in the concentrations of organic materials should be expressed as follows:

$$Log\frac{C}{C_0} = -(LI_{O,254}\phi_{254}\varepsilon_{254} + LI_{O,185}\phi_{185}\varepsilon_{185} + k_R[OH])t$$

$$= -k_{UV/Lamp2\_PW}t \qquad (9)$$

I_0: UV intensity (Einstein/sec)

ϕ: Quantum yield of photodegradation (mol/photon)

ε: Molar extinction coefficient of an organic material (/M/cm)

L: Reactor optical light path (cm)

$k_{UV/Lamp2\_PW}$: First-order rate constant for UV/Lamp2 (/sec)

3.3.2.2 Classification of photodegradability of PPCPs for applied UV

The first-order rate constant (k) for each PPCP makes it possible to compare the photodegradation effectiveness of UV for each PPCP when UV treatment was used to degrade the 30 PPCPs present in the test water. The k values of the 30 PPCPs obtained in the UV/Lamp1 and UV/Lamp2 treatment experiments were shown in Table 3-7.

The k values ($k_{UV/Lamp1\_PW}$) ranged from 6.0 E-05/sec (theophylline) to 2.4 E-02/sec (ketoprofen). For UV/lamp2 treatment, the k values ($k_{UV/Lamp2\_PW}$) ranged from 3.4 E-04/sec (theophylline) to 2.7 E-02/sec (ketoprofen). As a result, the average k of the 30 PPCPs for UV/lamp2 was about 1.4 times higher than that for UV/Lamp1.

The photodegradabilites of the 30 PPCPs investigated were compared by classifying into two groups: easily-degrading PPCPs with $k \geq$2.6 E-03/sec (equivalent to 90% degradation from the initial concentration within less than 15 min) and slowly-degrading PPCPs with k <6.4 E-04/sec (equivalent to 90% from the initial concentration after more than 1 hr) (See Table 3-7). Six PPCPs - ketoprofen, diclofenac, ceftiofur, sulfamethoxazole, sulfamonomethoxine and antipyrine - belonged to the category of easily-degrading PPCPs for UV/Lamp1. However, 10 PPCPs including isopropylantipyrine, disopyramide, ifenprodil and clenbuterol were classified as easily-degrading PPCPs for UV/Lamp2. On the other hand, 14 and 6 PPCPs were classified as slowly-degrading PPCPs for UV/Lamp1 and UV/Lamp2,

respectively. Consequently, it can be known that UV/Lamp2 treatment will be more effective in degrading the 30 PPCPs than UV/Lamp1.

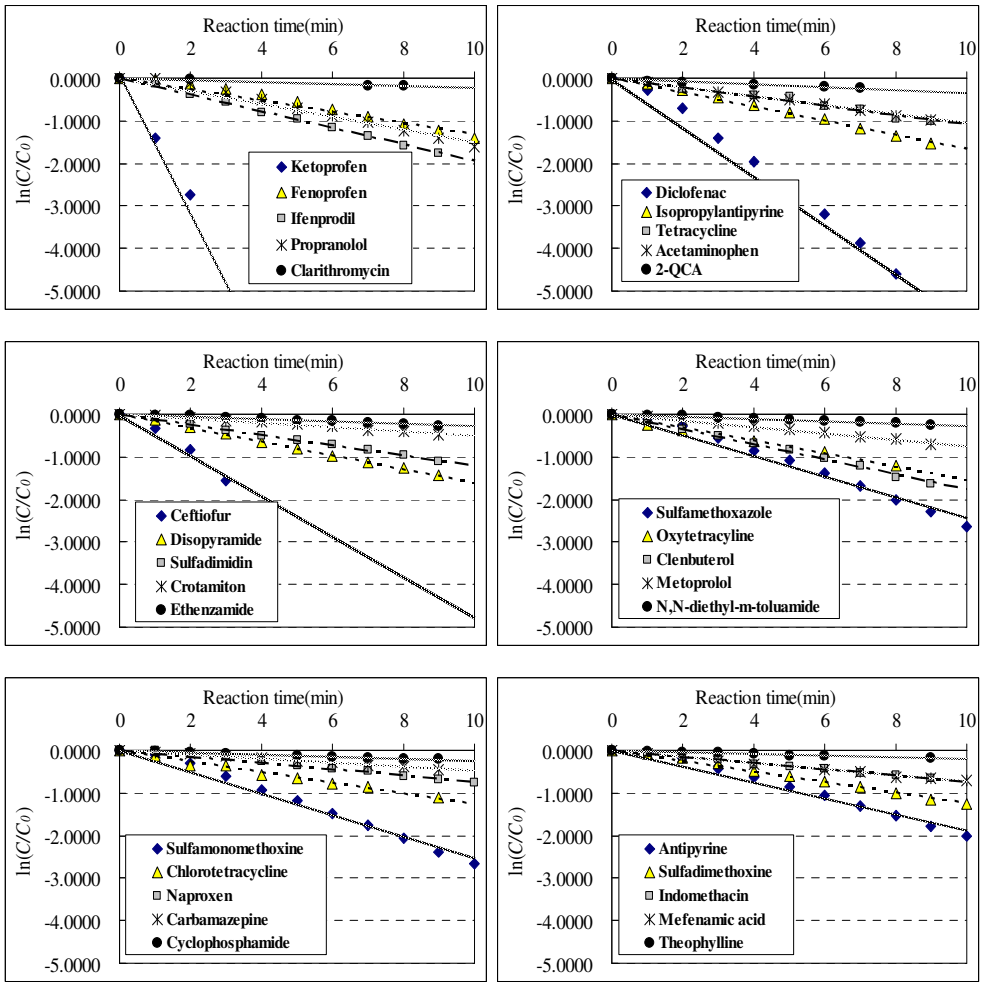


Fig. 3-6 Logarithmic relative residual concentrations of the 30 PPCPs spiked into PW during UV/Lamp2 treatment

Table 3-7 k values of the 30 PPCPs for UV/Lamp1 and UV/Lamp2

Name of PPCPs	Use	$k_{UV/Lamp1\_PW}$(/sec)	$k_{UV/Lamp2\_PW}$(/sec)	Amide bond	Amine bond
Ketoprofen	Analgesic	2.4E-02	2.7E-02		
Diclofenac	Analgesic	8.4E-03	9.6E-03		○
Ceftiofur	Antibiotics	6.6E-03	8.0E-03		○
Sulfamethoxazole	Antibiotics	3.6E-03	4.1E-03		○
Sulfamonomethoxine	Antibiotics	3.5E-03	4.2E-03		○
Antipyrine	Analgesic	3.2E-03	3.1E-03		
Fenoprofen	Analgesic	2.3E-03	2.2E-03		
Isopropylantipyrine	Analgesic	2.3E-03	2.8E-03		
Disopyramide	Antiarrhythmic agents	2.2E-03	2.6E-03	○	○
Oxytetracyline	Antibiotics	1.6E-03	2.5E-03	○	○
Chlorotetracycline	Antibiotics	1.5E-03	2.1E-03	○	
Sulfadimethoxine	Antibiotics	1.4E-03	2.1E-03		○
Ifenprodil	NMDA receptor antagonist	1.0E-03	3.2E-03		
Tetracycline	Antibiotics	8.6E-04	1.8E-03	○	○
Sulfadimizine	Antibiotics	8.1E-04	2.0E-03		○
Clenbuterol	Bronchodilator	7.1E-04	3.0E-03		○
Naproxen	Analgesic	5.2E-04	1.2E-03		
Indomethacin	Analgesic	5.1E-04	1.2E-03		
Propranolol	Antiarrhythmic agents	4.6E-04	2.5E-03		○
Acetaminophen	Analgesic	3.9E-04	1.8E-03	○	
Crotamiton	Anti-itch drug	3.1E-04	8.5E-04	○	
Metoprolol	Antiarrhythmic agents	2.3E-04	1.2E-03		○
Carbamazepine	Anticonvulsant	2.0E-04	8.0E-04	○	
Mefenamic acid	Analgesic	1.9E-04	1.2E-03		○
Clarithromycin	Antibiotics	1.8E-04	3.6E-04		
2-QCA	Carbadox intermediate	1.2E-04	6.0E-04		
Ethenzamide	Analgesic	9.5E-05	4.7E-04	○	
DEET	Insect repellents	9.2E-05	4.4E-04	○	
Cyclophosphamide	Antineoplastic agents	8.3E-05	4.0E-04	○	○
Theophylline	Bronchodilator	6.0E-05	3.4E-04		

* Black: easily-degrading PPCPs, Gray: slowly-degrading PPCPs

On the other hand, the acidic drugs ketoprofen, diclofenac and ceftiofur exhibited particularly high k values, irrespective of the applied UV lamps, indicating that these can be degraded very easily by UV irradiation. Contrarily, clarithromycin (an antibiotic), 2-QCA (a carbadox intermediate), ethenzamide (an analgesic), DEET (an insect repellent), cyclophosphamide (an antineoplastic) and theophylline (a bronchodilator) were classified as slowly-degrading PPCPs, irrespective of the UV/Lamp used. The $k_{UV/Lamp2\_PW}$ values of these PPCPs were still much lower than those of the others although the application of UV/Lamp2 caused significant increases in their degradations.

Among these PPCPs, enthenzamide, DEET and cyclophosphamide have amide bonds ($RCONR_2$) in their chemical structures, indicating that PPCPs consisting of amide bonds cannot be photolyzed easily with UV. Besides these three PPCPs, compounds such as

disopyramide, oxytetracycline, chlorotetracycline, tetracycline, acetaminophen, crotamiton and carbamazepine also have amide bonds. Among these, only disopyramide was classified as a fast-degrading PPCP. Therefore, PPCPs with amide bonds can be expected to exhibit low photodegradability under UV light. Four of the PPCPs that photolyzed very easily under UV light - diclofenac, ceftiofur, sulfamethoxazole and sulfamonomethoxine - had amine bonds (RNH_2, R_2NH, R_3N) in their chemical structures. However, the *k* values of the PPCPs with amine bonds were all quite different, indicating that the amine bond is not the main site attacked by UV energy during PPCP photodegradation.

Alternatively, as mentioned above, the $k_{UV/Lamp2\_PW}$ values were slightly higher than the $k_{UV/Lamp1\_PW}$ values, indicating that the average $k_{UV/Lamp2\_PW}$ value (3.1 E-03/sec) for the 30 PPCPs was 1.4 times higher for UV/lamp2 than for UV/lamp1. This in turn indicates that, in addition to direct photodegradation by UV irradiation, OH radicals formed by the photodegradation of water under a wavelength of 185 nm contributed to the degradation of PPCPs during UV/Lamp2 treatment. Under irradiation with UV emitted at a wavelength of less than 200 nm, water is photolyzed into hydrogen atoms and hydroxyl radicals, and other oxidative species such as hydrogen peroxide are also probably formed simultaneously (Heit *et al*., 1998). During the photocatalysis degradation of water with vacuum ultraviolet (VUV), hydroxyl radicals and other oxidants are formed according to the following reactions:

$$H_2O + VUV \rightarrow H\cdot + OH\cdot$$
$$OH\cdot + OH\cdot \rightarrow H_2O_2$$
$$H\cdot + O_2 \rightarrow HO_2\cdot$$

Han *et al* (2004) investigated the photocatalytic decomposition and mineralization of 4-chlorophenol, hydroquinone and 4-nitrophenol in an aqueous solution using two kinds of low-pressure mercury lamps: a UV lamp emitting light at 254 nm and a VUV lamp emitting light at both 254 and 185 nm. In the study, they found that, due to the contribution of the abundant and powerful oxidant, the OH radical, VUV irradiation performed the most efficient photocatalysis degradation of the organic materials. In this study, UV/Lamp2 also showed a better PPCPs photocatalysis degradation than UV/Lamp1. Therefore, the applicability of

UV/Lamp2 is expected in the area of water treatment.

3.3.3 Photodegradability of PPCPs in TW with UV/Lamp1

Fig. 3-7 compares UV/Lamp1 photodegradation results obtained in experiments using tested waters spiked with 30 PPCPs into pure water (PW) and biologically treated water (TW). Antineoplastic agent cyclophosphamide was one of the PPCPs highly resistant for UV and, it was expected that only 5% of its initial concentration (64 μg/L) would be degraded during UV/Lamp1 treatment for 10 min. While, 88% photodegradation was expected from antibiotic sulfamonomethoxine, indicating that sulfamonomethoxine will be degraded very easily with UV/Lamp1. Thus, considerably different photodegradation rates for the 30 PPCPs were observed for UV/Lamp1 treatment.

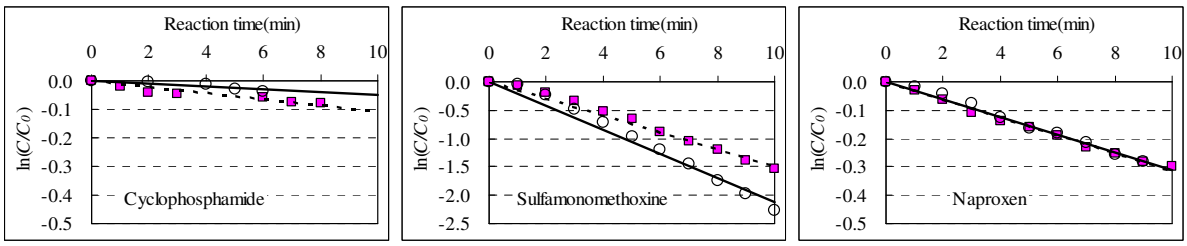


Fig. 3-7 Concentration decrease for cyclophosphamide, sulfamonomethoxine and naproxen with UV/Lamp1
(circle - PPCP in TW; rectangle - PPCP in PW)

Table 3-8 shows first-order rate constants for the reaction of each PPCP with UV obtained using equation (2) and Fig. 3-7. $k_{UV/Lamp1\_PW}$ and $k_{UV/Lamp1\_TW}$ values for the 30 PPCPs ranged from 6.0 E-05/sec (theophylline) to 2.4 E-02/sec (ketoprofen) and 1.8 E-04/sec (cyclophosphamide) to 2.2 E-02/sec (ketoprofen), respectively. Here, $k_{UV/Lamp1\_TW}$ indicates first-order rate constant obtained in UV/Lamp1 treatment experiments using TW spiked with the 30 PPCPs. In this study, the difference between photodegradability in PW and in TW for a PPCP was evaluated using a ratio of $k_{UV/Lamp1\_PW}$ value to $k_{UV/Lamp1\_TW}$ value for each PPCP. It was defined that the photodegradability of a PPCP was not affected by other constituents in TW if $k_{UV/Lamp1\_PW}/k_{UV/Lamp1\_TW}$ ratio ranges from 0.8 to 1.2 (for naproxen in Fig. 3-7) and,

however, the photodegradability was rather affected if $k_{UV/Lamp1\_PW}/k_{UV/Lamp1\_TW}$ ratio corresponds to over 1.2 (for cyclophosphamide in Fig. 3-7) or below 0.8 (for sulfamonomethoxine in Fig. 3-7). The results are shown in Table 3-8.

$k_{UV/Lamp1\_PW}/k_{UV/Lamp1\_TW}$ ratios of 11 PPCPs such as ketoprofen, diclofenac, antipyrine, isopropylantipyrine, naproxen and indomethacin (analgesics), sulfamethoxazole (antibiotic), disopyramide, metoprolol and propranolol (antiarrhythmic agents), and crotamiton (antiitch drug) ranged from 0.8 to 1.2. This means that photodegradation rates of the 11 PPCPs will be less affected by UV energy consumption of other DOM (dissolved organic matter) in water. Moreover, the 9 PPCPs except indomethacin and naproxen showed quantum yields in the range of 0.0148 (isopropylantipyrine) to 0.1131 (diclofenac), which are higher than those of other PPCPs (Table 3-6). Therefore, it was expected that UV energy absorbed involved very effectively in degradation of the PPCPs.

Photodegradability of 11 PPCPs including oxytetracycline, chlorotetracycline, tetracycline, sulfamonomethoxine, sulfadimethoxine and sulfadimidine (antibiotics), fenoprofen and acetaminophen (analgesics), anticonvulsant carbamazepine, NMDA receptor antagonist ifenprodil and bronchodilator clenbuterol reduced significantly when they were spiked into TW. This may be because UV energy absorbed to the 11 PPCPs decreased due to the consumption of UV energy by DOM in TW. Molar extinction coefficients of the 11 PPCPs ranged widely from 800 /M/cm to 19,799 /M/cm and, contrarily, quantum yields calculated for the 9 PPCPs except fenoprofen and sulfamonomethoxine were low to 0.0015 (carbamazepine) - 0.0098 (tetracycline). Therefore, the interference of UV energy absorption of the PPCPs by other organic materials in water such as DOM might mainly cause low photodegradation of the PPCPs during UV treatment.

Contrarily, ceftiofur and clarithromycin (antibiotics), mefenamic acid and ethenzamide (analgesics), carbadox intermediate 2-QCA, insect repellent DEET, antineoplastic agent cyclophosphamide and bronchodilator theophylline showed higher photodegradability when they were present in TW. This can be explained by an indirect production of radicals from reaction of UV with DOM in water. Doll *et al* (2003) have reported that NOM (natural organic matter) from Lake Hohloh in the southwest of Germany enhanced the photochemical degradation of carbamazepine, indicating that NOM can act as a precursor of reactive species.

Also, in sewage water, the degradation of these compounds could either decrease due to the competition with DOM for UV energy, or increase due to an indirect production of OH radicals from reaction of UV energy with DOM (Pereira *et al*., 2007). In this study, it can be also expected that reactive species were formed from organic materials in TW during UV treatment and promoted the degradation rates of the 8 PPCPs.

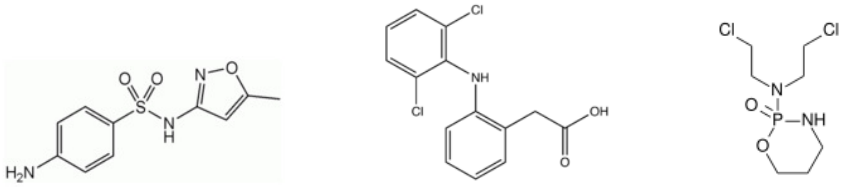
Table 3-8 First-order rate constants for the reaction of each PPCP with UV/Lamp1

PPCPs	$k_{UV/Lamp1\_PW}$(/sec)	R2	$k_{UV/Lamp1\_TW}$(/sec)	R2	$k_{UV/Lamp1\_PW}$ / $k_{UV/Lamp1\_TW}$ ratio
Ketoprofen	2.4E-02	0.9933	2.2E-02	0.9867	0.8 ~ 1.2
Diclofenac	8.4E-03	0.9812	7.2E-03	0.9866	
Sulfamethoxazole	3.6E-03	0.9759	3.1E-03	0.9837	
Antipyrine	3.2E-03	0.9865	2.7E-03	0.9933	
Isopropylantipyrine	2.3E-03	0.9818	2.0E-03	0.9925	
Disopyramide	2.2E-03	0.9908	1.9E-03	0.9940	
Naproxen	5.2E-04	0.9926	5.2E-04	0.9877	
Indomethacin	5.1E-04	0.9553	4.6E-04	0.9528	
Propranolol	4.6E-04	0.9708	3.9E-04	0.8200	
Crotamiton	3.1E-04	0.9642	3.0E-04	0.9740	
Metoprolol	2.3E-04	0.9259	2.2E-04	0.9519	
Sulfamonomethoxine	3.5E-03	0.9753	2.5E-03	0.9832	> 1.2
Fenoprofen	2.3E-03	0.9982	1.7E-03	0.9953	
Oxytetracyline	1.6E-03	0.9644	7.2E-04	0.9069	
Chlorotetracycline	1.5E-03	0.9206	1.0E-03	0.8198	
Sulfadimethoxine	1.4E-03	0.9936	1.1E-03	0.9867	
Ifenprodil	1.0E-03	0.9871	5.7E-04	0.9963	
Tetracycline	8.6E-04	0.9741	5.9E-04	0.9008	
Sulfadimidine	8.1E-04	0.9937	5.6E-04	0.9797	
Clenbuterol	7.1E-04	0.9812	3.7E-04	0.8717	
Acetaminophen	3.9E-04	0.9939	3.1E-04	0.9709	
Carbamazepine	2.0E-04	0.9750	1.6E-04	0.7787	
Ceftiofur	6.6E-03	0.9598	8.5E-03	0.9579	< 0.8
Mefenamic acid	1.9E-04	0.9548	2.8E-04	0.9659	
Clarithromycin	1.8E-04	0.9894	2.3E-04	0.8455	
2-QCA	1.2E-04	0.9922	1.6E-04	0.9975	
Ethenzamide	9.5E-05	0.8644	4.2E-04	0.9193	
DEET	9.2E-05	0.9147	3.3E-04	0.7873	
Cyclophosphamide	8.3E-05	0.8623	1.8E-04	0.7446	
Theophylline	6.0E-05	0.7934	2.0E-04	1.0000	

3.3.4 Discussion of PPCPs photodegradation based on chemical structure

Photodegradation characteristics of sulfamethoxazole, diclofenac and cyclophosphamide with UV/Lamp1 were dicussed based on their chemical structures presented in Fig. 3-8.

Sulfamethoxazole degraded the most rapidly with UV/Lamp1 from among nine antibiotics investigated in this study. Analgesics diclofenac belonging to the group of nonsteroidal anti-inflammatory drugs (NSAIDs) has frequently been detected in aquatic environments in many conturies including Switzerland and Japan (Buser *et al*., 1998; Okuda *et al*., 2007). Among the 30 PPCPs, photodegradation of cyclophosphamide was highly resistant against UV treatment. In the aquatic environment, the presence of cyclophosphamide used to treat various types of cancer has not been reported, however, it can be discharged into an aquatic environment from hospitals where cyclophosphamide is likely to be used very often.



<Sulfamethoxazole> <Diclofenac> <Cyclophosphamide>

Fig. 3-8 Chemical structures of sulfamethoxazole, diclofenac and cyclophosphamide

3.3.4.1 Photodegradation of sulfamethoxazole

It has been known that sulfamethoxazole is a derivative of sulfanilamide (sulfamine) and has a strong antibacterial power and low side effects in human. In addition to sulfamethoxazole, three kinds of sulfanilamide derivatives such as sulfamonomethoxine, sulfadimethoxine and sulfadimidine were included in a list of 30 PPCPs investigated in this study with -SO_2- group in their chemical structures. In particular, for antibiotics derived from sulfanilamide, only compounds with free amino groups in their chemical structures have antibacterial activity (Tanaka *et al*., 1992). In this study, which bond should be broken to invalidate their antibacterial activities during UV treatment was not investigated. However, some possible photodegradation reactions for UV treatment were discussed. When compounds with -SO_2- group are photolyzed with UV, -SO_2- groups can be separated from the compound by the breakage of bonds between -SO_2- and its side atoms. These compounds can degrade through the breakage of C-S bonds during UV photodegradation (Sugimori, 1998). Besides these two types of photodegradations, a breakage reaction of the N-H bond that all sulfanilamide derivatives have is expected.

Among four kinds of sulfanilamide derivatives, sulfamethoxazole and sulfamonomethoxine showed relatively high $k_{UV/Lamp1\_PW}$ values of 3.6 E-03/sec and 3.5 E-03/sec, respectively. Conversely, $k_{UV/Lamp1\_PW}$ values of sulfadimethoxine (1.4 E-03/sec) and sulfadimidine (8.1 E-04/sec) were low compared to sulfamethoxazole and sulfamonomethoxine. Generally, the photodegradation rates of compounds with similar chemical structures will also be similar because the same bond should be broken. However, photodegradation rates for four PPCPs derived from sulfanilamide were quite different, even though their chemical structures are very similar. This can be explained with the fact that other PPCPs which are simultaneously present in the tested water would affect photodegradations that would be similar, otherwise.

3.3.4.2 Photodegradation of diclofenac

NSAIDs diclofenac is a derivative of phenylacetic acid which is an organic compound containing a phenyl moiety and an acetic acid moiety. Diclofenac is also a carboxylic acid like most of the NSAIDs including ketoprofen, mefenamic acid, fenoprofen, naproxen and indomethacin (Nogrady and Weaver, 2005). Buser *et al*. (1998) have observed a significant elimination of diclofenac in the water of a natural lake in Switzerland, indicating that diclofenac degrades very easily during UV treatment.

Degradation of aliphatic amines (RNH_2, R_2NH, R_3N) by photo energy formed from short wavelengths is sometimes caused by the break of their C-N bonds, but most aliphatic amines mainly degrade by a breakage reaction of the N-H bond (Sugimori, 1998). Aromatic amines can also degrade in the same way and, therefore, diclofenac consisting of amino bonds of two benzene rings with Cl and RCOOH group, respectively, can degrade with UV photodegradation. On the other hand, it has been known that carboxylic acids would mainly degrade through the breakage of R-COOH bonds when they are photolyzed, which is similar to the photodegradation of aldehydes and ketones. However, the photoreactivity of derivatives from carboxylic acid is generally lower than that of aldehydes or ketones. For halogenated compounds, it has been known that the breakage of C-halogen atom bond could be caused by photodegradation (Sugimori, 1998). As a consequence, it is expected that degradation of diclofenac containing an amino group, carboxylic group and two chlorides in its chemical

structure as shown in Fig. 3-8 would result from the dehydrogenation of N-H bond, separation of -COOH from diclofenac molecular, and dechlorination of Cl from benzene ring.

Vogna *et al*. (2004b) investigated the photodegradation of diclofenac under UV treatment with/without H_2O_2. They found that UV irradiation of diclofenac increased the concentration of chloride in tested water. This means that when diclofenac is photolyzed with UV, the separation of Cl from benzene rings occurs. Consequently, it can be said that dechlorination is one of diclofenac degradation procedures in its UV photodegradation.

Among PPCPs investigated in this study, five kinds of PPCPs such as diclofenac, chlorotetracycline, clenbuterol, indomethacin and cyclophosphamide have C-halogen atom bonds in their chemical structures and for four PPCPs excluding cyclophosphamide, the halogen atom (Cl) is combined to benzene rings directly. Diclofenac was photolyzed rapidly ($k_{UV/Lamp1\_PW}$ = 8.4 E-03/sec) during UV treatment, while the other PPCPs exhibited very low $k_{UV/Lamp1\_PW}$ values (8.3 E-05/sec - 1.5 E-03/sec) compared to that of diclofenac. However, if the separation reaction of chloride from benzene ring occurs rapidly during UV photodegradation, chlorotetracycline, clenbuterol and indomethacin would be also degraded rapidly, similar to diclofenac. Therefore, it is considered that when diclofenac is photolyzed with UV, the dehydrogenation of N-H bond and separation reaction of -COOH from declofenac molecular would mainly be involved in the photodegradation of diclofenac.

Actually, among seven PPCPs classified as easily-degrading PPCPs in UV/Lamp1 treatment experiment, four PPCPs (diclofenac, ceftiofur, sulfamethoxazole, sulfamonomethoxine) have N-H bonds in their moleculars, indicating that the N-H bond may be broken easily by UV photodegradation. Moreover, three PPCPs (ketoprofen, diclofenac and ceftiofur) out of eight carboxylic acids such as 2-QCA, ceftiofur, diclofenac, fenoprofen, indomethacin, ketoprofen, mefenamic acid and naproxen included in a list of 30 PPCPs investigated in this study were classified as easily-degrading PPCPs. Consequently, it can be concluded that the dehydrogenation of N-H bond and breakage reaction of R-COOH can be considered as possible main reactions during diclofenac photodegradation with UV.

3.3.4.3 Photodegradation of cyclophosphamide

Amides ($RCONR_2$) are generally photolyzed by the breakage of R-CO or CO-N bond.

However, amides have the most stable of the carbonyl couplings due to their high resonance stabilization between the N-C and C-O bonds. DEET (*N,N*-diethyl-m-toluamide) which is the most common active ingredient in insect repellents and cyclophosphamide used to treat various types of cancer and some autoimmune disorders belong to amides. Among ten kinds of amides investigated in this study, six amides including DEET and cyclophosphamide were classified as slowly-degrading PPCPs in UV/Lamp1 treatment experiment (See Table 3-7), indicating that it would be difficult to degrade PPCPs with amide bond using UV photodegradation. In particular, cyclophosphamide showed the lowest photodegradation rate among PPCPs with amide bonds in their chemical structures. Moreover, cyclophosphamide has amide bonds and amine bonds in its chemical structure as shown in Fig. 3-8.

3.3.5 The effect of H_2O_2 addition on the PPCPs degradation during UV treatment

During UV/Lamp1 treatment, the effect of H_2O_2 addition on the photocatalysis degradations of 30 PPCPs was investigated. Tested water was prepared by spiking the 30 PPCPs into pure water (PW) and biologically treated water (TW). The tested water temperature was kept constantly at 20°C and pH of tested water was adjusted to 7. Initial H_2O_2 concentrations in tested water are adjusted to 8.2 mg/L and 6.1 mg/L for experiments using PW and TW, respectively. Concentration decreases of individual PPCPs obtained in UV/Lamp1/H_2O_2 experiments were presented in Fig. 3-9 and 3-10, which show that logarithmic relative residual concentrations of all the PPCPs decreased linearly with time. For UV/Lamp1/H_2O_2, concentration decrease of an organic material with time is expressed as follows (Lopez *et al*., 2003):

$$Log\frac{C}{C_0} = -(2.3LI_{O,254}\phi_{254}\varepsilon_{254} + k_R[OH\cdot])t = -k'_{UV/lamp1/H2O2}t \qquad (10)$$

where k_R and $k'_{UV/Lamp1/H2O2}$ represent second order rate constant and pseudo first-order rate constant for UV/H_2O_2 treatment, respectively. Pseudo first-order rate constants of the 30 PPCPs for UV/Lamp1/H_2O_2 treatments using PW ($k'_{UV/Lamp1/H2O2\_PW}$) and TW ($k'_{UV/Lamp1/H2O2\_TW}$) were calculated from equation (10). Table 3-9 shows pseudo first-order rate constants of the 30 PPCPs for UV/Lamp1/H_2O_2 treatments.

3.3.5.1 The effect of H_2O_2 addtion during UV/Lamp1 experiment using PW

Higher photocatalysis degradations of the 30 PPCPs were observed when H_2O_2 was added during UV treatment, due to the production of the highly reactive OH radicals by H_2O_2 photodegradation. $k_{UV/Lamp1\_PW}$ values ranged from 2.2 E-02/sec (ketoprofen) to 6.0 E-05/sec (theophylline) (Table 3-9), while $k'_{UV/Lamp1/H2O2\_PW}$ values from 2.5 E-02/sec (ketoprofen) to 9.8 E-04/sec (cyclophosphamide).

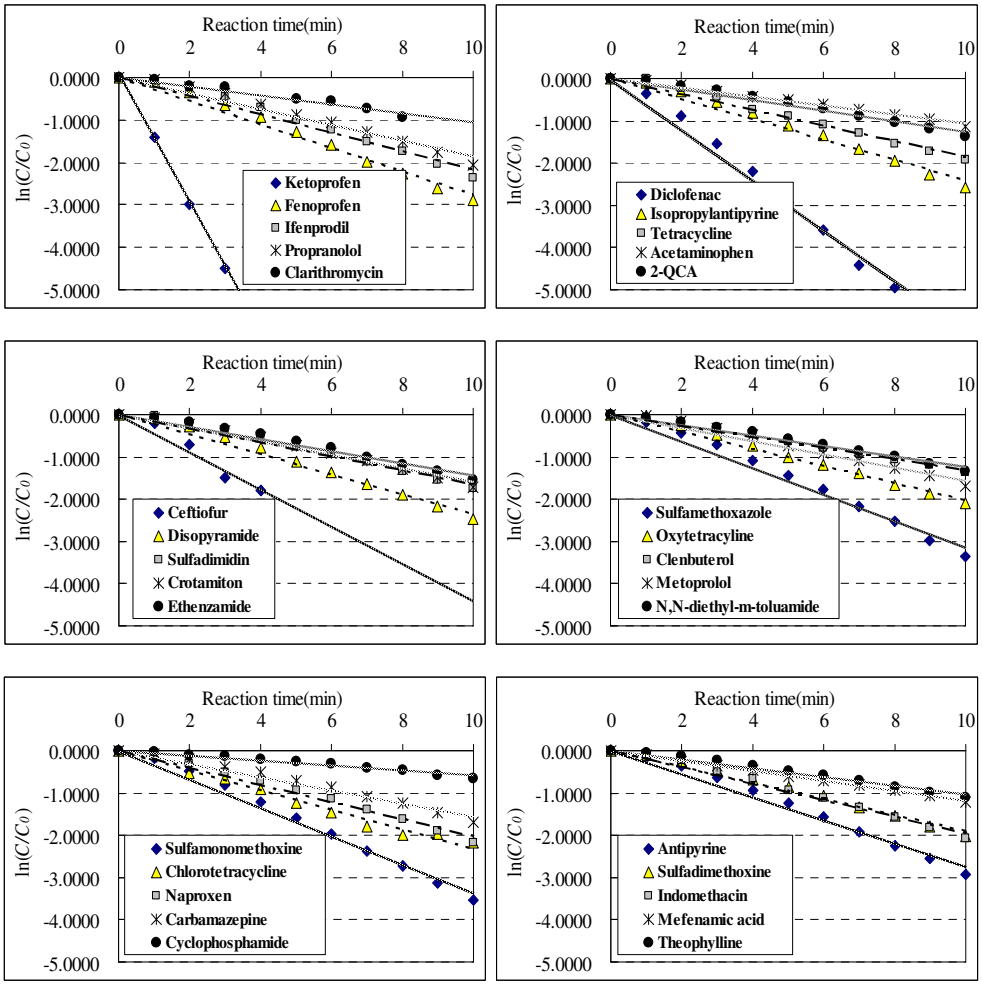


Fig. 3-9 Relative residual concentrations for the 30 PPCPs spiked into PW versus time during UV/Lamp1/H_2O_2 treatment

An average value of all the PPCPs was 4.2 E-03/sec, which is 1.9 times higher than that (2.2 E-02/sec) of $k_{UV/Lamp1\_PW}$ values obtained in experiment using only UV/Lamp1. In particular, it was observed that H_2O_2 addition was more effective in the photocatalysis degradation of PPCPs with low k values in UV treatment experiment. For example, k values of ethenzamide ($k_{UV/Lamp1\_PW}$: 9.5 E-05/sec), DEET ($k_{UV/Lamp1\_PW}$: 9.2 E-05/sec), theophylline

($k_{UV/Lamp1\_PW}$: 6.0 E-05/sec) and cyclophosphamide ($k_{UV/Lamp1\_PW}$: 8.3 E-05/sec) increased by a factor of 12 to 29 when 8.2 mg/L H_2O_2 was added during UV treatment. In addition, $k'_{UV/Lamp1/H2O2\_PW}$ values of carbamazepine, metoprolol, 2-QCA, clarithromycin and mefenamic acid that exhibited comparatively low $k_{UV/Lamp1\_PW}$ values also increased significantly more than 10 times compared to their $k_{UV/Lamp1\_PW}$ values. Contrarily, PPCPs degradable easily such as ketoprofen, ceftiofur and diclofenac showed the increase of k values by a factor of 1 to 3, and this result was compared with the PPCPs described above. Vogna *et al*. (2004b) have reported that diclofenac degradation was mainly caused by direct UV photodegradation during UV/H_2O_2 treatment, due to its very fast photodegradability.

3.3.5.2 The effect of H_2O_2 addtion during UV/Lamp1 experiment using TW

For experiments using 30 PPCPs in TW, $k_{UV/Lamp1\_TW}$ values ranged from 1.6 E-04/sec (2-QCA) to 2.4 E-02/sec (ketoprofen) as shown in Table 3-8 and an average value was 2.1 E-03/sec. However, $k'_{UV/Lamp1/H2O2\_TW}$ values were in the range of 5.2 E-04/sec (cyclophosphamide) to 2.0 E-02/sec (ketoprofen) (average value : 2.8 E-03/sec), showing that the increase of k values was not so significant compared to experiments using PPCPs in PW.

For experiments using TW, k values in UV/Lamp1/H_2O_2 treatment increased by a factor of 1 to 9 and, this is compared with the increase of 1 to 29 times in k values for experiments using PW. This may be due to the consumption of OH radicals by DOM and/or OH radicals scavengers such as HCO_3^- and CO_3^{2-} in tested water prepared with biologically treated water. Nevertheless, k values of tetracycline, indomethacin, crotamiton, carbamazepine, mefenamic acid, metoprolol and 2-QCA increased more than 5 times by H_2O_2 addition, indicating that photocatalysis degradation rates of the PPCPs will be less affected by DOM and/or scavengers of OH radicals during UV/Lamp1/H_2O_2 treatment compared to other PPCPs. Overall, average k value for all the PPCPs investigated increased by a factor of 1.3 by H_2O_2 addition during UV/Lamp1 treatment. Therefore, the effectiveness of H_2O_2 addition for PPCPs removal during UV treatment can be expected in real wastewater treatment process.

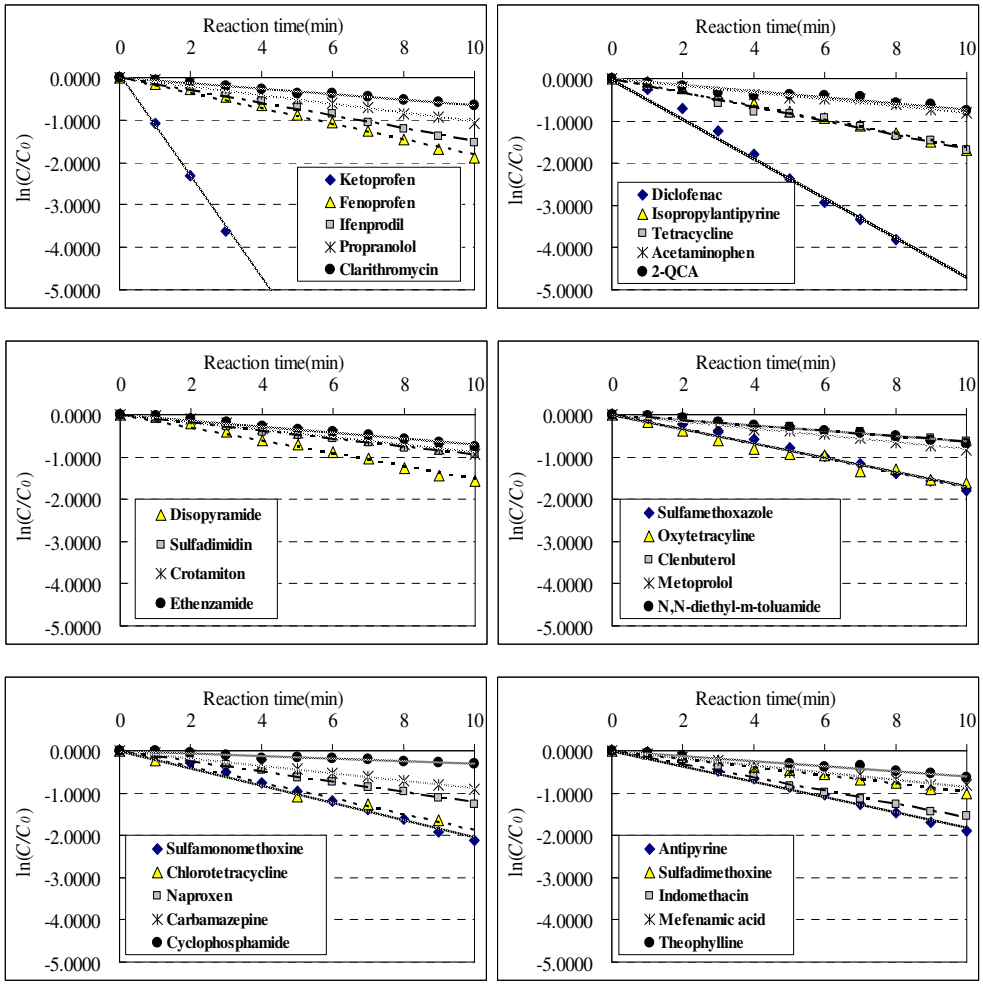


Fig. 3-10 Relative residual concentrations for the 30 PPCPs spiked into TW versus time during UV/Lamp1/H_2O_2 treatment

Table 3-9 Pseudo first-order rate constants of the 30 PPCPs for UV/Lamp1/H_2O_2 treatments

PPCPs	Use	$k'_{UV/Lamp1/H2O2\_PW}$(/sec)	$k'_{UV/Lamp1/H2O2\_TW}$(/sec)
Ketoprofen	Analgesic	2.5E-02	2.0E-02
Diclofenac		1.0E-02	7.8E-03
Fenoprofen		4.6E-03	3.0E-03
Antipyrine		4.6E-03	3.0E-03
Isopropylantipyrine		4.0E-03	2.7E-03
Naproxen		3.4E-03	2.0E-03
Indomethacin		3.2E-03	2.6E-03
Ethenzamide		2.4E-03	1.2E-03
Mefenamic acid		2.0E-03	1.4E-03
Acetaminophen		1.8E-03	1.3E-03
Disopyramide	Antiarrhythmic agents	3.9E-03	2.5E-03
Propranolol		3.1E-03	1.7E-03
Metoprolol		2.6E-03	1.3E-03
Ceftiofur	Antibiotics	7.4E-03	No data
Sulfamonomethoxine		5.6E-03	3.4E-03
Sulfamethoxazole		5.2E-03	2.8E-03
Chlorotetracycline		3.9E-03	3.1E-03
Oxytetracyline		3.4E-03	2.8E-03
Sulfadimethoxine		3.2E-03	1.6E-03
Tetracycline		3.1E-03	2.8E-03
Sulfadimizine		2.7E-03	1.6E-03
Clarithromycin		1.7E-03	1.1E-03
Carbamazepine	Anticonvulsant	2.6E-03	1.5E-03
Crotamiton	Anti-itch drug	2.7E-03	1.5E-03
Cyclophosphamide	Antineoplastic agents	9.8E-04	5.2E-04
Clenbuterol	Bronchodilator	2.2E-03	1.1E-03
Theophyline		1.7E-03	1.0E-03
2-QCA	Carbadox intermediate	2.1E-03	1.2E-03
DEET	Insect repellents	2.1E-03	1.1E-03
Ifenprodil	NMDA receptor antagonist	3.6E-03	2.5E-03

3.3.6 Estimation of UV dose for the effective PPCPs degradation

Table 3-10 shows UV/Lamp1 irradiation time and dose required for 90% degradation of each PPCP. These were calculated from *k* values obtained in UV/Lamp1 and UV/Lamp1/H_2O_2 treatment experiments using TW spiked with 30 PPCPs. UV/Lamp1 intensity of 0.384 mW/cm^2 was used for calculating UV dose introduced to tested water during each treatment. Firstly, for UV/Lamp1 alone treatment, UV irradiation time required for degrading each PPCP by 90% of initial concentration ranged from 1.6 min (ketoprofen) to 245.0 min (2-QCA) as shown in Table 3-10. It can be also known that more than 1 hour will be necessary for 90% degradation of 18 PPCPs including tetracycline, ifenprodil and sulfadimizine. For UV dose, 38 mJ/cm^2 to 5,644 mJ/cm^2 will be required for 90% degradation of the 30 PPCPs during UV/Lamp1 treatment. Considering that UV dose required for typical disinfection in

wastewater treatment plant is in a range of 40 mJ/cm^2 to 140 mJ/cm^2, it can be said that considerable UV dose will be needed for degrading PPCPs effectively. Moreover, only 3 PPCPs such as ketoprofen, ceftiofur and diclofenac can be degraded by more than 90% by only UV/Lamp1 treatment when UV dose of 140 mJ/cm^2 was introduced. This also tells that most of PPCPs will not be removed sufficiently in UV disinfection process in wastewater treatment plant known to a main source for PPCPs discharge into aquatic environment.

Table 3-10 UV irradiation time and dose required for the 90% degradation of each PPCP for UV/Lamp1

PPCPs	UV irradiation time (min) for UV	UV dose (mJ/cm^2) for UV	UV irradiation time (min) for UV/H_2O_2	UV dose (mJ/cm^2) for UV/H_2O_2
Ketoprofen	1.6	38	1.9	45
Ceftiofur	4.5	104	No data	No data
Diclofenac	5.3	123	4.9	113
Sulfamethoxazole	12.4	285	13.6	314
Antipyrine	14.2	328	12.7	293
Sulfamonomethoxine	15.5	358	11.3	261
Isopropylantipyrine	19.4	447	14.3	329
Disopyramide	20.1	463	15.1	348
Fenoprofen	22.7	522	12.7	292
Sulfadimethoxine	34.6	797	23.9	550
Chlorotetracycline	36.7	846	12.3	284
Oxytetracyline	50.9	1,174	13.5	310
Tetracycline	64.7	1,490	13.8	317
Ifenprodil	67.7	1,560	15.6	358
Sulfadimizine	68.7	1,584	24.3	561
Naproxen	73.3	1,690	18.9	434
Indomethacin	82.8	1,908	14.6	337
Ethenzamide	90.7	2,089	32.0	738
Propranolol	98.8	2,277	22.4	515
Clenbuterol	102.8	2,368	36.4	839
DEET	116.3	2,679	36.0	829
Acetaminophen	123.8	2,852	28.6	660
Crotamiton	126.5	2,915	26.1	602
Mefenamic acid	136.2	3,139	27.1	624
Clarithromycin	165.7	3,817	35.0	806
Metoprolol	171.8	3,959	28.5	657
Theophyline	195.1	4,496	38.4	884
Cyclophosphamide	225.7	5,201	73.6	1,695
Carbamazepine	235.0	5,413	26.3	605
2-QCA	245.0	5,644	31.5	727

Unlike only UV/Lamp1 treatment, for UV/Lamp1/H_2O_2 treatment, all the PPCPs except 7 PPCPs such as ethenzamide, clenbuterol, DEET, clarithromycin, theophylline, cyclophosphamide and 2-QCA were degraded by more than 90% by UV irradiation for 30 min (UV dose : 691 mJ/cm^2). It was also predicted that UV dose of 890 mJ/cm^2 will be sufficient for 90% degradation of even the 6 PPCPs except cyclophosphamide. Antineoplastic agent cyclophosphamide turned out as the most resistant PPCP among 30 PPCPs because considerable UV dose of 1,695 mJ/cm^2 was required for its 90% degradation in spite of H_2O_2 addition during UV/Lamp1 treatment. As a consequence, it can be concluded that much more UV dose than that necessary for typical disinfection will be needed to degrade more than 90% of each PPCP investigated in this study, regardless of H_2O_2 addition during UV/Lamp1 treatment.

3.4 Summary

Degradation characteristics of 30 PPCPs with UV and UV/H_2O_2 treatments were investigated using tested water prepared by spiking the 30 PPCPs simultaneously into pure water and secondary effluent. Each tested water was added into batch reactor with the effective volume of 22L and treated with UV or UV/H_2O_2. Two types of UV lamps were used; UV/Lamp1 emitting at the wavelength of 254nm, used for typical water disinfection, and UV/Lamp2 emitting at the wavelength of 254nm and 185nm. The findings from this study were as follows;

1) At the UV wavelength of 254nm, molar extinction coefficients of the 30 PPCPs ranged from 9 /M/cm (cyclophosphamide) to 19,799 /M/cm (oxytetracycline), indicating that photodegradabilites of the PPCPs will be very different according to individual PPCPs.

2) The concentration decrease of the 30 PPCPs with time followed 1st order kinetics, irrespective of UV lamps applied. Degradabilities of the 30 PPCPs were, therefore, classified and compared by 1st order rate constants. For UV/Lamp1 treatment, 6 PPCPs including ketoprofen and diclofenac and 14 PPCPs including theophylline, cyclophosphamide and DEET were classified as easily-degrading PPCPs (k≥2.6E-03 /sec) and slowly-degrading PPCPs (k<6.4E-04 /sec), respectively. On the other hand, 10 PPCPs and 6 PPCPs belonged to easily-degrading PPCPs and slowly-degrading PPCPs, respectively, for UV/Lamp2 treatment.

This result indicates that UV/Lamp2 was more effective for degrading PPCPs than UV/Lamp1. This might be due to the contribution of OH radicals formed during UV photodegradation of H_2O molecular by the wavelength of 185nm to the PPCPs degradations. Consequently, the applicability of UV/Lamp2 for degrading PPCPs in water was implied.

3) UV doses of 38 mJ/cm^2 to 5,644 mJ/cm^2 were needed for 90% degradation of the 30 PPCPs in secondary effluent. These UV doses are much higher than those required for typical disinfection (40 mJ/cm^2 ~ 140 mJ/cm^2). It can be known that considerable UV dose will be required for the effective removal of PPCPs in secondary effluent.

4) When the 30 PPCPs spiked into secondary effluent were treated with UV/Lamp1/H_2O_2, their degradation rates increased by a factor of about 1.3 comparing with those for UV/Lamp1. Especially, H_2O_2 addition improved significantly degradation rates of the PPCPs such as DEET and theophylline, which showed low photodegradation rates for UV/Lamp1 treatment. Considering that UV alone treatment is not so effective for the photodegradation of a lot of PPCPs, the combination of H_2O_2 with UV treatment will be a promising alternative treatment option for PPCPs removal.

5) All the PPCPs except 7 PPCPs including cyclophosphamide and 2-QCA (727 mJ/cm^2 ~ 1,695 mJ/cm^2) were degraded by more than 90% under UV dose of 691 mJ/cm^2 (contact time : 30 min) during UV/lamp1/H_2O_2 treatment. As a consequence, it is considered that UV/H_2O_2 treatment can contribute to the reduction of energy consumption for the effective PPCPs removal as well as the improvement of the photodegradation rates for the investigated PPCPs.

3.5 References

Andreozzi R., Raffaele M., Nicklas R., 2003, Pharmaceuticals in STP effluents and their solar photodegradation in aquatic environment, *Chemosphere* 50, 1319-1330

Baxendale J.H., Wilson J.A., 1957, The photolysis of hydrogen peroxide at high light intensity, *Trans. Faraday Soc.* 53, 344

Beltran F.J., Overjero G., Acedo B., 1993, Oxidation of atrazine in water by ultraviolet radiation combined with hydrogen peroxide, *Water Res.* 27, 1013-1021

Blatchley III E.R., Shen C., Scheible O.K., Robinson J.P., Ragheb K., Bergstrom D.E., Rokjer

D., 2007, Validation of large-scale, monochromatic UV disinfection systems for drinking water using dyed microspheres, *Water Res.*, doi:10.1016/j.watres.2007.08.019

Buser H.R., Poiger T., Muller M.D., 1998, Occurrence and fate of the pharmaceutical drug diclofenac in surface waters: rapid photodegradation in a lake, *Environ Sci Technol.* 32, 3449-3456

Cahill J.D., Furlong E.T., Burkhardt M.R., Kolpin D., Anderson LG, 2004, Determination of pharmaceutical compounds in surface-and ground-water samples by solid-phase extraction and high-performance liquid chromatography-electrospray ionization mass spectrometry, *J Chromatogr A* 1041, 171-180

Canonica S., Meunier L., von Gunten U., 2008, Phototransformation of selected pharmaceuticals during UV treatment of drinking water, *Water Res.* 42, 121-128

Doll T.E., Frimmel F.H., 2003, Fate of pharmaceuticals - photodegradation by simulated solar UV-light. *Chemosphere* 52, 1757-1769

Fukunaga A., Nagao R., Yamashita N., Tanaka H., 2007, A risk assessment approach using reliability analysis for pharmaceuticals in discharge from sewage treatment plants, 5th IWA Specialised Conference on Assessment and Control of Micropollutants / Hazardous Substances in Water, DECHEMA e.V., Frankfurt/Main, Germany, 569

Glaze W.H., Lay Y.S., Kang J.W., 1995, Advanced oxidation processes, a kinetic model for the oxidation of 1,2-dibromo-3-chloropropane in water by the combination of hydrogen peroxide and UV radiation, *Ind. Eng. Chem. Res* 34, 2314-2323

Guittonneau S., Contribution a l'etude de la photooxydation de quelques micropollutants organochlores en solution aqueuse en presence de peroxide d'hydrogen. Comparison de systemes oxidants: H_2O_2/UV, O_3/UV et O_3/H_2O_2, These de docteur, University of Poitiers, France.

Han W., Zhu W., Zhang P., Zhang Y., Li L., 2004, Photocatalytic degradation of phenols in aqueous solution under irradiation of 254 and 185 nm UV light, *Catalysis today* 90, 319-324

Heberer T., 2002, Occurrence, fate and removal of pharmaceutical residues in the aquatic environment: a review of recent research data, *Toxicol Lett.* 131, 5-17

Heit G., Neuner A., Saugy P.Y., Braun A.M., 1998, Vacuum-UV (172 nm) Actinometry - The

Quantum Yield of the Photolysis of Water, *J Phys Chem A* 102, 5551-5561

Huber M.M., Ternes T.A., 2005, Oxidation of pharmaceuticals during water treatment with chlorine dioxide, *Water Res.* 39, 3607-3617

Kobayashi Y., Yasojima M., Komori Y., Suzuki Y., Tanaka H., 2006, Removal Characteristics of Human Antibiotics during Wastewater Treatment in Japan, Water Practice and Technology doi10.2166/wpt.2006.059

Lopez A., Anna B., Giuseppe M., John K., 2003, Kinetic investigation on UV and UV/H_2O_2 degradations of pharmaceutical intermediates in aqueous solution, *J Photochem Photobiol A: Chem.* 156, 121-126

Mascolo G., Ciannarella R., Balest L., Lopez A., 2007, Effectiveness of UV-based advanced oxidation processes for the remediation of hydrocarbon pollution in the groundwater: A laboratory investigation, *J. Hazard. Mater.*, doi:10.1016/j.jhazmat.2007.07.120

Michael C., 2004, Mixture toxicity of the anti-inflammatory drugs diclofenac, ibuprofen, naproxen, and acetylsalicylic acid, *Ecotox Environ Safe* 59, 309-315

Nakada N., Komori K., Suzuki Y., 2007, Occurrence of 70 pharmaceuticals and personal care products in Tone River basin in Japan, *Wat Sci Tech.* 56, 133-140

Nghiem L.D., Schafer A.I., Elimelech M., 2005, Pharmaceutical Retention Mechanisms by Nanofiltration Membranes, *Environ Sci Technol.* 39, 7698-705

Nicole I., Laat J.D., Dore M., Duguet J.P., Bonnel C., 1990, Use of UV radiation in water treatment: Measurement of photonic flux by hydrogen peroxide actinometry, *Water Res.* 24, 157-168

Nogrady T., Weaver D.F., Medicinal chemistry - A molecular and biochemical approach, 3rd ed, Oxford university press, 2005, p.525

Okuda T., Kobayashi Y., Yamashita N., Tanaka H., 2007, Extraction of Pharmaceuticals from Activated Sludge and Behavior during Wastewater Treatment Process, Proceedings of Water Environment Federation/2007 Speciality Conference Series Compounds of Emerging Concern - What is on the Horizen, 160-171

Okuda T., Kobayashi Y., Nagao R., Yamashita N., Tanaka H., Tanaka S., Fuji S., Konishi C., Houwa I., 2008, Removal efficiency of 66 pharmaceuticals during wastewater treatment process in Japan, *Wat Sci Tech.* 57, 65-72

Pereira V.J., Weinberg H.S., Linden K.G., Singer P.C., 2007, UV degradation kinetics and modeling of pharmaceutical compounds in laboratory grade and surface water via direct and indirect photolysis at 254 nm, *Environ Sci Technol.* 41, 1682-1688

Plumlee M.H., Lopez-Mesas M., Heidlberger A., Ishida K.P., Reinhard M., 2008, N-nitrosodimethylamine (NDMA) removal by reverse osmosis and UV treatment and analysis via LC-MS/MS, *Water Res.* 42, 347-355

Richardson S.D., Ternes T.A., 2005, Water Analysis: Emerging Contaminants and Current Issues, *Anal.Chem.* 77, 3807-3838

Robinson P.R., Liu Q., Riddle A.M., Smith R.M., 2007, Modeling the impact of direct phototransformation on predicted environmental concentrations (PECs) of propranolol hydrochloride in UK and UV rivers, *Chemosphere* 66, 757-766

Sugimori A., Organic photochemistry, 4th ed, Tokyo:Shokabo, 1998, 162-191

Tanaka N., Nakamura S., Essentials of antibiotics, 4th ed, University of Tokyo press, 1992, 355

Thomas H., 2002, Occurrence, fate and removal of pharmaceutical residues in the aquatic environment: a review of recent research data, *Toxicology Letters* 131, 5-17

Tvrtko S., Till L., Roverta S., Amro M.H., Rebecca L.V., David E., 2004, Emerging contaminants-pesticides, PPCPs, microbial degradation products and natural substances as inhibitors of multixenobiotic defense in aquatic organisms, *Mutation Research* 552, 101-117

Vogna D., Marotta R., Andreozzi R., Napolitano A., M.d'Ischia, 2004a, Kinetic and chemical assessment of the UV/H_2O_2 treatment of antiepileptic drug carbamazepine, *Chemosphere* 54, 497-505

Vogna D., Marotta R., Napolitano A., Andreozzi R., d'Ischia M., 2004b, Advanced oxidation of the pharmaceutical drug diclofenac with UV/H_2O_2 and ozone, *Water Res.* 38, 414-422

Werner J.J., McNeill K., Arnold W.A., 2005, Environmental photodegradation of mefenamic acid, *Chemosphere* 58, 1339-1346

Ziolli R.L., Jardim W.F., 2003, Photochemical transformations of water-soluble fraction (WSF) of crude oil in marine waters A comparison between photolysis and accelerated degradation with TiO_2 using GC-MS and UVF, *J. Photochem. Photobiol.* 155, 243-252

Zwiener C., Frimmel F.H., 2003, Short-term tests with a pilot sewage plant and biofilm reactors for the biological degradation of the pharmaceutical compounds clofibric acid, ibuprofen, and diclofenac, *Science of the Total Environment* 309, 201-211

CHAPTER IV

REMOVAL CHARACTERISTICS OF PHARMACEUTICALS AND PERSONAL CARE PRODUCTS BY O_3-BASED PROCESSES

4.1 Introduction

Over the past few years, several studies have demonstrated that O_3 was very effective for the oxidation of PPCPs in water treatment process. A study showed that compared to other important micropollutants such as MTBE and atrazine, several PPCPs (bezafibrate, carbamazepine, diazepam, diclofenac, ibuprofen, iopromide, sulfamethoxazole and roxithromycin) reacted about two to three times faster with OH radicals, concluding that O_3 treatment and AOPs are promising processes for an efficient removal of PPCPs in drinking waters (Huber *et al*., 2003). A pilot study using O_3 treatment and UV-disinfection receiving effluent from a wastewater treatment plant has been reported that by applying 10-15 mgO_3/L (contact time : 18 min), all the PPCPs investigated as well as musk fragrances and estrone were no longer detected (Ternes *et al*., 2003). However, it was also found that iodinated X-ray contrast media such as diatrizoate, iopamidol, iopromide and iomeprol were still detected in appreciable concentrations.

During O_3 treatment, organic compounds are oxidized by O_3 molecules and OH radicals, which are formed as a consequence of O_3 decay. When H_2O_2 is added during O_3 treatment, the formation of OH radicals by the rapid decay of O_3 will be more accelerated (Rosenfeldt *et al*., 2006). O_3 treatment for synthetic pharmaceutical wastewater containing two human antibiotics and a veterinary antibiotic has been studied to enhance the biodegradability of the pharmaceutical (Balcioglu and Otker, 2003). The study showed that although O_3/H_2O_2

combination had no advantage for COD removal kinetics over the direct O_3 application at pH 7, the higher total removal rates of COD and UV_{254} were achieved by O_3/H_2O_2 process once adjusted optimum H_2O_2 concentration. The combined O_3/UV process has been widely studied due to a synergistic effect of several reactions such as direct UV photodegradation, direct O_3 treatment and OH radical oxidation. O_3/UV process has been employed for removing the organic contaminants in wastewater, drinking water and industrial wastewater (Lau *et al.*, 2007; Zou and Zhu, 2007).

As discussed above, O_3 treatment can be used as a very effective process for PPCPs removal in water and wastewater treatment plants. Moreover, it is thought that O_3/H_2O_2 and O_3/UV treatment could improve their removals. However, the numbers of PPCPs investigated were limited although a great variety of PPCPs may occur in the environment. Therefore, the data on the degradation characteristics of those PPCPs will be needed when wastewater treatment plants are designed for preventing the pollution of PPCPs in the aquatic environment. The objective of this study was to investigate the degradation characteristic and the removal potential of various PPCPs detected in the aquatic environment with O_3, O_3/UV and O_3/H_2O_2 treatments. Additionally, O_3 consumption needed for the effective PPCPs degradation was estimated. Structure of the research of this chapter is shown in Fig 4-1.

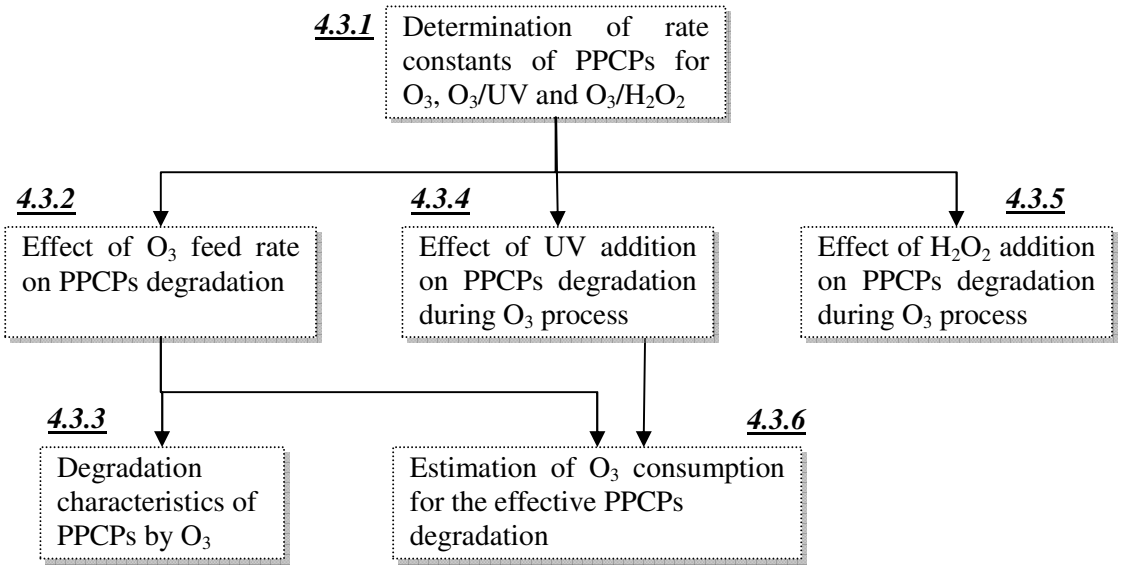


Fig. 4-1 Structure of this chapter

4.2 Methods and materials

4.2.1 PPCPs investigated and preparation of tested water

The 30 PPCPs used for this study were shown in Table 3-1. In order to examine the degradabilities of the 30 PPCPs with O_3, O_3/UV and O_3/H_2O_2, tested water was prepared by spiking the 30 PPCPs into pure water (PW) obtained from Nisso shoji Co., Ltd and biologically treated water (TW) delivered from the same sewage treatment plant mentioned in Chapter III. TOC concentration in PW was below 50 μg/L, and the pH and DOC concentration of the TW ranged from 6.8 to 7.1 and 7.1 mg/L to 12.4 mg/L, respectively. TW used for preparing tested water was filtered by GF/C filter (Whatman) before use.

The preparation procedure for tested water was the same as that for Chapter III. The initial concentrations of the 30 PPCPs in tested waters ranged from 4.7 μg/L (mefenamic acid) to 147.6 μg/L (sulfamonomethoxine).

4.2.2 Experimental setup and conditions

All the experiments were carried out using a cylindrical stainless reactor with an inside diameter of 30cm, a height of 108.7cm and an effective volume of 22L (Fig. 4-2). The temperature of tested water was maintained at 20°C by circulating hot water into a water jacket outside the reactor by a water circulator. The pH of tested waters spiked with the 30 PPCPs into PW were adjusted to 7.0 with phosphate buffer solution of 1M prepared by K_2HPO_4 and NaH_2PO_4 solution before each experiment. The pH adjustment of tested water prepared by TW was not done. All the experiments started by sparging O_3 gas continuously into the reactor filled with tested water. To confirm the potential of O_3 treatment and O_3-based AOPs for the PPCPs removal, we conducted 3 different treatment experiments such as O_3 treatment, O_3/UV and O_3/H_2O_2 treatment.

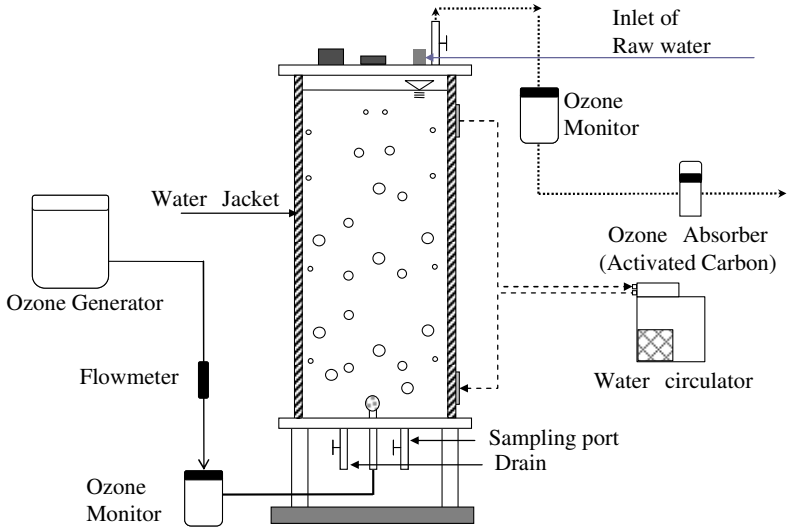


Fig. 4-2 Semi-batch reactor for O_3, O_3/H_2O_2 and O_3/UV experiments

4.2.2.1 Experimental conditions for O_3 treatment

For O_3 treatment, firstly the effect of O_3 feed rate on PPCPs degradation was investigated using tested water prepared by spiking the 30 PPCPs into PW. O_3 feed rates investigated were 0.15 mg/L/min, 0.3 mg/L/min and 0.6 mg/L/min, which were controlled by changing the concentration of O_3 gas supplying to the reactor into 3.3 mg/L, 6.6 mg/L and 13.2 mg/L, respectively. Flow rate of O_3 gas was maintained constantly to 1.0 L/min for all the experiments. Moreover, the degradation characteristic of PPCPs in real treated water by O_3 treatment was also investigated, and this experiment was performed by carrying out O_3 treatment (O_3 feed rate : 0.6 mg/L/min) for the 30 PPCPs spiked into TW.

Table 4-1 Experimental conditions

Applied treatments	O_3 feed rate (mg/L/min)	Applied UV lamp	Added H_2O_2 concentration
O_3	0.15 0.30 0.60	-	-
O_3/UV	0.15 0.30 0.60	UV 254nm	-
O_3/H_2O_2	0.60	-	2.3 mg/L 11.2 mg/L

4.2.2.2 Experimental conditions for O_3/UV treatment

An 8W low pressure mercury lamp that emits at 254 nm and of which the intensity was 0.384 mW/cm^2 was used for O_3/UV treatment. O_3/UV treatment was done for tested water prepared by TW under O_3 feed rates of 0.15 mg/L/min, 0.3 mg/L/min and 0.6 mg/L/min, respectively. The degradation of the 30 PPCPs in TW by O_3/UV was investigated at an O_3 feed rate of 0.6 mg/L/min.

4.2.2.3 Experimental conditions for O_3/H_2O_2 treatment

O_3/H_2O_2 treatment was done by adding H_2O_2 solution into tested water before O_3/H_2O_2 treatment. Initial H_2O_2 concentrations of 2.3 mg/L and 11.2 mg/L in tested water prepared by PW were used, and O_3 feed rate was 0.6 mg/L/min in both experiments.

4.2.3 Analytical method

The concentrations of the 30 PPCPs were measured simultaneously with LC/MS/MS. The measurement condition of LC/MS/MS, limit of detection (LOD) and limit of quantification (LOQ) were described in Chapter III. Dissolved O_3 concentration was measured with indigo method (Bader *et al*., 1981) measuring the absorbance at 600 nm wavelength by a spectrophotometer (UV-16000, Shimadzu). DOC (dissolved organic carbon) concentration was measured with a TOC analyzer (TOC-5000A, Shimadzu) and calculated from the difference of TOC (total organic carbon) and IC (inorganic carbon).

4.3 Results and discussion

4.3.1 Determination of rate constants of PPCPs for O_3, O_3/UV and O_3/H_2O_2 treatments

Generally, the degradation reaction of an organic compound with O_3 in semi-batch reactor is expressed as equation (1):

$$-\frac{d[C]}{dt} = k[C][O_3] \qquad (1)$$

where, [C] is the concentration of the organic compound; [O_3] is the concentration of dissolved O_3; k is the rate constant. If O_3 is not consumed by organic compounds *etc*, the increasing rate of dissolved O_3 in semi-batch reactor is expressed as equation (2):

$$\frac{d[O_3]}{dt} = k_L a([O_3]^* - [O_3]) - k_{O3}[O_3] \qquad (2)$$

where, $[O_3]^*$ is the saturated concentration of dissolved O_3, which is determined by the partial pressure and distribution coefficient of O_3 gas; k_La is the volumetric overall mass transfer coefficient (/h); k_{O3} is the rate constant of O_3 self decomposition (/h). As known in equation (2), when O_3 gas is supplied to the reactor the concentration of dissolved O_3 in the reactor increases with time. Moreover, if O_3 gas is supplied continuously, finally the concentration of dissolved O_3 will become constant ($k_L a([O_3]^* - [O_3]) = k_{O3}[O_3]$). Therefore, equation (1) can be expressed as pseudo first-order reaction such as equation (3):

$$-\frac{d[C]}{dt} = k'_{O3}[C] \qquad (3)$$

where, k'_{O3} is affected by the concentration of dissolved O_3 because k'_{O3} equals $k[O_3]$. However, for experiments using the same reactor, k'_{O3} value can be used as an indicator for the reactivity of an organic compound with O_3. By integrating equation (3), next equation is obtained.

$$\ln(C_t / C_0) = k'_{O3}t \qquad (4)$$

where, C_t is the concentration of an organic compound at the reaction time of t; C_0 is the initial concentration of the organic compound. On the other hand, for O_3/UV treatment, an organic compound is decayed by O_3 molecules, direct UV photodegradation and OH radicals formed by UV photodegradation of O_3. Therefore, the concentration decrease of the organic compound during O_3/UV treatment can be expressed as equation (5):

$$-\frac{d[C]}{dt} = (k[O_3] + LI_0\phi\varepsilon + k_R[OH\cdot])[C] \qquad (5)$$

Integrating equation (5)

$$Log(C_t / C_0) = (k[O_3] + 2.3LI_0\phi\varepsilon + k_R[OH\cdot])t = k'_{O3/UV}t \qquad (6)$$

where, L is reactor optical light path (cm); I_O is UV intensity (Einstein/sec); ϕ is quantum yield (mol/photon); ε is the molar extinction coefficient of the organic compound (/M/cm); k_R is the second order rate constant of OH radicals; [$OH\cdot$] is the concentration of OH radicals.

For O_3/H_2O_2 treatment, an organic compound will be degraded mainly by O_3 molecules and OH radicals and the concentration decrease of an organic compound can be, therefore, expressed by equation (7):

$$-\frac{d[C]}{dt} = (k[O_3] + k_R[OH\cdot])[C] \qquad (7)$$

Integrating equation (7), the following expression is obtained:

$$Log(C_t / C_0) = (k[O_3] + k_R[OH\cdot])t = k'_{O3/H2O2}t \qquad (8)$$

On the other hand, if ln (C_t/C_0) of an organic compound decreases linearly with time, the degradation reaction of the compound by each treatment can be regarded as pseudo first-order reaction. This time, pseudo first-order rate constants (k'_{O3}, $k'_{O3/UV}$, $k'_{O3/H2O2}$) for O_3, O_3/UV and O_3/H_2O_2 can be obtained from the slopes of each straight line.

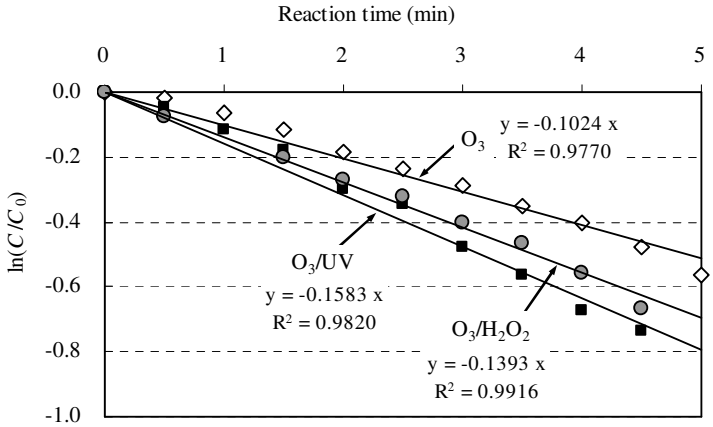


Fig. 4-3 Concentration decrease of DEET with time during O_3, O_3/UV and O_3/H_2O_2 treatments

Fig. 4-3 shows the concentration decrease of DEET for the reaction time of 5 min during O_3, O_3/UV and O_3/H_2O_2 treatments, which were conducted using tested water prepared by spiking 30 PPCPs simultaneously into PW. O_3 was supplied to the reactor at an O_3 feed rate of 0.6 mg/L/min in all the experiments. O_3/H_2O_2 treatment was done by supplying O_3 to tested water with the initial concentration of H_2O_2 of 11.2 mg/L. The concentration of DEET decreased linearly with time in all the experiments and it can be, therefore, said that the degradation reactions of DEET with O_3, O_3/UV and O_3/H_2O_2 follow pseudo first-order reaction. As shown in Fig. 4-3, k'_{O3} (pseudo first-order rate constant for O_3) of DEET was 0.1024 /min (1.7 E-03/sec), and $k'_{O3/H2O2}$ was slightly enhanced by 0.1393 /min (2.3 E-03/sec)

due to the contribution of OH radicals to the degradation of DEET. Moreover, it was observed that $k'_{O3/UV}$ increased by 0.1583 /min (2.6 E-03/sec) that thanks to the combination of UV with O_3. On the other hand, the linear concentration decrease for the reaction time of 5 min was shown in all the PPCPs selected in this study, irrespective of applied processes and therefore, pseudo first-order rate constants of the 30 PPCPs for each process could be obtained. The pseudo first-order rate constants were used for investigating and comparing the degradability of each PPCP by applied processes and the effects of O_3 feed rate, H_2O_2 addition and UV combination during O_3 treatment on the degradation of the 30 PPCPs.

4.3.2 Effect of O_3 feed rate on PPCPs degradation during O_3 treatment

Fig. 4-4 compares pseudo first-order rate constants of the 30 PPCPs when different O_3 feed rates (0.15 mg/L/min, 0.3 mg/L/min and 0.6 mg/L/min) were used during O_3 treatment. The experiments were carried out with tested water spiked the 30 PPCPs into PW. Pseudo first-order rate constants obtained in experiments performed by O_3 feed rates of 0.15 mg/L/min, 0.3 mg/L/min and 0.6 mg/L/min express as $k'_{O3(0.15)\_PW}$, $k'_{O3(0.3)\_PW}$ and $k'_{O3(0.6)\_PW}$, respectively. $k'_{O3(0.15)\_PW}$ values were in a low range of 1.4 E-04/sec (theophylline) to 6.0 E-03/sec (mefenamic acid), while considerably high $k'_{O3(0.3)\_PW}$ and $k'_{O3(0.6)\_PW}$ values of 7.4 E-04/sec (ethenzamide) to 1.5 E-02/sec (oxyteracycline) and 9.3 E-04/sec (cyclophosphamide) to 1.8 E-02/sec (mefenamic acid), respectively were obtained. Average rate constants of all the PPCPs for O_3 feed rates of 0.15 mg/L/min, 0.3 mg/L/min and 0.6 mg/L/min were also calculated as 1.2 E-03/sec, 3.3 E-03/sec and 4.7 E-03/sec, respectively, showing that high O_3 dose led to fast PPCPs degradation. $k'_{O3(0.15)\_PW}$ values of almost all PPCPs increased by a factor of more than 2 with the increased O_3 feed rate (0.3 mg/L/min and 0.6 mg/L/min).

On the other hand, when tested water was treated with O_3 feed rates of 0.15 mg/L/min, 0.3 mg/L/min and 0.6 mg/L/min for the reaction time of 5 min, the amounts of O_3 consumed per the volume of the reactor were 0.7 mg O_3/L, 1.4 mg O_3/L and 2.6 mg O_3/L, respectively. Therefore, the ratio of average rate constant (/sec) to the amount of O_3 consumed per the volume of the reactor (mg O_3/L) was calculated to investigate the degradation efficiency for the PPCPs at each O_3 feed rate based on the amount of O_3 consumed during each treatment.

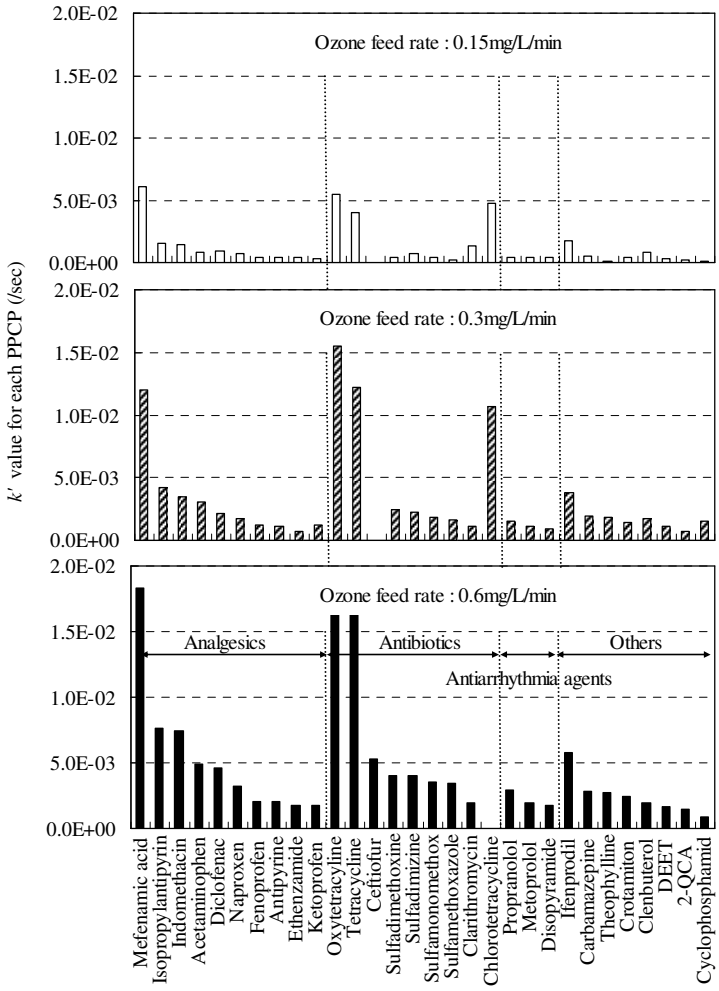


Fig. 4-4 k' values for the 30 PPCPs obtained during O_3 treatment using different O_3 feed rates

The calculation showed that the value was highest in O_3 feed rate of 0.3 mg/L/min (2.2 E-03L/mg O_3·sec), while 1.6 E-03L/mg O_3·sec and 1.8 E-03L/mg O_3·sec were obtained in O_3 feed rates of 0.15 mg/L/min and 0.6 mg/L/min, respectively. The values were calculated only for 28 PPCPs due to lacks of data for ceftiofur and chlorotetracyline. In water, O_3 is decayed by chain reaction as equation (9) ~ (14). Especially, equation (14) is a fast reaction and causes O_3 and OH radicals consumptions for waters with low scavenger (DOC, alkalinity) concentrations, resulting in the reduction of the oxidation capacity in the system (von Gunten, 2003). In this study, the pH of all the tested waters was maintained at 7.0 by phosphate buffer solution. Therefore, the reason why the degradation efficiency of PPCPs to the amount of O_3 consumed for O_3 feed rate of 0.6 mg/L/min was lower than for 0.3 mg/L/min may be that OH radicals and O_3 were consumed faster by excess O_3 which could be formed when relatively

high O_3 feed rate (0.6 mg/L/min) was used, resulting in low degradation efficiency of the PPCPs. This means that the appropriate O_3 dose should be investigated first for the efficient removal of target compounds by O_3 treatment.

$$O_3 + OH^- \rightarrow HO_2^- + O_2 \qquad k = 70\text{M}^{-1}\text{s}^{-1} \qquad (9)$$

$$O_3 + HO_2^- \rightarrow {}^{\bullet}OH + O_2^{\bullet-} + O_2 \qquad k = 2.8 \times 10^6\text{M}^{-1}\text{s}^{-1} \qquad (10)$$

$$O_3 + O_2^{\bullet-} \rightarrow O_3^{\bullet-} + O_2 \qquad k = 1.6 \times 10^9\text{M}^{-1}\text{s}^{-1} \qquad (11)$$

$$HO_3^{\bullet} \rightarrow {}^{\bullet}OH + O_2 \qquad k = 1.4 \times 10^5\text{s}^{-1} \qquad (12)$$

$$O^{\bullet-} + H_2O \rightarrow {}^{\bullet}OH + OH^- \qquad k = 10^8\text{s}^{-1} \qquad (13)$$

$${}^{\bullet}OH + O_3 \rightarrow HO_2^{\bullet} + O_2 \qquad k = 1 \times 10^8\text{M}^{-1}\text{s}^{-1} \sim 2 \times 10^9\text{M}^{-1}\text{s}^{-1} \qquad (14)$$

4.3.3 Degrdadation characteristics of PPCPs by O_3

When O_3 was supplied by a feed rate of 0.6 mg/L/min, 3 PPCPs such as analgesic mefenamic acid and tetracycline antibiotics (oxytetracycline and tetracycline) showed the highest rate constants (1.8 E-02/sec, 1.6 E-02/sec and 1.6 E-02/sec, respectively) among the PPCPs, indicating that O_3 will be very effective for their degradation. Contrarily, insect repellent DEET, carbadox intermediate 2-QCA and antineoplastic agent cyclophosphamide turned out to be very resistant for O_3 from their very low rate constants (17 E-03/sec, 1.5 E-03/sec and 9.3 E-04/sec, respectively). Here, O_3 degradation characteristics of these several PPCPs was discussed.

4.3.3.1 O_3 degradation of tetracyclines

Tetracyclines have been used as antibiotics for human and animal, and its consumption in the United States and Europe was estimated to 5,500tons/year in the mid-1990s (Chopra and Roberts, 2001). There are some studies on the fast degradation of tetracycline with O_3. It has been reported that tetracycline reacted very quickly with O_3, even though total organic carbon

analyses revealed that it was not mineralized at all (Dalmazio *et al*., 2007). They proposed that during O_3 treatment the C11a-C12 double bond of tetracycline was attacked by O_3 and O_3 reaction at the C2-C3 double bond occurred by subsequent O_3 attack (Fig. 4-5).

Dodd *et al* (2006) have measured O_3 and OH radical reaction kinetics for 14 antibacterial compounds from nine structural families. In their study, C11a-C12 double bond, C2-C3 double bond and tertiary amine were proposed as expected sites of O_3 attack, and they showed that tetracycline reacted rapidly with O_3 in a wide range of pH. 3 kinds of tetracyclines (tetracycline, chlorotetracycline and oxytetracycline) with a similar chemical structure were included in a list of 30 PPCPs investigated, and all the tetracyclines showed a similar degradation rate.

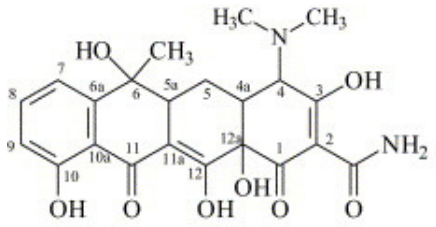


Fig. 4-5 Chemical structure of tetracycline

4.3.3.2 O_3 degradation of DEET and cyclophosphamide

Insect repellent DEET and antineoplastic agent cyclophosphamide were observed to be very resistant for O_3. There seems to be no information on the O_3 degradation of these PPCPs. Costanzo *et al* (2007) discussed a preliminary risk assessment for DEET in the aquatic environment based on its new and existing toxicity data, and showed that risk to aquatic biota at observed environmental concentrations is minimal. However, they suggested that further investigation on the risk should be done because it is detected in the aquatic environment very frequently.

Cyclophosphamide is also known to a cytotoxic drug, which is a group of compounds used in chemotherapy which prevent or disrupt cell division. Steger-Hartmann *et al* (1997) assessed the biological degradability of cyclophosphamide using the Zahn-Wellens/EMPA test (OECD 302B) and a laboratory scale sewage treatment plant. In both test, cyclophosphamide showed very poor degradability and might, therefore, enter into the water cycle. This means

that additional processes following biological process will be necessary for ensuring high removal efficiency of cyclophosphamide, even though its effect on aquatic environment still remains unclear. On the other hand, Johnson *et al* (2008) have suggested that occurrence of cytotoxic drugs in water is not desirable because a mixture of cytotoxic drugs as well as a single cytotoxic drug can affect aquatic environment.

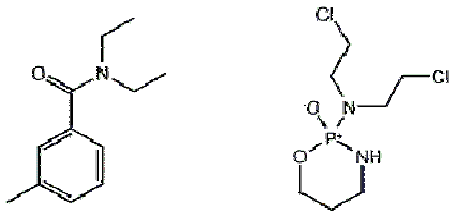


Fig. 4-6 Chemical structures of DEET and cyclophosphamide

4.3.3.3 O_3 degradation of sulfonamides

In this study, the degradation of 4 sulfonamides (sulfamethoxine, sulfadimizine, sulfamonomethoxine and sulfamethoxazole) with O_3 was investigated. Sulfonamide compounds, derivatives from sulfanilamide (sulfamine), have been known to be more antibacterial than sulfanilamide and have a low risk of side effects (Tanaka and Nakamura, 1992). Huber *et al* (2003) investigated the oxidation of PPCPs using conventional O_3 treatment and O_3-based AOPs. The study showed that when O_3 of 1 mg/L was utilized at pH 7~8, half-life time of sulfamethoxazole was below 0.5sec, indicating that it is completely transformed during O_3 treatment and O_3-based AOPs. In addition, they expected the aromatic amino group as the main reaction site of O_3 during O_3 degradation of sulfamethoxazole. They also suggested that rate constants of all sulfonamides will be very similar to the rate constant ($\sim 2.5\times10^{6} M^{-1}s^{-1}$) of sulfamethoxazeol for O_3 reaction because the reactive group (aromatic amine) is characteristic for all the compounds in sulfonamides group. In this study, 4 sulfonamides showed almost same rate constants (3.5 E-03/sec ~ 4.0 E-03/sec) for O_3 feed rates of 0.6 mg/L/min, although a rather wide range of rate constants were obtained for 0.15 mg/L/min and 0.3 mg/L/min.

4.3.4 Effect of UV on PPCPs degradation during O_3 treatment

Fig. 4-7 compares pseudo first-order rate constants ($k'_{O3(0.15)/UV\_PW}$, $k'_{O3(0.3)/UV\_PW}$ and $k'_{O3(0.6)/UV\_PW}$) of the 30 PPCPs for O_3 treatment with/without UV under O_3 feed rates of 0.15 mg/L/min, 0.3 mg/L/min and 0.6 mg/L/min, respectively. Each symbol in Fig. 4-7 indicates corresponding PPCP investigated. The combination of UV during O_3 treatment led to the distinct improvement of degradation rates of most of the PPCPs for 0.15 mg/L/min and 0.6 mg/L/min. While, for O_3 feed rate of 0.3 mg/L/min, UV addition could not improve the degradation of 14 PPCPs including mefenamic acid, tetracyclines, carbamazepine and cyclophosphamide. As known in Fig. 4-7, rate constants of 4 PPCPs such as mefenamic acid and tetracyclines (tetracycline, oxytetracycline, chlorotetracycline) increased or decreased slightly for all the O_3/UV treatments compared to O_3 treatments.

It was also observed that among the 14 PPCPs, the increase of rate constants of the 10 PPCPs such as carbamazepine and cyclophosphamide were relatively lower than for other PPCPs, irrespective of O_3 feed rate during O_3/UV treatments. Therefore, it can be expected that the 14 PPCPs would be degraded very fast with O_3 than with OH radicals compared to other PPCPs. On the contrary, rate constants of several PPCPs such as ketoprofen, diclofenac, sulfamethoxazole and antipyrine increased considerably by UV addition during O_3 treatment. Especially, ketoprofen and diclofenac showed much higher rate constants than for O_3 treatment, irrespective of O_3 feed rate (Fig. 4-7). Chapter III showed that ketoprofen was degraded very easily with UV, and direct UV photodegradation mainly contributed to its degradation during UV/H_2O_2 treatment. In this study, it is, therefore, thought that direct UV photodegradation rather than OH radicals involved in such a fast ketoprofen degradation during O_3/UV treatment.

On the other hand, when O_3 feed rates of 0.15 mg/L/min, 0.3 mg/L/min and 0.6 mg/L/min were used during O_3/UV treatment, O_3 of 0.6 mg/L, 1.3 mg/L and 2.7 mg/L was consumed, respectively. The degradation efficiency of the 30 PPCPs for each treatment was compared based on the ratio of average rate constant (/sec) for all the PPCPs to the O_3 consumption per the volume of reactor (mg O_3/L). As a result, during O_3/UV treatment 6.9 E-03L/mgO_3·sec, 3.8 E-03L/mgO_3·sec and 3.3 E-03L/mgO_3·sec were obtained for O_3 feed rates of 0.15 mg/L/min, 0.3 mg/L/min and 0.6 mg/L/min, respectively, showing the apparently

increased values, compared to for O_3 treatment as described above.

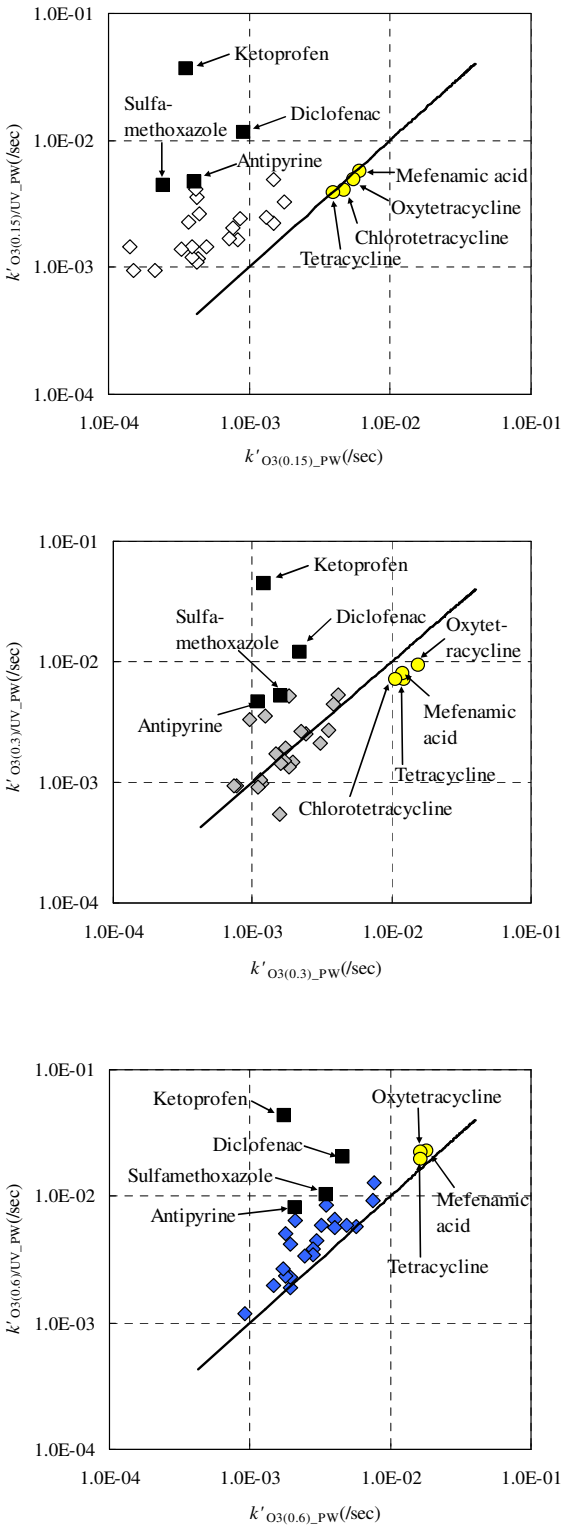


Fig. 4-7 Comparison of rate constants of the 30 PPCPs for O_3 treatment with/without UV

(a) O_3 feed rate : 0.15 mg/L/min, (b) O_3 feed rate : 0.3 mg/L/min and (c) O_3 feed rate : 0.6 mg/L/min

However, in contrast to O_3 treatment, it was characteristic that the highest degradation efficiency was shown at O_3 feed rate of 0.15 mg/L/min, indicating that required O_3 dose can be reduced by the combination of UV during O_3 treatment.

4.3.5 Effect of H_2O_2 addition on PPCPs degradation during O_3 treatment

Fig. 4-8 compares rate constants of the 30 PPCPs for O_3/H_2O_2 treatment with $k'_{O3(0.6)\_PW}$ values obtained for O_3 treatment using O_3 feed rate of 0.6 mg/L/min. Tested water prepared by PW spiked with the 30 PPCPs was used for the experiments using O_3/H_2O_2 treatment. Initial H_2O_2 concentrations in tested water were 2.3 mg/L and 11.2 mg/L, and therefore, rate constants obtained in the experiments were expressed by $k'_{O3(0.6)/H2O2(2.3)\_PW}$ and $k'_{O3(0.6)/H2O2(11.2)\_PW}$, respectively. Here, the degradation rates of 28 PPCPs were discussed except ceftiofur and chlorotetracycline of which the data were not available.

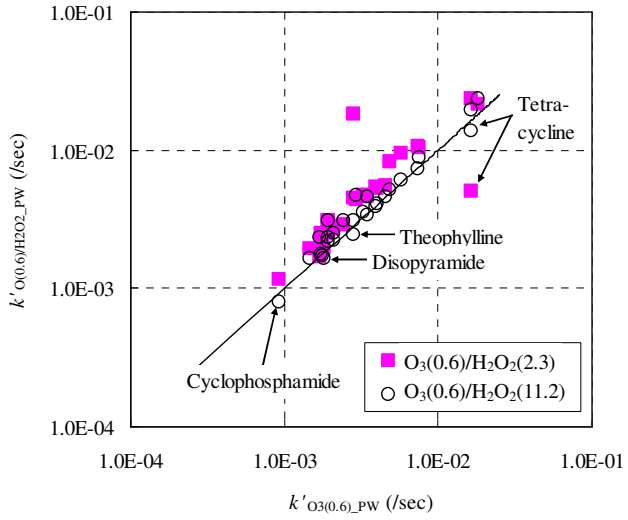


Fig. 4-8 Comparison of rate constants of the 30 PPCPs for O_3 treatment with/without H_2O_2 addition

As a result, the presence of initial H_2O_2 concentration of 2.3 mg/L during O_3 treatment promoted the degradation rates of 26 PPCPs by 1.1 to 6.5 times of those for O_3 treatment (Fig. 4-8). This is due to the contribution of OH radicals formed by the reaction of equation (15), although very low rate constant (5.1 E-03/sec) was obtained in tetracycline.

$$2O_3 + H_2O_2 \rightarrow 2OH\cdot + 3O_2 \qquad (15)$$

Contrarily, rate constants of only 17 PPCPs including clarithromycin and propranolol increased by 1.1 to 1.6 times of those for O_3 treatment when initial H_2O_2 concentration of 11.2 mg/L was used for O_3 treatment. In particular, even slightly lower rate constants than for O_3 treatment were shown in 4 PPCPs such as cyclophosphamide, disopyramide, tetracycline and theophylline. Moreover, average rate constants of the 28 PPCPs for 2.3 mg/L and 11.2 mg/L were 6.2 E-03/sec and 5.1 E-03/sec, respectively. Consequently, high H_2O_2 concentration of 11.2 mg/L did not cause higher degradation rates of PPCPs. This can be explained that OH radicals can be scavenged by H_2O_2 in water as equation (16) (von Gunten, 2003), leading to low degradation rate of target compounds.

$$OH\cdot + H_2O_2 \rightarrow HO_2 + H_2O \qquad (16)$$

Therefore, it is considered that when high initial H_2O_2 concentration of 11.2 mg/L was added, OH radicals formed by the reaction of equation (15) were scavenged by excess H_2O_2 added during O_3 treatment, and as a consequent, lower rate constants than those for O_3/H_2O_2 treatment using initial H_2O_2 concentration of 2.3 mg/L were obtained. Finally, it can be concluded that it will be important to determine the appropriate H_2O_2 dose for O_3 treatment in order to improve degradation rates of PPCPs by the addition of H_2O_2 during O_3 treatment.

4.3.6 O_3 consumption required for 90% degradation of PPCPs during O_3 and O_3/UV treatments

Table 4-2 shows O_3 consumptions and relative residual concentration of each PPCP at reaction times of 5 min, 10 min, 20 min and 30 min during O_3 treatment (O_3 feed rate of 0.6 mg/L/min). Here, the achievement of relative residual concentration of 0.1 (90% degradation) was used for investigating the potential of O_3 treatment for the degradation of 30 PPCPs in TW.

Firstly, it can be seen that the degradation rate of each PPCP increased with the increasing O_3 consumption in both the cases, and O_3 consumption with time was a little higher in tested water prepared by spiking the 30 PPCPs into TW due to DOM (dissolved organic matters) present originally in TW. For tested water using PW, when O_3 of 6.3 mg/L was

consumed, relative residual concentrations of all the PPCPs decreased by less than 0.1 except chlorotetracycline. However, when using TW as tested water, relative residual concentration of chlorotetracycline was 0.1 at O_3 consumption of 2.8 mg/L, indicating that this compound will be degraded very easily even by low O_3 dose.

Table 4-2 Variation of O_3 consumptions and relative residual concentration of each PPCP with time during O_3 treatment

Tested water		Pure water +30 PPCPs				Treated water +30 PPCPs			
Used process		O_3 (0.6 mg/L/min)				O_3 (0.6 mg/L/min)			
Reaction time		5min	10min	20min	30min	5min	10min	20min	30min
Consumed O_3		2.6mg/L	4.2mg/L	6.3mg/L	7.9mg/L	2.8mg/L	4.6mg/L	7.0mg/L	8.9mg/L
Isopropylantipyrine	Analgesic	< 0.1	-	-	-	0.2	< 0.1	-	-
Mefenamic acid		< 0.1	-	-	-	< 0.1	-	-	-
Indomethacin		≤ 0.1	< 0.1	-	-	0.3	< 0.1	-	-
Acetaminophen		0.2	< 0.1	-	-	0.4	< 0.1	-	-
Diclofenac		≤ 0.3	< 0.1	-	-	0.5	< 0.1	-	-
Naproxen		0.3	< 0.1	-	-	0.5	≤ 0.1	< 0.1	-
Antipyrine		0.5	0.1	< 0.1	-	≤ 0.7	0.4	< 0.1	-
Ethenzamide		0.6	0.2	< 0.1	-	0.7	0.5	0.2	< 0.1
Fenoprofen		0.5	0.2	< 0.1	-	0.7	0.4	0.1	< 0.1
Ketoprofen		0.6	0.2	< 0.1	-	0.8	0.5	0.2	< 0.1
Propranolol	Antiarrhythmic agents	≤ 0.4	< 0.1	-	-	0.6	0.2	< 0.1	-
Metoprolol		0.5	0.2	< 0.1	-	0.7	≤ 0.5	≤ 0.2	< 0.1
Disopyramide		≤ 0.6	≤ 0.3	< 0.1	-	0.8	0.5	0.3	< 0.1
Oxytetracyline	Antibiotics	< 0.1	-	-	-	< 0.1	-	-	-
Tetracycline		< 0.1	-	-	-	< 0.1	-	-	-
Ceftiofur		0.2	< 0.1	-	-	0.4	< 0.1	-	-
Sulfadimethoxine		≤ 0.3	< 0.1	-	-	0.5	< 0.1	-	-
Sulfadimizine		≤ 0.3	< 0.1	-	-	0.5	< 0.1	-	-
Sulfamethoxazole		0.3	< 0.1	-	-	0.6	0.1	< 0.1	-
Sulfamonomethoxine		≤ 0.4	< 0.1	-	-	0.5	0.1	< 0.1	-
Clarithromycin		≤ 0.6	≤ 0.2	< 0.1	-	0.7	0.4	< 0.1	-
Chlorotetracycline		No data				0.1	< 0.1	-	-
Ifenprodil	NMDA receptor antagonist	0.1	< 0.1	-	-	0.4	< 0.1	-	-
Clenbuterol	Bronchodilator	0.5	< 0.1	-	-	≤ 0.7	0.4	< 0.1	-
Theophylline	Bronchodilator	0.4	< 0.1	-	-	≤ 0.7	0.2	≤ 0.2	≤ 0.2
Carbamazepine	Anticonvulsant	0.4	< 0.1	-	-	0.6	0.2	≤ 0.2	≤ 0.2
Crotamiton	Anti-itch drug	0.4	< 0.1	-	-	0.6	0.3	< 0.1	-
2-QCA	Carbadox intermediate	0.6	0.3	< 0.1	-	≤ 0.7	≤ 0.5	≤ 0.2	< 0.1
DEET	Insect repellents	0.6	0.2	< 0.1	-	0.7	0.5	0.2	< 0.1
Cyclophosphamide	Antineoplastic agents	0.8	0.6	0.1	< 0.1	≤ 0.8	0.7	0.5	0.3
No. of PPCPs degraded by ≥ 90%		6	20	29	29	4	15	22	27

On the other hand, when using tested water prepared by TW, cyclophosphamide showed relative residual concentration of 0.3 in spite of O_3 consumption of 8.9 mg/L. Therefore, more O_3 dose will be required for ensuring 90% degradation of cyclophosphamide in real sewage treated water. Relative residual concentrations of carbamazepine and theophylline were indicated as less than 0.2 even at the O_3 consumption of 8.9 mg/L because their peaks were not detected for LC/MS/MS analysis. However, it is expected that when more than 90% of them would be degraded at O_3 consumption of 8.9 mg/L because their relative residual concentrations were 0.2 at O_3 consumption of 4.6 mg/L.

From these results, it can be known that O_3 dose of less than 6.3 mg/L will be needed for degrading the 30 PPCPs with concentrations ranging of 13.4~144.0 μg/L by more than 90% if there is no component consuming O_3 in the water such as drinking water. While, O_3 dose of about 8.9 mg/L will be necessary for ensuring 90% degradation of PPCPs in biologically treated water with DOC concentration of 12.7 mg/L. However, less O_3 dose may be required for ensuring the degradation efficiency obtained in semi-batch reactor because O_3 reactors in water and wastewater treatment plants are operated by continuous flow type.

Table 4-3 shows O_3 consumption and relative residual concentration of individual PPCPs at each reaction time during O_3/UV treatment using O_3 feed rate of 0.6 mg/L/min. O_3 consumption for 30 min was rather higher than for O_3 treatment due to direct UV photodegradation of O_3 molecules, while the amounts of O_3 consumed for 10 min were almost the same to for O_3 treatment. Nevertheless, relative residual concentrations of less than 0.1 were obtained in 28 PPCPs except cyclophosphamide and ceftiofur when using PW as tested water. This was compared with for O_3 treatment that only 20 PPCPs showed relative residual concentration of less than 0.1. As known in Table 4-2 and Table 4-3, such a significant difference was not observed when using tested water prepared by TW, probably due to the consumption of OH radicals by scavengers such as DOM and alkalinity in TW. Consequently, it is considered that the improvement of PPCPs degradation by the combination of UV during O_3 treatment can be expected in water treatment process with relatively clean water matrix.

Table 4-3 Variation of O_3 consumptions and relative residual concentration of each PPCP with time during O_3/UV treatment

Tested water		Pure water +30 PPCPs				Treated water +30 PPCPs			
Used process		O_3 (0.6 mg/L/min)/UV				O_3 (0.6 mg/L/min)/UV			
Reaction time		5min	10min	20min	30min	5min	10min	20min	30min
Consumed O_3		2.7mg/L	4.5mg/L	7.4mg/L	10.6mg/L	2.6mg/L	4.5mg/L	7.7mg/L	10.6mg/L
Antipyrine	Analgesic	< 0.1	-	-	-	0.4	< 0.1	-	-
Diclofenac		< 0.1	-	-	-	< 0.1	-	-	-
Indomethacin		< 0.1	-	-	-	0.2	< 0.1	-	-
Isopropylantipyrine		< 0.1	-	-	-	0.2	< 0.1	-	-
Ketoprofen		< 0.1	-	-	-	< 0.1	-	-	-
Acetaminophen		0.1	< 0.1	-	-	0.4	< 0.1	-	-
Fenoprofen		0.1	< 0.1	-	-	0.4	≤ 0.2	< 0.1	-
Ethenzamide		0.5	< 0.1	-	-	0.8	0.5	0.2	< 0.1
Mefenamic acid		≤ 0.5	< 0.1	-	-	0.1	< 0.1	-	-
Naproxen		≤ 0.2	< 0.1	-	-	≤ 0.5	≤ 0.2	< 0.1	-
Disopyramide	Antiarrhythmic agents	0.2	< 0.1	-	-	0.5	0.2	< 0.1	-
Propranolol		≤ 0.3	< 0.1	-	-	0.5	≤ 0.2	< 0.1	-
Metoprolol		0.5	< 0.1	-	-	0.8	< 0.1	-	-
Chlorotetracycline	Antibiotics	< 0.1	-	-	-	< 0.1	-	-	-
Oxytetracyline		< 0.1	-	-	-	< 0.1	-	-	-
Sulfadimethoxine		< 0.1	-	-	-	0.4	≤ 0.1	< 0.1	-
Sulfamethoxazole		< 0.1	-	-	-	0.3	< 0.1	-	-
Sulfamonomethoxine		< 0.1	-	-	-	0.2	< 0.1	-	-
Tetracycline		< 0.1	-	-	-	< 0.1	< 0.1	-	-
Sulfadimizine		0.2	< 0.1	-	-	0.4	0.1	< 0.1	-
Clarithromycin		≤ 0.6	< 0.1	-	-	≤ 0.7	≤ 0.4	< 0.1	-
Ceftiofur		No data				No data			
Ifenprodil	NMDA receptor antagonist	0.1	< 0.1	-	-	0.2	< 0.1	-	-
Clenbuterol	Bronchodilator	0.2	< 0.1	-	-	0.7	0.3	< 0.1	-
Theophylline	Bronchodilator	0.3	< 0.1	-	-	0.6	0.2	< 0.1	-
Carbamazepine	Anticonvulsant	0.3	< 0.1	-	-	0.6	0.3	< 0.1	-
Crotamiton	Anti-itch drug	0.3	< 0.1	-	-	0.6	0.3	< 0.1	-
DEET	Insect repellents	≤ 0.5	< 0.1	-	-	≤ 0.8	0.5	0.2	< 0.1
2-QCA	Carbadox intermediate	0.6	0.1	< 0.1	-	≤ 0.8	≤ 0.6	0.3	< 0.1
Cyclophosphamide	Antineoplastic agents	≤ 0.7	≤ 0.4	< 0.1	-	0.9	≤ 0.8	≤ 0.5	≤ 0.3
No. of PPCPs degraded by ≥ 90%		14	28	29	29	6	16	25	28

4.4 Summary

The effect of O_3 feed rate and the addition of H_2O_2 or UV on the degradation rates of 30 PPCPs was investigated during O_3 treatment using semi-batch reactor. The concentration of each PPCP decreased linearly with time, indicating that their reactions with O_3, O_3/H_2O_2 and O_3/UV follow pseudo 1st order kinetics. Therefore, the degradability of each PPCP was compared by pseudo 1st order rate constant.

1) The degradabilities (pseudo 1st order rate constants) of individual PPCPs increased with the increased O_3 feed rate (0.15 mg/L/min, 0.3 mg/L/min, 0.6 mg/L/min). However, the degradation efficiency (the ratio of pseudo 1st order rate constant (/sec) to the amount of O_3 consumed per the volume of the reactor (mgO_3/L)) for the 30 PPCPs was the highest for O_3 feed rate of 0.3 mg/L/min (2.2E-03 L/mgO_3·sec). This indicates that the introduction of high O_3 concentration could not contribute to the improvement of the degradabilites per O_3 consumed although it improved the degradation rates of the PPCPs.

2) The degradation rate of each PPCP increased considerably by the combination of UV with O_3 treatment, and the lowest O_3 feed rate of 0.15 mg/L/min showed the most efficiency PPCPs degradation (6.9E-03 L/mgO_3·sec). This means that O_3 dose required for the effective PPCP removal can be reduced for O_3/UV treatment. On the other hand, the degradation rates of 14 PPCPs including mefenamic acid, tetracyclines, carbamazepine and cyclophosphamide did not improve so much during O_3/UV treatment, implying that the PPCPs will react more easily with O_3 than OH radicals.

3) For O_3/H_2O_2 treatment, initial H_2O_2 concentration of 2.3 mg/L and 11.2 mg/L was combined with O_3 treatment (0.6 mg/L/min). As a result, H_2O_2 addition increased the degradation rates of 26 PPCPs by factors of 1.1 to 6.5 comparing with for O_3 alone treatment. However, lower degradation rates showed when initial H_2O_2 concentration was 11.2 mg/L, maybe due to the scavenging effect of O_3 and OH radicals by excess H_2O_2.

4) Finally, O_3 consumptions required for 90% degradation of each PPCP for O_3 and O_3/UV treatment were calculated. For O_3 treatment, O_3 consumption of 6.3 mg/L was necessary for 90% degradation of all the 30 PPCPs spiked into pure water. While, for O_3/UV treatment, O_3 consumption of 4.5 mg/L could achieve 90% degradation of each PPCP. On the other hand, comparatively high O_3 consumptions of 8.9 mg/L and 7.7 mg/L were required for

O_3 and O_3/UV treatments carried out with tested water spiked with the 30 PPCPs, respectively. These O_3 consumptions resulted from semi-batch experiments (initial dissolved ozone concentration in tested water = 0 mg/L), and less O_3 consumption will be, therefore, needed for real O_3 and O_3/UV treatment facilities because real treatment facilities are operated by supplying continuously O_3 gas into O_3 and O_3/UV reactors.

4.5 References

Balcioglu I.A., Otker M., 2003, Treatmetn of pharmaceutical wastewater containing antibiotics by O_3 and O_3/H_2O_2 processes, *Chemosphere* 50, 85-95

Chopra, I., Roberts, M., 2001, Tetracycline antibiotics: Mode of Action, Applications, Molecular Biology, and Epidemiology of Bacterial Resistance, *Microbiol Mol Biol*., Rev.65, 232-233

Costanzo S.D., Watkinson A.J., Murby E.J., Kolpin D.W., Sandstrom M.W., 2007, Is there a risk associated with the insect repellent DEET(N,N-diethyl-m-toluamide) commonly found in aquatic environments?, *Sci Total Environ.* 384, 214-220

Dalmazio I., Almeida M. O., Augusti R., 2007, Monitoring the Degradation of Tetracycline by Ozone in Aqueous Medium Via Atmospheric Pressure Ionization Mass Spectrometry, *J. Mass Spec.* 18, 679-687

Dodd M.C., Buffle M.O., von Gunten U., 2006, Oxidation of antibacterial molecules by aqueous ozone: moiety-specific reaction kinetics and application to ozone-based wastewater treatment, *Environ Sci Technol.* 40, 1969-1977

Huber M.M., Canonica S., Park G., von Gunten U., 2003, Oxidation of pharmaceuticals during ozonation and advanced oxidation processes, *Environ Sci Technol.* 37, 1016-1024

Johnson A.C., Jurgens M.D., Williams R.J., Kummerer K., Kortenkamp A., Sumpter J.P., 2008, Do cytotoxic chemotherapy drugs discharged into rivers pose a risk to the environment and human health? An overview and UK case study, *J. Hydrol.* 348, 167-175

Kim I.H., Tanaka H., Iwasaki T., Takubo T., Morioka T., Kato Y., 2008, Classification of the degradability of 30 pharmaceuticals in water with ozone, UV and H_2O_2, *Wat Sci Technol.* 57, 195-200

Lau T.K., Chu W., Graham N., 2007, Reaction pathways and kinetics of butylated

hydroxyanisole with UV, ozonation, and UV/O_3 processes, *Water Res.* 41, 765-774

Nakada N., Komori K., Suzuki Y., 2007, Occurrence of 70 pharmaceuticals and personal care products in Tone River basin in Japan, *Wat Sci Tech.* 56, 133-140

Okuda T., Kobayashi Y., Nagao R., Yamashita N., Tanaka H., Tanaka S., Fuji S., Konishi C., Houwa I., 2008, Removal efficiency of 66 pharmaceuticals during wastewater treatment process in Japan, *Wat Sci Technol.* 57, 65-71

Rosenfeldt E.J., Linden K.G., Canonica S., von Gunten U., 2006, Comparison of the efficiency of ·OH radical formation during ozonation and the advanced oxidation processes O_3/H_2O_2 and UV/H_2O_2, *Water Res.* 40, 3695-3704

Steger-Hartmann T., Kummerer K., Hartmann A., 1997, Biological degradation of cyclophosphamide and its occurrence in sewage water, *Ecotox Environ Safe.* 36, 174-179

Susan D.R., Ternes T.A., 2005, Water Analysis: Emerging Contaminants and Current Issues, *Anal Chem.* 77, 3807-3838

Tanaka N., Nakamura S., Essentials of antibiotics, Fourth edition, University of Tokyo press, 1992, 355

Ternes T.A., Stuber J., Herrmann N., McDowell D., Ried A., Kampmann M., Teiser B., 2003, Ozonation: A tool for removal of pharmaceuticals, contrast media and musk fragrances from wastewater?, *Water Res.* 37, 1976-1982

von Gunten U., 2003, Ozonation of drinking water: Part I. Oxidation kinetics and product formation, *Water Res.* 37, 1443-1467

Zou L., Zhu B., The synergistic effect of ozonation and photocatalysis on color removal from reused water, *J. Photochem Photobiol A*: Chem., doi:10.1016/j.jphotochem.2007.11.008 (2007)

CHAPTER V

INVESTIGATION ON THE REMOVAL PERFORMANCE FOR PHARMACEUTICALS AND PERSONAL CARE PRODUCTS BY UV-BASED PROCESSES IN BENCH SCALE PLANT

5.1 Introduction

A great variety of pharmaceuticals and personal care products (PPCPs) have been produced for human and veterinary health in the medical field. The environmental fate and effects of the PPCPs have been studied over the last few years. Cleuvers (2004) demonstrated that diclofenac, ibuprofen, naproxen and acetylsalicylic acid exhibit the stronger toxicities when they coexist in water than when they exist alone. This means that more studies are still needed to confirm the adverse effects of PPCPs on human health and ecosystem. On the other hand, much attention has been paid to the safety of tap water and treated wastewater because of the lack of water resources and water reuse. While, there is a growing concern regarding the occurrence of PPCPs in the aquatic environment (Heberer *et al*., 2002; Smital *et al*., 2004). These PPCPs have been detected in samples from all aquatic environment such as river water, ground water and drinking water and the main source of them has been known as the effluent from wastewater treatment plant (Halling-Sørensen *et al*., 1998; Kanda *et al*., 2003). There are also several investigations showing that PPCPs are not eliminated during wastewater treatment and also not biodegraded in the environment (Ternes, 1998; Daughton *et al*., 1999; Nakada *et al*., 2006; Okuda *et al*., 2008).

On the other hand, there seems to be almost no studies on the removal of PPCPs in secondary effluent by UV and UV/H_2O_2 processes using demonstration scale plant. In this

study, therefore, the removal performance of UV and UV/H_2O_2 processes was investigated using bench scale plant. The experiments were carried out ,based on the results from Chapter III (UV dose required for the effective removal of the 30 PPCPs: 38 mJ/cm^2 to 5,644 mJ/cm^2 for UV alone process). Moreover, the appropriate amount of H_2O_2 addition during UV process was investigated for the 90% removal of all the PPCPs detected in secondary effluent. Finally, energy consumption and operating costs were estimated for each process considering the effective PPCPs removal. The research structure of this chapter is shown in Fig. 5-1.

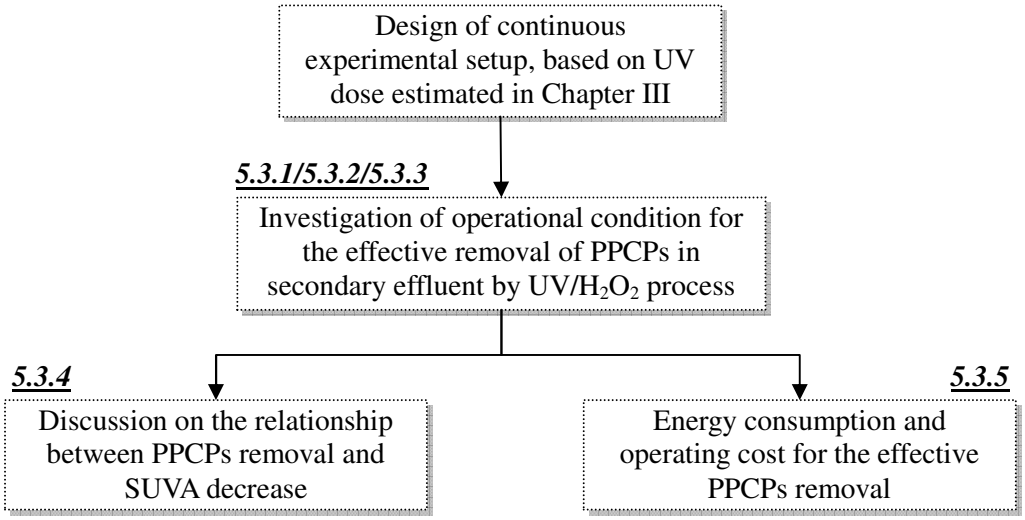


Fig. 5-1 Structure of this chapter

5.2 Methods and materials

5.2.1 Experimental setup and operational conditions

Experiment setup used in this study consists of three reactors (R1, R2 and R3) connected in series (Fig. 5-2). The effective volume and HRT (hydraulic retention time) of a reactor are 35L and 5 min, respectively. Secondary effluent from sewage treatment plant was used after filtered by sand filtration as tested water during all the experiments. The pH of the tested water was 6.7, and DOC and UV_{254} ranged from 2.6 mg/L to 3.9 mg/L and 0.053 /cm to 0.064 /cm, respectively.

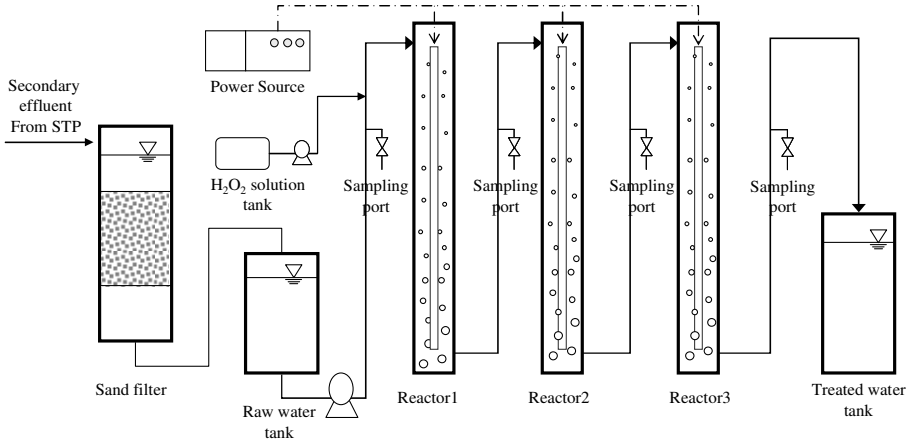


Fig. 5-2 Experimental setup for UV and UV/H_2O_2 treatments

In order to investigate UV dose and energy consumption for the effective removal of PPCPs in secondary effluent by UV and UV/H_2O_2 processes, 2 kinds of UV lamps that emit at the wavelength of 254 nm were used for experiments; a 65W low pressure mercury lamp with UV output of 21.8W_{UV} (UV_{65W} Lamp) and a 41W low pressure mercury lamp with UV output of 13.6W_{UV} (UV_{41W} Lamp). UV_{65W} and UV_{41W} lamps have the UV intensities of 1.025 mW/cm^2 and 0.639 mW/cm^2, respectively. UV treatments with and without H_2O_2 addition were performed for each UV lamp. For UV treatments, all the 3 reactors were operated under UV irradiation, while only R1 was operated during UV/H_2O_2 treatments. The same 3 UV lamps were placed inside each reactor and air was supplied continuously from the bottom to each reactor at a flow rate of 0.5 L/min for efficient UV irradiation to tested water during all the experiments. The initial H_2O_2 concentrations in tested water were maintained to 1.1 mg/L, 3.1 mg/L and 6.0 mgL for UV_{41W}/H_2O_2 treatments, and 1.2 mg/L, 3.1 mg/L and 6.2 mg/L for UV_{65W}/H_2O_2 treatments.

Table 5-1 Operational conditions

Applied UV lamp	UV alone process	UV/H_2O_2 process	
	Operated reactor	Initial H_2O_2 concentration	Operated reactor
UV_{41W} Lamp	R1, R2, R3	1.1 mg/L 3.1 mg/L 6.0 mg/L	R1
UV_{65W} Lamp	R1, R2, R3	1.2 mg/L 3.1 mg/L 6.2 mg/L	R1

5.2.2 Pretreatment of sample for PPCPs quantification with LC/MS/MS

Fig. 5-2 shows pretreatment procedure of each sample for PPCPs quantification with LC/MS/MS. Firstly, a sample of 1,000ml taken from sampling port in outlet of each reactor was filtered with GF/B (pore size: 1.0μm) and then, EDTA of 1g was added to the filtrate. Afterwards, PPCPs in the filtrate were concentrated in Oasis HLB cartridge (Waters, 6cc/100mg) by the concentrator (Waters, Sep-Pak concentrator SPC-10). The Oasis HLB cartridge conditioned in advance with 3ml methanol and 6ml distilled water was used for the concentration. After concentrating, the cartridge was dehydrated by a pneumatic pump for 1 hr in order to avoid the remaining of water in the cartridge, and PPCPs were eluted from the dehydrated cartridge with 6ml methanol. The eluted solution was volatilized with N_2 gas and then, dissolved again with 1ml mixed solution of 0.1% formic acid and methanol. This solution of 1ml was used for PPCPs quantification with LC/MS/MS.

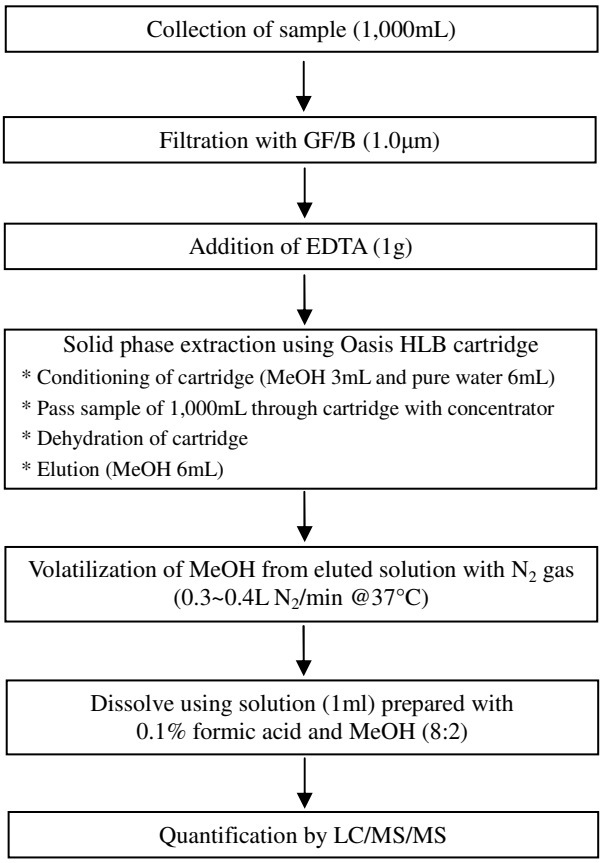


Fig. 5-3 Pretreatment procedure of sample for PPCPs quantification

5.2.3 Analytical methods

The concentrations of PPCPs were measured simultaneously with UPLC/MS/MS. AQUITY UPLC (Waters) was used for UPLC and Quattro micro API Tandem mass spectrometer (Waters) for MS/MS. The control of UPLC/MS/MS system and the treatment of data acquired during operation of LC/MS/MS were managed by MassLynxTM Software (Waters). For simultaneous quantification of PPCPs, gradient elution analysis method by varying the polarity of mobile phase with time was adopted and 62 PPCPs could be quantified simultaneously by UPLC/MS/MS.

Table 5-2 shows the measurement condition of UPLC/MS/MS in details, and ionization conditions, LODs (Limit Of Detections) and LOQs (Limit Of Quantifications) for the 62 PPCPs are shown in Table 5-3. LODs and LOQs for simultaneous analysis of the PPCPs were determined by measuring standard solutions with the concentration of 0.5 μg/L, 1 μg/L, 5 μg/L, 10 μg/L, 50 μg/L, 100 μg/L and 200 μg/L for individual PPCPs with UPLC/MS/MS. Using the concentrations obtained by measurements of 5 times for each standard solution, average value and standard deviation value for each PPCP were calculated. Afterwards, a variation coefficient, which is defined as a ratio of standard deviation value to average value, was calculated. Based on the standard deviation (σ) of standard solution at the lowest concentration with the variation coefficient of less than 20%, LOD (3σ) and LOQ (10σ) were calculated.

DOC (dissolved organic carbon) concentration was measured with a TOC analyzer (TOC-5000A, Shimadzu) and calculated from the difference of TOC (total organic carbon) and IC (inorganic carbon). A spectrophotometer (UV-16000, Shimadzu) was used for measuring the absorbance at 254 nm (UV_{254}). DMP (2,9-dimethyl-1,10-phenanthroline) method was adopted for the measurement of H_2O_2 concentration in sample (Baga *et al.*, 1988).

Table 5-2 Measurement condition for LC/MS/MS analysis

<UPLC : UPLC AQUITY>

- Column : Waters AQUITY^{IM} UPLC BEH C18 2.1mm×100mm,1.7μm
- Column Temp. : 60℃
- Flow rate : 0.35ml/min
- Injection volume : 10μl
- Mobile Phase : A 0.1% Formic acid B Methanol
- Gradient :

Time(min)	A(%)	B(%)
0	90	10
2	90	10
8	75	25
14	45	55
16	45	55
19	5	95
21	5	95
21.01	90	10

<MS/MS : Quattro micro API>

- Ionization : Electrospray Ionization(ESI)
- Spray Voltage : 0.5kV 3.5kV
- Source Temp. : 120℃ 120℃
- Capillary Temp. : 400℃ 350℃

Table 5-3 Ionization conditions, LOD and LOQ for 62 PPCPs

No.	PPCPs	Positive(+) or Negative(-)	Precursor ion (m/z)	Product ion (m/z)	Cone Voltage (V)	Collision Energy (eV)	LOD (μg/L)	LOQ (μg/L)
1	Azithromycin	+	749.5	591.4	40	25	0.06	0.19
2	Clarithromycin	+	748.9	157.9	30	20	0.18	0.61
3	Erythromycin	+	734.5	158.1	18	26	0.14	0.46
4	Roxithromycin	+	837.7	679.4	25	20	0.07	0.24
5	Tylosin	+	916.5	174.0	45	40	0.07	0.23
6	Ciproflxacin	+	332.2	231.0	25	35	0.31	1.02
7	Enrofloxacin	+	360.2	245.2	30	26	0.05	0.16
8	Levofloxacin	+	362.1	317.8	28	18	0.39	1.31
9	Norfloxacin	+	320.1	276.0	28	18	0.15	0.51
10	Sulfadimethoxine	+	311.0	155.8	28	22	0.06	0.21
11	Sulfadimidine	+	279.0	185.7	24	18	0.10	0.34
12	Sulfamerazine	+	265.2	155.9	25	18	0.20	0.66
13	Sulfamonomethoxine	+	281.0	155.7	24	18	0.49	1.64
14	Ampicillin	+	350.3	105.8	16	20	0.58	1.94
15	Benzylpenicillin Potassium	+	335.0	289.0	34	25	1.04	6.47
16	Ceftiofur	+	524.0	240.8	20	16	4.62	15.41
17	Oxytetracycline	+	461.1	425.9	16	18	0.20	0.68
18	Tetracycline hydrochloride	+	445.1	409.7	20	18	0.02	0.08
19	Diclazuril	-	406.9	335.7	32	18	0.41	1.38
20	Nicarbazin	-	301.0	136.8	18	12	0.21	0.69
21	Sulfamethoxazole	+	254.0	155.9	25	15	0.16	0.55
22	Trimethoprim	+	291.0	229.8	32	26	0.11	0.35
23	2-quinoxaline carboxylic acid	+	175.0	128.9	20	15	0.31	1.03
24	Chloramphenicol	-	320.9	151.7	24	14	0.35	1.17
25	Griseofulvin	+	353.1	214.9	25	25	0.17	0.58
26	Lincomycin	+	407.2	125.8	28	28	0.14	0.47
27	Novobiocin	+	613.3	188.7	20	32	0.22	0.73
28	Salinomycin	-	749.6	240.9	48	34	0.44	1.48
29	Tiamulin	+	494.4	192.1	25	20	0.03	0.10
30	Acetaminophen	+	152.0	109.8	25	16	0.25	0.84
31	Antipyrine	+	189.1	76.7	30	35	0.11	0.36
32	Ethenzamide	+	166.0	148.9	15	10	0.09	0.29
33	Fenoprofen	+	243.0	196.9	12	12	0.56	1.87
34	Indomethacin	+	357.8	138.9	20	18	0.20	0.65
35	Isopropylantipyrine	+	231.0	188.8	32	22	0.04	0.13
36	Ketoprofen	+	255.1	209.0	25	15	0.50	1.68
37	Mefenamic acid	+	242.0	224.6	12	18	0.28	0.94
38	Naproxen	+	231.0	184.7	16	16	0.26	0.88
39	Crotamiton	+	204.1	68.7	30	20	0.07	0.24
40	Diclofenac sodium	+	297.6	215.2	12	26	0.66	2.19
41	Carbamazepine	+	237.1	194.0	25	20	0.05	0.16
42	Ifenprodil	+	326.2	308.1	30	20	0.07	0.23
43	Primidone	+	219.3	162.1	20	10	1.06	3.52
44	Atenolol	+	267.1	189.8	28	18	0.41	1.38
45	Disopyramide	+	340.2	239.0	20	15	0.06	0.19
46	Metoprolol	+	268.2	115.9	30	20	0.12	0.42
47	Propranolol hydrochloride	+	260.1	182.7	24	18	0.06	0.19
48	Diltiazem hydrochloride	+	415.1	177.7	24	22	0.02	0.05
49	Dipyridamole	+	505.3	384.9	50	42	0.04	0.13
50	Nalidixic acid	+	233.3	215.1	35	14	0.09	0.30
51	Salbutamol	+	240.3	148.0	18	20	0.32	1.05
52	Theophylline	+	181.5	123.9	30	20	0.22	0.73
53	Bezafibrate	+	362.0	316.0	20	14	0.35	1.16
54	Clenbuterol	+	277.0	202.9	20	15	0.21	0.72
55	Caffeine	+	195.0	137.7	28	18	0.14	0.48
56	Carbazochrome	+	237.0	219.7	12	8	0.23	0.77
57	Clofibric acid	-	213.1	126.9	20	13	0.13	0.42
58	Cyclophosphamide	+	260.9	139.7	24	22	0.20	0.66
59	N,N-diethyl-m-toluamide	+	192.1	118.8	25	15	0.03	0.11
60	Furosemide	-	329.1	205.1	30	20	0.19	0.64
61	Pirenzepine	+	352.1	112.7	26	22	1.04	3.47
62	Sulpiride	+	342.0	213.7	32	32	0.02	0.05

5.3 Results and discussion

5.3.1 PPCPs detected in tested water

38 PPCPs were detected in secondary effluent used for tested water in this study. Fig. 5-4 shows average, maximum and minimum concentrations of the 38 PPCPs. As therapeutic classes, 11 kinds of antibiotics including clarithromycin and levofloxacin, 7 analgesics including ketoprofen and diclofenac and 4 antiarrhythmic agents such as disopyramide, atenolol, metoprolol and propranolol were mainly present in the tested water. A variety of PPCPs such as anticonvulsants (carbamazepine and primidone), 2 vasodilators (dipyridamole and diltiazem), diuretic (furosemide), antineoplastic agent (cyclophosphamide) and peptic ulcer drug (pirenzepine) were also present, showing that sewage treatment plant is a main source of PPCPs contaminants of aquatic environment. Among the 38 PPCPs, antibiotic clarithromycin showed the highest concentration of 481 ng/L. Subsequently, antiitch drug crotamiton, antipsychotic drug sulpiride, insect repellent DEET, antibiotic clarithromycin and levofloxacin and antiarrhythmic agent disopyramide exhibited high concentration of over 100 ng/L in tested water.

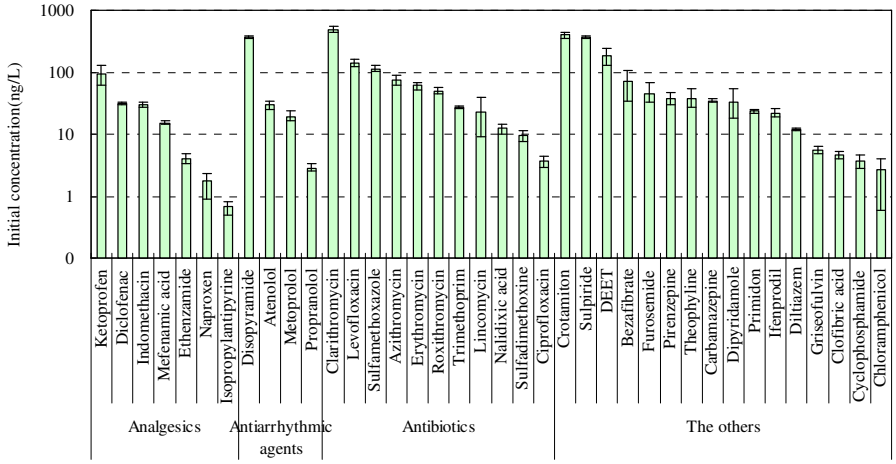


Fig. 5-4 Average, maximum and minimum concentrations of 38 PPCPs detected in tested water

Nakada *et al* (2006) have surveyed the occurrences of 6 analgesics, 2 phenolic antiseptics, 4 amide pharmaceuticals, 3 phenolic endocrine disrupting chemicals and 3 natural estrogens

for influents and secondary effluents of 5 sewage treatment plants in Tokyo. They reported the occurrences of crotamiton, ketoprofen, carbamazepine and mefenamic acid as PPCPs detected from the tested water used in this study. Especially, they found that PPCPs with the highest concentration in secondary effluents was crotamiton (245 ng/L ~ 968 ng/L). In our study, crotamiton showed the second highest concentration ranging from 347 ng/L to 448 ng/L. Although the occurrence of the compound has not been reported in other countries, it has often been detected in several sewage treatment plants of Japan over the past few years. Okuda *et al* (2008) also reported the occurrence of crotamiton in influent and effluent of a sewage treatment plant in Japan, and concluded that biological treatment process could not remove the compound effectively, based on its low removal efficiency (30% or less) obtained in their survey.

Heberer *et al* (2002) have reported that for analgesic diclofenac average concentrations ranging from 3.02 μg/L to 2.51 μg/L occurred in influents and effluents of sewage treatment plants in Berlin, Germany, indicating that the compound is one of the most concerning PPCPs in water cycle. Antibiotic sulfamethoxazole has been reported to be detected up to 410 ng/L in groundwater by Sacher *et al* (2001). The occurrences of sulfonamides antibiotics such as sulfamethoxazole and sulfadimethoxine in aquatic environment have been often reported by many researchers (Okuda *et al*., 2008; Holm *et al*., 1995). Anticonvulsant carbamazepine has been found in sewage and surface water very frequently (Ternes, 1998; Heberer *et al*., 2001). On the other hand, ethenzamide, naproxen and isopropylantipyrine (analgesics), propranolol (antiarrhythmic agent), sulfadimethoxine and ciprofloxacin (antibiotics), griseofulvin (antifungal drug), clofibric acid (lipid modifying agent), cyclophosphamide (antineoplastic agent) and chlorampenicol (antimicrobial drug) showed relatively low concentrations ranging from 1 ng/L to 10 ng/L compared to other PPCPs.

5.3.2 PPCPs removal with UV_{41W} lamp and H_2O_2

In order to investigate the removal performance of UV and UV/H_2O_2 processes for the 38 PPCPs, UV and UV/H_2O_2 processes experiments were first performed using UV_{41W} lamp with a low output of 13.6W_{UV}. In this study, a goal of 90% removal efficiency was set to compare the performance for PPCPs removal of each process. Table 5-4 compares the removal

efficiency of each PPCP at contact times of 5 min (R1), 10 min (R1+R2) and 15 min (R1+R2+R3) during UV_{41W} process. UV dose introduced to each reactor in this study was 575 mJ/cm^2, which is much higher than 40 mJ/cm^2 to 140 mJ/cm^2 required for typical disinfection (Pereira *et al*., 2007).

It can be seen in Table 5-4 that many PPCPs were not removed effectively during UV_{41W} process although their removal efficiencies increased slightly according to the increase of contact time. Especially, 15 PPCPs including cyclophosphamide (antineoplastic agent), DEET (insect repellent) and carbamazepine (anticonvulsant) showed low removal efficiency of below 50% despite the introduction of UV dose of 1,725 mJ/cm^2. Mefenamic acid, ethenzamide, metoprolol, clarithromycin, carbamazepine, theophylline, cyclophosphamide and DEET known to be resistant for UV irradiation also belong to the 15 PPCPs (Kim *et al*., 2008).

Contrarily, diclofenac, isopropylantipyrine and ketoprofen (analgesics), sulfamethoxazole (antibiotic), diltiazem and dipyridamole (vasodilators) and clofibric acid (lipid modifying agent) were thought to be susceptible for UV irradiation compared to other PPCPs because they were removed by more than 90% even at UV dose of 575 mJ/cm^2 (contact time : 5 min). It was demonstrated in Chapter III that several PPCPs such as ketoprofen and diclofenac can be degraded very easily with UV irradiation. However, considerable UV dose will be necessary for efficient PPCPs removal with UV_{41W} process.

Table 5-4 Removal efficiency of individual PPCPs at each reactor during UV_{41W} process

Use	PPCPs	UV_{41W} process		
		R1	R2	R3
Analgesics	Diclofenac	> 98	> 98	> 98
	Ketoprofen	98	98	99
	Isopropylantipyrine	> 95	> 95	> 95
	Naproxen	55	70	> 87
	Indomethacin	40	62	77
	Ethenzamide	13	21	29
	Mefenamic acid	5	25	44
Antiarrhythmic agents	Disopyramide	89	97	99
	Atenolol	36	35	57
	Propranolol	23	39	65
	Metoprolol	21	29	42
Antibiotics	Sulfamethoxazole	93	98	99
	Ciprofloxacin	> 89	> 89	> 89
	Nalidixic acid	78	97	> 99
	Sulfadimethoxine	75	90	94
	Levofloxacin	22	17	54
	Trimethoprim	19	23	34
	Lincomycin	19	34	42
	Clarithromycin	13	27	38
	Erythromycin	11	15	22
	Azithromycin	10	14	25
	Roxithromycin	9	15	25
The others	Diltiazem	96	100	100
	Dipyridamole	96	99	100
	Clofibric acid	93	> 97	> 97
	Chloramphenicol	> 87	> 87	> 87
	Furosemide	79	96	100
	Ifenprodil	62	85	95
	Crotamiton	41	67	81
	Griseofulvin	40	60	78
	Bezafibrate	31	54	68
	Pirenzepine	28	48	51
	Sulpiride	15	19	29
	Carbamazepine	13	23	33
	Theophyline	10	16	22
	DEET	7	17	25
	Cyclophosphamide	2	13	11
	Primidon	1	16	21

In order to accomplish 90% removal efficiencies for all the PPCPs, H_2O_2 solution was added during UV process. The different initial H_2O_2 concentrations (1.1 mg/L, 3.1 mg/L and 6.0 mg/L) in tested water were used during UV_{41W} process. The removal efficiencies of individual PPCPs at contact time of 5 min during UV_{41W} and UV_{41W}/H_2O_2 processes were indicated and compared in Table 5-5.

The removal efficiency of each PPCP ranged from 1% (primidon) to >98% (diclofenac) during UV_{41W} process, while drastic increase in the removal efficiency was observed when H_2O_2 was added (22% (theophylline) ~ 100% (diltiazem), 32% (theophylline) ~ 100% (diltiazem) and 73% (theophylline) ~ 100% (diltiazem) for 1.1 mg/L, 3.1 mg/L and 6.0 mg/L of initial H_2O_2 concentrations during UV_{41W} process, respectively). In particular, it was shown that 7 PPCPs such as mefenamic acid, azithromycin, roxithromycin, theophylline, DEET, cyclophosphamide and primidon improved most remarkably in their removal efficiencies by the addition of H_2O_2.

Consequently, it was expected that by the combination of H_2O_2 with UV process, more efficient PPCPs removal could be achieved at lower UV dose comparing to UV_{41W} process. However, 90% removals for all the 38 PPCPs could not be achieved even by UV_{41W}/H_2O_2 process because 7 PPCPs such as azithromycin, erythromycin, primidon, chloramphenicol, naproxen, cyclophosphamide and theophylline showed the removal efficiencies of 88%, 87%, 87%, >83%, >81%, 78% and 73%, respectively despite the combination of the initial H_2O_2 concentration of 6.0 mg/L with UV_{41W} process.

Table 5-5 Removal efficiency of each PPCP at contact time of 5 min during UV_{41W} and UV_{41W}/H_2O_2 processes

Use	PPCPs	UV_{41W}	UV_{41W}/H_2O_2 (1.1mg/L)	UV_{41W}/H_2O_2 (3.1mg/L)	UV_{41W}/H_2O_2 (6.0mg/L)
Analgesics	Diclofenac	> 98	> 98	> 98	> 98
	Ketoprofen	98	99	99	100
	Isopropylantipyrine	> 95	> 95	> 94	> 95
	Naproxen	55	> 88	> 86	> 81
	Indomethacin	40	78	96	> 99
	Ethenzamide	13	66	94	> 97
	Mefenamic acid	5	60	> 98	> 98
Antiarrhythmic agents	Disopyramide	89	94	97	99
	Atenolol	36	70	92	98
	Propranolol	23	82	> 98	> 98
	Metoprolol	21	65	88	97
Antibiotics	Sulfamethoxazole	93	94	97	98
	Ciprofloxacin	> 89	> 89	> 90	> 91
	Nalidixic acid	78	90	> 99	> 99
	Sulfadimethoxine	75	81	91	96
	Levofloxacin	22	56	91	95
	Trimethoprim	19	63	87	95
	Lincomycin	19	73	94	98
	Clarithromycin	13	54	82	94
	Erythromycin	11	46	63	87
	Azithromycin	10	49	75	88
	Roxithromycin	9	52	78	93
The others	Diltiazem	96	100	100	100
	Dipyridamole	96	99	99	99
	Clofibric acid	93	96	96	> 97
	Chloramphenicol	> 87	> 42	> 82	> 83
	Furosemide	79	92	97	100
	Ifenprodil	62	88	97	100
	Crotamiton	41	73	90	97
	Griseofulvin	40	63	> 97	> 97
	Bezafibrate	31	72	91	97
	Pirenzepine	28	65	86	93
	Sulpiride	15	45	76	94
	Carbamazepine	13	65	90	98
	Theophyline	10	22	32	73
	DEET	7	53	81	93
	Cyclophosphamide	2	26	58	78
	Primidon	1	56	77	87

5.3.3 PPCPs removal with UV_{65W} lamp and H_2O_2

UV_{65W} lamp with a higher output of 21.8W_{UV} was used aiming at the improvement of the PPCPs removal performance by the introduction of more much UV dose because 90% removals for all the PPCPs could not be achieved by UV_{41W} and UV_{41W} /H_2O_2 processes under the experiment conditions carried out in this study. Table 5-6 indicates the removal efficiency of individual PPCPs at each reactor during UV_{65W} process.

It can be known that only 17 PPCPs including diclofenac and ketoprofen (analgesics), disopyramide (antiarrhythmic agent), sulfamethoxazole and ciprofloxacin (antibiotics) and clofibric acid (lipid modifying agent) could be removed by more than 90% in spite of the introduction of UV dose of 2,768 mJ/cm^2 (contact time : 15 min, R3). On the other hand, 11 PPCPs such as ethenzamide, metoprolol, azithromycin, roxithromycin, erythromycin, DEET, carbamazepine, sulpiride, primidon, theophylline and cyclophosphamide showed the removal efficiency of less than 50%, indicating that the PPCPs would be very resistant for UV. This result is compared with that for UV_{41W} process that removed 15 PPCPs by less than 50% at a contact time of 15 min. It was also observed that the removal efficiency of each PPCP increased slightly by the application of UV_{65W} lamp comparing to UV_{41W} process thanks to much UV dose used. However, considerable UV energy will still be needed for the efficient removal of a variety of PPCPs in secondary effluent.

Table 5-7 compares the removal efficiency of each PPCPs during UV_{65W} and UV_{65W} /H_2O_2 processes. The initial H_2O_2 concentrations used for UV_{65W}/H_2O_2 process were 1.2 mg/L, 3.1 mg/L and 6.2 mg/L and the contact time was 5 min (R1) for all the experiments. The UV dose introduced for 5 min was 923 mJ/cm^2. The removal efficiencies for UV_{65W}/H_2O_2 processes using the initial H_2O_2 concentration of 1.2 mg/L, 3.1 mg/L and 6.2 mg/L ranged from 31% (theophylline) to 100% (diltiazem), 63% (theophylline) to 100% (diltiazem) and >89% (naproxen) to 100% (diltiazem), respectively, showing that the removal efficiency improved significantly comparing to for UV_{41W} /H_2O_2 process. On the other hand, during UV_{65W} process 17 PPCPs and 32 PPCPs were removed by more than 90% when initial H_2O_2 concentrations were 1.2 mg/L and 3.1 mg/L, respectively. Beside naproxen, all the 37 PPCPs detected in tested water could be removed by more than 90% for UV_{65W}/H_2O_2 process using the initial H_2O_2 concentration of 6.2 mg/L.

Table 5-6 Removal efficiency of individual PPCPs at each reactor during UV_{65W} process

Use	PPCP	UV_{65W}		
		R1	R2	R3
Analgesics	Diclofenac	> 98	> 98	> 98
	Ketoprofen	97	99	99
	Isopropylantipyrine	> 92	> 92	> 92
	Indomethacin	51	77	90
	Mefenamic acid	25	53	> 98
	Naproxen	22	> 71	> 71
	Ethenzamide	21	33	44
Antiarrhythmic agents	Disopyramide	94	99	99
	Propranolol	35	65	81
	Atenolol	31	46	59
	Metoprolol	22	40	50
Antibiotics	Sulfamethoxazole	94	99	99
	Ciprofloxacin	> 93	> 93	> 93
	Nalidixic acid	87	> 99	> 99
	Sulfadimethoxine	84	94	97
	Levofloxacin	30	51	76
	Lincomycin	22	38	57
	Clarithromycin	21	38	52
	Trimethoprim	20	34	52
	Azithromycin	11	19	38
	Roxithromycin	10	19	32
	Erythromycin	2	17	31
The others	Diltiazem	100	100	100
	Clofibric acid	> 98	> 98	> 98
	Dipyridamole	98	98	100
	Chloramphenicol	> 91	> 91	> 91
	Furosemide	86	98	100
	Ifenprodil	74	92	98
	Bezafibrate	54	73	86
	Crotamiton	50	80	90
	Griseofulvin	50	68	83
	Pirenzepine	21	52	67
	DEET	20	31	48
	Carbamazepine	17	31	45
	Sulpiride	16	28	38
	Primidon	13	27	41
	Theophyline	11	15	20
	Cyclophosphamide	6	19	28

Table 5-7 Removal efficiency of each PPCP at contact time of 5 min during UV_{65W} and UV_{65W}/H_2O_2 processes

Use	PPCPs	UV_{65W}	UV_{65W}/H_2O_2 (1.2mg/L)	UV_{65W}/H_2O_2 (3.1mg/L)	UV_{65W}/H_2O_2 (6.2mg/L)
Analgesics	Diclofenac	> 98	> 98	> 98	> 98
	Ketoprofen	97	99	> 99	> 99
	Isopropylantipyrine	> 92	> 94	> 92	> 93
	Indomethacin	51	92	> 99	> 99
	Mefenamic acid	25	> 98	> 98	> 98
	Naproxen	22	> 80	> 86	> 89
	Ethenzamide	21	83	> 98	> 98
Antiarrhythmic agents	Disopyramide	94	98	99	100
	Propranolol	35	> 98	> 98	> 98
	Atenolol	31	90	98	> 98
	Metoprolol	22	79	96	> 99
Antibiotics	Sulfamethoxazole	94	97	99	100
	Ciprofloxacin	> 93	> 93	> 93	> 91
	Nalidixic acid	87	> 99	> 99	> 99
	Sulfadimethoxine	84	91	96	> 99
	Levofloxacin	30	82	94	99
	Lincomycin	22	84	97	> 98
	Clarithromycin	21	69	93	99
	Trimethoprim	20	79	94	100
	Azithromycin	11	64	84	97
	Roxithromycin	10	69	92	98
	Erythromycin	2	58	87	98
The others	Diltiazem	100	100	100	100
	Clofibric acid	> 98	> 97	> 97	> 98
	Dipyridamole	98	98	98	98
	Chloramphenicol	> 91	> 86	> 91	> 90
	Furosemide	86	98	> 99	> 99
	Ifenprodil	74	94	100	100
	Bezafibrate	54	88	97	> 99
	Crotamiton	50	86	96	99
	Griseofulvin	50	76	> 97	> 97
	Pirenzepine	21	66	92	> 98
	DEET	20	71	91	99
	Carbamazepine	17	81	96	100
	Sulpiride	16	60	93	98
	Primidon	13	70	86	95
	Theophyline	11	31	63	91
	Cyclophosphamide	6	50	79	> 93

5.3.4 The variation of SUVA during UV and UV/H_2O_2 processes for PPCPs removal

Specific UV absorbance (SUVA) is the absorbance (/cm) of a sample at 254 nm normalized for dissolved organic carbon (DOC, mg/L), and has been known to be strongly correlated to the aromaticity percentage (Weishaar *et al.*, 2003). The aromaticity content of a sample decreases along the cleavage of the aromatic rings by UV or UV/H_2O_2 process. All the PPCPs investigated in this study have aromatic ring in their chemical structures and, therefore, the decrease of SUVA can be related to the degradation of PPCPs.

The removal efficiency of SUVA was 16% for UV_{41W} process, while for UV_{41W} /H_2O_2 process using initial H_2O_2 concentrations of 1.1 mg/L, 3.1 mg/L and 6.0 mg/L, the SUVA decreased by 23%, 28% and 37%, respectively (Fig. 5-5). The SUVA of tested waters ranged from 0.014 L/mg·cm to 0.016 L/mg·cm for the experiments using UV_{65W} lamp, which are a little less than for the experiments using UV_{41W} lamp (0.021 L/mg·cm ~ 0.024 L/mg·cm). The difference in SUVA would be driven from different experiment days. For the experiments using UV_{65W} lamp, SUVA decreased more significantly compared to for UV_{41W} and UV_{41W} /H_2O_2 processes, and the removal efficiencies were 15%, 29%, 41% and 52% for UV_{65W}, UV_{65W}/H_2O_2 (1.2 mg/L), UV_{65W}/H_2O_2 (3.1 mg/L) and UV_{65W}/H_2O_2 (6.2 mg/L) processes, respectively.

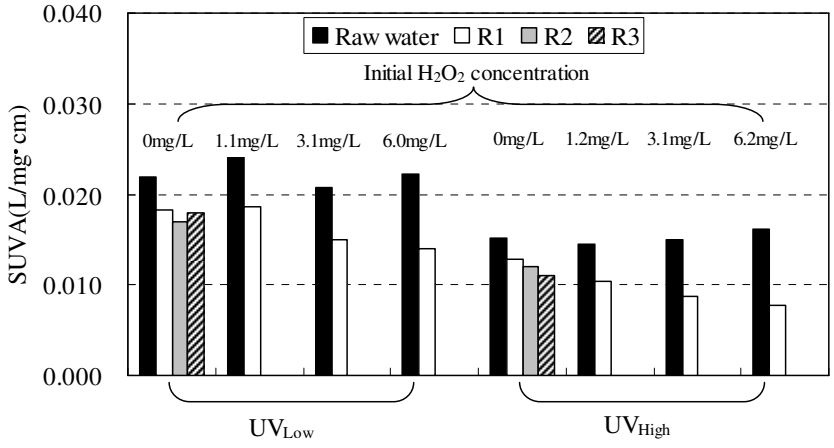


Fig. 5-5 The decrease of SUVA during UV and UV/H_2O_2 processes

On the other hand, the number of PPCPs removed by more than 90% increased linearly with the decrease of SUVA, irrespective of UV lamp applied (Fig. 5-6). The number of PPCPs with a removal efficiency of more than 90% increased from 7 to 37 as the removal efficiency of SUVA increased from 15% to 52%. It has been reported that SUVA of secondary effluent can be decreased by around 60% with ozonation (Kim, 2005). In this study, 37 PPCPs were removed by 90% when SUVA decreased by 52% and, therefore, it is considered that the 60% decrease of SUVA can ensure the high removal efficiency of a variety of PPCPs in secondary effluent.

Fig. 5-7 shows the relation between the number of PPCPs removed by more than 90% and SUVA in treated water. It was observed that the number increased as SUVA decreased, irrespective of UV lamp applied. However, low SUVA is not necessarily likely to ensure the high removal efficiency of PPCPs. For example, SUVA was 0.014 L/mg·cm when 31 PPCPs were removed by more than 90% (UV_{41W} process), while only 10 PPCPs were removed by more than 90% despite very low SUVA of 0.013 L/mg·cm in treated water (UV_{65W} process). Therefore, it can be known that it will be difficult to expect the PPCPs removal from the decrease of SUVA in treated water.

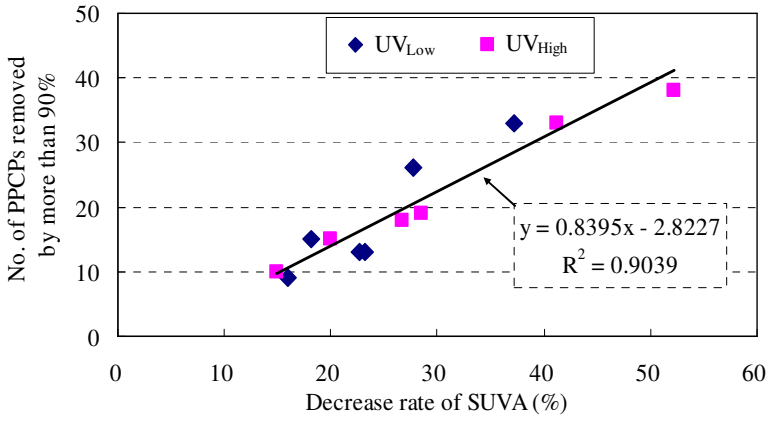


Fig. 5-6 PPCPs removal according to the removal efficiency of SUVA

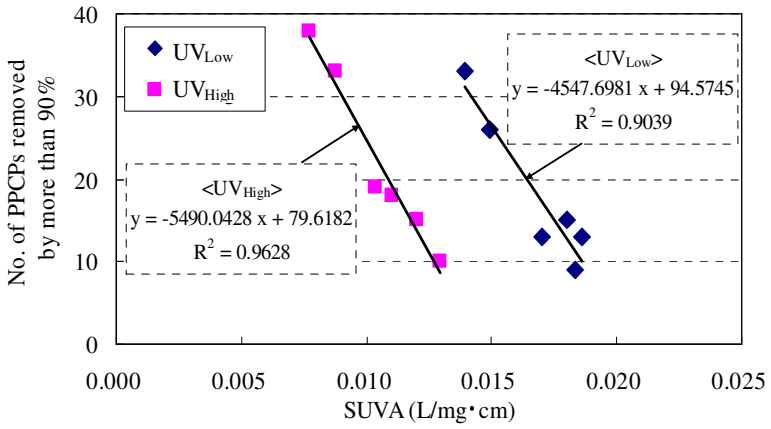


Fig. 5-7 PPCPs removal according to the decrease of SUVA

5.3.5 Energy consumption and operating cost

The cost evaluation of UV/H_2O_2 process was performed as the procedure described by Sutherland *et al* (2004) and Mascolo *et al* (2008). Cost caused by added H_2O_2 amount and electrical energy of UV used occupies most of the process cost for UV and UV/H_2O_2 processes. Firstly, an electrical energy introduced can be calculated using the following general equation:

Electrical energy (kWh/m^3) = 1,000 × UV power (kW)/60 × flow (L/min) + electrical energy for H_2O_2 production (kWh/m^3) (1)

Electrical energy for H_2O_2 production was calculated on the basis of CO_2 amount generated for producting H_2O_2 (The Ministry of Economy, Trade and Industry, 2003). Fig. 5-8 indicates the number of PPCPs removed by more than 90% according to electrical UV energy introduced during UV and UV/H_2O_2 processes. When UV alone was used, the number increased slightly with the increased electrical energy, irrespective of the applied UV lamp, and the increasing tendency in the number was almost the same. From these, it can be known that the removal effectiveness of PPCPs will increase linearly according to the increase of the introduced electrical energy. When the electrical energy of 1.56 kWh/m^3, which is the maximum electrical energy introduced for UV alone process, was used, only 17 out of the 38 PPCPs were removed by more than 90%. Therefore, it will be inevitable to introduce considerable electrical UV energy for the effective removal of a variety of PPCPs by UV alone process.

On the other hand, it was observed that the addition of H_2O_2 for UV process can result in the very effective PPCPs removal even at the introduction of low electrical energy. Moreover, the removal effectiveness increased with the increased initial H_2O_2 concentration when the same UV lamp was used, and in this study, 37 PPCPs could be removed by more than 90% when initial H_2O_2 concentration in tested water was 6.2 mg/L for UV_{65W} process (consumed electrical energy : 0.54 kWh/m^3).

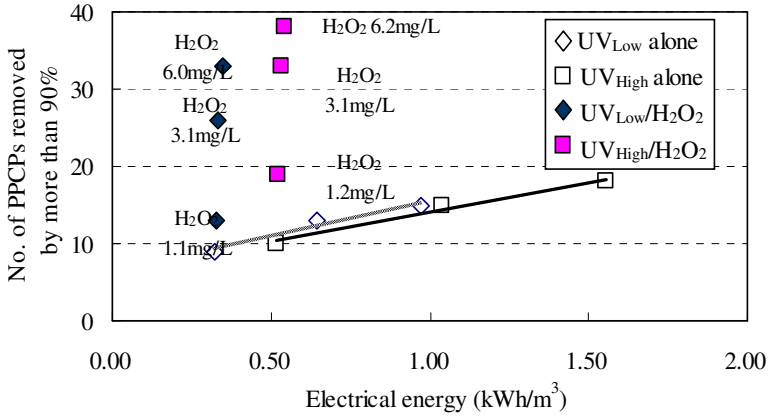


Fig. 5-8 PPCPs removal performance according to electrical UV energy introduced

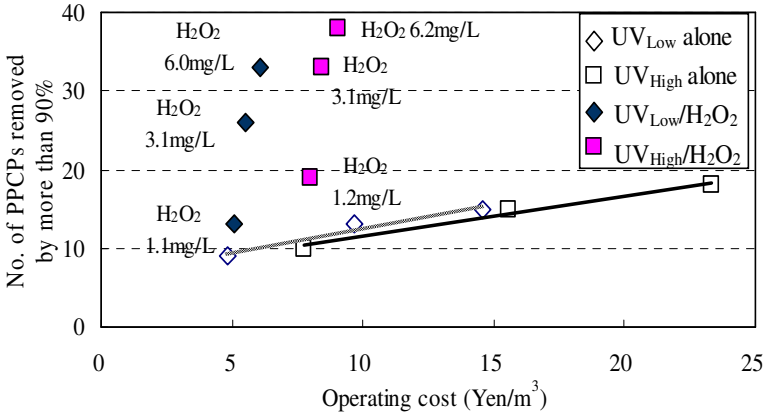


Fig. 5-9 PPCPs removal performance according to estimated operating cost

The operating cost of UV/H_2O_2 process can be calculated with using following equation (Mascolo *et al*., 2008);

Operating cost = [EE/O × log (C_i/C_f) × unit cost of electrical energy] + H_2O_2 cost (2)

where the cost of lamp replacement was not considered. Electrical energy in equation (1) can be expressed as follow;

Electrical energy (kWh/m^3) =EE/O ×log (C_i/C_f) (3)

where EE/O is the electrical energy necessary for one order removal of the investigated pollutant; C_i *and* C_f the initial and final concentration, respectively. Here, the log (C_i/C_f) was calculated to 1 because this study was focused on the 90% removal of the investigated PPCPs. Therefore, equation (2) can be expressed as follow;

Operating cost = [Electrical energy (kWh/m^3) × unit cost of electrical energy] + H_2O_2 cost (4)

15 Yen/kWh and 151.3 Yen/kg were used for the unit cost of electrical energy and cost of H_2O_2, respectively.

Fig. 5-9 shows the number of PPCPs removed by more than 90% and the operating cost calculated by equation (4) for each process. For UV alone process, it can be known that the PPCPs removal effectiveness to the increase of the operating cost did not improve so significantly despite the considerable increase of operating cost. Contrarily, for UV/H_2O_2 process, the slight increase of operating cost caused by the H_2O_2 addition led to the significant improvement for the PPCPs removal performance. This time, the operating cost ranged from 5.1 Yen/m^3 to 6.1 Yen/m^3 and 8.0 Yen/m^3 to 9.1 Yen/m^3 for UV_{41W}/H_2O_2 and UV_{65W}/H_2O_2 processes, respectively. Therefore, it can be concluded that the combination of H_2O_2 with UV process will be much more cost-effective than UV alone process that will cause the high consumption of electrical UV energy for the 90% removal PPCPs.

5.4 Summary

The performance of UV and UV/H_2O_2 processes for the PPCPs removal was investigated using secondary effluent. In addition, operating costs required for the accomplishment of appropriate PPCPs removal by the applied processes were estimated.

1) 38 PPCPs were detected in secondary effluent used for tested water in this study. The concentration ranged from 1 μg/L to 481 μg/L. As therapeutic classes, 11 antibiotics including clarithromycin and levefloxacin, 7 analgesics including ketoprofen and diclofenac and 4 antiarrhythmic agents such as disopyramide, atenolol, metoprolol and propranolol were mainly present. Besides, various PPCPs such as anticonvulsants (carbamazepine, primidone), vasodilators (dipyridamole, diltiazem), diuretic (furosemide), antineoplastic agent (cyclophosphamide) and peptic ulcer drug (pirenzepine) were also present in secondary

effluent. The side effects of PPCPs on the aquatic environment and human body have not been known yet, however, PPCPs in water environment should be removed in aspect of precautionary principles.

2) Only 17 of 38 PPCPs were removed by more than 90% despite UV dose of 2,768 mJ/cm^2 (contact time : 15 min) during UV process, showing that considerable UV dose will be required for the effective PPCPs removal by UV alone process. This also shows that it will be difficult to accomplish good PPCPs removals by typical UV disinfection process (UV dose : 40 mJ/cm^2 ~ 140 mJ/cm^2, contact time : a few secs).

3) On the other hand, the PPCPs removal by UV alone process improved significantly by the combination of H_2O_2 with UV process. Except naproxen (>89%), 37 PPCPs were removed by more than 90% at the operational condition of UV dose of 923 mJ/cm^2 (contact time : 5 min) and initial H_2O_2 concentration of 6.2 mg/L. As a consequence, the combination of UV and H_2O_2 made it possible to reduce UV dose at least by more than 3 times comparing with for UV alone process.

4) The number of PPCPs removed by more than 90% increased linearly with the increased removal efficiency of SUVA, irrespective of applied processes. On the other hand, the removal efficiency of SUVA was 52% at at the operational condition of UV dose of 923 mJ/cm^2 and initial H_2O_2 concentration of 6.2 mg/L. From these results, it was expected that SUVA removal of more than 50% ensures the effective removal of various PPCPs by UV or UV/H_2O_2 processes.

5) Electrical energy required for the effective PPCPs removal by UV/H_2O_2 process was 0.54 kW per 1 m^3 target water (Operational condition : UV dose : 923 mJ/cm^2, H_2O_2 : 6.2 mg/L), showing that UV/H_2O_2 process can reduce energy consumption and operating cost considerably, comparing with UV alone process, and, therefore, be utilized as a treatment option for water reuse.

5.5 References

Andreozzi R., Raffaele M., Nicklas R., 2003, Pharmaceuticals in STP effluents and their solar photodegradation in aquatic environment, *Chemosphere* 50, 1319-1330

Bader H., Hoigne J., 1981 Determination of ozone in water by the indigo method, *Water Res.*

15, 449-456

Baga A.N., Johnson G.R.A., Nazhat N.B., Saadalla-Nazhat R.A., 1988, A simple spectrophotometric determination of hydrogen peroxide at low concentrations in aqueous solution, *Anal. Chem. Acta.* 204, 349-353

Blatchley III E.R., Shen C., Scheible O.K., Robinson J.P., Ragheb K., Bergstrom D.E., Rokjer D., 2007, Validation of large-scale, monochromatic UV disinfection systems for drinking water using dyed microspheres, *Water Res.*, doi:10.1016/j.watres.2007.08.019

Canonica S., Meunier L., von Gunten U., 2008, Phototransformation of selected pharmaceuticals during UV treatment of drinking water, *Water Res.* 42, 121-128

Cleuvers, M., 2004, Mixture toxicity of the anti-inflammatory drugs diclofenac, ibuprofen, naproxen, and acetylsalicylic acid, *Ecotoxicology and Environmental Safety* 59, 309-315

Daughton C.G. and Ternes T.A., 1999, Pharmaceuticals and Personal Care Products in the Environment: Agents of Subtle hange?, *Environmental Health Perspectives* 107, 907-938

Doll T.E., Frimmel F.H., 2003, Fate of pharmaceuticals - photodegradation by simulated solar UV-light. *Chemosphere* 52, 1757-1769

Halling-Sørensen B., Nielsen S.N., Lanzky P.F., Ingerslev F., Lutzhoft H.C.H., Jorgensen S.E., 1998, Occurrence, fate and effects of pharmaceutical substances in the environment- A review, *Chemosphere* 36, 357-393

Heberer T., Verstraeten I.M., Meyer M.T., Mechlinski A., Reddersen K., 2001, Occurrence and fate of pharmaceuticals during bank filtration-preliminary results from investigations in Germany and the United States, *Water Resources Update* 120, 4-17

Heberer T., 2002, Occurrence, fate and removal of pharmaceutical residues in the aquatic environment: a review of recent research data, *Toxicology Letters* 131, 5-17

Holm J.V., Rugge K., Bjerg P.L., Christensen T.H., 1995, Occurrence and distribution of pharmaceutical organic compounds in the groundwater downgradient of a landfill (Grindsted, Denmark), *Environ. Sci. technol* 29, 1415-1420

Japan sewage works association, Sewage test methods - Supplemental preliminary version (cryptosporidium and Endocrine Disrupters Chapter), 2002

Kanda R., Griffin P., James H.A. and Fothergill J., 2003, Pharmaceutical and personal care products in sewage treatment works, *J. Environ. Monit.* 5, 823-830

Kim H.S., 2005, Behavior and control of by-products during ozone and ozone/hydrogen peroxide treatments of sewage effluent, Department of Urban & Environmental Engineering, Kyoto University, Kyoto

Kim I.H., Tanaka H., Iwasaki T., Takubo T., Morioka T., Kato Y., 2008, Classification of the degradability of 30 pharmaceuticals in water with ozone, UV and H_2O_2, *Wat Sci Technol.*, 57, 195-200

Lopez A., Anna B., Giuseppe M., John K., 2003, Kinetic investigation on UV and UV/H_2O_2 degradations of pharmaceutical intermediates in aqueous solution, *J. Photochem. and Photobiol.* 156, 121-126

Mascolo G., Ciannarella R., Balest L., Lopez A., 2007, Effectiveness of UV-based advanced oxidation processes for the remediation of hydrocarbon pollution in the groundwater: A laboratory investigation, *J. Hazard. Mater.*, doi:10.1016/j.jhazmat.2007.07.120

Mascolo G., Ciannarella R., Balest L., Lopez A., 2008, Effectiveness of UV-based advanced oxidation processes for the remediation of hydrocarbon pollution in the groundwater: A laboratory investigation, *J. Hazardous Materials* 152, 1138-1145

Nakada N., Taniishima T., Shinohara H., Kiri K., Takada H., 2006, Pharmaceutical chemicals and endocrine disrupters in municipal wastewater in Tokyo and their removal during activated sludge treatment, *Water Res.* 40, 3297-3303

Okuda T., Kobayashi Y., Nagao R., Yamashita N., Tanaka H., Tanaka S., Fuji S., Konishi C., Houwa I., 2008, Removal efficiency of 66 pharmaceuticals during wastewater treatment process in Japan, *Wat Sci Technol.* 57, 65-71

Pereira V.J., Weinberg H.S., Linden K.G., Singer P.C., 2007, UV degradation kinetics and modeling of pharmaceutical compounds in laboratory grade and surface water via direct and indirect photolysis at 254 nm, Environmental science and technology 41, 1682-1688

Plumlee M.H., Lopez-Mesas M., Heidlberger A., Ishida K.P., Reinhard M., 2008, N-nitrosodimethylamine (NDMA) removal by reverse osmosis and UV treatment and analysis via LC-MS/MS, *Water Res.* 42, 347-355

Sacher F., Lange F.Th., Brauch H.-J., Blankenhorn I., 2001, Pharmaceuticals in groundwaters. Analytical methods and results of a monitoring program in Baden-Wurttemberg, Germany. *J.Chromatogr. A* 938, 199-210

Smital T., Luckenbach T., Sauerborn R., Hamdoun A.M., Vega R. L., Epel D., 2004, Emerging contaminants-pesticides, PPCPs, microbial degradation products and natural substances as inhibitors of multixenobiotic defense in aquatic organisms, *Mutation Research* 552, 101-117

Sutherland J., Adams C., Kekobad J., 2004, Treatment of MTBE by air stripping, carbon adsorption, and advanced oxidation: technical and economic comparison for five groundwaters, *Water Res.* 38, 193-205

Ternes T.A., 1998, Occurrence of drugs in German sewage treatment plants and rivers, *Water Res.* 32, 3245-3260

The Ministry of Economy, Trade and Industry, Report for guideline of environment-friendly water treatment technology, 2003

Weishaar J. L., Aiken G. R., Bergamaschi B. A., Fram M. S., Fujii R., Mopper K., 2003, Evaluation of Specific Ultraviolet Absorbance as an Indicator of the Chemical Composition and Reactivity of Dissolved Organic Carbon, *Environ. Sci. Technol.* 37, 4702-4708

Ziolli R.L., Jardim W.F., 2003, Photochemical transformations of water-soluble fraction (WSF) of crude oil in marine waters A comparison between photolysis and accelerated degradation with TiO_2 using GC-MS and UVF, *J. Photochem. Photobiol.* 155, 243-252

CHAPTER VI

INVESTIGATION ON THE REMOVAL PERFORMANCE FOR PHARMACEUTICALS AND PERSONAL CARE PRODUCTS BY O_3-BASED PROCESSES IN BENCH SCALE PLANT

6.1 Introduction

Wastewater is generally treated in wastewater treatment plants (WWTPs) before it is discharged into receiving waters. Nevertheless, WWTPs is known as the main source of PPCPs in the aquatic environment (Halling-Sørensen *et al*., 1998; Kanda *et al*., 2003). If the consumption of PPCPs is not reduced, the improvement of WWTPs will be one of the options to prevent the release of the PPCPs into the aquatic environment. As mentioned before, conventional activated sludge treatment was shown to degrade PPCPs to various extents (Ternes, 1998; Daughton *et al*., 1999; Nakada *et al*., 2006; Okuda *et al*., 2008). Therefore, advanced treatment technologies have to be implemented to achieve further removal of PPCPs. O_3 process has been shown to have a high potential for the removal of PPCPs in drinking water (Huber *et al*., 2003) and wastewater (Ternes, 2003). They reported that O_3 doses ranging from 5 mg/L to 15 mg/L led to a complete degradation of most of the PPCPs except for iodinated X-ray contrast media.

The combined O_3/UV process has been widely studied due to a synergistic effect of several reactions such as direct UV photodegradation, direct O_3 process and OH radical oxidation. O_3/UV process has been employed for the removal of the organic contaminants in wastewater, drinking water and industrial wastewater (Lau *et al*., 2007; Zou *et al*., 2007). However, limited information is available on the effectiveness of O_3/UV processes for PPCPs

removal although they have been known as very effective processes for PPCPs removal.

In Chapter IV, most of the PPCPs were degraded by more than 90% at O_3 consumptions of 6.3 mg/L and 4.5 mg/L for O_3 and O_3/UV treatments, respectively, when using tested water prepared by PW spiked with the 30 PPCPs, indicating that O_3 dose can be reduced by the combination of UV during O_3 treatment. Based on these results, in this study the removal performance of O_3-based processes (O_3 and O_3/UV processes) for the PPCPs detected in secondary effluent was investigated using bench-scale experimental setup with a treatment capacity of $10m^3$/day. Moreover, electrical energy and operating cost required for an effective PPCPs removal by the applied processes were estimated. Research structure in this chapter is shown in Fig. 6-1.

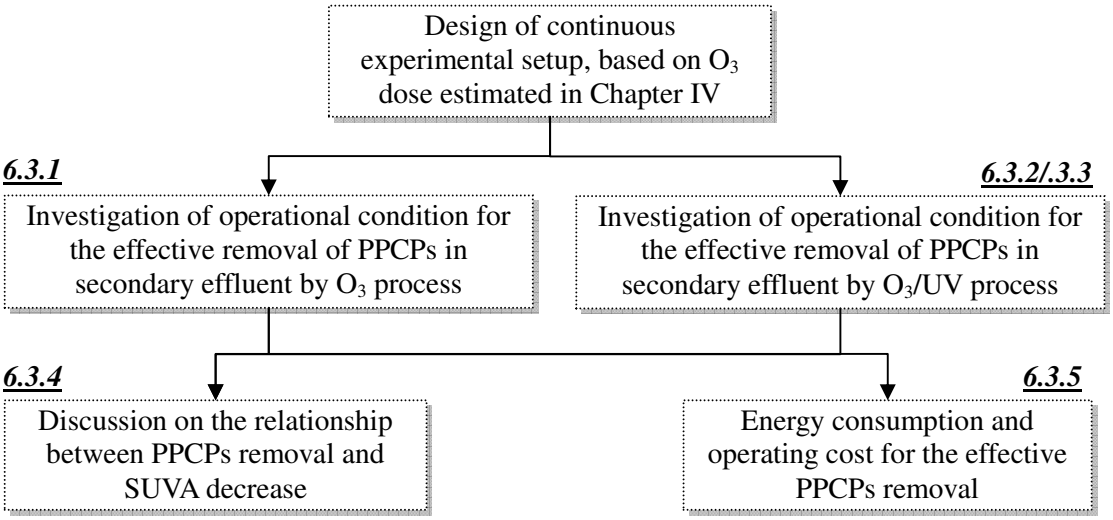


Fig. 6-1 Structure of this chapter

6.2 Materials and methods

6.2.1 Experimental setup

Experiment setup consists of three reactors (Reactor 1 (R1), Reactor 2 (R2) and Reactor 3 (R3)) connected in series (Fig. 6-2). In this study, only R1 and R2 were operated for all the experiments. The effective volume and hydraulic retention time (HRT) a reactor are 35L and 5 min, respectively. In order to ensure stable flux state, UV irradiation and O_3 injection, each process was operated more than 3 HRT before samples were taken.

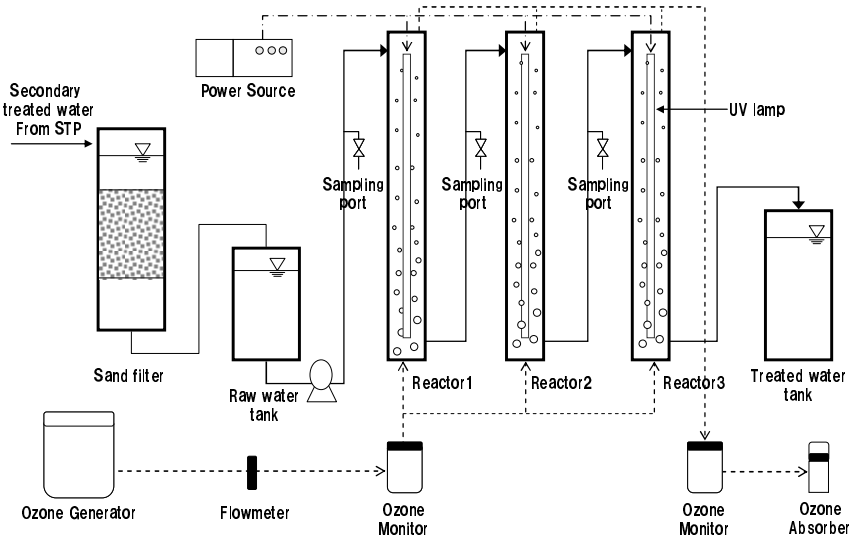


Fig. 6-2 Experimental setup for O_3-based processes

To investigate the effectiveness of O_3 process for PPCPs removal, treatment experiments using different O_3 doses were performed. O_3/UV process was carried out using different O_3 dose and UV lamps with different UV intensity.

Table 6-1 shows the operational conditions investigated in this study. O_3 process was performed at different O_3 doses of 2 mg/L, 4 mg/L and 6 mg/L. The concentrations of injected O_3 gas were 14 mg/L, 28 mg/L and 42 mg/L for O_3 doses of 2 mg/L, 4 mg/L and 6 mg/L, respectively. O_3 gas was injected to R1 and R2 at a rate of 0.5 L/min, respectively. For O_3/UV process, 2 types of UV lamps (21.5 W and 65 W low pressure mercury UV lamps) were used. Here, 2 UV lamps (UV wavelength : 254 nm, Length of lamp : 1,556 mm) were described as $UV_{21.5W}$ lamp and UV_{65W} lamp, respectively, and O_3/UV process using these UV lamps were also as $O_3/UV_{21.5W}$ process and O_3/UV_{65W} process. $UV_{21.5W}$ and UV_{65W} lamps have UV output of 7.2 W and 21.8 W, and UV intensity of 0.339 mW/cm^2 and 1.025 mW/cm^2, respectively. 3 UV lamps are placed inside each reactor and the same O_3 doses (2 mg/L, 4 mg/L and 6 mg/L) with for O_3 process were applied. O_3, $O_3/UV_{21.5W}$ and O_3/UV_{65W} processes were operated on different days. All the samples taken during O_3-based processes were purged by N_2 gas immediately after sampling in order to remove residual O_3 in sample and stop the reaction of PPCPs with O_3.

Table 6-1 Operational conditions

O_3		$O_3/UV_{21.5W}$			O_3/UV_{65W}		
Run	O_3 dose	Run	O_3 dose	UV lamp	Run	O_3 dose	UV lamp
Run1	2 mg/L	Run4	2 mg/L	Not used	Run8	2 mg/L	Not used
Run2	4 mg/L	Run5	2 mg/L	R1, R2	Run9	2 mg/L	R1, R2
Run3	6 mg/L	Run6	4 mg/L	R1, R2	Run10	4 mg/L	R1, R2
-	-	Run7	6 mg/L	R1, R2	Run11	6 mg/L	R1, R2

6.2.2 PPCPs investigated

Secondary effluent was used as tested water in this study. The pH, DOC and UV254 of the tested water ranged from 6.5 to 6.8, 2.7 mg/L to 3.4 mg/L and 0.0514 /cm to 0.0779 /cm, respectively. 37, 35 and 38 PPCPs were detected in the tested water for O_3, $O_3/UV_{21.5W}$ and O_3/UV_{65W} processes, respectively.

Table 6-2 The name and use of PPCPs detected in tested water

No.	PPCP	Use	No.	PPCP	Use
1	Acetaminophen	Analgesic	21	Atenolol	Antiarrhythmic agent
2	Diclofenac		22	Disopyramide	
3	Ethenzamide		23	Metoprolol	
4	Indomethacin		24	Propranolol	
5	Isopropylantipyrine		25	Carbamazepine	Anticonvulsant
6	Ketoprofen		26	Primidone	
7	Mefenamic acid		27	Griseofulvin	Antifungal drug
8	Naproxen		28	Crotamiton	Anti-itch drug
9	Azithromycin	Antibiotic	29	Chloramphenicol	Antimicrobial drug
10	Ciprofloxacin		30	Cyclophosphamide	Antineoplastic agent
11	Clarithromycin		31	Sulpiride	Anti-psychotic drug
12	Erythromycin		32	Clenbuterol	Bronchodilator
13	Levofloxacin		33	Theophylline	
14	Lincomycin		34	Furosemide	Diuretic
15	Nalidixic acid		35	DEET	Insect repellent
16	Roxithromycin		36	Bezafibrate	Lipid modifying agent
17	Sulfadimethoxine		37	Clofibric acid	
18	Sulfamerazine		38	Ifenprodil	NMDA receptor antagonist
19	Sulfamethoxazole		39	Pirenzepine	Peptic ulcer drug
20	Trimethoprim		40	Diltiazem	Vasodilator
			41	Dipyridamole	

The number of the PPCPs detected in the tested water during all the investigated treatments was 41 including eight analgesics, twelve antibiotics and four antiarrhythmic agents (Table 6-2).

The concentrations of the detected PPCPs ranged from 2 ng/L (isopropylantipyrine) to 402 ng/L (clarithromycin), 2 ng/L (isopropylantipyrine) to 774 ng/L (clarithromycin) and 1 ng/L (isopropylantipyrine) to 503 ng/L (clarithromycin) for O_3, $O_3/UV_{21.5W}$ and O_3/UV_{65W} processes, respectively.

6.2.3 Analytical methods

The concentrations of the 30 PPCPs were measured simultaneously with LC/MS/MS. The measurement condition of LC/MS/MS, limit of detection (LOD) and limit of quantification (LOQ) were described in Chapter V.

DOC (dissolved organic carbon) concentration was measured with a TOC analyzer (TOC-5000A, Shimadzu) and calculated from the difference of TOC (total organic carbon) and IC (inorganic carbon). Dissolved ozone concentration was measured with indigo method (Bader *et al*., 1981) measuring the absorbance at 600 nm wavelength by a spectrophotometer (UV-16000, Shimadzu). This spectrophotometer was also used for measuring the absorbance at 254 nm (UV_{254}).

6.3 Results and discussion

6.3.1 Effect of O_3 dose on the PPCPs removal during O_3 process

The effect of O_3 dose on the PPCPs removal in secondary effluent was investigated. The O_3 doses used for O_3 process were 2 mg/L, 4 mg/L and 6 mg/L. 37 PPCPs ranging from 2 ng/L (isopropylantipyrine) to 402 ng/L (clarithromycin) in their concentration were detected in secondary effluent used as tested water. Table 6-3 shows removal efficiencies of the 37 PPCPs during O_3 process for 10 min (R1+R2) performed at each O_3 dose. The removal efficiency of PPCPs decreased by less than limit of detection (LOD) after O_3 treatment was calculated to 100%. 25 PPCPs including carbamazepine, crotamiton and diclofenac were removed by more than 90% even at O_3 dose of 2 mg/L, showing that O_3 was very effective for the PPCPs removal. It was also observed that the increase of O_3 dose could achieve the effective PPCPs removal.

Among 11 antibiotics (sulfadimethoxine, trimethoprim, erythromycin, lincomycin, roxithromycin, levofloxacin, sulfamethoxazole, azithromycin, ciprofloxacin, clarithromycin and nalidixic acid), 10 antibiotics beside nalidixic acid could be removed by more than 90%, irrespective of O_3 dose. 3 antibiotics such as levofloxacin, ciprofloxacin and nalidixic acid belong to quinoline antibiotics, however, only nalidixic acid showed low removal efficiency of 66% at O_3 dose of 2 mg/L although higher O_3 dose (more than 4 mg/L) could remove the compound by more than 90%. Quinoline, a representative of Nitrogen-heterocyclic compounds has been known to be degraded more easily by OH radicals than by O_3 (Wang *et al*., 2004). Therefore, advanced oxidation processes (AOPs) such as O_3/UV and O_3/H_2O_2 are also expected to ensure the efficient removal of the PPCP. Ketoprofen (analgesic), which has known to be degraded very easily by UV (Kim *et al*., 2008), also showed low removal efficiency of 73% at O_3 dose of 2 mg/L. Except ketoprofen and nalidixic acid, atenolol, metoprolol and disopyramide (antiarrhythmic agent), bezafibrate and clofibric acid (lipid modifying agent), ethenzamide (analgesic), chloramphenicol (antimicrobial drug), DEET (insect repellent), griseofulvin (antifungal drug) and primidone (anticonvulsant) also showed less than 90% in their removal efficiency at low O_3 dose of 2 mg/L.

Table 6-3 Removal efficiency of the 37 PPCPs for O_3 process (Run1, Run 2 and Run3, contact time: 10min)

No.	Use	PPCPs	O_3 dose : 2 mg/L (O_3 consumption : 1.6 mg/L)	O_3 dose : 4 mg/L (O_3 consumption : 3.0 mg/L)	O_3 dose : 6 mg/L (O_3 consumption : 4.4 mg/L)
1	Analgesics	Indomethacin	> 99	> 99	> 99
2		Isopropylantipyrine	> 98	> 97	> 97
3		Diclofenac	> 98	> 97	> 98
4		Mefenamic acid	> 98	> 98	> 98
5		Naproxen	> 86	> 83	> 89
6		Ethenzamide	74	96	> 98
7		Ketoprofen	73	91	97
8	Antiarrhythmic agents	Propranolol	> 98	> 98	> 98
9		Atenolol	89	> 98	> 98
10		Metoprolol	86	> 99	> 99
11		Disopyramide	74	96	100
12	Antibiotics	Roxithromycin	100	98	100
13		Erythromycin	100	100	100
14		Trimethoprim	100	100	100
15		Sulfadimethoxine	100	100	100
16		Lincomycin	> 99	> 99	> 99
17		Levofloxacin	98	100	98
18		Sulfamethoxazole	97	100	100
19		Azithromycin	97	100	100
20		Ciprofloxacin	93	> 97	> 95
21		Clarithromycin	90	99	100
22		Nalidixic acid	66	96	> 99
23	Anticonvulsant	Carbamazepine	100	100	100
24		Primidone	51	85	87
25	Antifungal drug	Griseofulvin	62	86	> 98
26	Anti-itch drug	Crotamiton	100	100	100
27	Antimicrobial drug	Chloramphenicol	69	> 90	> 90
28	Anti-psychotic drug	Sulpiride	100	100	100
29	Bronchodilator	Theophylline	96	> 99	99
30	Diuretic	Furosemide	> 99	100	100
31	Insect repellent	DEET	67	88	93
32	Lipid modifying agent	Bezafibrate	83	99	100
33	Lipid modifying agent	Clofibric acid	74	84	> 97
34	NMDA receptor antagonist	Ifenprodil	97	100	100
35	Peptic ulcer drug	Pirenzepine	> 96	> 96	> 95
36	Vasodilator	Dipyridamole	100	100	100
37		Diltiazem	100	100	100

On the other hand, the removal efficiency of clofibric acid, chloramphenicol, DEET,

griseofulvin and primidone improved by more than 80% when O_3 dose of 4 mg/L was applied. Moreover, all the PPCPs except primidone (87%) were removed by more than 90% at O_3 dose of 6 mg/L. Consequently, it is considered that O_3 dose of 6 mg/L can ensure the efficient removal of the investigated PPCPs for O_3 alone process.

Fig. 6-3 compares dissolved ozone and O_3 consumption for each O_3 process. As shown in Fig. 6-3, it was found that high O_3 dose increased O_3 consumption and dissolved ozone concentration. Dissolved ozone can react with bromide in water and lead to the formation of bromate (Wert *et al.*, 2007). Bromate regulation is now being proposed at a maximum contaminant level of 10 μg/L in drinking water in U.S.EPA. Carcinogenesis of bromate has been found (Kurokawa *et al.*, 1983) and, therefore, concerns on the control of bromate formation are increasing. In 2003, Japan has set the bromate regulation of 10 μg/L in drinking water (The Ministry of Health, Labour and Welfare, Japan, 2003a,b). Bromate has also been known to remain in the water once formed (von Gunten U., 2003b). Therefore, the formation potential of bromate should be considered especially when O_3 alone process was applied. Moreover, it will be desirable that the ecological risk which can be caused by PPCPs intermediates formed during O_3 process is investigated in order to ensure the effectiveness of O_3 process for PPCPs removal.

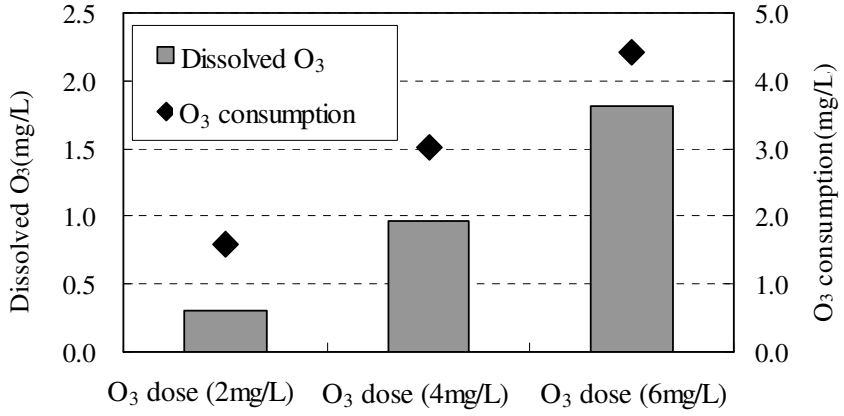


Fig. 6-3 Comparison of dissolved ozone and O_3 consumption during O_3 process

6.3.2 Effect of $UV_{21.5W}$ addition on the PPCPs removal during O_3 process

Here, the effect of UV combination with O_3 process on the PPCPs removal was

investigated. $UV_{21.5W}$ lamp was combined during O_3 processes performed using O_3 dose of 2 mg/L, 4 mg/L and 6 mg/L. As a control experiment, O_3 alone process was carried out at O_3 dose of 2 mg/L. In this study, 35 PPCPs were detected in tested water, and their concentrations ranged from 2 ng/L (isopropylantipyrine) to 774 ng/L (clarithromycin).

6.3.2.1 O_3 process

Fig. 6-4 indicates the removal efficiency of the 35 PPCPs during O_3 process at O_3 dose of 2 mg/L (contact time: 10 min). Rather low removal efficiency (11% (ethenzamide) ~ 100% (mefenamic acid)) was obtained comparing with the result (51% (primidone) ~ 100% (carbamazepine)) in 6.3.1 (O_3 dose: 2 mg/L). The decreased removal efficiency might be caused by the difference in the quality of tested water. For O_3 process in 6.3.1, specific UV absorbance (SUVA) was 0.018 L/mg·cm (DOC: 3.0 mg/L, UV254: 0.0546 /cm), while SUVA of 0.024 L/mg·cm (DOC: 3.2 mg/L, UV254: 0.0779 /cm) was shown in this experiment. High SUVA means that more O_3-consuming organic materials are included in tested water. Moreover, the difference in water quality is also demonstrated by that O_3 absorption rate (84%) in this experiment was rather higher than for the experiment (79%) in 6.3.1, and O_3 consumption (1.7mg/L) was also slightly higher than for 6.3.1 (1.6 mg/L). It is thought that the difference led to the decreased PPCPs removal efficiency (No. of PPCPs removed by more than 90% : 16 out of the 35 PPCPs) despite the same O_3 dose of 2mg/L.

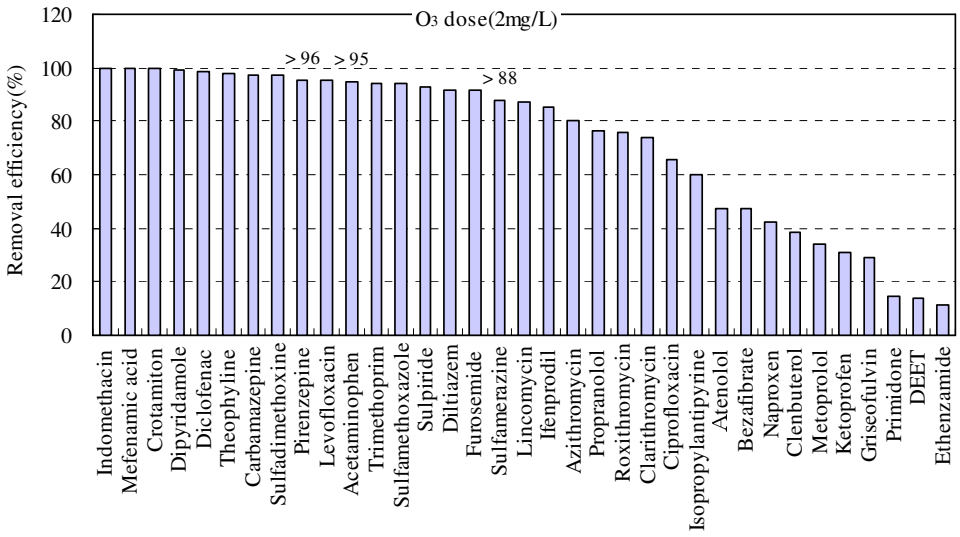


Fig. 6-4 Removal efficiency of the 35 PPCPs during O_3 process (Run 4, contact time: 10 min)

6.3.2.2 $O_3/UV_{21.5W}$ process

Table 6-4 compares the removal efficiency of each PPCP during O_3 process (Run 4) and $O_3/UV_{21.5W}$ processes (Run 5, 6 and 7) for contact time of 10 min. UV dose introduced for 10 min was 1,220 mJ/cm^2. Each signal in Table 6-4 represents individual PPCPs. For $O_3/UV_{21.5W}$ process at O_3 dose of 2 mg/L, it was observed that the removal efficiency of many PPCPs was lower than even for O_3 alone process. Several researchers have reported that PPCPs react very fast with O_3 molecular (Huber *et al*., 2003). However, most of O_3 molecular would be photolyzed by UV when low O_3 dose is used, and low dissolved ozone concentration shown in Fig. 6-5 proves this fact. During O_3/UV process organic materials are mainly degraded by OH radicals formed through UV photodegradation of O_3 molecular and/or by direct UV photodegradation (JOA, 2004). However, OH radicals can be consumed easily by other organic materials and/or scavengers such as HCO_3^- and CO_3^{2-} in water (von Gunten U., 2003a). On the other hand, our previous study showed that a variety of PPCPs were quite resistant for UV photodegradation (Kim *et al*., 2008). Therefore, it is considered that a lower removal efficiency of many PPCPs during $O_3/UV_{21.5W}$ process (O_3 dose: 2 mg/L) than O_3 alone process might be caused by the consumption of OH radicals by scavengers.

On the other hand, average removal efficiency of the 35 PPCPs was 74% (12% (ethenzamide) ~ 100% (diclofenac)) when $UV_{21.5W}$ was combined with O_3 dose of 2 mg/L. While, the average removal efficiency increased significantly by 90% (64% (ethenzamide) ~ 100% (diclofenac)) and 95% (77% (propranolol) ~ 100% (diclofenac)) as O_3 dose increased by 4 mg/L and 6 mg/L, respectively. Several PPCPs such as sulfamerazine (>89%), propranolol (77%), ethenzamide (79%), primidone (84%), DEET (87%) and griseofulvin (88%) were still less than 90% in their removal efficiency in spite of the combination of $UV_{21.5W}$ and O_3 dose of 6 mg/L. Ethenzamide and DEET showed low degradability for O_3 comparing with other PPCPs in Chapter IV. As a consequence, it is thought that more O_3 dose or UV dose will be necessary for the effective removal of all the PPCPs detected in tested water.

Table 6-4 Removal efficiency of each PPCP during O_3 process (Run 4) and $O_3/UV_{21.5W}$ process(Run 5, 6 and 7) for contact time of 10 min

No.	PPCP	O_3 dose : 2mg/L (O_3 consumption : 1.7 mg/L)	O_3 dose(2mg/L)/UV (O_3 consumption : 1.7 mg/L)	O_3 dose(4mg/L)/UV (O_3 consumption : 3.3 mg/L)	O_3 dose(6mg/L)/UV (O_3 consumption : 4.9 mg/L)
1	Indomethacin	100	99	100	100
2	Mefenamic acid	100	100	100	100
3	Crotamiton	100	88	100	100
4	Dipyridamole	99	99	99	99
5	Diclofenac	99	> 99	> 99	> 99
6	Theophyline	98	95	96	97
7	Carbamazepine	97	95	98	98
8	Sulfadimethoxine	97	95	98	98
9	Pirenzepine	> 96	87	> 95	> 95
10	Levofloxacin	95	87	98	97
11	Acetaminophen	> 95	83	88	95
12	Trimethoprim	94	92	96	96
13	Sulfamethoxazole	94	96	99	99
14	Sulpiride	93	37	93	99
15	Diltiazem	92	96	96	96
16	Furosemide	91	95	98	98
17	Sulfamerazine	> 88	90	> 93	> 89
18	Lincomycin	87	89	88	> 97
19	Ifenprodil	85	97	98	97
20	Azithromycin	80	68	91	97
21	Propranolol	76	73	74	77
22	Roxithromycin	76	59	91	97
23	Clarithromycin	74	61	92	98
24	Ciprofloxacin	66	59	> 95	> 94
25	Isopropylantipyrine	60	> 98	> 98	> 98
26	Atenolol	47	49	82	91
27	Bezafibrate	47	57	87	96
28	Naproxen	42	15	66	90
29	Clenbuterol	38	81	86	92
30	Metoprolol	34	21	79	91
31	Ketoprofen	31	94	99	100
32	Griseofulvin	29	66	74	88
33	Primidone	15	19	71	84
34	DEET	14	27	75	87
35	Ethenzamide	11	12	64	79

6.3.2.3 Dissolved O_3 and O_3 consumption

For O_3 process at O_3 dose of 2 mg/L, the combination of $UV_{21.5W}$ decreased dissolved ozone concentration (Fig. 6-5). While $O_3/UV_{21.5W}$ process could not remove effectively organic materials including PPCPs in tested water. Removal efficiencies of SUVA were only 40.4% and 42.2% for O_3 and $O_3/UV_{21.5W}$ processes (O_3 dose: 2 mg/L), indicating that organic materials which are degradable by O_3 or O_3/UV still remained. It has been reported that SUVA of secondary effluent can be decreased by around 60% with O_3 process (Kim, 2005).

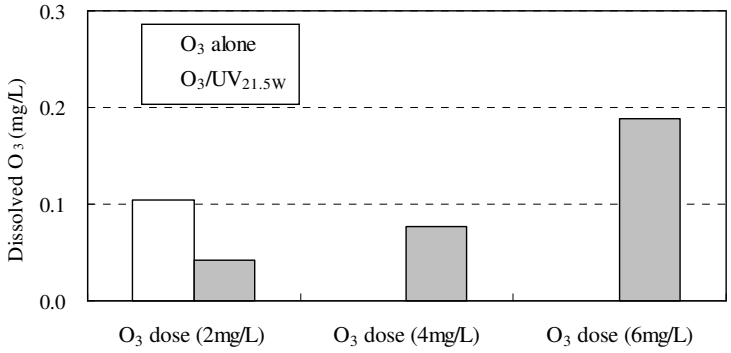


Fig. 6-5 Dissolved ozone concentration during O_3 (Run 4) and $O_3/UV_{21.5W}$ (Run 5, 6 and 7) processes

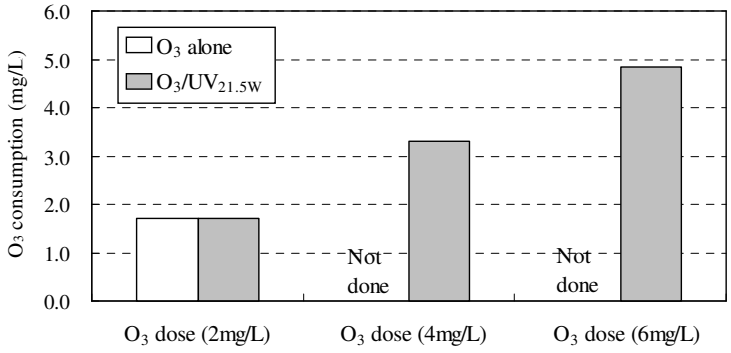


Fig. 6-6 O_3 consumption during O_3 (Run 4) and $O_3/UV_{21.5W}$ (Run 5, 6 and 7) processes

On the other hand, for $O_3/UV_{21.5W}$ process, the increase of O_3 dose led to the increased O_3 consumption (Fig. 6-6) and the improvement of the PPCPs removal (Table 6-4). However, the increased O_3 dose caused the increase of dissolved ozone (Fig. 6-5) which can form bromate through the reaction with bromide. It has been reported that O_3 dose of 2 mg/L resulted in the oxidation of approximately 40% of MTBE, and approximately 70% was oxidized by O_3 dose of 4 mg/L, whereas bromate formation increased considerably when the O_3 dose increased

(von Gunten, 2003b). The application of O_3/H_2O_2 process can suppress the bromate formation by the reduction of HOBr with H_2O_2/HO_2^-. However, the presence of H_2O_2 during O_3 process can not ensure the complete suppression of bromate formation due to the oxidation of bromide by O_3 (von Gunten U., 2003b). Similarly, O_3/UV process may also cause the bromate formation especially if high O_3 dose is used. Therefore, sufficient O_3 degradation will be necessary in applying O_3/UV process, and for this, the appropriate combination of O_3 dose and UV dose should be investigated.

6.3.3 Effect of UV_{65W} addition on the PPCPs removal during O_3 process

Although comparatively good PPCPs removal could be achieved by the $O_3/UV_{21.5W}$ process at high O_3 dose, residual dissolved O_3 concentration increased by approximately 0.2 mg/L when O_3 dose was 6 mg/L. Therefore, UV_{65W} lamp with a UV intensity of 1.025 mW/cm^2 was applied during O_3 process in order to induce the decrease of residual dissolved ozone concentration as well as the effective PPCPs removal by enhancing the UV photodegradation effectiveness for O_3. In this study, 38 PPCPs were detected in tested water, and their concentrations ranged from 1 ng/L (isopropylantipyrine) to 503 ng/L (clarithromycin).

6.3.3.1 O_3 process

Fig. 6-7 indicates the removal efficiency of the 38 PPCPs during O_3 alone process (Run 8, O_3 dose: 2 mg/L, contact time: 10 min) carried out as a control experiment for O_3/UV_{65W} processes. Among the 38 PPCPs, the removal efficiency of more than 90% was obtained in 25 PPCPs, similar to for O_3 process (O_3 dose: 2 mg/L) in 6.3.1. SUVA of the tested water was 0.020 L/mg·cm (DOC: 2.9 mg/L, UV_{254}: 0.0569 /cm), which is a little higher than for O_3 alone process using O_3 dose of 2 mg/L in 6.3.1 (0.018 L/mg·cm). The removal efficiency of the 38 PPCPs ranged from 45% (primidone) to 100% (diclofenac).

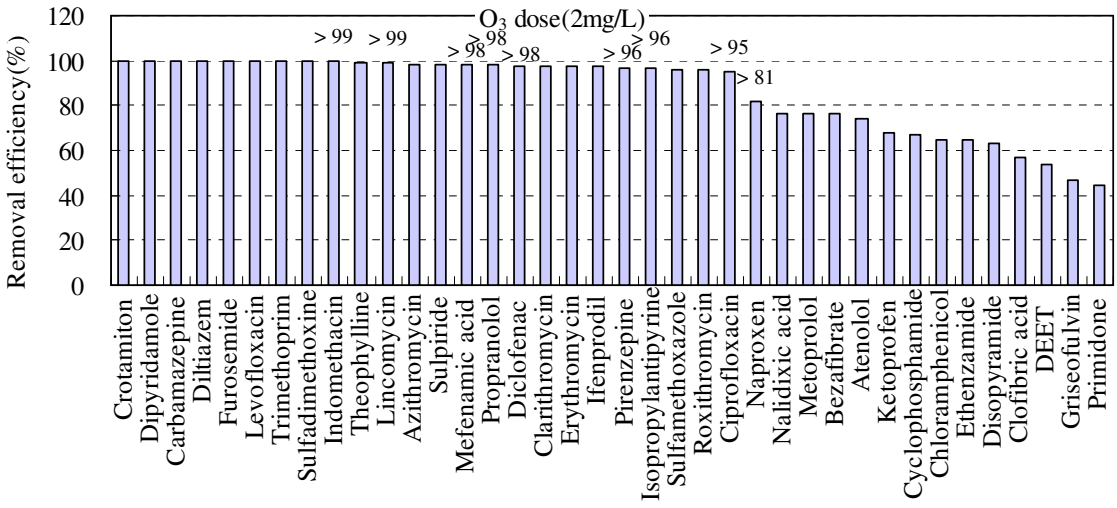


Fig. 6-7 Removal efficiency of the 38 PPCPs during O_3 process (Run 8, contact time: 10 min)

6.3.3.2 O_3/UV_{65W} process

Table 6-5 compares the removal efficiency of each PPCP during O_3 process (Run 8) and O_3/UV_{65W} process (Run 9, 10 and 11) for contact time of 10 min. UV dose introduced for 10 min was 1,846 mJ/cm^2. A very effective and stable removal for the 38 PPCPs could be achieved, and this is compared with for $O_3/UV_{21.5W}$ process (Table 6-4). However, similar to for $O_3/UV_{21.5W}$ process, the combination of low O_3 dose (2 mg/L) with UV_{65W} could not improve the PPCPs removal so significantly comparing to for O_3 process (Run 8).

Contrarily, all the PPCPs except DEET (89%), primidone (86%), cyclophosphamide (86%) and chloramphenicol (>73%) showed the removal efficiency of more than 90% by the combination of UV_{65W} with O_3 dose of 4 mg/L. In addition, all the PPCPs were removed by almost 100% when O_3 dose of 6 mg/L and UV_{65W} were combined. As a consequence, it is considered that O_3 dose of approximately 4mg/L will be needed for the effective PPCPs removal when UV_{65W} lamp is applied.

Table 6-5 Removal efficiency of each PPCP during O_3 process (Run 8) and O_3/UV_{65W} process (Run 9, 10 and 11) for contact time of 10 min

No.	PPCPs	O_3 dose : 2mg/L (O_3 consumption : 1.6 mg/L)	O_3 dose(2mg/L)/UV (O_3 consumption : 1.8 mg/L)	O_3 dose(4mg/L)/UV (O_3 consumption : 3.4 mg/L)	O_3 dose(6mg/L)/UV (O_3 consumption : 5.3 mg/L)
1	Crotamiton	100	98	100	100
2	Dipyridamole	100	100	100	100
3	Carbamazepine	100	97	100	100
4	Diltiazem	100	100	100	100
5	Furosemide	100	100	100	100
6	Levofloxacin	100	92	98	100
7	Trimethoprim	100	98	99	100
8	Sulfadimethoxine	100	100	100	100
9	Indomethacin	> 99	> 99	> 99	> 99
10	Theophylline	99	93	99	99
11	Lincomycin	> 99	> 99	> 99	> 99
12	Azithromycin	98	86	99	99
13	Sulpiride	98	68	97	99
14	Mefenamic acid	> 98	> 98	> 98	> 98
15	Propranolol	> 98	> 98	> 98	> 98
16	Diclofenac	> 98	> 98	> 97	> 97
17	Clarithromycin	98	88	99	100
18	Erythromycin	97	84	98	100
19	Ifenprodil	97	100	100	100
20	Pirenzepine	> 96	93	> 98	> 97
21	Isopropylantipyrine	> 96	> 96	> 96	> 96
22	Sulfamethoxazole	96	99	100	100
23	Roxithromycin	96	84	98	99
24	Ciprofloxacin	> 95	> 91	> 90	> 87
25	Naproxen	> 81	> 86	> 90	> 88
26	Nalidixic acid	77	> 99	> 99	> 99
27	Metoprolol	76	81	96	> 99
28	Bezafibrate	76	90	97	100
29	Atenolol	74	73	93	> 99
30	Ketoprofen	67	99	99	99
31	Cyclophosphamide	67	56	86	> 88
32	Chloramphenicol	65	> 88	> 73	> 89
33	Ethenzamide	64	76	> 98	> 98
34	Disopyramide	63	100	100	100
35	Clofibric acid	57	> 97	> 98	> 98
36	DEET	54	66	89	97
37	Griseofulvin	47	73	> 97	> 97
38	Primidone	45	58	86	> 95

6.3.3.3 Dissolved O_3 and O_3 consumption

Fig. 6-8 and 6-9 show dissolved O_3 concentration and O_3 consumption for O_3/UV_{65W} process. Due to the effective O_3 degradation of UV_{65W} lamp, a concentration of residual dissolved O_3 was very low (less than 0.06 mg/L) even when O_3 dose of 6 mg/L was used during O_3/UV_{65W} process (Fig. 6-8). This was compared with 0.19 mg/L and 1.8 mg/L for $O_3/UV_{21.5W}$ and O_3 alone processes, respectively. Therefore, it is thought that the application of UV_{65W} lamp will be of great advantage to reduce residual ozone during O_3/UV process.

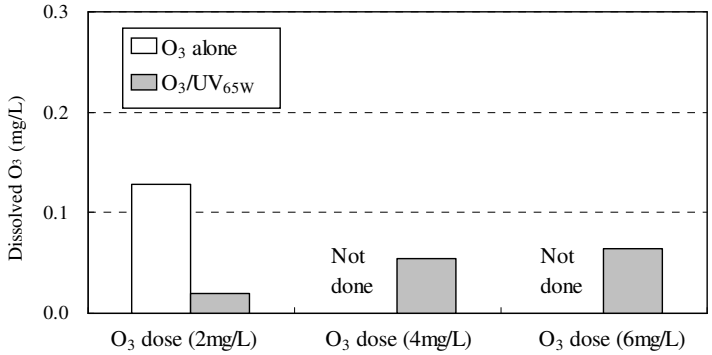


Fig. 6-8 Dissolved O_3 concentration during O_3 (Run 8) and O_3/UV_{65W} (Run 9, 10 and 11) processes

On the other hand, it was expected that more O_3 would be consumed during O_3/UV_{65W} process because higher UV intensity were used in this study. SUVAs were also almost the same (0.019 L/mg·cm ~ 0.024 L/mg·cm for $O_3/UV_{21.5W}$ process, 0.019 L/mg·cm ~ 0.022 L/mg·cm for O_3/UV_{65W} process). However, almost the same or a little more O_3 was consumed despite much more effective PPCPs removal by O_3/UV_{65W} process comparing to for $O_3/UV_{21.5W}$ process. Therefore, it can be expected that the direct UV photodegradation contributed to the PPCPs removal more than a little.

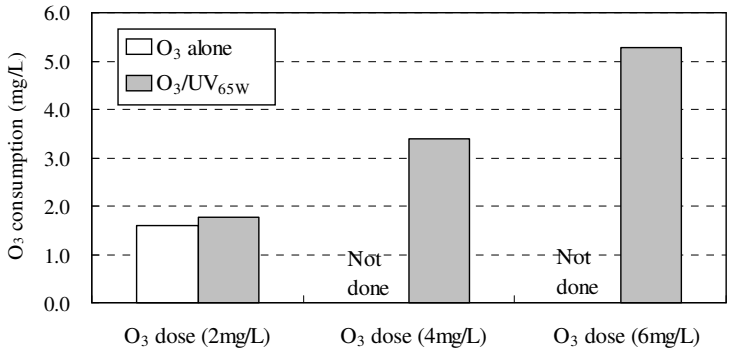


Fig. 6-9 O_3 consumption during O_3 (Run 8) and O_3/UV_{65W} (Run 9, 10 and 11) processes

6.3.4 Relationship between the PPCPs removal efficiency and SUVA decrease

Specific UV absorbance (SUVA) is the absorbance (/cm) of a sample at 254 nm normalized for dissolved organic carbon (DOC, mg/L), and has been known to be strongly correlated to the aromaticity percentage (Weishaar *et al*., 2003). The decrease in SUVA demonstrates the decrease of a variety of aromatic compounds including PPCPs. Consequently, the higher SUVA in water will need more O_3 demand.

Fig. 6-10 shows the removal efficiency of SUVA and the number of PPCPs removed by more than 90% during each process. Initial SUVA in tested water ranged from 0.018 L/mg·cm to 0.024 L/mg·cm, and decreased by 0.007 L/mg·cm to 0.014 L/mg·cm with O_3 and O_3/UV processes for contact time of 10 min. As shown in Fig. 6-10, the removal efficiency of SUVA increased with the increase of O_3 dose. The highest removal efficiency was approximately 60±5% and obtained when O_3 dose was 6 mg/L, irrespective of applied processes. The removal efficiency of SUVA for O_3/UV process was a little more remarkable than for O_3 process. The difference might be led to the contribution of OH radicals, which are generally considered to react relatively unselectively with organic compounds, to the degradation of aromatic compounds.

It was also observed that the number of PPCPs removed by more than 90% increased with the increase of removal efficiency in SUVA. For O_3 and O_3/UV_{65W} processes, the removal efficiency of SUVA was more than 48% (O_3 dose: more than 4 mg/L) when among the detected PPCPs, more than 30 PPCPs were removed by more than 90%. Therefore, it is thought that the removal efficiency of SUVA of more than 48% can ensure the effective

removal of a variety of PPCPs although the removal efficiencies of PPCPs are sometimes affected by the difference in water quality.

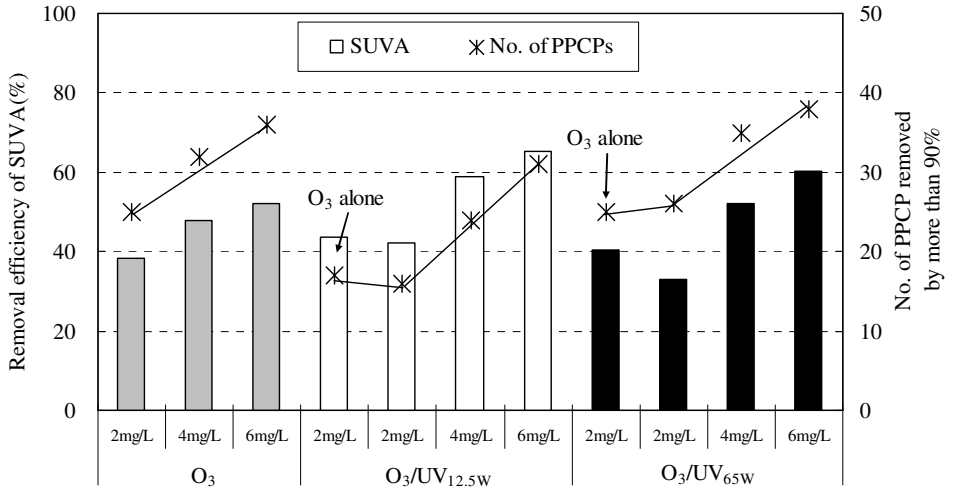


Fig. 6-10 Decrease of SUVA and No. of PPCPs removed by more than 90% during each process

6.3.5 Energy consumption and operating cost

Electrical energy and operating cost required during O_3 and O_3/UV processes for the PPCPs removal were calculated. Firstly, 15 kWh (6kWh for equipment for oxygen supply, 9kWh for O_3 generator) was used for an electrical energy required for generating 1kg O_3 gas. Power consumptions of the used UV lamps were 23.7 W and 72 W for $UV_{21.5W}$ and UV_{65W}, respectively, considering a leeway of 10%. 15 Yen per electrical energy of 1 kWh was applied for the calculation of operating cost. Tables 6-6, 6-7 and 6-8 show calculated electrical energy, operating costs and the number of PPCPs removed by more than 90% obtained in O_3 and O_3/UV processes. For O_3 alone process, average O_3 dose of 6.7 mg/L has been used for the water reuse in sewage treatment plants in Japan (JS, 2004). In this study, 35 out of 37 PPCPs were removed by more than 90% when O_3 dose of 6 mg/L was used. Consequently, it can be expected that most of PPCPs will be removed effectively at a level of O_3 dose used for existing water reuse projects. An electrical energy of 0.09 kWh/m^3 for O_3 dose of 6 mg/L (contact time: 10 min) is expected to be required, and operating cost was calculated as 1.4 Yen/m^3 as shown in Table 6-6.

Table 6-6 Electrical energy and operating cost required for O_3 process

Applied process	O_3 alone					
O_3 dose	2 mg/L (O_3 consumption : 1.6mg/L)		4 mg/L (O_3 consumption : 3.0mg/L)		6 mg/L (O_3 consumption : 4.4mg/L)	
	R1 : 1mg/L	R2 : 1mg/L	R1 : 2mg/L	R2 : 2mg/L	R1 : 3mg/L	R2 : 3mg/L
Contact time (min)	5 min	10 min	5 min	10 min	5 min	10 min
Electrical energy (kWh/m^3)	0.02	0.03	0.03	0.06	0.05	0.09
No. of PPCPs removed by ≥ 90% / No. of detected PPCPs	15 / 34	24 / 37	22 / 37	32 / 37	29 / 37	35 / 37
Operating cost (Yen/m^3)	0.2	0.5	0.5	0.9	0.7	1.4

Table 6-7 Electrical energy and operating cost required for $O_3/UV_{21.5W}$ process

Applied process	$O_3/UV_{21.5W}$					
O_3 dose	2 mg/L (O_3 consumption : 1.7mg/L)		4 mg/L (O_3 consumption : 3.3mg/L)		6 mg/L (O_3 consumption : 4.9mg/L)	
	R1 : 1mg/L	R2 : 1mg/L	R1 : 2mg/L	R2 : 2mg/L	R1 : 3mg/L	R2 : 3mg/L
Contact time (min)	5 min	10 min	5 min	10 min	5 min	10 min
Electrical energy for O_3 (kWh/m^3)	0.02	0.03	0.03	0.06	0.05	0.09
Electrical energy for UV (kWh/m^3)	0.17	0.34	0.17	0.34	0.17	0.34
Total electrical energy (kWh/m^3)	0.19	0.37	0.20	0.40	0.22	0.43
No. of PPCPs removed by ≥ 90% / No. of detected PPCPs	7 / 25	15 / 35	10 / 35	23 / 35	16 / 35	31 / 35
Operating cost (Yen/m^3)	2.8	5.6	3.0	6.0	3.2	6.5

Table 6-8 Electrical energy and operating cost required for O_3/UV_{65W} process

Applied process	O_3/UV_{65W}					
O_3 dose	2 mg/L (O_3 consumption : 1.8mg/L)		4 mg/L (O_3 consumption : 3.4mg/L)		6 mg/L (O_3 consumption : 5.3mg/L)	
	R1 : 1mg/L	R2 : 1mg/L	R1 : 2mg/L	R2 : 2mg/L	R1 : 3mg/L	R2 : 3mg/L
Contact time (min)	5 min	10 min	5 min	10 min	5 min	10 min
Electrical energy for O_3 (kWh/m^3)	0.02	0.03	0.03	0.06	0.05	0.09
Electrical energy for UV (kWh/m^3)	0.51	1.03	0.51	1.03	0.51	1.03
Total electrical energy (kWh/m^3)	0.53	1.06	0.54	1.09	0.56	1.12
No. of PPCPs removed by ≥ 90% / No. of detected PPCPs	15 / 38	24 / 38	24 / 38	34 / 38	27 / 38	35 / 38
Operating cost (Yen/m^3)	7.9	15.9	8.2	16.3	8.4	16.8

On the other hand, for $O_3/UV_{21.5W}$, the required electrical energy increased considerably due to the combination of UV treatment. An electrical energy and operating cost ranged from

0.19 kWh/m^3 to 0.43 kWh/m^3 and 2.8 Yen/m^3 to 6.5 Yen/m^3, respectively during $O_3/UV_{21.5W}$ for 10 min at O_3 dose of 2 mg/L, 4 mg/L and 6 mg/L. Nevertheless, only 7 to 31 out of the detected PPCPs exhibited the removal efficiency of more than 90%.

In contrast to $O_3/UV_{21.5W}$ process, the removal efficiency of PPCPs increased significantly when UV_{65W} was combined with O_3 process. In particular, O_3/UV_{65W} process at O_3 dose of 6 mg/L could remove 35 PPCPs by more than 90%. However, as seen in Table 6-8, a considerable electrical energy was required due to the application of UV lamps with high power consumption. From Table 6-8, it can be known that at least an electrical energy of 1.09 kWh/m^3 (O_3 dose: 4 mg/L, contact time: 10 min) will be needed for the effective PPCPs removal by O_3/UV process. It is obvious that O_3/UV process leads to much more energy consumption than O_3 process. However, the applicability of this process for the PPCPs removal should be investigated, considering several questions such as incomplete oxidation of organic materials by O_3 and the formation of by-products, and the improvement of disinfection effectiveness by the introduction of UV as well as a required electrical energy.

6.4 Summary

The effectiveness of O_3-based processes (O_3 and O_3/UV processes) for the removal performance of PPCPs using bench-scale experimental setup was investigated.

1) 37 PPCPs were detected in secondary effluent used as tested water in this study. O_3 dose of 6 mg/L (O_3 consumption : 4.4 mg/L) was required for 90% removal of all the PPCPs except primidone (87%) for O_3 process. However, 24 PPCPs including carbamazepine, crotamiton and diclofenac were removed by more than 90% even at a low O_3 dose of 2 mg/L (O_3 consumption : 1.6 mg/L), indicating that O_3 process can be used as a technology for the effective removal of various PPCPs in secondary effluent.

2) For O_3/UV process, two types of UV lamps ($UV_{21.5W}$, UV_{65W}) were combined with O_3 doses of 2 mg/L, 4mg/L and 6mg/L, respectively. As a result, all the detected PPCPs were removed by more than 90% when UV_{65W} lamps and O_3 dose of 6 mg/L (O_3 consumption : 5.3 mg/L) were combined (Contact time : 10 min, UV dose : 1,846 mJ/cm^2). On the other hand, all the PPCPs except DEET (89%), primidone (86%), cyclophosphamide (86%) and chloramphenicol (>73%) showed removal efficiencies of more than 90% even when UV_{65W}

lamps and O_3 dose of 4 mg/L (O_3 consumption : 3.4 mg/L) were combined, showing that a lot of PPCPs can be removed effectively under this operational condition.

3) For O_3 and O_3/UV_{65W} processes using O_3 dose of over 4 mg/L (O_3 consumption : over 3.4 mg/L), more than 30 PPCPs showed the removal efficiency of more than 90% when SUVA decreased by more than 48%. Similarly to UV-based processes, it was thought that about 50% decrease in SUVA could ensure the effective PPCPs removal.

4) Electrical energy consumed for the effective PPCPs removal was 0.09 kWh/m^3 for O_3 process (O_3 dose : 6 mg/L). Whereas, O_3/UV process (O_3 dose : 4 mg/L, UV dose : 1,846 mJ/cm^2) needed comparatively high electrical energy of 1.09 kWh/m^3. Consequently, it can be known that O_3 process is more cost-effective process than O_3/UV process in the removal performance of PPCPs.

5) For O_3 process, the formation of bromate regulated in drinking water as well as the removal performance of PPCPs should be also taken into consideration. Although O_3/UV process needs high energy consumption, the process has several advantages such as the suppression of bromate formation and the additional disinfection effect by UV. It is, therefore, thought that O_3/UV process cannot be excluded in applying as technology for water reuse.

6.5 References

Bader H., Hoigne J., 1981, Determination of ozone in water by the indigo method, *Water Res.* 15, 449-456

Balcioglu I.A., Otker M., 2003, Treatmetn of pharmaceutical wastewater containing antibiotics by O_3 and O_3/H_2O_2 processes, *Chemosphere* 50, 85-95

Daughton C.G. and Ternes T.A., 1999, Pharmaceuticals and Personal Care Products in the Environment: Agents of Subtle change?, *Environmental Health Perspectives* 107, 907-938

Halling-Sørensen, B., Nielsen S.N., Lanzky P.F., Ingerslev F., Lutzhoft H.C.H., Jorgensen S.E., 1998, Occurrence, fate and effects of pharmaceutical substances in the environment- A review, *Chemosphere* 36, 357-393

Heberer T., 2002, Occurrence, fate and removal of pharmaceutical residues in the aquatic environment: a review of recent research data, *Toxicology Letters* 131, 5-17

Huber M.M., Canonica S., Park G.Y., von Gunten U., 2003 Oxidation of pharmaceuticals

during ozonation and advanced oxidation processes, *Environ. Sci. Technol.* 37, 1016-1024

JOA, 2004, Ozone handbook, Japan Ozone Association, Tokyo, Japan

JS, 2004, Technology Development Division, Japan Sewage Works, Japan

Kanda R., Griffin P., James H.A. and Fothergill J., 2003, Pharmaceutical and personal care products in sewage treatment works, *J. Environ. Monit.* 5, 823-830

Kim H.S., 2005, Behavior and control of by-products during ozone and ozone/hydrogen peroxide treatments of sewage effluent, Department of Urban & Environmental Engineering, Kyoto University, Kyoto

Kim I. H., Tanaka H., Iwasaki T., Takubo T., Morioka T., Kato Y., 2008, Classification of the degradability of 30 pharmaceuticals in water with ozone, UV and H_2O_2, Wat Sci Technol., 57, 195-200

Kurokawa Y., Hayashi Y., Maekawa A., Takahashi M., Kokubo T., Odashima S., 1983, Carcinogenicity of potassium bromate administered orally to F344 rats, *J. Natl. Cancer Inst.* 71, 965-972

Lau T.K., Chu W., Graham N., 2007, Reaction pathways and kinetics of butylated hydroxyanisole with UV, ozonation, and UV/O_3 processes, *Water Res.* 41, 765-774

Lopez A., Anna B., Giuseppe M., John K., 2003, Kinetic investigation on UV and UV/H_2O_2 degradations of pharmaceutical intermediates in aqueous solution, *J. Photoch. Photobio A* 156, 121-126

Nakada N., Taniishima T., Shinohara H., Kiri K., Takada H., 2006, Pharmaceutical chemicals and endocrine disrupters in municipal wastewater in Tokyo and their removal during activated sludge treatment, *Water Res.* 40, 3297-3303

Okuda T., Kobayashi Y., Nagao R., Yamashita N., Tanaka H., Tanaka S., Fuji S., Konishi C., Houwa I., 2008, Removal efficiency of 66 pharmaceuticals during wastewater treatment process in Japan, *Wat Sci Technol.* 57, 65-71

Rosenfeldt E.J., Linden K.G., Canonica S., von Gunten U., 2006 Comparison of the efficiency of ·OH radical formation during ozonation and the advanced oxidation processes O_3/H_2O_2 and UV/H_2O_2, *Water Res.* 40, 3695-3704

Smital T., Luckenbach T., Sauerborn R., Hamdoun A.M., Vega R. L., Epel D., 2004, Emerging contaminants-pesticides, PPCPs, microbial degradation products and natural

substances as inhibitors of multixenobiotic defense in aquatic organisms, *Mutation Research* 552, 101-117

Ternes T.A., 1998, Occurrence of drugs in German sewage treatment plants and rivers, *Water Res.* 32, 3245-3260

Ternes T.A., Stuber J., Herrmann N., McDowell D., Ried A., Kampmann M., Teiser B., 2003 Ozonation: A tool for removal of pharmaceuticals, contrast media and musk fragrances from wastewater?, *Water Res.* 37, 1976-1982

The Ministry of Health, Labour and Welfare, Japan, 2003a, A ministerial ordinance No. 101

The Ministry of Health, Labour and Welfare, Japan, 2003b, Notification No. 261

von Gunten U., 2003a, Ozonation of drinking water: Part I. Oxidation kinetics and product formation, *Water Res.* 37, 1443-1467

von Gunten U., 2003b, Ozonation of drinking water: Part II. Disinfection and by-product formation in presence of bromide, iodide or chlorine, *Water Res.* 37, 1469-1487

Wang X., Huang X., Zuo C., Hu H., 2004, Kinetics of quinoline degradation by O_3/UV in aqueous phase, *Chemosphere* 55, 733–741

Weishaar J. L., Aiken G. R., Bergamaschi B. A., Fram M. S., Fujii R., Mopper K., 2003, Evaluation of Specific Ultraviolet Absorbance as an Indicator of the Chemical Composition and Reactivity of Dissolved Organic Carbon, *Environ. Sci. Technol.* 37, 4702-4708

Wert E.C., Rosario-Ortiz F.L., Drury D.D., Snyder S.A., 2007, Formation of oxidation byproducts from ozonation of wastewater, *Water Res.* 41, 1481-1490

Zou L., Zhu B., 2007, The synergistic effect of ozonation and photocatalysis on color removal from reused water, *J. Photochem. Photobiol A.*, doi:10.1016/j.jphotochem.2007.11.008

CHAPTER VII

DISCUSSION ON THE APPLICABILITY OF UV/H_2O_2, O_3 AND O_3/UV PROCESSES AS TECHNOLOGIES FOR SEWAGE REUSE UNDER CONSIDERING THE REMOVAL OF PHARMACEUTICALS AND PERSONAL CARE PRODUCTS

7.1 Introduction

The demand for water will increase with the dramatic increase of the world's population by the year 2020 (U.S. EPA, 2004). However, available water resources have been already limited in many areas of the world and therefore, water reuse will be necessary for extending available water resources. It has been reported that the majority of states in U.S. have regulations regarding water reuse on a volume basis is growing at an estimated 15 percent per year (U.S. EPA, 2004). In Japan, the amount of reclaimed water in 2005 was about 200 million m^3, which corresponds to just 1.4% of total effluent from sewage treatment plants (STPs) (The Ministry of Land, Infrastructure and Transport of Japan, 2005). However, in recent years there has been a growing interest in water reuse according to the lack of water resources and the advanced technologies for water treatment such as membrane treatment and advanced oxidation processes (AOPs). The manual for the quality of water reclaimed from treated water of STP was prepared by the Ministry of Land, Infrastructure and Transport of Japan in April, 2005. Moreover, a committee for promoting the reuse of secondary effluent was organized in 2008. Table 7-1 shows application types and purposes of the water reclaimed from secondary effluent of wastewater treatment plants.

Table 7-1 Application types and purposes of the reclaimed water

Application type	Purpose
Urban reuse	- Irrigation of public parks and recreation centers, athletic fields, school yards and playing fields, highway medians and shoulders, and landscaped areas surrounding public buildings and facilities - Irrigation of landscaped areas surrounding single-family and multi-family residences, general wash down, and other maintenance activities - Irrigation of landscaped areas surrounding commercial, office, and industrial developments - Irrigation of golf courses - Commercial uses such as vehicle washing facilities, laundry facilities, window washing, and mixing water for pesticides, herbicides, and liquid fertilizers - Ornamental landscape uses and decorative water features, such as fountains, reflecting pools, and waterfalls - Dust control and concrete production for construction projects - Fire protection through reclaimed water fire hydrants - Toilet and urinal flushing in commercial and industrial buildings
Industrial reuse	- Cooling water, boiler make-up water, industrial process water
Agricultural reuse	- Agricultural irrigation
Environmental and Recreational reuse	- Natural and Man-made Wetlands - Recreational and Aesthetic Impoundments - Stream Augmentation
Groundwater recharge	- Establishment of saltwater intrusion barriers in coastal aquifers - Provision of further treatment for future reuse - Augmentation of potable or nonpotable aquifers - Provision of storage of reclaimed water for subsequent retrieval and reuse - Control or prevention of ground subsidence
Augmentation of potable supplies	- Surface water augmentation and groundwater recharge for indirect potable reuse - Direct potable water reuse

On the other hand, it will be very important to consider the health assessment of pathogenic microorganisms, chemical constituents and endocrine disrupters for the reuse of secondary effluent. Especially, the effect of the chemical constituents should be considered when reclaimed water is used for potable reuse, food crop irrigation or aquaculture. U.S. EPA suggests advanced water treatment facilities such as MBR and UV treatment in the guidelines for water reuse for ensuring the safety from chemical constituents, however, the guideline of

Japan has not treated with it yet. At the present, the concentration of residual chlorine is being regulated by the guideline on the use of the reclaimed water of Japan for the microbiological safety of the reclaimed water.

Much attention has been paid to PPCPs (pharmaceuticals and personal care products) as a kind of chemical constituents for the past few years. The effective degradation with chlorine is limited on only a few PPCPs such as diclofenac, indomethacine and naproxen although it is quite good disinfectant (Energy, Environment and Sustainable Development, 2004). In addition, there are a variety of organic compounds including PPCPs in secondary effluent and, therefore, the formation potential of disinfection by products (DBPs) is concerned during chlorination. Therefore, alternative methods are necessary to be investigated for reducing a risk of the reclaimed water caused by chemical constituents as well as pathogenic microorganisms. Up to now, our research group has studied and reported the effectiveness of O_3-based and UV-based processes for the PPCPs removal.

The objective of this chapter was to suggest the applicability as a technology for the reclamation of secondary effluent of investigated processes.

7.2 Methods

When evaluating the applicability of a process for the reclaimed water, factors such as reliability, operating and maintenance costs, practicality, disinfection effectiveness and potential adverse effects should be considered. Here, in terms of energy consumption, disinfection effectiveness, the formation potential of DBPs and ecological risk decrease, UV/H_2O_2, O_3 and O_3/UV processes were evaluated in order to suggest an appropriate process for the reclamation of secondary effluent. Fig 7-1 shows proposed procedure of appropriate process for water reuse considering the PPCPs removal.

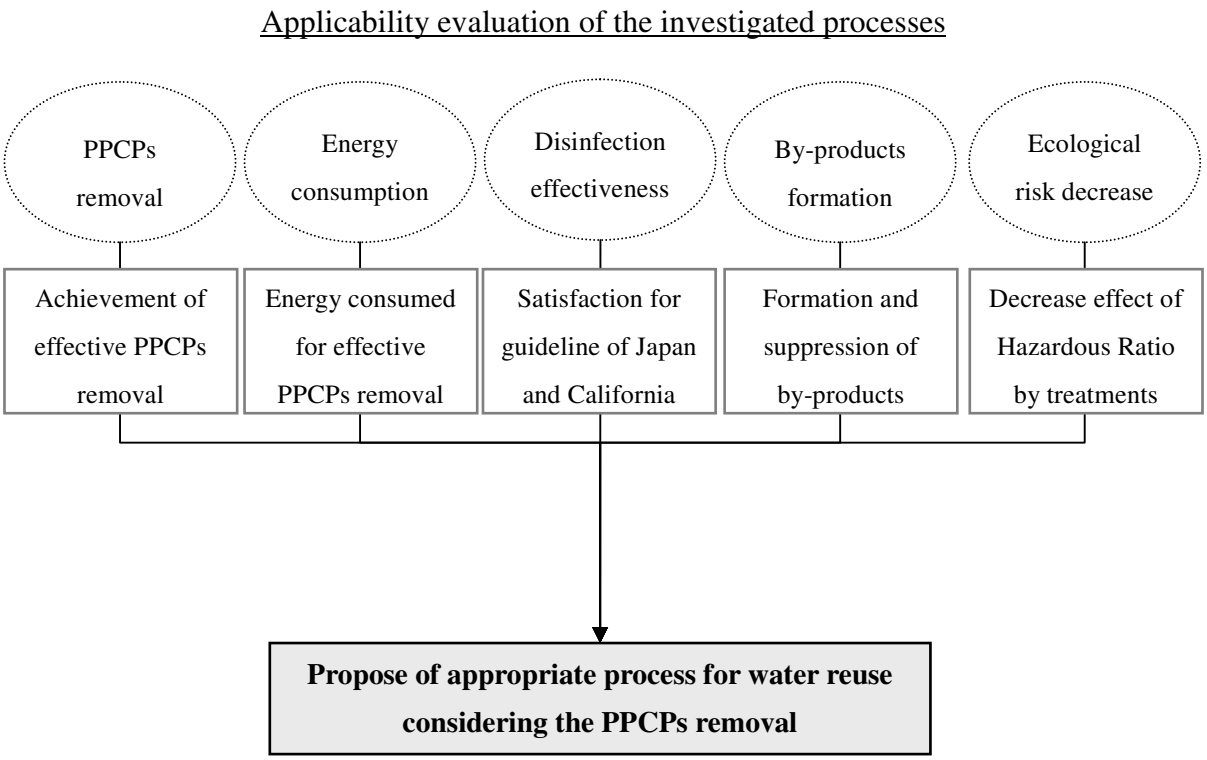


Fig. 7-1 Propose procedure of appropriate process for water reuse considering the PPCPs removal

PPCPs removal and energy consumption The electrical energy consumed for a pollutant removal is a powerful scale-up parameter and a measure of the removal performance in a fixed volume of contaminated water as a function of the applied specific energy dose. Therefore, energies consumed for the processes investigated in this study were calculated based on operational conditions that showed an effective PPCPs removal for each process. Afterwards, the most energy-saving process for an effective PPCPs removal from secondary effluent was suggested. Moreover, the energy consumptions were compared with those for other pollutants reported in previous studies. In this investigation, UV process was not considered because removal efficiencies of most of PPCPs detected in secondary effluent were less than 90% in spite of considerable energy consumption (UV dose : 2,768 mJ/cm^2 for UV_{High}, 1,725 mJ/cm^2 for UV_{Low}) (Fig 7-2).

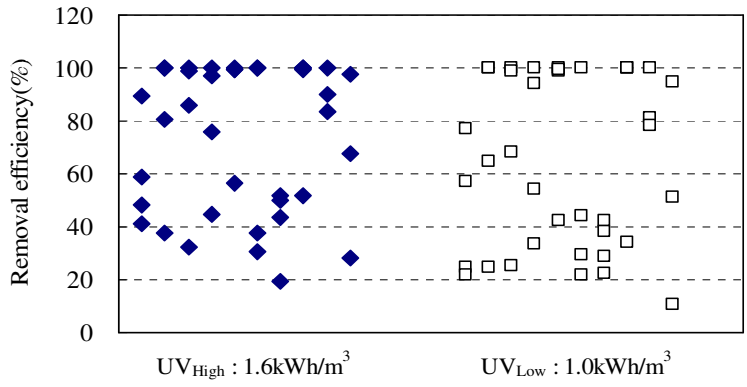


Fig. 7-2 Removal efficiency of the 38 PPCPs by UV_{High} and UV_{Low} treatments

Disinfection effectiveness In urban settings, where there is a high potential for human exposure to reclaimed water used for landscape irrigation and toilet flushing *etc*, the reclaimed water must assure minimum health risk. The facilities producing secondary effluent can become water reclamation plants with the addition of enhanced disinfection processes.

The guideline for water reuse of Japan requires that total coliform does not exceed 1,000/100ml for urban and recreational reuse (a tentative regulation). Therefore, Residual chlorine is necessary for meeting this regulation when secondary effluent is reclaimed in Japan. In the California Title 22 criteria, average total coliform should be less than 2.2/100 ml or 23/100ml according to the application of reclaimed water (Table 7-2).

Table 7-2 Regulations of coliform for the reclaimed water in California

Application	Total coliform	
Unrestricted urban reuse Agricultural reuse – Food crops Unrestricted recreational reuse Restricted recreational reuse	2.2/100ml (Avg)	23/100ml (Max in 30days)
Restricted urban reuse Agricultural reuse – Non-food crops	23/100ml (Avg)	240/100ml (Max in 30days)
Groundwater recharge Indirected potable reuse	Case-by-case	

Groundwater recharge and indirect potable reuse are determined on a case-by-case basis.

The most common disinfectant is chlorine, however, O_3 and UV can be also used at wastewater treatment plants as prominent disinfectants. Therefore, the disinfection performance as well as the effective PPCPs removal by the investigated processes was evaluated.

By-products formation By-product which can be formed for the degradation of an organic compound is one of the most important issues in the area of physicochemical process using oxidants such as O_3, H_2O_2 and UV. There are several cases that by products are more problematic than parent product. For example, several aldehydes including formaldehyde, acetaldehyde and trichloroacetaldehyde can be produced during ozonation (Richardson *et al*., 2007). Formaldehyde has been known to induce gene mutation in bacteria, mammalian cells and in rat nasal epithelia *in vivo* although in vivo genotoxicity of formaldehyde is difficult to assess for humans due to its highly reactive nature (Richardson *et al*., 2007).

Moreover, Chloroacetaldehyde has been shown to cause liver tumors in rodents (Daniel *et al*., 1992). Bromate (BrO_3^-) can also be produced primarily by ozonation when source waters contain high levels of bromide (Richardson S.D, 1998). It has been known that among the regulated DBPs (disinfection by products), bromate is most carcinogenic in laboratory animals (Muellner *et al*., 2007). On the other hand, advance oxidation processes (AOPs) such as UV/H_2O_2 and O_3/UV are promising technologies for mineralizing organic compounds. However, intermediate AOPs result in the partial oxidation of organic compounds into more biodegradable compounds such as aldehydes and carboxylic acids (Tuhkanen, 2004). Therefore, rigorous treatment should be applied for the complete mineralization of organic compounds. Here, the formation potential of by-products was discussed based on the results from laboratory and bench scale experiments, and previous studies performed by other researchers.

Ecological risk decrease Screening evaluation has been carrying out for determining the priority of compounds which require more investigations due to their relatively high ecological risks. Initial ecological risk assessment is widely used as a tool for the screening evaluation and in this assessment, the priority is determined by the ratio of predicted

environmental concentration (PEC) to predicted no effect concentration (PNEC), called by Hazard Ratio (H/R). In this study, concentrations of individual PPCPs before and after treatment by each process were used instead of PEC in calculating H/R. No observed effect concentration (NOEC) divided by assessment factor (100) was used as a PNEC of each PPCP. NOEC was obtained from algae growth inhibition test using *Pseudokirchneriella subcapitata* (Korshikov) F.Hindak (Fukunaga, 2008). In this study, H/R was defined as the ratio of the concentration of a PPCP at each reactor during each process to NOEC. Decrease effect for ecological risk by each process was assessed using the H/R. During each process 38 PPCPs were dectected in tested water, however, H/Rs were calculated only for 30 PPCPs of which NOECs were available (Table 7-3).

Table 7-3 NOEC and PNEC for 30 PPCPs

No.	PPCP	Use	Formula	Water solubility (mg/L)	pKa	NOEC(mg/L)	PNEC(mg/L)
1	Diclofenac	Analgesics	$C_{14}H_{11}C_{l2}NO_2$	2.4E+00	4.15	6.25	6.3E-02
2	Indomethacin		$C_{19}H_{16}ClNO_4$	9.4E-01	4.5	50	5.0E-01
3	Isopropylantipyrine		$C_{14}H_{18}N_2O$	3.0E+06	-	1.56	1.6E-02
4	Ketoprofen		$C_{16}H_{14}O_3$	5.1E+01	4.45	0.0156	1.6E-04
5	Mefenamic acid		$C_{15}H_{15}NO_2$	2.0E+01	4.2	5	5.0E-02
6	Naproxen		$C_{14}H_{14}O_3$	1.6E+01	4.15	6.25	6.3E-02
7	Atenolol	Antiarrhythmic agent	$C_{14}H_{22}N_2O_3$	1.3E+04	9.6	6.25	6.3E-02
8	Azithromycin	Antibiotics	$C_{38}H_{72}N_2O_{12}$	7.1E+00	8.74	0.0156	1.6E-04
9	Chloramphenicol		$C_{11}H_{12}C_{l2}N_2O_5$	2.5E+03	5.5	0.125	1.3E-03
10	Ciprofloxacin		$C_{17}H_{18}FN_3O_3$	3.0E+04	6.09	2.5	2.5E-02
11	Clarithromycin		$C_{38}H_{69}NO_{13}$	3.4E-01	8.99	0.0156	1.6E-04
12	Erythromycin		$C_{37}H_{67}NO_{13}$	1.4E+00	8.88	0.0313	3.1E-04
13	Levofloxacin		$C_{18}H_{20}FN_3O_4$	-	5.5, 8.0	0.625	6.3E-03
14	Lincomycin		$C_{18}H_{34}N_2O_6S$	9.3E+02	7.6	0.00781	7.8E-05
15	Nalidixic acid		$C_{12}H_{12}N_2O_3$	1.0E+02	8.6	25	2.5E-01
16	Sulfadimethoxine		$C_{12}H_{14}N_4O_4S$	3.4E+02	-	0.625	6.3E-03
17	Sulfamethoxazole		$C_{10}H_{11}N_3O_3S$	6.1E+02	5.94	0.156	1.6E-03
18	Trimethoprim		$C_{14}H_{18}N_4O_3$	4.0E+02	7.12	6.25	6.3E-02
19	Carbamazepine	Anticonvulsant	$C_{15}H_{12}N_2O$	1.8E+01	-	6.25	6.3E-02
20	Primidone		$C_{12}H_{14}N_2O_2$	5.0E+02	-	12.5	1.3E-01
21	Crotamiton	Anti-itch drug	$C_{13}H_{17}NO$	5.5E+02	-	6.25	6.3E-02
22	Cyclophosphamide	Antineoplastic agent	$C_7H_{15}C_{l2}N_2O_2P$	4.0E+04	-	50	5.0E-01
23	Sulpiride	Anti-psychotic drug	$C_{15}H_{23}N_3O_4S$	2.3E+03	9.12	12.5	1.3E-01
24	Theophylline	Bronchodilator	$C_7H_8N_4O_2$	7.4E+03	8.81	50	5.0E-01
25	Diltiazem	Calcium channel blockers	$C_{22}H_{26}N_2O_4S$	4.7E+02	7.7	0.625	6.3E-03
26	DEET	Insect repellent	$C_{12}H_{17}NO$	9.1E+02	-	50	5.0E-01
27	Bezafibrate	Lipid regulating agent	$C_{19}H_{20}ClNO_4$	3.4E-01	3.4	25	2.5E-01
28	Clofibric acid	Lipid regulating agent	$C_{10}H_{11}ClO_3$	5.8E+02	-	25	2.5E-01
29	Pirenzepine	Muscarinic receptor antagonists	$C_{19}H_{21}N_5O_2$	1.7E+01	1.8,7.9	25	2.5E-01
30	Ifenprodil	NMDA receptor antagonist	$C_{21}H_{27}NO_2$	2.6E+02	9.05, 9.69	0.0391	3.9E-04

7.3 Results and discussion

7.3.1 Energy consumption for the effective PPCPs removal

7.3.1.1 Energy consumption by UV/H_2O_2, O_3 and O_3/UV processes

In this study, a goal of 90% removal efficiency was set to compare the performance for PPCPs removal of each process. For UV/H_2O_2 process, 90% removal of 37 PPCPs could be achieved when initial H_2O_2 concentration in tested water was 6.2 mg/L during UV treatment using 65 W low pressure mercury lamp with UV output of 21.8WUV (UV intensity of applied UV lamp : 1.025 mW/cm^2). Introduced UV dose (UV intensity x contact time) was 923 mJ/cm^2. During O_3 process, O_3 dose of 6mg/L (Concentration of O_3 gas : 42 mg/L, Flow rate of O_3 gas : 1.0 L/min, Contact time : 10 min., O_3 consumption : 4.4 mg/L) was necessary for 90% removal of all the PPCPs except primidone (87%) and naproxen (>89%).

For O_3/UV process, most of the PPCPs were removed by more than 90% when UV dose of 1,846 mJ/cm^2 was combined with O_3 dose of 4 mg/L (Concentration of O_3 gas : 28 mg/L, Flow rate of O_3 gas : 1.0 L/min, Contact time : 10 min., O_3 consumption : 3.4 mg/L). 90% removal could not be accomplished in cyclophosphamide, primidone, DEET and chloramphenicol, however, high removal efficiencies of 86%, 86%, 89% and >73%, respectively were obtained. Consequently, it can be known that the combination of UV treatment with O_3 process caused the decrease of O_3 dose, showing a similar removal performance for PPCPs.

The amount of energy consumed during the operation of each process for achieving 90% removal was estimated. For the estimation, the electricity consumption of 72 W per UV lamp was used. The electricity consumption required for O_3 generation of 1 kg was 15 kWh. The energy for supplying H_2O_2 solution to the reactor was not considered. As a result, the energies of 0.54 kWh/m^3, 0.09 kWh/m^3 and 1.09 kWh/m^3 were consumed during UV/H_2O_2, O_3 and O_3/UV processes, respectively for the accomplishment of efficient PPCPs removal. Based on this result, it was found that UV/H_2O_2 and O_3/UV processes would need quite high electricity consumptions by the introduction of UV, comparing to O_3 process. Therefore, it can be concluded that among the investigated processes, O_3 process will be the most advantageous process in aspect of energy consumption.

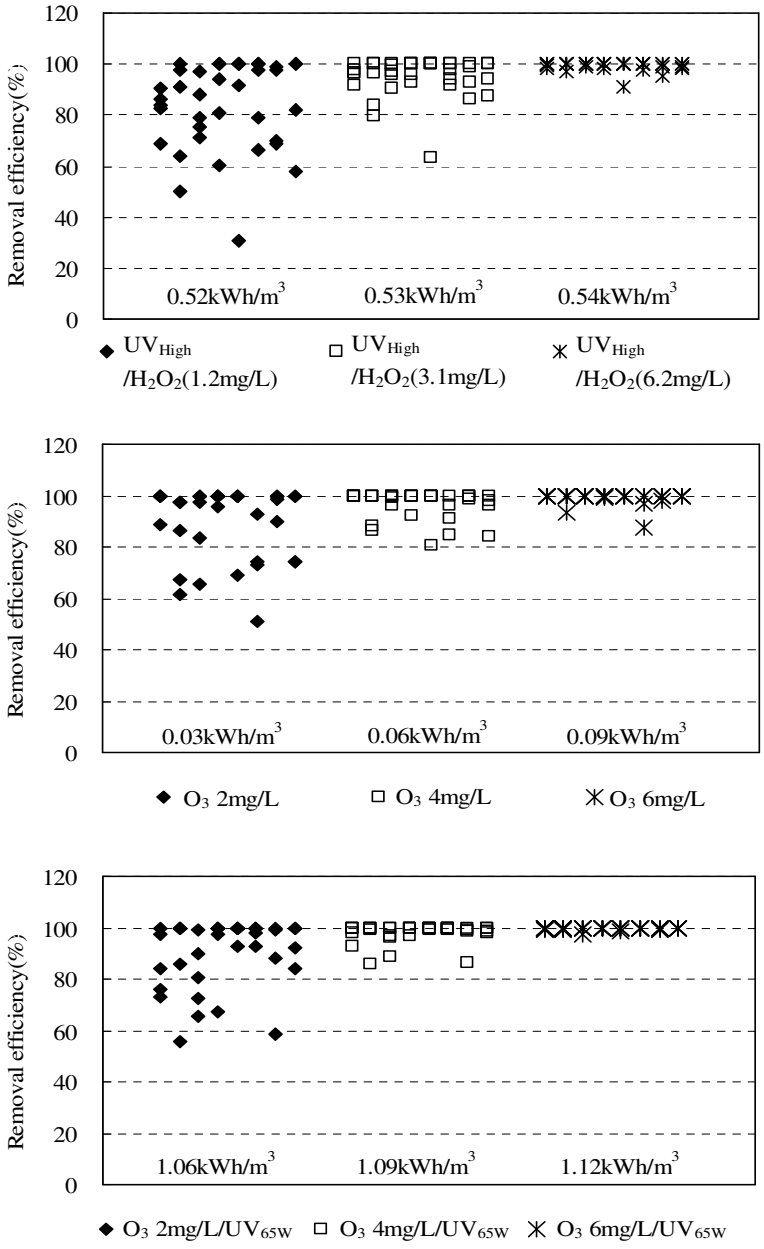


Fig. 7-3 Comparison of removal efficiency of PPCPs by each process

7.3.1.2 Electrical energy required for the removal of other micropollutants

Here, the energy consumptions of each process for PPCPs removal and for the removal of other micropollutants such as methyl-*tert*-butyl-eter (MTBE) and atrazine reported in previous studies were investigated and compared. Table 7-4 shows the energy consumption required for 1Log removal of individual compounds by each process.

Mascolo *et al* (2008) have performed a preliminary operation cost evaluation of

UV/H_2O_2 process for the remediation of groundwater polluted by MTBE, benzene, toluene, *p*-xylene, styrene and ethylbenzene using batch experiment. In the study, they showed that the electrical energy necessary for a one order magnitude of removal of the investigated pollutants was 2.8 kWh/m^3. This corresponds to more than 5 times of the electrical energy (0.54 kWh/m^3) required for 90% removal of the PPCPs investigated in this study.

Table 7-4 Energy consumption required for 1Log removal of each all the compound

Compounds	Energy consumption (kWh/m^3)		
	UV/H_2O_2	O_3	O_3/UV
This study	0.54 (Secondary effluent)	0.09 (Secondary effluent)	1.09 (Secondary effluent)
MTBE(methyl-*tert*-butyl-eter)	1.2 ~ 8.6 [i] (Groundwater)	-	1.0 [ii] (Drinking water)
MTBE, bezene, toluene, *p*-xylene, styrene	2.8 [iii] (Groundwater)	-	-
BTEX	0.5 ~ 1.3 [iv] (Groundwater)	-	-
Atrazine	2.6 ~ 7.9 [iv] (Groundwater)	-	-
1,4-dioxane	0.5 ~ 1.6 [iv] (Groundwater)	-	-
C.I. Reactive Red2	-	2.1 [v] (Milli-Q)	4.2 [v] (Milli-Q)
Iopromide	-	0.3 [ii] (Drinking water)	-

i) Sutherland *et al*. 2008

ii) Sona *et al*., 2006

iii) Mascolo *et al*., 2008

iv) Calgon carbon oxidation technologies, 1996

v) Wu and Ng, 2008

Sutherland *et al* (2004) have also reported that the electrical energy necessary for a one order removal (EE/O) of MTBE in groundwater samples by pilot scale UV/H_2O_2 process ranged from 1.2 to 8.6 kWh/m^3. It was also known that EE/O values for other compounds are 0.5-1.3 kWh/m^3 for BTEX, 2.6-7.9 kWh/m^3 for atrazine, and 0.5-1.6 kWh/m^3 for 1,4-dioxane (Calgon carbon oxidation technologies, 1996). Comparing to the results from these previous studies, it can be known that efficient PPCPs removal by UV/H_2O_2 process can be achieved with relatively less energy consumption than other micropollutants.

On the other hand, Wu and Ng (2008) have calculated EE/O values for the decolorization

of C.I. Reactive Red2, dye with the most commonly used anchor in batch experiments using O_3, O_3/H_2O_2 and O_3/UV. They reported that for O_3 process, at pH 7 EE/O value was 2.1 kWh/m^3 and, O_3/UV process needed 2 times higher electrical energy (4.2 kWh/m^3) than for O_3 process. It can be known that the EE/O values are quite high comparing to 0.09 kWh/m^3 for O_3 process and 1.09 kWh/m^3 for O_3/UV process obtained in this study although a rather high concentration of the compound was used for the experiment.

Sona *et al* (2006) calculated the EE/O values for the removal of iopromide and MTBE in batch O_3 and O_3/UV experiments. The EE/O values for the compounds spiked in drinking water were 0.3 kWh/m^3 and 1.0 kWh/m^3 for iopromide and MTBE, respectively. Iopromide, a contrast medium has been known to be very stable compound, however, no contrast media were not contained in the investigated PPCPs in this study. Therefore, more electrical energy could be necessary than 0.09 kWh/m^3 if considering the efficient removal of contrast media such as iopromide by O_3 process. However, it can be known that iopromide needs less electrical energy than MTBE although it is a compound with very low degradability among PPCPs. From these results, it can be concluded that effective PPCPs removal can be achieved by the introduction of less electrical energy comparing to for other pollutants, irrespective of the investigated processes.

7.3.2 The disinfection effectiveness during UV/H_2O_2, O_3 and O_3/UV processes

7.3.2.1 UV/H_2O_2 process

UV doses required for the effective PPCPs removal were compared with those for the removal of pathogenic microorganisms. Fig 7-4 shows UV doses required for the effective pathogenic microorganisms and PPCPs removal.

In guidelines for sewer maintenance of Japan (2003), UV doses of 150-200 mJ/cm^2, 200-300 mJ/cm^2 and 300-500 mJ/cm^2 are recommended for 1log, 2log and 3log removal of total coliform in secondary effluent. Kruithof *et al* (2007) have investigated on the potential of UV/H_2O_2 process for organic contaminants control and primary disinfection using surface water. Under UV dose of 540 mJ/cm^2 (about 0.5 kWh/m^3) and H_2O_2 of 6 mg/L, pesticide (atrazine), *N*-Nitrosodimethylamine (NDMA), MTBE, dioxane, endocrine disruptor

(bisphenol A), microcystine and pharmaceuticals (diclofenac, ibuprofen) were removed by more than 80%. Moreover, 3log disinfection for *Cryptosporidium* and *Giardia* were obtained at the UV dose of less than 20 mJ/cm^2 and no reinfection of protozoa was observed at the UV dose of more than 45 mJ/cm^2. The highest UV dose for disinfection was 105 mJ/cm^2 needed for the inactivation of spores of *Sulphite Reducing Clostridia*. This means that UV/H_2O_2 process showed very good disinfection effectiveness under the operational condition for removing organic pollutants sufficiently.

It can be known in Fig 7-4 that *E.coli* and *cryptosporidium* are inactivated very easily even by UV dose of 5-18 mJ/cm^2 and 2-12 mJ/cm^2, respectively (Hijnen *et al.*, 2006). UV doses of 56-167 mJ/cm^2 can remove by 1-3log of Adenovirus type 40, which is the most UV-resistant waterborne pathogen known.

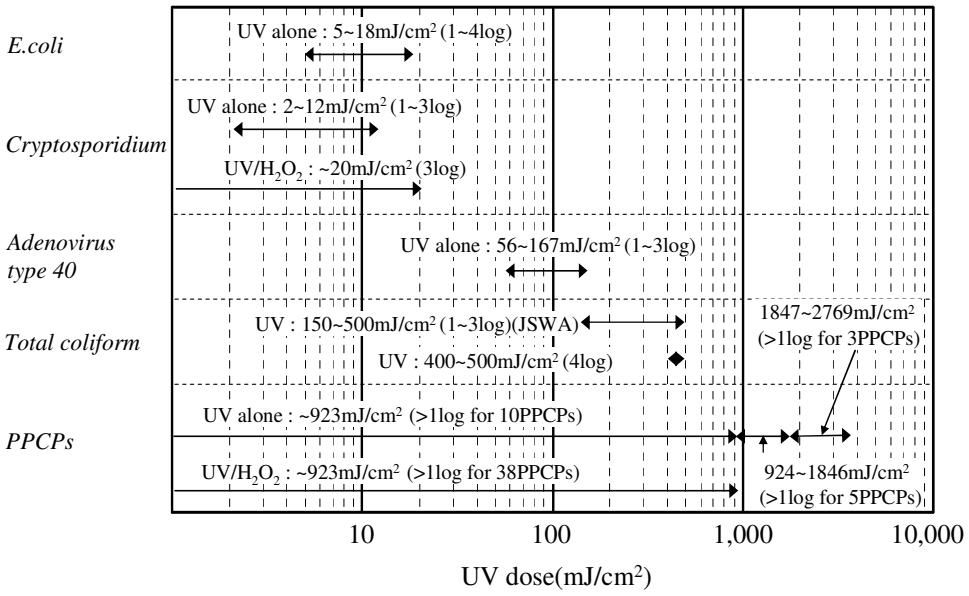


Fig. 7-4 UV doses for the effective pathogenic microorganisms and PPCPs removal

On the other hand, among 38 PPCPs, only 18 including diclofenac and isopropylantipyrine (analgesics), disopyramide (antiarrhythmic agent), ciprofloxacin and sulfamethoxazole (antibiotics) and clofibric acid (lipid modifying agent) could be removed by more than 90% in spite of the introduction of UV dose of 2,769 mJ/cm^2 during UV alone process (contact time : 15 min). Contrarily, the combination of H_2O_2 with UV process resulted in the significant decrease of UV dose. All the detected PPCPs were removed by more than

90% under UV dose of 923 mJ/cm^2 when initial H_2O_2 concentration of 6.2 mg/L was used during UV process. The disinfection effective for total coliforms with UV increases linearly with the increased UV dose (Paraskeva and Graham, 2005). This shows that 5 log disinfection for total coliform can be obtained under the operational condition (UV dose : 923 mJ/cm^2, Initial H_2O_2 concentration : 6.2 mg/L).

7.3.2.2 O_3 process

O_3 has been known to be a very effective disinfectant for advanced wastewater treatment plant effluent, and it can also inactivate viral and bacterial pathogens very rapidly (U.S. EPA, 2004). Moreover, some toxic, mutagenic, or carcinogenic compounds found in wastewaters can be more readily biodegraded after ozonation. Coliform is often used for evaluating the disinfection effectiveness by a disinfectant and several researchers have studied on the inactivation of coliform by ozone (Farooq *et al*., 1983; Smeets *et al*., 2006). In general, total coliform of less than 3,000 /cm^3 can be achieved at O_3 dose of 5 mg/L for secondary effluent including low organic compounds and/or NO_2^- (Japan Sewage Works Association, 2003).

Paraskeva and Graham (2005) examined the effect of three potential disinfection methods - ozonation, UV irradiation and microfiltration - on the removal of *E. coli* and total coliforms from a typical secondary municipal effluent. They showed that O_3 doses of 1-1.5 mg/L, 2.5 mg/L, 2.5-5 mg/L, 5-7.5 mg/L and 7.5-10 mg/L can ensure total coliforms reduction of 1log, 2log, 3log, 4log and 5log, respectively. Moreover, their results strongly indicated that transferred ozone dose was the most important parameter in the ozone treatment, but contact time was not a critical parameter. According to the U.S. EPA (1986), most plants have been reported to operate at 10-15 min contact times.

On the other hand, Xu *et al.* (2002) investigated wastewater disinfection by ozone at pilot scale on wastewater effluents. They found that O_3 dose of 4.8 mg/L with 4 min HRT was enough for total inactivation of enteroviruses (>2.9 log inactivation). In this study, O_3 dose required for an effective PPCPs removal in this study was 6 mg/L (O_3 consumption : 4.4 mg/L). This O_3 dose will also guarantee effluent water quality standard (< 3,000 /cm^3) for total coliform even though 4.4 mg/L is slightly lower than O_3 dose (5 mg/L) using for the disinfection of secondary effluent in Japan. In addition, Fig 7-5 shows that O_3 dose of 2.5

mg/L can inactivate total coliform of 2log. From this result, it is expected that total coliform inactivation required for the reclaimed water in Japan could be achieved with an effective PPCPs removal. On the other hand, O_3 doses of 7.5-10 mg/L are necessary for inactivating total coliform of 5log (Paraskeva and Graham, 2005). Therefore, 3log disinfection for total coliform is expected for O3 alone process using O_3 dose of 4.4 mg/L. However, it can be known that more than O_3 dose of 5 mg/L will be needed for satisfying the guidelines on the reclaimed water in the California Title 22 criteria (4-5log disinfection). The installation of rapid sand filter or biofilter before O_3 process is recommended because O_3 demand increase due to the consumption of O_3 by various constituents such as organic compounds or NO_2^- when secondary effluent is reclaimed (Japan Sewage Works Association, 2003). These processes will improve the disinfection effectiveness of O_3 for total coliform reducing O_3 demand.

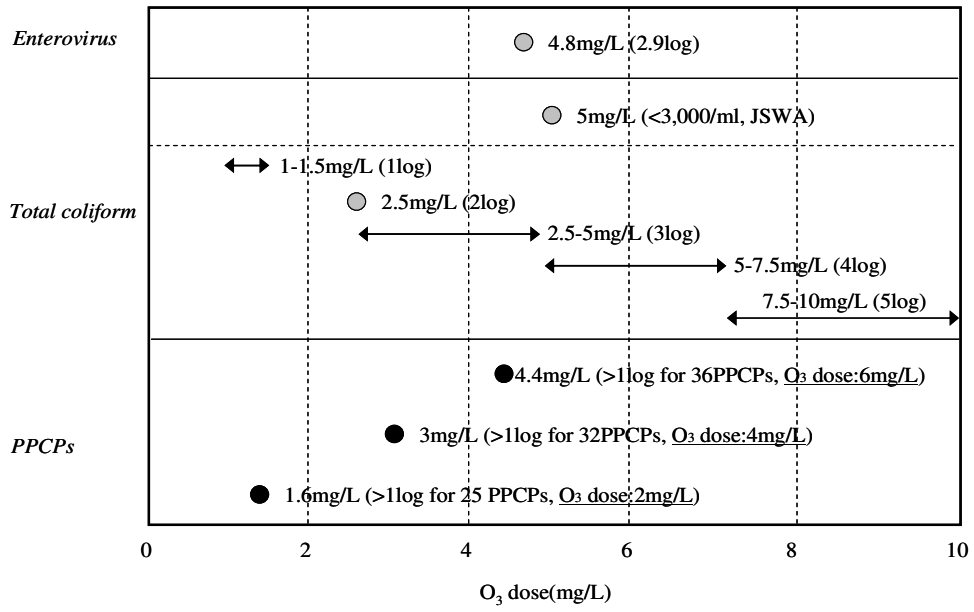


Fig. 7-5 O_3 doses for the effective pathogenic microorganisms and PPCPs removal

7.3.2.3 O_3/UV process

Information on the disinfection effectiveness of O_3/UV process appears to be not sufficient because most of studies on the process have been conducted for the removal of organic compounds. Jung *et al* (2007) evaluated the effect of O_3, UV, O_3/UV, O_3-UV and UV-O_3 processes for the disinfection of *Bacillus subtilis* spores which have often been used as a

surrogate microorganism for *Cryptosporidium parvum* oocysts. They found that among the investigated five processes, O_3/UV process showed the greatest synergistic effect in disinfecting *Bacillus subtilis* spores. This might be because the inactivation of *Bacillus subtilis* spores was affected by OH radicals as well as ozone and UV during O_3/UV process. OH radicals can play an important role in the inactivation of microorganisms, mainly due to the destruction of their cell membranes or walls (von Sonntag, 1986). Therefore, O_3/UV process is expected to be more effective for disinfection than O_3 process owing to the contribution of OH radicals formed by UV photodegradation of O_3 to the inactivation of pathogenic microorganisms as well as the destruction of pathogenic microorganisms by direct UV irradiation. In this study, the effective PPCPs removal was achieved for O_3/UV process using O_3 dose of 4 mg/L (O_3 consumption : 3.4 mg/L) and UV dose of 1,846 mJ/cm^2. Considering the synergistic effect of O_3/UV process for disinfection, it is thought that 5log disinfection for total coliform can be acquired with the operational condition.

7.3.3 The formation of by-products by UV/H_2O_2, O_3 and O_3/UV processes

7.3.3.1 The formation of by-products of PPCPs during each process

Fig. 7-6 shows the profile of dissolved organic carbon (DOC) concentration with time when tested waters spiked with 30 PPCPs including analgesics, antiarrhythmia agents, antibiotics and brondiodilators were treated with UV/H_2O_2, O_3 and O_3/UV processes. The initial concentrations of the 30 PPCPs in tested water ranged from 5 μg/L to 119 μg/L. UV/H_2O_2 process was carried out using batch reactor with an effective volume of 22L and, UV lamp that emits at the wavelength of 254 nm and the initial H_2O_2 concentration of 4.9 mg/L were used. O_3 process was performed by semi-batch experiment supplying O_3 gas to batch reactor continuously at O_3 feed rate of 0.3 mg/L/min (Concentration of O_3 gas : 6.6mg/L, Flow rate of O_3 gas : 1 L/min). O_3/UV process was carried out using O_3 feed rate of 0.3 mg/L/min and UV lamp applied in UV/H_2O_2 process.

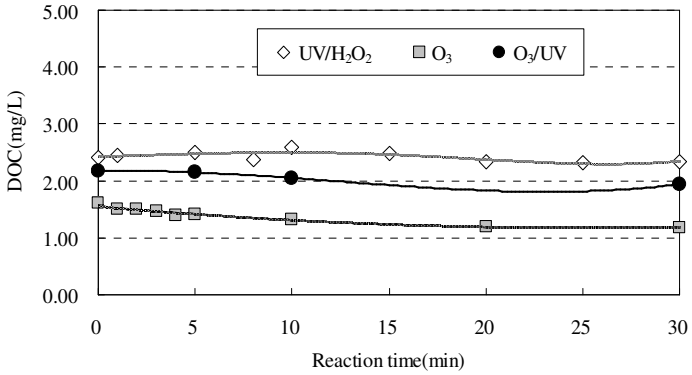


Fig. 7-6 Profile of DOC concentration with time during each process

It can be known in Fig. 7-6 that DOC concentration decreased very slightly during the reaction time of 30 min. However, most of PPCPs dereased by less than limit of detection (LOD) in their concentrations for 5-15 min, irrespective of applied processes. Therefore, it was expected that a variety of by products would be generated during the processes.

7.3.3.2 The formation of bromate during each process

Fig 7-7 shows the formation of bromate under O_3 doses of 3 mg/L (O_3 consumption : 2.2 mg/L), 6 mg/L (O_3 consumption : 3.9 mg/L) and 12 mg/L (O_3 consumption : 7.0 mg/L) during O_3 process using bench scale experimental setup. The contact time of each reactor is 5 min and O_3 gas was supplied to Reactors 1 and 2 (O_3 gas flow rate/reactor : 0.5 L/min). Bromide concentrations in raw water ranged from 62 μg/L to 80 μg/L.

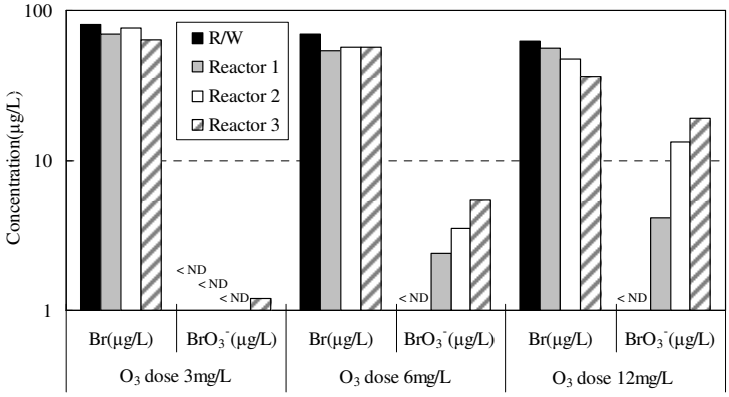


Fig. 7-7 Formation of bromate during O_3 process

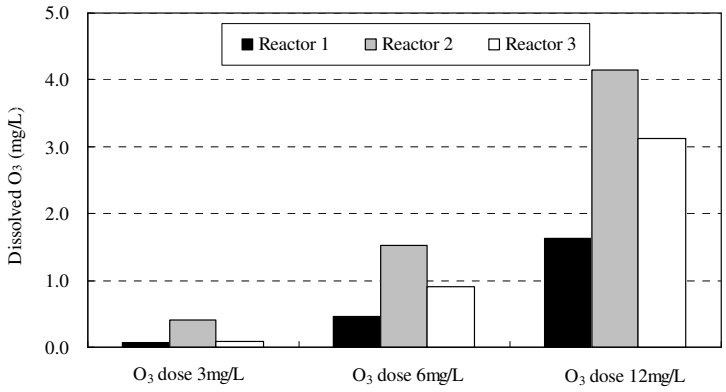


Fig. 7-8 Profile of dissolved O_3 during O_3 process

As shown in Fig. 7-7, bromate concentration increased with the increased O_3 dose and contact time. Kim (2005) reported that bromate formation increased linearly as CT (concentration × contact time) value increased, and the formation rate of bromate was mainly affected by initial bromide concentration. On the other hand, it can be known that the formation potential of bromate will increase when dissolved O_3 concentration is high (Fig. 7-8) although the removal efficiency of PPCPs improved with the increase of O_3 dose as mentioned before.

Fig. 7-9 shows the profile of bromate during UV/H_2O_2, O_3 and O_3/UV processes. No bromate formation showed during UV process combined with H_2O_2 concentration of 8 mg/L. For O_3 process, bromate concentrations in samples from reactor 1 and 2 increased by 1.4 μg/L and 4.4 μg/L, respectively, under O_3 dose of 6 mg/L. Contrarily, bromate concentration in sample from reactor 2 decreased by 2.3 μg/L in O_3/UV process although the same O_3 dose of 6 mg/L was applied. It was described in Chapter 6 that the PPCPs removal was improved by the combination of UV with O_3 process. Dissolved O_3 concentrations in reactor 1 and 2 were 0.4 mg/L and 1.7 mg/L during O_3 process, while for O_3/UV process, dissolved O_3 concentration of about 0.1 mg/L was shown in both reactors because of the direct photodegradation of O_3 molecular by UV irradiation. Thus, it can be concluded that bromate formation potential can be suppressed by lowering dissolved O_3 concentration.

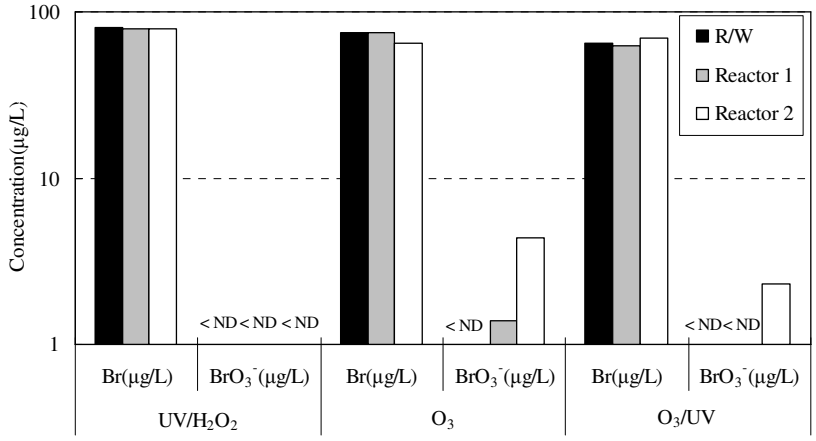


Fig. 7-9 Formation of bromate during UV/H_2O_2, O_3, O_3/UV processes

7.3.3.3 Review on the formation of by-products during each process

PPCPs may be transformed by a variety of water treatment processes during their release to the aquatic environment. Consequently, the aquatic environment may be exposed to a mixture of the parent PPCPs and any resulting transformation products. The increasing concern is the potential toxicity of the transformation products to humans through drinking water as well as aquatic organisms (Li *et al*., 2008). Here, the formation potential of by products during the degradation of PPCPs by UV/H_2O_2, O_3 and O_3/UV processes was discussed.

Vogna *et al* (2004a) has investigated the oxidation of diclofenac, a widely used anti-inflammatory drug, with UV/H_2O_2 and O_3 treatments. In their study, both UV/H_2O_2 and O_3 turned out effective treatment methods for inducing diclofenac degradation. When tested water spiked with diclofenac of 0.001M was treated for 90 min by UV/H_2O_2 process, diclofenac showed the degree of mineralization of 39%, which was calculated by total organic carbon (TOC) abatement. O_3 treatment showed slightly lower mineralization of 32% than for UV/H_2O_2 treatment for 90 min although diclofenac was degraded completely within 10 min. The degradation of carbamazepine with UV/H_2O_2 treatment was investigated in their other study (Vogna *et al*., 2004b). They found that TOC of about 35% was removed when carbamazepine in aqueous solution (2.0×10^{-2}mM) was degraded completely for about 4 min, showing the formation of a series of acridine intermediates which are more toxic and hazardous than carbamazepine.

There seems to be relatively many studies on the degradation of pharmaceuticals with O_3 (Andreozzi *et al*., 2005; Lange *et al*., 2006; Dantas *et al*., 2007; Seitz *et al*., 2008; Dantas *et al*., 2008; Li *et al*., 2008). Andreozzi *et al* (2005) has studied and reported on the ozonation of amoxicillin (5.0×10^{-4}M) added to aqueous solution which was saturated with ozone ($[O_3] = 1.6\times10^{-4}$M) previously. In the study, more than 90% of amoxicillin was converted during ozonation of 4 min, while very low TOC removal of 18.2% was observed for longer ozonation time of 20 min. As a consequent, they suggested that further investigations will be necessary to assess the ecotoxicities of the intermediates and products formed during ozonation of amoxicilline.

Seitz *et al* (2008) found that for ozonation of iomeprol, a representative iodinated X-ray contrast medium, unknown by-products were formed and detected from the effluent of an ozone reactor in a full-scale water treatment works as well as their batch studies. Dantas *et al* (2008) also observed that after 15 min of ozonation (0.4g O_3/L), the complete sulfamethoxazole abatement was almost achieved with just 10% of mineralization. From these previous studies, it can be known that it will be difficult to achieve the complete mineralization of PPCPs by ozonation. Dantas *et al* (2007) have assessed the biodegradability and acute toxicity of by products formed from ozonation of bezafibrate, a largely used lipid regulator. They demonstrated that ozonation is an appropriate process to improve the biodegradability and slow down the toxicity of water containing bezafibrate, based on the increased ratio of BOD_5/COD by ozonation.

There seems to be very few studies on the formation of by products during the degradation of PPCPs by O_3/UV process. Gong *et al* (2007) have done O_3 and O_3/UV treatment experiments for the biotreated effluent of a municipal wastewater treatment in order to investigate the effects of O_3 and O_3/UV on organic fractions. Dissolved organic matter (DOM) was separated into four fractions: hydrophobic acids, non-acid hydrophobics, transphilics and hydrophilics. As a result, they observed that ozone was not effective for reducing dissolved oxygen carbon (DOC) due to its sequential reaction with aromatic hydrophobics, trasphilics and hydrophilics. Contrarily, O_3/UV process was effective for removing all four DOM fractions.

From these results, it is likely to be difficult to accomplish the complete mineralization of

PPCPs by UV/H_2O_2 and O_3 process. There may be a great variety of PPCPs in the aquatic environment. This may be why it will be much more difficult work to consider the mineralization of all the PPCPs by wastewater treatment processes. Therefore, after and before treatment by the processes, risk assessment for treated water should be performed to investigate the effect of the treated water on the aquatic system and human health.

7.3.3.4 Review on the formation and suppression of bromate during O_3 process

Adverse health consequences associated with the reuse of raw or improperly treated wastewater were well documented. As a consequence, water reuse regulations and guidelines are principally directed at public health protection, and generally are based on the control of both health significant microorganisms and chemical contaminants especially for indirect potable reuse applications. For indirect potable reuse, treated wastewater is mixed with surface and/or groundwater, and the mix typically receives additional treatment before entering the water distribution system.

On the other hand, for O_3 process, dissolved O_3 can react with bromide in water and lead to the formation of bromate as mentioned above. Bromate is known to be carcinogenic and, therefore, concerns on the control of bromate formation are increasing. Bromate regulation is now being proposed at a maximum contaminant level of 10 μg/L in drinking water in U.S.EPA. In 2003, Japan has also set the bromate regulation of 10 μg/L in drinking water. Therefore, if considering indirect potable reuse applications, bromate is needed to be controlled during treatment of secondary effluent.

Bromate can be formed when O_3 dose exceeds the O_3 demand of the water. Wert *et al* (2007) observed that at O_3 doses above 3.1 mg/L, a linear relationship was obtained between bromate formation and O_3 dose during bench- and pilot-scale testing. They also reported that bromate formation during O_3/H_2O_2 treatment was due to residual O_3. Kim (2005) demonstrated that more than 3log inactivation of total coliform and 90% removal of EDCs could be achieved when the ratio of O_3 consumed to initial DOC concentration was set to 1.0 during O_3 process. Moreover, he observed that no bromate was formed under the operational condition. Bench scale experiments showed that for O_3 process, the ratios of O_3 consumed to initial DOC concentration were 0.5, 1.0 and 1.6 for O_3 doses of 2 mg/L, 4 mg/L and 6 mg/L,

respectively (Chapter VI). It can be, therefore, said that O_3 dose of 4 mg/L will be desirable in terms of the suppression of bromate formation. However, the effective removal of PPCPs detected in secondary effluent could be achieved under O_3 dose of 6 mg/L.

On the other hand, Kim (2005) reported that when the molar ratio of H_2O_2 added to O_3 consumed was over 0.5, dissolved O_3 was completely suppressed, resulting in no bromate formation. Moreover, this study showed that O_3/UV process could be an alternative treatment option for the control of bromate formation (7.3.3.2) and the effective PPCPs removal (Chapter VI).

From these results, the formation potential of bromate caused by residual O_3 can be pointed out as a defect of O_3 process. Bromate formation for O_3 process can be controlled by selecting appropriate O_3 dose considered initial DOC concentration of the water. In this study, it was thought that the operational condition (O_3 dose of 6 mg/L) which achieved an effective PPCPs removal could cause bromate formation because the ratio of O_3 consumed to initial DOC concentration was over 1.0 and SUVA was less than 0.013L/mg·cm, suggested by Kim (2005). On the other hand, the combination of H_2O_2 or UV with O_3 can ensure the suppression of bromate formation. Especially, this study demonstrated that O_3/UV process could accomplish an effective removal of all the PPCPs detected in secondary effluent.

7.3.4 Decrease effect for ecological risk by each process

Figs. 7-10~13 show the variation of H/Rs of the 30 PPCPs by each process. Among the 30 PPCPs, PPCPs that showed high H/R in tested water were clarithromycin (2.3~3.6), ketoprofen (0.4~0.8), azithromycin (0.4~0.6), erythromycin (0.2) and lincomycin (0.1~0.3). Clarithromycin was classified as a candidate compound that further assessment is required due to its very high H/R (5.7), which was calculated using PEC and PNEC. On the other hand, the sum of H/Rs of other 25 PPCPs ranged from 0.1 to 0.2, which is negligible comparing with those of the five PPCPs mentioned above.

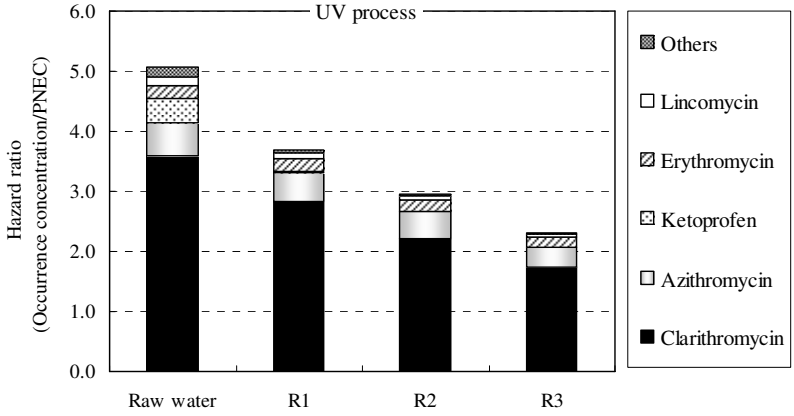


Fig. 7-10 Variation of H/Rs of the 30 PPCPs by UV process

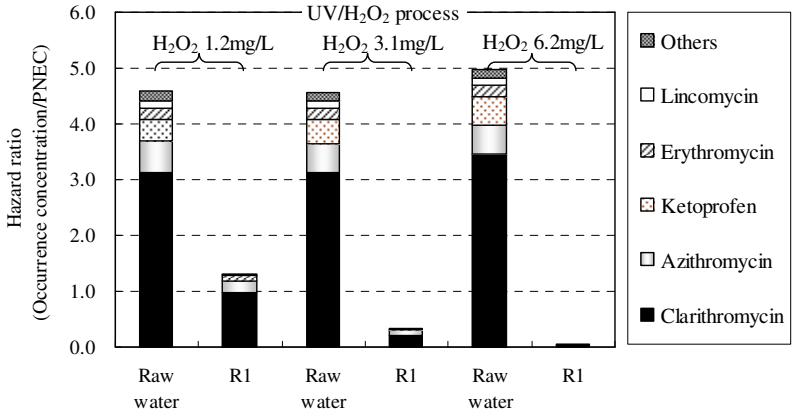


Fig. 7-11 Variation of H/Rs of the 30 PPCPs by UV/H_2O_2 process

For UV process (Fig. 7-10), H/R decreased gradually passing through each reactor (R1, R2 and R3). In particular, H/R of ketoprofen in tested water was 0.4, however, it decreased by almost 0 in R1 (contact time: 5 min), indicating that UV process can reduce the ecological risk caused by ketoprofen very fast. It was also observed that H/Rs of other 25 PPCPs decreased by almost 0 in R1. On the other hand, three macrolide antibiotics such as clarithromycin, azithromycin and erythromycin showed highly high H/Rs of 0.2 to 1.7 even after UV treatment for 15 min (R3, Introduced UV dose : 2,768 mJ/cm^2). It is, therefore, thought that considerable UV dose will be needed to decrease the ecological risk caused by PPCPs by UV alone process.

H/R in treated water from R1 was about 1.3 when initial H_2O_2 concentration of 1.2 mg/L was combined with UV process (Fig. 7-11). The addition of initial H_2O_2 concentrations of 3.1

mg/L and 6.2 mg/L during UV process could decrease the H/Rs by 0.3 and 0.1, respectively. In contrast to UV process, significant decrease effect for ecological risk was shown for short contact time of 5 min.

Fig. 7-12 shows H/R at each reactor during O_3 process. It can be seen that very low H/Rs were obtained comparing with other processes, irrespective of O_3 dose. Moreover, the H/Rs decreased significantly with the increased O_3 dose, showing that O_3 process will be very effective for reducing ecological risk caused by parent PPCPs. However, as mentioned above, various intermediates can be formed for the degradation of organic compounds by O_3. In this study, H/Rs of the intermediates were not considered.

For O_3/UV process (Fig. 7-13), the decrease of H/R during the contact time of 5 min (R1) was not so significant, however, the contact time of 10 min (R2) reduced the H/R considerably. H/Rs for O_3/UV process also decreased gradually the increased O_3 dose. Consequently, UV/H_2O_2, O_3 and O_3/UV processes could reduce total H/Rs of the 30 PPCPs ranging from 3.8 to 5.0 in tested water by very low level (less than 1.0).

Therefore, it can be concluded that these processes will play an important role in reducing the ecological risk caused by a variety of parent PPCPs in secondary effluent of STP.

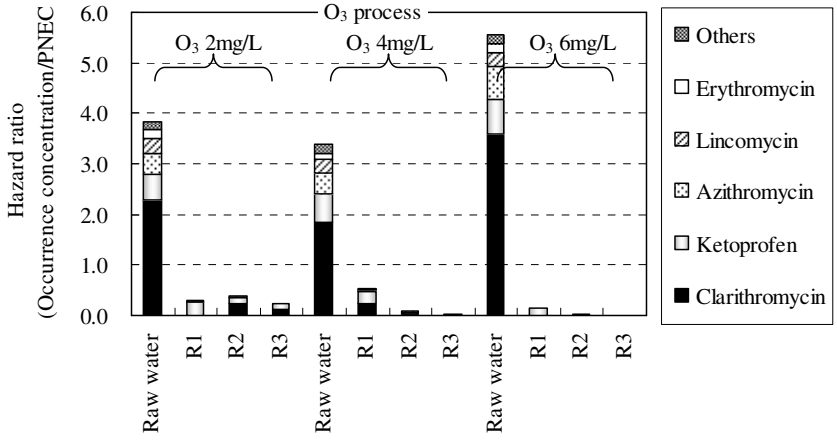


Fig. 7-12 Variation of H/Rs of the 30 PPCPs by O_3 process

※ O_3 consumption : 1.6 mg/L, 3.0 mg/L and 4.4 mg/L for O_3 doses of 2 mg/L, 4 mg/L and 6 mg/L, respectively.

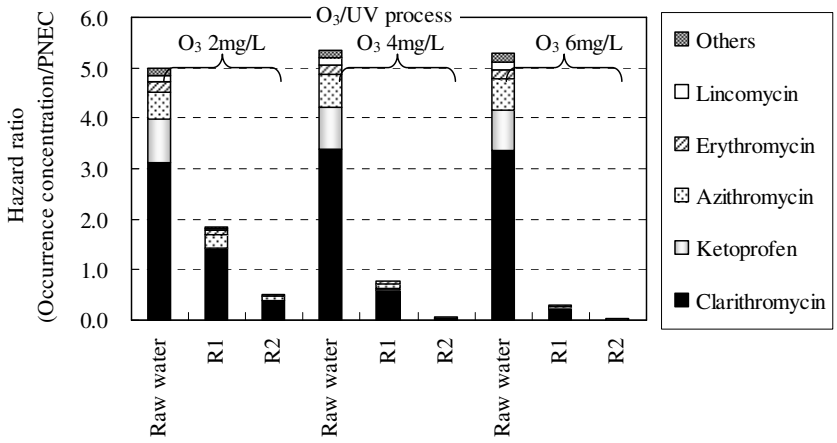


Fig. 7-13 Variation of H/Rs of the 30 PPCPs by O_3/UV process

※ O_3 consumption : 1.8 mg/L, 3.4 mg/L and 5.3 mg/L for O_3 doses of 2 mg/L, 4 mg/L and 6 mg/L, respectively.

7.3.5 Propose of appropriate process for water reuse

Additional concerns have been raised regarding the fate and transport of trace organic compounds. These include endocrine disruptors and PPCPs (pharmaceuticals and personal care products) that are present in municipal wastewaters. None of these individual compounds are regulated for the reclaimed water. Although no illnesses to date have been directly connected to the use of reclaimed water, it is recommended to continue with ongoing research for these compounds in terms of precautionary principles. The performance of O_3, UV/H_2O_2 and O_3/UV processes for the PPCPs removal was investigated in this study. Based on the results from the investigations and previous studies, the applicability of the processes as a technology for sewage reuse was evaluated. Effective PPCPs removal was achieved by the introduction of less electrical energy comparing to for other pollutants such as MTBE, BTEX and atrazine, irrespective of the investigated processes (7.3.1.2). In addition, UV/H_2O_2, O_3 and O_3/UV processes reduced total H/Rs of the 30 PPCPs in tested water by very low level (7.3.4). Therefore, the disinfection effectiveness and the potential of by-product formation are critical factors in evaluating the applicability of the investigated processes as a technology of water reuse.

For O_3 process, O_3 dose of 6 mg/L (O_3 consumption : 4.4 mg/L) was necessary for the effective removal of the 37 PPCPs detected in secondary effluent. About 4log inactivation of

total coliform can be expected under this operational condition (Fig. 7-5). In Japan, total coliform in the effluent from wastewater treatment plant must be less than 3,000 /ml. Therefore, the removal efficiency of total coliform which the investigated processes should achieve for water reuse was calculated from 3,000 /ml. As a result, 3log and 4~5log inactivations are necessary to meet the guideline for water reuse of Japan (1,000/100 ml) and California Title 22 criteria (Table 7-2), respectively. Consequently, it is expected that O_3 dose of 6 mg/L can meet the guideline for water reuse of Japan and the water quality required for restricted urban and agricultural (non-food crops) reuses in the California Title 22 criteria by accomplishing about 4log inactivation of total coliform. On the other hand, the formation potential of bromate is likely to be high under O_3 dose of 6 mg/L (7.3.3.4). Therefore, the combination of UV or H_2O_2 with O_3 process is recommended to suppress bromate formation, for direct and indirect potable reuses. In addition, UV/H_2O_2 process can be a treatment option in terms of bromate suppression.

UV/H_2O_2 (UV dose : 923 mJ/cm^2, H_2O_2 : 6.2 mg/L) and O_3/UV (O_3 consumption : 3.4 mg/L (O_3 dose : 4 mg/L), UV : 1,846 mJ/cm^2) processes discussed in this chapter can be expected to achieve more than 5log inactivation of total coliform (7.3.2.1). Moreover, no bromate will be formed during UV/H_2O_2 process, and the combination of UV with O_3 process also can suppress the formation of bromate by blocking the reaction of residual O_3 with Br through the photodegradation of residual O_3 (7.3.3). Therefore, the processes can be applied for unrestricted urban reuse, agricultural reuse (food crops) and recreational reuse as well as restricted urban and agricultural (non-food crops) reuses of sewage water although much more energy consumption will be necessary comparing to for O_3 process.

On the other hand, various by-products from the parent PPCPs degradation can be formed for all the investigated processes. There are a great variety of PPCPs used for human health and, therefore, it is very difficult to investigate the by-products from all the PPCPs. In this case, risk assessment for the water treated with the processes will be useful for investigating the adverse effects from the by-products. In this study, decrease effect of ecological risk before and after treatment was evaluated for the parent PPCPs. As a result, it was observed that ecological risk caused by the parent PPCPs could be reduced considerably after treatments, irrespective of the applied processes. Therefore, the investigated processes

can be used as treatment options for indirect potable reuse, recreational reuse and groundwater reuse *etc* of sewage water in terms of ecological risk decrease for the parent PPCPs, although the adverse effect by by-products are still questioned.

Table 7-5 Applicable reuses by the investigated processes

Items		O_3	UV/H_2O_2	O_3/UV
		* O_3 dose : 6 mg/L (O_3 consump.:4.4 mg/L)	* UV dose : 923 mJ/cm^2, H_2O_2 : 6.2 mg/L	* O_3 dose : 4 mg/L (O_3 consump.:3.4 mg/L), UV dose : 1,846mJ/cm^2
Energy consumption for effective PPCPs removal		0.09 kWh/m^3	0.54 kWh/m^3	1.09 kWh/m^3
Disinfection effectiveness		3log inactivation of total coliform	More than 5log inactivation of total coliform	
By-products	PPCPs by-products	Formation potential of various by-products from PPCPs degradation		
	Bromate	Bromate formation potential	No bromate formation	Suppression of bromate formation
Ecological risk		Hazardous ratio for 30 PPCPs : less than 0.1		
Applicable reuses		- Urban and recreational reuse (Japan) - Restricted urban / agricultural reuse (non-food crops) (California)	- Urban and recreational reuse (Japan) - Unrestricted and restricted urban / agricultural (food and non-food crops) / recreational reuse (California)	

7.4 Summary

In this chapter, the applicability of O_3, UV/H_2O_2 and O_3/UV processes as technologies for water reuse considering PPCPs removal was investigated. The PPCPs removal efficiency and energy consumption for each process were compared and discussed for this investigation. In addition, the formation potential of disinfection by products (DBPs), disinfection effectiveness and decrease effect for ecological risk of the investigated processes were also discussed. The results are as follows;

1) Electrical energies required for the effective removal of PPCPs in secondary effluent were 0.09 kWh/m^3, 0.54 kWh/m^3 and 1.09 kWh/m^3 for O_3 (O_3 dose : 6 mg/L, O_3

consumption : 4.4 mg/L), UV/H_2O_2 (UV dose : 923 mJ/cm^2, H_2O_2 : 6.2 mg/L) and O_3/UV (O_3 dose : 4 mg/L, O_3 consumption : 3.4 mg/L, UV dose : 1,846 mJ/cm^2) processes, respectively, showing that O_3 process is the most cost-effective treatment option for the PPCPs removal. On the other hand, it is considered that PPCPs removal by the investigated processes requires less electrical energy than for other micropollutants such as MTBE, atrazine and 1,4-dioxane.

2) 4 log inactivation of total coliform was expected to be achieved by O_3 process at O_3 dose of 6 mg/L, while more than 5 log inactivation by UV/H_2O_2 (UV dose : 923 mJ/cm^2, H_2O_2 : 6.2 mg/L) and O_3/UV (O_3 dose : 4 mg/L, UV dose : 1,846 mJ/cm^2) processes could be achieved. Therefore, in case that the number of total coliform in secondary effluent is 3,000 /ml, these processes can meet sufficiently the guideline for water reuse of Japan (1,000/100ml). On the other hand, O_3 process (O_3 dose : 6 mg/L) can be used as a treatment method for restricted urban reuse and agricultural reuse (non-food crops) requiring the number of total coliform of less than 23/100ml. However, in order to obtain the reclaimed water for unrestricted urban reuse, agricultural reuse (food crops) and unrestricted/restricted recreational reuse considering the effective PPCPs removal, UV/H_2O_2 and O_3/UV processes should be applied.

3) O_3 process at O_3 dose of 6 mg/L (O_3 consumption : 4.4 mg/L) showed the effective PPCPs removal, however, the formation of bromate is expected for O_3 process using O_3 dose of more than 4 mg/L (O_3 consumption : 3.0 mg/L). In particular, bromate formation will be a critical issue when the reclaimed water is used for direct/indirect potable reuses. Therefore, in order to suppress the bromate formation as well as achieve the effective PPCPs removal, O_3/UV process will be appropriate. For O_3/UV process, residual O_3 will be degraded by UV photodegradation, and, therefore, the formation reaction of bromate (reaction of O_3 with Br^-) will be suppressed. UV/H_2O_2 process will be also a profitable process because no bromate will be formed during the process.

4) The ecological risk evaluation showed that each process could decrease the ecological risk caused by parent PPCPs considerably. This means that the investigated processes can play an important role in reducing unpredictable side effects caused by PPCPs in the aquatic environment.

7.5 References

Andreozzi R., Canterino M., Marotta R., Paxxeus N., 2005, Antibiotic removal from wastewaters: The ozonation of amoxicillin, Journal of Hazardous Materials 122, 243-250

Calgon Carbon Oxidation Technologies. AOT handbook. Markham, Ontario, Canada: Calgon Carbon Corporation, 1996

Daniel F.B., DeAngelo A.B., Stober J.A., Olson G.R., Page N.P., 1992, Hepatocarcinogenicity of chloral hydrate, 2-chlororacetaldehyde and dichloroacetic acid in the male B6C3F1 mouse, Fundam. *Appl. Toxicol.* 19, 159-168

Dantas R.F., Canterino M., Marotta R., Sans C., Esplugas S., Andreozzi R., 2007, Bezafibrate removal by means of ozonation: Primary intermediates, kinetics, and toxicity assessment, *Water Res.* 41, 2525-2532

Dantas R.F., Contreras S., Sans C., Esplugas S., 2008, Sulfamethoxazole abatement by means of ozonation, *Journal of Hazardous Materials* 150, 790-794

Energy, Environment and Sustainable Development, Assessment of technologies for the removal of pharmaceuticals and personal care products in sewage and drinking water facilities to improve the indirect potable water reuse, POSEIDON, Detailed report related to the overall project duration: January 1st, 2001-June 30th, August, 2004

Farooq S., Akhlaque S., 1983, Comparative response of mixed cultures of bacteria and virus to ozonation, *Water Res.* 17, 809–812

Fukunaga, 2008, Evaluation on Ecotoxicity of Urban Water: A Case Study of Yodo River System, Department of Urban & Environmental Engineering, Kyoto University, Kyoto

Gong J., Liu Y., Sun X., 2007, O_3 and UV/O_3 oxidation of organic constituents of biotreated municipal wastewater, *Water Res.*(2007), doi:10.1016/j.watres.2007.09.020

Hijnen W.A.M., Beerendonk E.F., Medema G.J., 2006, Inactivation credit of UV radiation for viruses, bacteria and protozoan (oo)cysts in water: A review, Water Res. 40 (2006), 3-22

Japan Sewage Works Association, Guidelines for sewer maintenance, 2003

Jung Y.J., Oh B.S., Kang J.W., 2007, Synergistic effect of sequential or combined use of ozone and UV radiation for the disinfection of Bacillus subtilis spores. *Water Res.*(2007), doi:10.1016/j.watres.2007.10.008

Kim H.S., 2005, Behavior and control of by-products during ozone and ozone/hydrogen

peroxide treatments of sewage effluent, Department of Urban & Environmental Engineering, Kyoto University, Kyoto

Kim I. H., Tanaka H., Iwasaki T., Takubo T., Morioka T., Kato Y., 2008, Classification of the degradability of 30 pharmaceuticals in water with ozone, UV and H_2O_2, *Wat Sci Technol.* 57, 195-200

Kruithof J.C., Kamp P.C., Martijn B.J., 2007, UV/H_2O_2 Treatment: A practical solution for organic contaminant control and primary disinfection, *Ozone: Science & Engineering* 29, 273-280

Lange F., Cornelissen S., Kubac D., Sein M.M., von Sonntag J., Hannich C.B., Golloch A., Heipieper H.J., Moder M., von Sonntag C., 2006, Degradation of macrolide antibiotics by ozone: A mechanistic case study with clarithromycin, *Chemosphere* 65, 17-23

Li K., Yediler A., Yang M., Schulte-Hostede S., Wong M.H., 2008, Ozonation of oxytetracycline and toxicological assessment of its oxidation by-products, *Chemosphere*, doi:10.1016/j.chemosphere.2008.02.008

The ministry of Land, Infrastructure and Transport of Japan, Manual for water reuse of sewage treated water, 2005

Mascolo G., Ciannarella R., Balest L., Lopez A., 2008, Effectiveness of UV-based advanced oxidation processes for the remediation of hydrocarbon pollution in the groundwater: A laboratory investigation, *Journal of Hazardous Materials* 152, 1138-1145

Muellner M.G., Wagner E.D., McCalla K., Richardson S.D., Woo Y.T., Plewa M.J., 2007, Haloacetonitriles vs. regulated haloacetic acids; are nitrogen containing DBPs more toxic? *Environ. Sci. Technol.* 41, 645-651

Paraskeva P. and Graham N.J.D., 2005, Treatment of a secondary municipal effluent by ozone, UV and microfiltration: microbial reduction and effect on effluent quality, *Desalination* 186, 47–56

Richardson S.D., 1998, Drinking water disinfection by-products, Encyclopedia Environ. *Anal. Remed.* 3, 1398-1421

Richardson S.D., Plewa M.J., Wagner E.D., Schoeny R., DeMarini D.M., 2007, Occurrence, genotoxicity, and carcinogenicity of regulated and emerging disinfection by-products in drinking water: A review and roadmap for research, *Mutation Research* 636, 178-242

Seitz W., Jiang J.Q., Schulz W., Weber W.H., Maier D., Maier M., 2008, Formation of oxidation by-products of the iodinated X-ray contrast medium iomeprol during ozonation, *Chemosphere* 70, 1238-1246

Smeets P.W.M.H., van der Helm A.W.C., Dullemont Y.J., Rietveld L.C., van Dijk J.C., Medema G.J., 2006, Inactivation of Escherichia coli by ozone under bench-scale plug flow and full-scale hydraulic conditions, *Water Res.* 40, 3239-3248

Sona M., Baus C., Brauch H.J., 2006, UV Irradiation versus combined UV / Hydrogen Peroxide and UV / Ozone Treatment for the Removal of Persistent Organic Pollutants from Water, International Conference Ozone and UV, Wasser Berlin rlin, April 3rd 2006, 69-76

Sutherland J., Adams C., Kekobad J., 2004, Treatment of MTBE by air stripping, carbon adsorption and advanced oxidation: technical and economic comparison for five groundwaters, *Water Res.* 38, 193-205

Tuhkanen T.A., 2004, UV/H_2O_2 processes. In: Parsons, S. (Ed.), Advanced Oxidation Processes for Water and Wastewater Treatment. IWA Publishing, London, UK, pp. 86-110

US EPA, EPA/625/1-86/021, 1986.

U.S. EPA, Guidelines for Water Reuse, EPA/625/R-04/108, September 2004

Vogna D., Marotta R., Napolitano A., Andreozzi R., d'Ischia M., 2004a, Advanced oxidation of the pharmaceutical drug diclofenac with UV/H_2O_2 and ozone, *Water Res.* 38, 414-422

Vogna D., Marotta R , Andreozzi R., Napolitano A., d'Ischia M., 2004b, Kinetic and chemical assessment of the UV/H_2O_2 treatment of antiepileptic drug carbamazepine, *Chemosphere* 54, 497-505

von Sonntag C., 1986, Disinfection by free radicals and UV-radiation, *Water Supply: Rev.J.Int. Water Supply Assoc.* 4, 11-18

Wert E.C., Rosario-Ortiz F.L., Drury D.D., Snyder S.A., 2007, Formation of oxidation byproducts from ozonation of wastewater, *Water Res.* 41, 1481-1490

Wu C.H., Ng H.Y., 2008, Degradation of C.I. Reactive Red2 (RR2) using ozone-based systems: Comparisons of decolorization efficiency and power consumption, *Journal of Hazardous Materials* 152, 120-127

Xu P., Janex M.L., Savoye P., Cockx A., Lazarova V., 2002, Wastewater disinfection by ozone: main parameters for process design, *Water Res.* 36, 1043-1055

CHAPTER VIII

CONCLUSION AND RECOMMENDATIONS

8.1 Conclusions

There has been little information that pharmaceuticals and personal care products (PPCPs) have any adverse health effects. Nevertheless, water reclamated from secondary effluent of wastewater treatment plant as well as drinking water should be free from the PPCPs to minimize the unpredictable risk. Therefore, a sufficient removal of PPCPs in wastewater treatment plants (WWTPs) known to a main PPCPs source into the aquatic environment is inevitable. However, it has not been known that which PPCP is relevant to the aquatic environment because a great variety of PPCPs are used for human health and animal breed, unlike other micropollutants.

Indicators for evaluating environmental relevance of a micropollutant include occurrence, fate and detection frequency in the aquatic environment, and its ecological toxicity and degradability. This study provides information on the degradability of various PPCPs by physicochemical processes such as UV-based (UV and UV/H_2O_2) and O_3-based processes (O_3, O_3/H_2O_2 and O_3/UV). Besides, the main achievements of this study are as follows; 1) UV doses, O_3 doses, the energy consumptions and operating costs required for the effective removal of PPCPs were obtained, and 2) considering the disinfection effectiveness, the formation potential of by products and the decrease effect of ecological risk by the introduction of each process as well as the removal efficiency of PPCPs and energy consumption, the removal performance of each process for PPCPs was discussed integratedly. These results are available as operating data for the prevention of PPCPs discharge into the aquatic environment and water reuse of secondary effluent in WWTPs.

Main findings from this study are described below by each chapter.

In Chapter III, the photodegradation characteristics of PPCPs detected often in aquatic environment with UV treatment were examined. Moreover, the effectiveness of H_2O_2 addition for PPCPs degradation during UV treatment was investigated. Finally, UV doses required for the effective removal of each PPCP were estimated. This information is useful for expecting the removal potential of UV process for various PPCPs in water and wastewater treatment plant. The major findings are as follows.

1) At the UV wavelength of 254nm, molar extinction coefficients of the 30 PPCPs ranged from 9 /M/cm (cyclophosphamide) to 19,799 /M/cm (oxytetracycline), indicating that photodegradabilites of the PPCPs will be very different according to individual PPCPs.

2) The concentration decrease of the 30 PPCPs with time followed 1st order kinetics, irrespective of UV lamps applied. Degradabilities of the 30 PPCPs were, therefore, classified and compared by 1st order rate constants. For UV/Lamp1 that emits at the wavelength of 254nm, 6 PPCPs including ketoprofen and diclofenac and 14 PPCPs including theophylline, cyclophosphamide and DEET were classified as easily-degrading PPCPs ($k \geq$2.6E-03 /sec) and slowly-degrading PPCPs ($k <$6.4E-04 /sec), respectively. On the other hand, 10 PPCPs and 6 PPCPs belonged to easily-degrading PPCPs and slowly-degrading PPCPs, respectively, for UV/Lamp2 that emits at the wavelength of 185nm and 254nm. This result indicates that UV/Lamp2 was more effective for degrading PPCPs than UV/Lamp1. This might be due to the contribution of OH radicals formed during UV photodegradation of H_2O molecular by the wavelength of 185nm to the PPCPs degradations. Consequently, the applicability of UV/Lamp2 for degrading PPCPs in water was implied.

3) UV doses of 38 mJ/cm^2 to 5,644 mJ/cm^2 were needed for 90% degradation of the 30 PPCPs in secondary effluent. These UV doses are much higher than those required for typical disinfection (40 mJ/cm^2 ~ 140 mJ/cm^2). It can be known that considerable UV dose will be required for the effective removal of PPCPs in secondary effluent.

4) When the 30 PPCPs spiked into secondary effluent were treated with UV/Lamp1/H_2O_2, their degradation rates increased by a factor of about 1.3 comparing with those for UV/Lamp1. Especially, H_2O_2 addition improved significantly degradation rates of the PPCPs such as DEET and theophylline, which showed low degradation rates for UV/Lamp1 treatment.

Considering that UV alone treatment is not so effective for the degradation of a lot of PPCPs, the combination of H_2O_2 with UV treatment will be a promising alternative treatment option for PPCPs removal.

5) All the PPCPs except 7 PPCPs including cyclophosphamide and 2-QCA (727 mJ/cm^2 ~ 1,695 mJ/cm^2) were degraded by more than 90% under UV dose of 691 mJ/cm^2 (contact time : 30 min) during UV/lamp1/H_2O_2 treatment. As a consequence, it is considered that UV/H_2O_2 treatment can contribute to the reduction of energy consumption for the effective PPCPs removal as well as the improvement of the degradation rates for the investigated PPCPs.

The objective of Chapter IV was to investigate the degradation characteristic and the removal potential of various PPCPs detected in aquatic environment with O_3, O_3/UV and O_3/H_2O_2 treatments. Additionally, O_3 consumption needed for the effective PPCPs degradation was estimated. The major findings are as follows.

1) The degradabilities (pseudo 1st order rate constants) of individual PPCPs increased with the increased O_3 feed rate (0.15 mg/L/min, 0.3 mg/L/min, 0.6 mg/L/min). However, the degradation efficiency (the ratio of pseudo 1st order rate constant (/sec) to the amount of O_3 consumed per the volume of the reactor (mgO_3/L)) for the 30 PPCPs was the highest for O_3 feed rate of 0.3 mg/L/min (2.2E-03 L/mgO_3·sec). This indicates that the introduction of high O_3 concentration could not contribute to the improvement of the degradabilites per O_3 consumed although it improved the degradation rates of the PPCPs.

2) The degradation rate of each PPCP increased considerably by the combination of UV with O_3 treatment, and the lowest O_3 feed rate of 0.15 mg/L/min showed the most efficiency PPCPs degradation (6.9E-03 L/mgO_3·sec). This means that O_3 dose required for the effective PPCP removal can be reduced for O_3/UV treatment. On the other hand, the degradation rates of 14 PPCPs including mefenamic acid, tetracyclines, carbamazepine and cyclophosphamide did not improve so much during O_3/UV treatment, implying that the PPCPs will react more easily with O_3 than OH radicals.

3) For O_3/H_2O_2 treatment, initial H_2O_2 concentration of 2.3 mg/L and 11.2 mg/L was combined with O_3 treatment (0.6 mg/L/min). As a result, H_2O_2 addition increased the

degradation rates of 26 PPCPs by factors of 1.1 to 6.5 comparing with for O_3 alone treatment. However, lower degradation rates showed when initial H_2O_2 concentration was 11.2 mg/L, maybe due to the scavenging effect of O_3 and OH radicals by excess H_2O_2.

4) Finally, O_3 consumptions required for 90% degradation of each PPCP for O_3 and O_3/UV treatment were calculated. For O_3 treatment, O_3 consumption of 6.3 mg/L was necessary for 90% degradation of all the 30 PPCPs spiked into pure water. While, for O_3/UV treatment, O_3 consumption of 4.5 mg/L could achieve 90% degradation of each PPCP. On the other hand, comparatively high O_3 consumptions of 8.9 mg/L and 7.7 mg/L were required for O_3 and O_3/UV treatments carried out with tested water spiked with the 30 PPCPs, respectively. These O_3 consumptions resulted from semi-batch experiments (initial dissolved ozone concentration in tested water = 0 mg/L), and less O_3 consumption will be, therefore, needed for real O_3 and O_3/UV treatment facilities because real treatment facilities are operated by supplying continuously O_3 gas into O_3 and O_3/UV reactors.

In Chapter V, the removal performance of UV and UV/H_2O_2 processes was investigated using bench scale plant. Moreover, the appropriate amount of H_2O_2 addition during UV process was investigated for the 90% removal of all the PPCPs detected in secondary effluent. Finally, energy consumption and operating costs were estimated for each process considering the effective PPCPs removal. The major findings are as follows.

1) 38 PPCPs were detected in secondary effluent used for tested water in this study. The concentration ranged from 1 μg/L to 481 μg/L. As therapeutic classes, 11 antibiotics including clarithromycin and levefloxacin, 7 analgesics including ketoprofen and diclofenac and 4 antiarrhythmic agents such as disopyramide, atenolol, metoprolol and propranolol were mainly present. Besides, various PPCPs such as anticonvulsants (carbamazepine, primidone), vasodilators (dipyridamole, diltiazem), diuretic (furosemide), antineoplastic agent (cyclophosphamide) and peptic ulcer drug (pirenzepine) were also present in secondary effluent. The side effects of PPCPs on the aquatic environment and human body have not been known yet, however, PPCPs in water environment should be removed in aspect of precautionary principles.

2) Only 17 of 38 PPCPs were removed by more than 90% despite UV dose of 2,768

mJ/cm^2 (contact time : 15 min) during UV process, showing that considerable UV dose will be required for the effective PPCPs removal by UV alone process. This also shows that it will be difficult to accomplish good PPCPs removals by typical UV disinfection process (UV dose : 40 mJ/cm^2 ~ 140 mJ/cm^2, contact time : a few secs).

3) On the other hand, the PPCPs removal by UV alone process improved significantly by the combination of H_2O_2 with UV process. Except naproxen (>89%), 37 PPCPs were removed by more than 90% at the operational condition of UV dose of 923 mJ/cm^2 (contact time : 5 min) and initial H_2O_2 concentration of 6.2 mg/L. As a consequence, the combination of UV and H_2O_2 made it possible to reduce UV dose at least by more than 3 times comparing with for UV alone process.

4) The number of PPCPs removed by more than 90% increased linearly with the increased removal efficiency of SUVA, irrespective of applied processes. On the other hand, the removal efficiency of SUVA was 52% at at the operational condition of UV dose of 923 mJ/cm^2 and initial H_2O_2 concentration of 6.2 mg/L. From these results, it was expected that SUVA removal of more than 50% ensures the effective removal of various PPCPs by UV or UV/H_2O_2 processes.

5) Electrical energy required for the effective PPCPs removal by UV/H_2O_2 process was 0.54 kW per 1 m^3 target water (Operational condition : UV dose : 923 mJ/cm^2, H_2O_2 : 6.2 mg/L), showing that UV/H_2O_2 process can reduce energy consumption and operating cost considerably, comparing with UV alone process, and, therefore, be utilized as a treatment option for water reuse.

In Chapter VI, the removal performance O_3-based processes (O_3 and O_3/UV processes) for the PPCPs detected in secondary effluent was investigated using bench-scale experimental setup with a treatment capacity of 10 m^3/day. Moreover, electrical energy and operating cost required for an effective PPCPs removal by the applied processes were estimated. The major findings are as follows.

1) 37 PPCPs were detected in secondary effluent used as tested water in this study. O_3 dose of 6 mg/L (O_3 consumption : 4.4 mg/L) was required for 90% removal of all the PPCPs except primidone (87%) for O_3 process. However, 24 PPCPs including carbamazepine,

crotamiton and diclofenac were removed by more than 90% even at a low O_3 dose of 2 mg/L (O_3 consumption : 1.6 mg/L), indicating that O_3 process can be used as a technology for the effective removal of various PPCPs in secondary effluent.

2) For O_3/UV process, two types of UV lamps ($UV_{21.5W}$, UV_{65W}) were combined with O_3 doses of 2 mg/L, 4mg/L and 6mg/L, respectively. As a result, all the detected PPCPs were removed by more than 90% when UV_{65W} lamps and O_3 dose of 6 mg/L (O_3 consumption : 5.3 mg/L) were combined (Contact time : 10 min, UV dose : 1,846 mJ/cm^2). On the other hand, all the PPCPs except DEET (89%), primidone (86%), cyclophosphamide (86%) and chloramphenicol (>73%) showed removal efficiencies of more than 90% even when UV_{65W} lamps and O_3 dose of 4 mg/L (O_3 consumption : 3.4 mg/L) were combined, showing that a lot of PPCPs can be removed effectively under this operational condition.

3) For O_3 and O_3/UV_{65W} processes using O_3 dose of over 4 mg/L (O_3 consumption : over 3.4 mg/L), more than 30 PPCPs showed the removal efficiency of more than 90% when SUVA decreased by more than 48%. Similarly to UV-based processes, it was thought that about 50% decrease in SUVA could ensure the effective PPCPs removal.

4) Electrical energy consumed for the effective PPCPs removal was 0.09 kWh/m^3 for O_3 process (O_3 dose : 6 mg/L). Whereas, O_3/UV process (O_3 dose : 4 mg/L, UV dose : 1,846 mJ/cm^2) needed comparatively high electrical energy of 1.09 kWh/m^3. Consequently, it can be known that O_3 process is more cost-effective process than O_3/UV process in the removal performance of PPCPs.

5) For O_3 process, the formation of bromate regulated in drinking water as well as the removal performance of PPCPs should be also taken into consideration. Although O_3/UV process needs high energy consumption, the process has several advantages such as the suppression of bromate formation and the additional disinfection effect by UV. It is, therefore, thought that O_3/UV process cannot be excluded in applying as technology for water reuse.

In Chapter VII, the applicability as a technology for the reclamation of secondary effluent of O_3, UV/H_2O_2 and O_3/UV processes was discussed based on the energy consumption, the formation potential of disinfection by products (DBPs), disinfection effectiveness and decrease effect for ecological risk. The main results obtained in this chapter are as follows;

1) Electrical energies required for the effective removal of PPCPs in secondary effluent were 0.09 kWh/m^3, 0.54 kWh/m^3 and 1.09 kWh/m^3 for O_3 (O_3 dose : 6 mg/L, O_3 consumption : 4.4 mg/L), UV/H_2O_2 (UV dose : 923 mJ/cm^2, H_2O_2 : 6.2 mg/L) and O_3/UV (O_3 dose : 4 mg/L, O_3 consumption : 3.4 mg/L, UV dose : 1,846 mJ/cm^2) processes, respectively, showing that O_3 process is the most cost-effective treatment option for the PPCPs removal. On the other hand, it is considered that PPCPs removal by the investigated processes requires less electrical energy than for other micropollutants such as MTBE, atrazine and 1,4-dioxane.

2) 4 log inactivation of total coliform was expected to be achieved by O_3 process at O_3 dose of 6 mg/L, while more than 5 log inactivation by UV/H_2O_2 (UV dose : 923 mJ/cm^2, H_2O_2 : 6.2 mg/L) and O_3/UV (O_3 dose : 4 mg/L, UV dose : 1,846 mJ/cm^2) processes could be achieved. Therefore, in case that the number of total coliform in secondary effluent is 3,000 /ml, these processes can meet sufficiently the guideline for water reuse of Japan (1,000/100ml). On the other hand, O_3 process (O_3 dose : 6 mg/L) can be used as a treatment method for restricted urban reuse and agricultural reuse (non-food crops) requiring the number of total coliform of less than 23/100ml. However, in order to obtain the reclaimed water for unrestricted urban reuse, agricultural reuse (food crops) and unrestricted/restricted recreational reuse considering the effective PPCPs removal, UV/H_2O_2 and O_3/UV processes should be applied.

3) O_3 process at O_3 dose of 6 mg/L (O_3 consumption : 4.4 mg/L) showed the effective PPCPs removal, however, the formation of bromate is expected for O_3 process using O_3 dose of more than 4 mg/L (O_3 consumption : 3.0 mg/L). In particular, bromate formation will be a critical issue when the reclaimed water is used for direct/indirect potable reuses. Therefore, in order to suppress the bromate formation as well as achieve the effective PPCPs removal, O_3/UV process will be appropriate. For O_3/UV process, residual O_3 will be degraded by UV photodegradation, and, therefore, the formation reaction of bromate (reaction of O_3 with Br^-) will be suppressed. UV/H_2O_2 process will be also a profitable process because no bromate will be formed during the process.

4) The ecological risk evaluation showed that each process could decrease the ecological risk caused by parent PPCPs considerably. This means that the investigated processes can play an important role in reducing unpredictable side effects caused by PPCPs in the aquatic

environment.

8.2 Recommendations for future research

1) This study was performed for the effective removal of PPCPs in secondary effluent of WWTPs, a main PPCPs source into the aquatic environment, by UV-based and O_3-based processes. However, there are almost no studies for the effluent from hospital wastewater treatment plant where higher concentration of PPCPs is likely to be present. In aspect of the control of the point source for PPCPs, it will be also desirable to conduct this kind of investigation.

2) This study focused on the removal of parent PPCPs, however, various by products can be formed during degradation of parent PPCPs by physicochemical processes, especially O_3 treatment, due to its selective reactivity on compounds. Moreover, the evaluation on the decrease effect of ecological risk after physicochemical treatment processes was also conducted only based on the concentration decrease of parent PPCPs. In order to evaluate the applicability of physicochemical processes for the PPCPs removal, it will be necessary to know more about the formation potential of by-products after the treatments and the ecological risk of by-products formed.

ACKNOWLEDGEMENT

First of all, I would like to express my deepest appreciation to Dr. Hiroaki Tanaka, Professor of Department of Urban and Environmental engineering, Kyoto University. I greatly thank him for his enthusiastic instruction and support during the whole study period. His positive and practical ideas encouraged me to think about what I should do.

I would like to express my sincere gratitude to Professor Hiroshi Tsuno and Professor Yoshihisa Shimizu for their valuable comments and review of this dissertation. I wish they would give such good comments for other students, also.

Dr. Naoyuki Yamashita provided me helpful advice and guidance throughout the study period. Dr. Shuhei Tanaka and Dr. Norihide Nakada also gave useful information and comments on the study. I could not forget their friendly helps. I really thank Mr. Yasuhiro Kato of Metawater Co., Ltd and Mr. Takeshi Takubo of Iwasaki Co., Ltd for their valuable cooperation. I was honored to have a chance to perform this study with them who are specialists in the fields of O_3 and UV technologies.

Special thanks go to all staffs and students in Research Center for Environmental Quality Management (RCEQM), Kyoto University. Especially, I must thank to Mr. Yoshikazu Kobayashi and Mr. Takashi Okuda who were members of PPCPs research group for their timely helps. I also appreciate Ms. Yuki Hayabara for giving me advice in languages.

I appreciate great support from all members in Kyoto Rakunan Rotary club. I do not know how to say thanks to Mr. and Mrs. Shibutani, my counselor in the Rotary club. I do never forget their sincere consideration and kindness.

Finally, it seems quite hard to express appreciation and love for my family with words. I promise to live my whole life for them, especially for Kyoung-mi Lim, my sole wife and Ga-eun Kim, my angelic daughter and Gyu-hyun Kim, my naughty son.