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A Dissertation for the Degree of Doctor of Philosophy

**The applicability of advanced oxidation processes
for micropollutant removal
in small-scale sewage treatment facilities
and assessment of greenhouse gas emissions**

소규모 오수처리시설에서 미량오염물질 처리를 위한
고도산화공정 적용 가능성과
온실가스 발생량 평가에 관한 연구

February, 2020

By

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Major in Environmental Health Sciences, Graduate School of Public Health

Seoul National University

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A dissertation submitted in partial fulfillment of
the requirements for the degree of
Doctor of Philosophy in Public Health

Graduate School of Public Health at
Seoul National University

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ABSTRACT

The applicability of advanced oxidation processes for micropollutant removal in small-scale sewage treatment facilities and assessment of greenhouse gas emissions

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In the areas where public sewage treatment systems are not provided, private sewage treatment facilities should be used to purify sewage. However, micropollutants such as pharmaceuticals and to biological degradation. Therefore, it is assumed that the private sewage treatment facilities discharge the micropollutants into its receiving water. The micropollutants introduced into surface water disrupt natural aquatic ecosystems, and even cause health effects to humans. Various advanced treatments are under study to remove non-biodegradable pollutants in water. Among them, advanced oxidation processes (AOPs) are expected to be suitable for application to small-scale sewage treatment facilities operated by part-

time workers. However, AOPs can be strongly affected by radical scavengers in water. The AOPs are also considered as the main source of the greenhouse gas (GHG) emissions in wastewater treatment facilities due to high consumption of chemicals and electric power. Less research, however, has been conducted to monitor the behavior of micropollutants in small-scale sewage treatment facilities and to improve the treatment efficiency in terms of sustainable low-carbon growth.

Therefore, the thesis examined the removal efficiency of micropollutants in small-scale private sewage treatment facilities and improved the treatment efficiency considering low-carbon growth. The study (1) investigated the occurrence and removal of ten micropollutants such as acetaminophen, bisphenol-A (BPA), caffeine, carbamazepine, diclofenac, ibuprofen, metoprolol, naproxen, sulfamethazine, and sulfamethoxazole in small-scale wastewater treatment facilities (WTFs). It also examined the effects of WTF effluent on micropollutants concentration change of the surrounding water. The study (2) conducted the effects of natural water components on degradation kinetics and mechanisms of BPA in AOPs to confirm the applicability of AOPs in the small-scale sewage treatment facilities. The study (3) estimated and compared the amounts of GHG emissions from AOPs ($\text{H}_2\text{O}_2/\text{UV}$, TiO_2/UV , and O_3) during BPA removal to provide the basic data for low-carbon development. The specific study results are as follows.

In the study (1), we investigated the occurrence and removal of the target

micropollutants in the small-scale WTFs used in the rural communities in Korea. In addition, the effect of WTFs on its receiving water was investigated by examination of changes in concentrations of micropollutants at upstream and downstream. Micropollutants were detected ranging from 9 to 13,346 ng/L in WTF and 2 to 164 ng/L in receiving water. The composition profile of micropollutants in WTF influent was not significantly different by provinces, suggesting that the consumption pattern of these micropollutants did not show regional variation in Korea. The removal efficiencies of the selected micropollutants at the WTFs ranged from 12% (carbamazepine) to 88% (acetaminophen), lower than conventional removal by STPs but higher than septic tanks using anaerobic treatment. The concentrations of selected micropollutants upstream of the receiving water were generally lower compared to those observed downstream, indicating that effluent from WTFs was the pollutions source of selected micropollutants. The per capita discharge loads (mg/d/1000 inhabitants) of WTFs and annual emissions rates (kg/year) from private WTFs in Korea were estimated for the selected micropollutants. As the results of this chapter, small-scale private sewage treatment facilities are not able to properly treat micropollutants and are discharging to surface water.

In the study (2), the effects of environmentally relevant concentrations of natural water components (pH, nitrate, carbonate/bicarbonate, and humic acid) on the kinetics and degradation mechanisms of BPA during UV photolysis and H₂O₂/UV process were examined. During UV photolysis, BPA removal efficiency

was increased at higher solution pH but BPA degradation was more efficient in acid medium during H₂O₂/UV process. The presence of NO₃⁻ (0.04 - 0.4 mM) and CO₃²⁻/HCO₃⁻ (0.4 - 4 mM) ions increased BPA degradation during UV photolysis. Humic acid less than 3 mg/L promoted BPA degradation, but greater than 5 mg/L of humic acid inhibited BPA degradation in the UV photolysis. During the H₂O₂/UV reactions, all natural water components (humic acid, CO₃²⁻/HCO₃⁻, and NO₃⁻) reduced degradation kinetics of BPA. In particular, humic acid showed high scavenger effect because it contains a large amount of organic matter. While eight byproducts (m/z = 122, 136, 139, 164, 181, 244, 273, 289) were identified in UV/ NO₃⁻ photolysis, four (m/z = 122, 136, 164, 244) and three byproducts (m/z = 122, 136, 164) were observed during UV/NO₃⁻/CO₃²⁻/HCO₃⁻ photolysis and UV/CO₃²⁻/HCO₃⁻ photolysis, respectively. On the other hand, regardless input ions, four byproducts (m/z = 122, 136, 164, 244) were detected in all H₂O₂/UV reactions. From the results of the identified byproducts, degradation mechanisms were proposed. Our results showed that the NO₃⁻ and CO₃²⁻/HCO₃⁻ changed the degradation mechanism of BPA during UV photolysis but the ions did not affect the formation of byproducts in H₂O₂/UV process.

In the study (3), greenhouse gas (GHG) emissions and degradation rate constants (k_{obs}) during the degradation of bisphenol-A in the H₂O₂/UV, TiO₂/UV, and ozonation processes were estimated to provide the low-carbon growth. Experiments were conducted at laboratory scale. During the H₂O₂/UV process, the fastest

degradation rate constant ($k_{obs} = 0.353 \text{ min}^{-1}$) was observed at 4 mM of H_2O_2 , while the minimum GHG emission was achieved at 3 mM of H_2O_2 . During the TiO_2/UV process, the fastest rate constant ($k_{obs} = 0.126 \text{ min}^{-1}$) was achieved at 2,000 mg/L of TiO_2 , while the minimum GHG emission was observed at 400 mg/L of TiO_2 . During the ozonation process, GHG emissions were minimal at 4 mg/L of O_3 , and it was different from the fastest rate constant. The carbon footprint assessment revealed that for the treatment of 1 m^3 of water contaminated with 0.04 mM BPA, the $\text{H}_2\text{O}_2/\text{UV}$ process had the smallest carbon footprint ($0.565 \text{ kg CO}_2 \text{ eq/m}^3$), followed by the TiO_2/UV process ($3.445 \text{ kg CO}_2 \text{ eq/m}^3$) and the ozonation process ($3.897 \text{ kg CO}_2 \text{ eq/m}^3$). Our results imply that the increase in rate constant might not be the optimal parameter for reducing GHG emissions in AOPs. Moreover, manufacturing and usage stages accounted for the majority of GHG emissions in AOPs (> 95%).

The comprehensive research results of this thesis are as follows. (1) The small-scale private WTFs were not able to completely remove micropollutants in water and discharged this water to the surface water. Therefore, small-scale private WTFs need a supplementary treatment process to improve the treatment efficiency of micropollutants. (2) In the AOP ($\text{H}_2\text{O}_2/\text{UV}$), the degradation kinetics were reduced by natural water components. However, natural water components did not affect byproduct formation. Thus, a sufficient amount of oxidant should be added to apply AOP in small-scale private WTFs. (3) GHG emissions from AOPs can be reduced by adjusting operating conditions. In addition, the use of low-carbon oxidants and

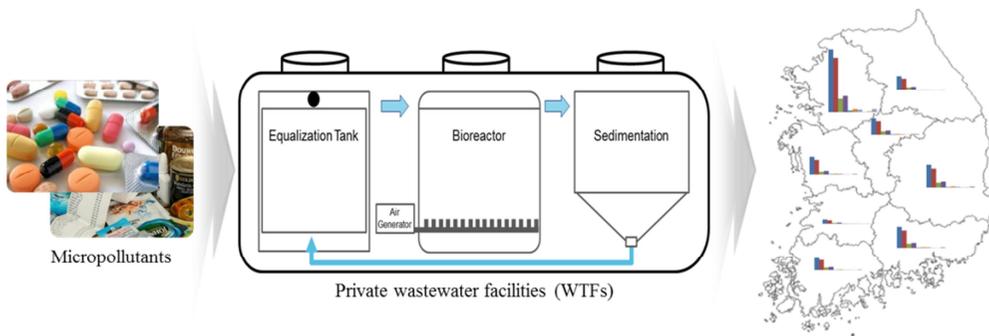
renewable power can reduce large amount of GHG emissions from AOPs. It is expected that healthier ecosystem will be created in nature and population by applying the results of this dissertation.

Keywords: micropollutants, private wastewater treatment facilities, advanced oxidation process, greenhouse gas emissions, carbon footprint, natural water components

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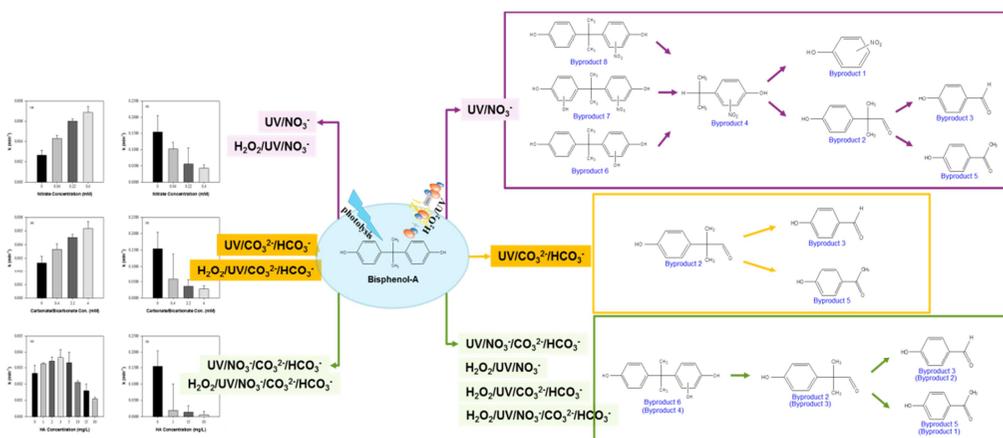
Graphical abstracts and highlights

Chapter 2: The occurrence and fate of micropollutants in small-scale wastewater treatment facilities in rural community and their impact on receiving water



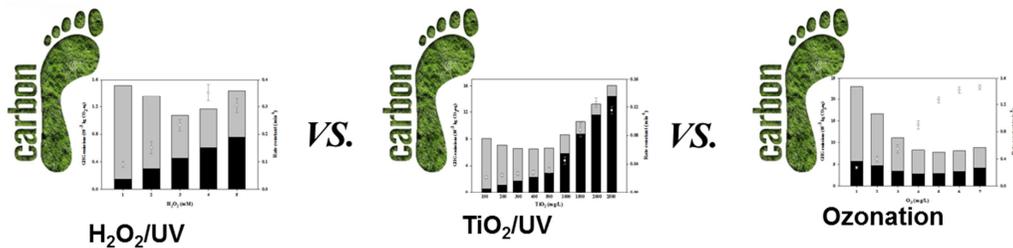
- Occurrence and removal of micropollutants in small-scale WTFs was examined.
- WTFs showed lower removal efficiencies for the target micropollutants than conventional sewage treatment plants.
- WTF effluent was the major source of micropollutants contamination in the surrounding surface water.
- The per capita discharge loads of target micropollutants in WTFs were calculated.
- The total annual emissions (kg/yr) of the target micropollutants from private WTFs in Korea were calculated.

Chapter 3: Effect of natural water components on the kinetics and degradation mechanism of bisphenol-A during UV photolysis and H₂O₂/UV process



- During UV photolysis, BPA removal efficiency was increased at higher solution pH but BPA degradation was more efficient in acid medium in H₂O₂/UV.
- NO₃⁻ and CO₃²⁻/HCO₃⁻ acted only as a promoter for UV photolysis of BPA.
- Humic acid acted as both promoter and scavenger for UV photolysis of BPA.
- NO₃⁻, CO₃²⁻/HCO₃⁻, and humic acid inhibited the BPA degradation during the H₂O₂/UV process.
- NO₃⁻, CO₃²⁻/HCO₃⁻ affected the degradation mechanisms of BPA during UV photolysis, but they had no effect on byproduct formation during H₂O₂/UV process.

Chapter 4: Greenhouse gas emissions during the degradation of bisphenol-A in advanced oxidation processes: A Comparative Study of H_2O_2/UV , TiO_2/UV , and O_3



- GHG emissions were estimated during the removal of bisphenol-A in H_2O_2/UV , TiO_2/UV , and O_3 processes.
- There were three different types of GHG emissions during AOPs.
- The conditions to increase the rate constant (k_{obs}) of BPA may not be optimal in terms of GHG emissions.
- The carbon footprint concept was used to compare GHG emissions of AOPs.
- H_2O_2/UV showed the smallest carbon footprint among the studied AOPs.
- In AOPs, GHG emissions mainly come from the manufacturing and usage stages.

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List of Abbreviations

$\cdot\text{OH}$	hydroxyl
$^1\text{O}_2$	singlet oxygen
ACT	acetaminophen
AOP	advanced oxidation Process
APF	aminophenyl fluorescence
BAU	business as usual
BOD	biological oxygen demand
BPA	bisphenol-A
CB	Chungcheongbuk
CBM	carbamazepine
CFF	caffeine
CH ₄	methane
CN	Chungcheongnam
CO ₂	dioxide
CO ₃ ²⁻	carbonate
CO ₃ ²⁻	carbonate radicals
COD	chemical oxygen demand
COP	conference of the parties
DCF	diclofenac
DOM	dissolved organic matter
E°	redox potential
e ⁻ _{CB}	band electrons

EDC	endocrine disrupting compound
EE/O	electric energy consumption per order
EPA	Environmental Protection Agency
Eq.	equation
GB	Gyeongsangbuk
GG	Gyeonggi
GHG	greenhouse gas
GN	Gyeongsangnam
GW	Gangwon
GWP	global warming potential
h^+_{VB}	band holes
H_2O_2	hydrogen peroxide
HA	humic acid
HCl	hydrochloric acid
HCO_3^-	bicarbonate
HCO_3^\bullet	bicarbonate radicals
HFC	hydrofluorocarbons
HO_2^-	hydroperoxide anion
HO_2^\bullet	hydroperoxyl radicals
HRT	hydraulic retention time
IBU	ibuprofen
INDC	intended nationally detected contribution
IPCC	intergovernmental panel on climate change
JB	Jeollabuk

JN	Jeollanam
KEITI	Korea Environmental Industry and Technology Institute
KMnO ₄	permanganate
KMOE	Ministry of Environment of Korea
k _{obs}	degradation rate constant
K _{ow}	octanol-water partition coefficient
LCA	life cycle assessment
LCI	life cycle inventory
LOD	limit of detection
LOQ	limit of quantification
LULUCF	land use land-use change and forestry
MTP	metoprolol
N ₂ O	nitrous oxide
Na ₂ S ₂ O ₃	Sodium thiosulfate
NaOH	sodium hydroxide
NO ₂	nitrate
NO ₂ [•]	nitrite radical
NO ₃ ⁻	nitrate
NOAEL	no observed adverse effect level
NP	nonylphenol
NPX	naproxen
NSAID	non-steroidal anti-inflammatory drug
O [•]	singlet oxygen
O ₂	oxygen

$O_2^{\cdot-}$	superoxide anions
O_3	ozone
OECD	organization for economic cooperation and development
OWC	organic wastewater contaminant
PFC	perfluorocarbon
pK_a	aci dissociation constant
ppb	part per billion
PPCP	pharmaceuticals and personal care products
ppt	part per trillion
PTFE	polytetrafluoroethylene
r^2	regression coefficient
RfD	reference dose
ROS	reactive oxygen species
RQ	risk quotients
S/N	signal-to-noise
SD	standard deviation
SF_6	sulfur hexafluoride
SMA	sulfamethazine
SMZ	sulfamethoxazole
SS	suspended solid
STE	Septic tank effluent
STP	sewage treatment plants
TiO_2	titanium dioxide
TN	total nitrogen

TP	total phosphorus
UNCED	United Nations Conference on Environment and Development
UNFCCC	Framework Convention on Climate Change
UPLC	ultra performance liquid chromatography
UV	ultraviolet
WTF	wastewater treatment facility
WWTP	wastewater treatment plant
ε	molar absorption coefficient

Chapter 1.

Introduction

1.1. Backgrounds

The human desire to become more prosperous requires tens of millions of chemicals. However, the chemicals are unintentionally released into wastewater treatment systems during the manufacturing, use, and disposal. These micropollutants (chemicals that exist in very small traces in water) are introduced into the wastewater treatment systems through various channels including human excreta, water activities, leakage, and runoff (Stackelberg et al., 2007; Kümmerer 2008). The public wastewater treatment systems handle most of the micropollutants, but in some areas where the public wastewater treatment systems are not provided, the private sewage treatment systems remove the contaminants in water (Figure 1.1).

Pollutants such as suspended solid (SS), biological oxygen demand (BOD), total nitrogen (TN), and total phosphorus (TP) can be easily removed in the private sewage treatment systems. However, some micropollutants such as pharmaceuticals and endocrine disrupting compounds (EDCs) have been known about their persistence for the conventional wastewater treatment systems (Mompelat et al., 2009; Behera et al., 2011; Ratola et al., 2012). Therefore, the untreated micropollutants from the private sewage treatment systems can be discharged into its receiving water. The micropollutants in natural water disrupt the eco-system through acute and chronic exposure. Furthermore, micropollutants dissolved in rivers, lakes, and reservoirs will cause adverse health effects to human through

various exposure paths such as drinking water, aquatic activities, and food intake (Vos et al., 2000; Brophy et al., 2012). Therefore, the occurrence of the micropollutants in surface water made people uneasy. New technologies to purify non-biodegradable micropollutants have also been consistently required.

The public wastewater treatment systems have a small burden on the application of various latest treatment technologies because many users pay for a fee. However, the private sewage treatment systems have a small number of users, which puts an economic burden on the application of the latest technology (Matamoros et al., 2009). Therefore, when applying advanced treatment facilities for the removal of micropollutants in private sewage treatment systems, the applicability should be examined in various aspects as well as treatment efficiency. Among them, advanced oxidation processes (AOPs) provide a viable and effective attenuation option for the removal of non-biodegradable micropollutants in the private wastewater systems because the processes can be operated by a part-time operator.

AOPs destruct contaminants by generation of strong oxidants, which highly reactive molecules such as hydroxyl-radicals, singlet oxygen or bi/carbonate radicals (Andreozzi et al., 1999). However, the large limitation of applying AOPs to the private sewage treatment systems is that the processes are severely affected by scavengers in water. Natural water components such as nitrate (NO_3^-), carbonate/bicarbonate ($\text{CO}_3^{2-}/\text{HCO}_3^-$), and humic acid are ubiquitous in natural water. These compounds can inhibit the degradation of pollutants by reacting with OH

radicals and scattering of light (Fukushima et al., 2000; Grebel et al., 2010; Keen et al., 2012; Hofman-Caris et al., 2015). Therefore, in order to assess the applicability of AOPs for removal of non-biodegradable micropollutant in private sewage treatment systems, the impact of the natural water components on AOPs must be evaluated.

AOPs consume enormous energy and chemicals during purification. This results in large amounts of greenhouse gas (GHG) emissions into the atmosphere. Anthropogenic emissions of GHG have been attracting public attention due to the substantial increase of the concentration of these gases in the atmosphere. An excess amount of GHGs released into the atmosphere cause climate change. Thus, many countries have taken action to reduce the anthropogenic GHG emissions. Wastewater treatment plants (WWTPs) and sewage treatment plants (STPs) are considered as the important sources of GHG emissions (Gu et al., 2016). The amounts of GHG emissions from WWTPs and STPs depend on the operating methods and applied technologies (Giaccherini et al., 2017). Therefore, it is necessary to study GHG emissions according to various wastewater treatment technologies for sustainable development.

In order to address the problems that we face, the limitation of the current state should be clearly understood. Consequently, the monitoring research of micropollutants in private wastewater treatment systems must be accompanied. The next step is to implement an assessment of applicable treatment technologies to

improve the efficiency of private sewage treatment systems. Finally, the applicable treatment technology should be evaluated in terms of GHG emissions for low-carbon sustainable development. These factors not only enable micropollutants to be removed more efficiently from the private sewage treatment systems, but also help policymakers and planner make better decisions.

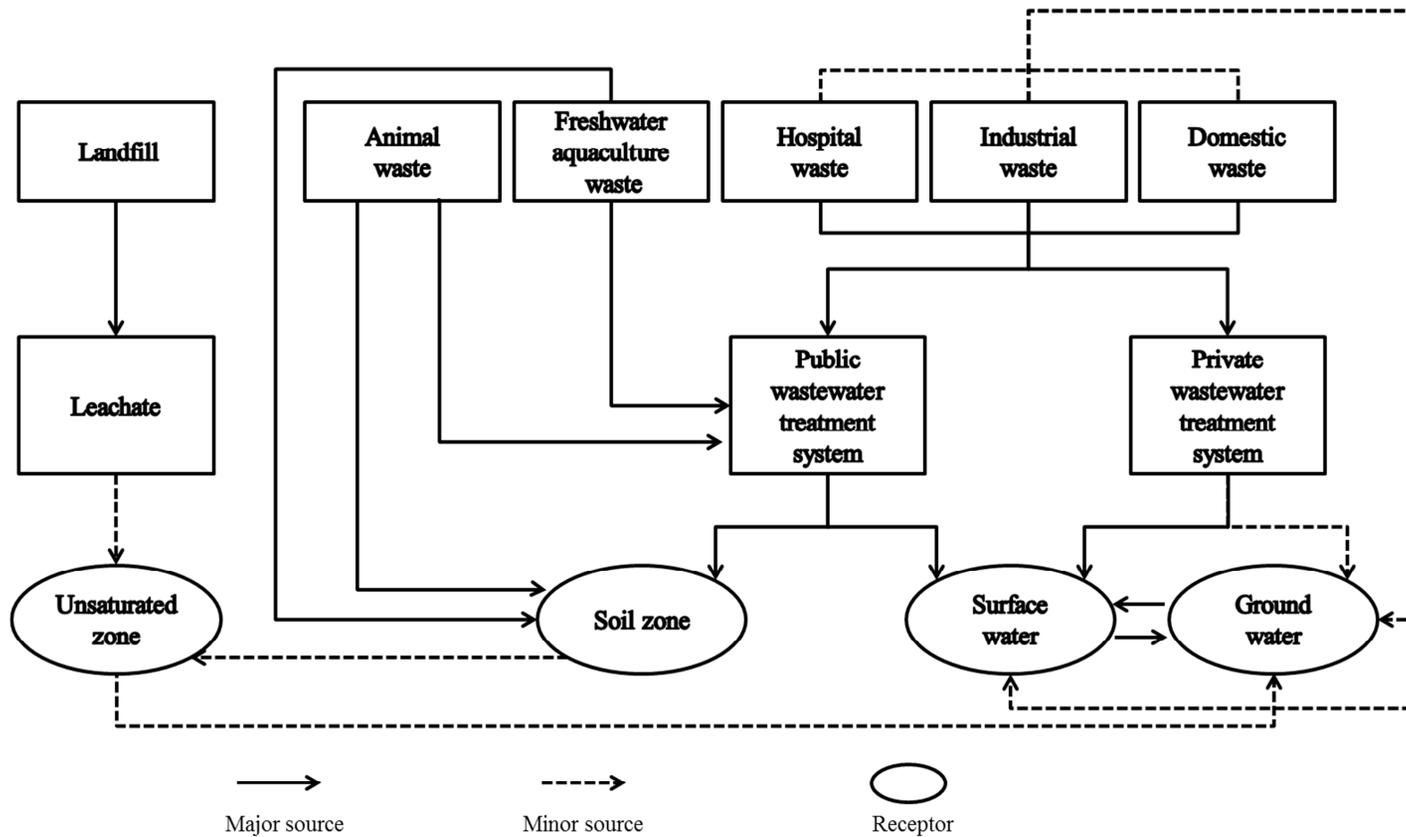


Figure 1.1 Potential sources and pathways of micropollutants in soil and water (Heberer 2002; Díaz-Cruz and Barceló 2008).

1.2. Micropollutants in environment

1.2.1. Micropollutants in water

There are a variety of terms for the chemicals in water such as emerging pollutants, contaminants of emerging concerns, and emerging substances. However, these terms are all related to health risk. The health risks for unknown chemicals are unclear to conclude as hazardous materials because a lot of unidentified chemicals can be present in the group. The definition of the micropollutant, on the other hand, is pollutants present in very small traces in water, and the term can cover the range for pollutants in many ways (EEA 2012). Micropollutants contain various compounds such as pesticides, medicines, flame retardants, perfumes, and insulating foams, etc. (IEF 2009). Among these, pharmaceuticals and EDCs are frequently detected in water.

Pharmaceuticals and EDCs are used in various places to help human life. However, the chemicals in water have received growing attention in recent year as micropollutants due to their possible threats to aquatic ecosystem and human health. As an important group of micropollutants with massive studies in recent years, pharmaceuticals and EDCs have been found to be ubiquitous in the surface water and wastewater throughout the world (Tauxe-Wuersch et al., 2005; Lishman et al., 2006).

Pharmaceuticals are available at hospitals, pharmacies, and convenience stores. Some pharmaceuticals such as acetaminophen, ibuprofen, and naproxen are available without a prescription. However, the chemicals are not completely absorbed in the body, and they will be excreted as excreta (Thomas and Foster 2005; Kosma et al., 2017). The chemicals also can be leaked from the manufacturing, usage, and disposal phase and enter the eco-system (Kim et al., 2016; Kay et al., 2017).

EDCs are used as raw materials for plastic products, flame retardants, personal care products. EDCs are extracted during manufacturing, usage, and disposal processes, and are introduced into the water (Birkett 2003). Also, EDCs that enter the body are excreted and cause water pollution (Staniszewska et al., 2015).

Pharmaceuticals and EDCs that are not fully used and enter the aquatic ecosystems are disrupting the ecosystem in various ways such as reducing productivity and producing resistant bacteria (Goksøyr 2006; Kim and Aga 2007, Cevalco et al., 2008). However, we are already accustomed to the convenience of life brought by these chemicals, so it is not easy for us to reduce the use of the chemicals. As a result, concentrations of micropollutants in wastewater treatment systems continue to increase. Therefore, monitoring research is needed to assess treatment efficiencies of the wastewater treatment systems and to improve the removal efficiencies of the systems.

1.2.2. Selection and properties of the target chemicals

Target micropollutants for monitoring

Ten micropollutants were selected to study the behavior and removal in small-scale sewage treatment systems. Huge amounts of domestic sewage, commercial wastewater, and factory wastewater are entered together into public STPs but all influent of small-scale sewage treatment systems are from domestic sewage. Considering the capacity of treatment volume and the time using small-scale sewage treatment systems, the concentration of micropollutants in small-scale sewage treatment systems can be lower than in public STPs. Therefore, the targeted substances were screened for high annual production in Korea (Table 1.1), and the high concentration in surface water and wastewater from previous studies (Table 1.2).

The selected pharmaceuticals were acetaminophen (ACT), caffeine (CFF), carbamazepine (CBM), diclofenac (DCF), ibuprofen (IBU), naproxen (NPX), metoprolol (MTP), sulfamethoxazole (SMZ), sulfamethazine (SMA). The selected pharmaceuticals have been produced more than 800 kg/yr in Korea, and previous research showed significant concentrations in surface water and wastewater (Table 1.1). In addition, according to European Commission (2003), the pharmaceutical producing annually more than 600 kg can affect environment.

Among the EDCs, bisphenol-A (BPA) was selected as a target micropollutant. Nam et al. (2015) conducted the importance out of 27 EDCs. At the results, nonylphenol (NP) and BPA were chosen based on the annually production (> 1 000 000 kg/yr in the domestic industry) and frequent detection in surface water. However, the use of NP in household cleaners, inks, and paints is prohibited in Korea (KMOE 2007). Therefore, we selected BPA as a target micropollutant in this study. BPA was significantly detected in surface water and wastewater in Korea (Table 1.2).

ACT, DCF, IBU, and NPX can be classified in analgesics/anti-inflammatories. DCF, IBU, and NPX are well-known non-steroidal anti-inflammatory drugs (NSAIDs). DCF, IBU, and NPX are used for analgesic, antipyretic, and anti-inflammatory actions. ACT is used as analgesic but it has weak anti-inflammatory properties. Occasionally, ACT is known as NSAIDs, but it has too weak effect on anti-inflammatory. These compounds work in various ways on peripheral and central nervous systems, and are widely used to relieve pain in almost all diseases (Bueno et al., 2012). These substances are readily available without prescription. Santos et al. (2010) reported that NSAIDs were the most commonly detected in the environment among therapeutics classes.

SMA and SMZ are classified as antibiotics. Antibiotics are constantly introduced into the environment and are often considered 'pseudo-persistent' (Deng et al., 2016). Among them, sulfonamides are widely used because of their broad antimicrobial

activity against both gram-positive and gram-negative bacteria (Morrow and Roberts 2001). SMA and SMZ are used as a preventive and therapeutic agent for bacterial diseases in both livestock and humans (Dantas et al., 2008; Kümmerer 2009). Most of the antibiotics are released into the water through livestock farms, human feces, and flooding. Huang et al. (2011) reported that the SMZ is the most commonly detected in municipal wastewater effluents among sulfonamides, and SMA is the most frequently found in agricultural runoff.

CFF is the most common central nervous system and metabolic stimulant. CFF is used as an ingredient in coffee, tea, chocolate, cocoa, and soft drinks. It is also a component of pharmaceuticals such as analgesics and cold medicines (Gardinali and Zhao 2002). The extensive use of CFF makes hundreds of tons of production produced each year. The high concentration of CFF in water results from extensive use. Also, due to the high solubility of CFF, it may present at a high level in water (Seiler et al., 1999).

CBM is an anticonvulsant medication and commonly used for epilepsy and neuropathic pain. The chemical is frequently detected in the water because it is difficult to remove in the conventional wastewater treatment systems. CBM is also susceptible to be accumulated in single microorganisms such as algae (Nikolaou et al., 2007). Due to the low removal efficiency and frequent detection, CBM has become a representative micropollutant in water.

MTP is classified as a beta-blocker. The chemical is used for hypertension and angina. Monitoring studies of MTP have been rarely carried out, but several previous studies have shown high concentrations in water. Ternes et al. (2001) measured 2,080 ng/L of MTP in German STP effluent. Recently, Schriks et al. (2010) detected MTP concentration < 2,100 ng/L in Netherland drinking water. This result showed that MTP is a non-degradable compound in wastewater treatment systems.

BPA is a plasticizer used in a wide variety of applications such as plastics, rubbers, and resins (Piotrowska et al., 2005). When we only think of the convenience of plastic products, the production of BPA will grow more than ever before. However, BPA unfortunately causes reproductive, breast cancer by either way mimicking a hormone or blocking humoral effects (Murray et al., 2007). BPA is also a representative micropollutant in water due to the low removal efficiency and frequent detection.

Considering the annual production in Korea and previous research of selected micropollutants in surface water and wastewater, they will be sufficiently detectable in small-scale sewage treatment systems. Molecular weights of the target micropollutants varied from 150 to 300. There was no substance similar to molecular weights. Thus, the target micropollutants can be separated from a column and detected relatively easily in chromatographic analysis.

Bisphenol -A for the AOP study

Bisphenol-A (4-(2-(4-hydroxyphenyl)propan-2-yl)-phenol, BPA) is one of the most frequently detected micropollutants in the environment (Muhamad et al., 2016). BPA has become a famous compound in food cans and beverage containers manufacturing in 1950s. Rubin (2011) reported that the annual production of BPA was more than 8 billion pounds. The vast output of BPA comes from a variety of utilization. The chemical can be used as a raw material for polycarbonate plastics and epoxy resins, which are used in food cans, drink packages, bottle tops, and water supply pipes. Recently, it has reported that approximately 95% of BPA was used in the industrial production of polycarbonates and epoxy resins (Careghini et al., 2015). Although BPA is in high demand and very useful for industrial productions, the utilization of the chemical is linked to human and ecological health issues (Erlor and Novak 2010).

The adverse effects of BPA on human health are revealed by the epidemiological and animal studies in laboratory. It is generally believed that BPA acts as agonists or antagonists toward the endocrine system. Therefore, the chemical that enters a body can alter the activity of response elements of genes, block natural hormones from binding to their receptors, or act as a hormone mimic to its receptor (Rogers et al., 2013; Yüksel et al., 2013). The reactions cause metabolic disease, thyroid hormone function, albuminuria, oxidative stress, inflammation, epigenetics and gene expression (Rochester 2013). Moreover, the early exposure of BPA may

bring about the development of chronic diseases such as prostate and breast cancer, Type 2 diabetes, obesity as well as impaired brain development (Anderson et al., 2012).

However, standards or guidelines for the limit of BPA in drinking water sources have not been established. Undoubtedly, the low quality of drinking water affects public health, but little is known about the chronic effects of daily exposure to low level BPA (Sodré et al., 2010). Some agencies only provide the recommended exposure to BPA. The US Environmental Protection Agency (EPA) has established the tolerable daily intake (50 ug/kg (body weight)/day), and the oral reference dose (100 ug/L) as a total allowable concentration of BPA in drinking water (Rubin 2011; Willhite et al., 2008).

The wastewater treatment facilities such as WWTPs and STPs play an important role in removing BPA in water. However, due to the low removal efficiency of BPA, it was detected at 890 ng/L in Saudi Arabia WWTPs (Alidina et al., 2014). Also, 336 ng/L of BPA was reported in Han River in South Korea (Ra et al., 2011). Similarly, BPA concentrations ranged from 8.24 - 263 ng/L were detected in Songhua River in China (Zhang et al., 2014). BPA was also found in surface water and near-bottom water (5.0 - 277.9 ng/L) in the coastal zone of the Gulf of Gdansk (Staniszewska et al., 2015).

Because of the huge amount of annual production, low removal efficiency, and health effects, the presence of BPA in aquatic environment has been a major concern

over the last decade. Therefore, studies to remove BPA in wastewater should be prioritized over any other micropollutants.

BPA is known as a moderately removal (40-70%) pollutant in WWTPs (Luo et al., 2014). Thus, the BPA study in AOPs can represent degradation kinetic at which substances such as nonylphenol, sulfamethoxazole, durion, and bezafibrate with similar removal efficiency as BPA can be seen in AOPs. Moreover, in terms of organic structure, BPA is constituted of phenolic group with hydroxyl group joined in aromatic rings. Thus, BPA is also representative of toxic pollutants with phenyl structures because it consists of two phenyl groups. In addition, if properly decomposed, it can be completely mineralized to CO₂ and H₂O. For the reason, it also has many advantages as a target chemical for assessing GHG emissions at STPs since direct GHG emissions of BPA can be excluded from aerobic STPs. However, aerobic conditions must be ensured to exclude CH₄ emissions. Nevertheless, BPA has limitations that cannot be represented for substances containing nitrogen.

Table 1.1 Annual productions and occurrences in water of target micropollutants in Korea.

Compounds	Annual production (kg/yr) ^a	Commercial use
Acetaminophen (ACT)	765,730	Analgesic, antipyretic
Bisphenol-A (BPA)	148,000 ^b	Plasticizer
Caffeine (CFE)	1,823,657 ^c	Stimulant
Carbamazepine (CBM)	8,897	Anticonvulsant medication
Diclofenac (DCF)	7,092	Non-steroidal anti-inflammatory drugs
Ibuprofen (IBU)	145,849	Non-steroidal anti-inflammatory drugs
Naproxen (NPX)	69,274	Non-steroidal anti-inflammatory drugs
Metoprolol (MTP)	801	Beta-blocker
Sulfamethazine (SMA)	14,797 ^d	Antibiotics
Sulfamethoxazole (SMZ)	12,296	Antibiotics

a: KMOE 2011; b KMOE 2007; c: KFDA 2007; d: KFDA 2006

Table 1.2 Occurrence of the target micropollutants in the aquatic environment.

Compounds	Water sample	Country	Concentration (ng/L)	References
Acetaminophen				
	Surface water	Korea	5 - 127	Choi et al., 2008
	Surface water	Serbia	78,170	Grujić et al., 2009
	Ground water	USA	380	Barnes et al., 2008
	STP influent	Spain	24,600 - 29,000	Gómez et al., 2007
	STP effluent	Spain	32 -4,300	Gómez et al., 2007
	Hospital effluent	Taiwan	62,250	Lin and Tsai 2009
Bisphenol-A				
	Surface water	Korea	4.5 - 61	Yoon et al., 2010
	Surface water	USA	6,000	Benotti et al., 2008
	Surface water	Europe	10	Klečka et al., 2009
	Surface water	Germany	28 - 68	Loos et al., 2010b
	Surface water	China	1,194 - 1,574	Zhou et al., 2009
	Surface water	Canada	6,100	Kleywegt et al., 2011
	Surface water	Japan	500 - 900	Kang and Kondo 2006
	Surface water	Greece	55 - 162	Stasinakis et al., 2012
	Ground water	Europe	79 - 2,299	Loos et al., 2010a
	STP influent	UK	1,105	Hernando et al., 2004
	STP effluent	UK	19.2	Hernando et al., 2004

Table 1.2 Continued.

Compounds	Water sample	Country	Concentration (ng/L)	References
Caffeine				
	Surface water	Korea	78,170	Choi et al., 2008
	Surface water	Germany	65 - 67,98	Loos et al., 2010b
	Surface water	Denmark	65 - 382	Matamoros et al., 2012
	Surface water	China	339	Yang et al., 2013
	Ground water	Spain	4 - 50	Teijon et al., 2010
	Ground water	Europe	189	Loos et al., 2010b
	Ground water	USA	290	Fram and Belitz 2011
	STP influent	India	16 - 60,500	Subedi et al., 2015
	STP effluent	India	0 - 51,700	Subedi et al., 2015
Carbamazepine				
	Surface water	Korea	4 - 595	Kim et al., 2009
	Surface water	USA	6.8	Benotti et al., 2008
	Ground water	Europe	12 -390	Loos et al., 2010a
	Ground water	France	10.4	Vulliet and Cren-Olivé 2011
	Ground water	Germany	< 50	Müller et al., 2012
	Hospital effluent	Spain	30 - 70	Gómez et al., 2006
	STP influent	India	22 - 726	Subedi et al., 2015
	STP effluent	India	88 - 900	Subedi et al., 2015

Table 1.2 Continued.

Compounds	Water sample	Country	Concentration (ng/L)	References
Diclofenac				
	Surface water	Korea	8.8 - 127	Kim et al., 2007
	Surface water	France	< 35	Vulliet et al., 2011
	Surface water	Greece	0.8 - 1,043	Stasinakis et al., 2012
	Surface water	UK	0.5 - 261	Kasprzyk-Hordern et al., 2009
	Surface water	Costa Rica	14 - 266	Spongberg et al., 2011
	Ground water	France	9.7	Vulliet and Cren-Olivé 2011
	Ground water	Germany	3,050	Müller et al., 2012
	Ground water	Europe	0 -24	Loos et al., 2010a
	STP influent	Australia	< 2,000	Ying et al., 2009
	STP effluent	Australia	< 100	Ying et al., 2009
Ibuprofen				
	Surface water	Korea	11 - 37	Kim et al., 2007
	Surface water	UK	114 - 2,370	Roberts and Thomas 2006
	Surface water	Canada	0.98 - 79	Kleywegt et al., 2011
	Surface water	China	< 1 417	Peng et al., 2008
	Ground water	USA	3 110	Barnes et al., 2008
	STP influent	India	686 - 4,460	Subedi et al., 2015
	STP effluent	India	< 1,890	Subedi et al., 2015

Table 1.2 Continued.

Compounds	Water sample	Country	Concentration (ng/L)	References
Naproxen				
	Surface water	Korea	20 - 483	Kim et al., 2007
	Surface water	Canada	1 - 87	Kleywegt et al., 2011
	Surface water	China	< 328	Peng et al., 2008
	Surface water	France	< 6.4	Vulliet et al., 2011
	Surface water	Germany	70	Hernando et al., 2006
	Ground water	Spain	145 - 263	Teijon et al., 2010
	Ground water	France	1.2	Vulliet and Cren-Olivé 2011
	STP influent	Sweden	250	Bendz et al., 2005
	STP effluent	Sweden	3,650	Bendz et al., 2005
Metoprolol				
	Surface water	Spain	90	Huerta-Fontela et al., 2010
	Surface water	France	0.5 - 2	Vulliet et al., 2011
	Surface water	China	24.8	Yu et al., 2011
	Surface water	Sweden	47	Daneshvar et al., 2010
	Surface water	UK	7 - 10	Kasprzyk-Hordern et al., 2009
	Surface water	USA	12	Batt et al., 2008
	STP influent	China	121	Yu et al., 2011
	STP effluent	Sweden	274	Daneshvar et al., 2010

Table 1.2 Continued.

Compounds	Water sample	Country	Concentration (ng/L)	References
Sulfamethazine				
	Surface water	Korea	310 - 9,120	Ok et al., 2011
	Surface water	China	100	Wei et al., 2011
	Surface water	China	5.25	Li et al., 2012
	Ground water	USA	360	Barnes et al., 2008
	STP influent	Korea	132	Behera et al., 2011
	STP effluent	Korea	114	Behera et al., 2011
Sulfamethoxazole				
	Surface water	Korea	5 - 82	Choi et al., 2008
	Surface water	Italy	402	Perret et al., 2006
	Surface water	Canada	0.2 - 284	Kleywegt et al., 2011
	Surface water	Costa Rica	11 - 56	Spongberg et al., 2011
	Surface water	Taiwan	0.3 - 0.6	Lin et al., 2011
	Surface water	USA	< 38	Wang et al., 2011a
	Ground water	Europe	2 - 38	Loos et al., 2010a
	Ground water	France	3	Vulliet and Cren-Olivé 2011
	Hospital effluent	Taiwan	1,335	Lin and Tsai 2009
	STP influent	India	195 - 2,260	Subedi et al., 2015
	STP effluent	India	< 318	Subedi et al., 2015

1.2.3. Wastewater treatment systems for micropollutants removal

Fate of the target micropollutant in wastewater treatment systems

The water pollution sources are divided into a point source and a non-point source. Point pollution source is a single identifiable source (Lapworth et al., 2012). Industrial wastewater, hospital wastewater, and domestic wastewater are point sources. On the other hand, it is difficult to identify the non-point pollution source as they occur in the over board geographical scales (Daughton and Ternes 1999; Lapworth et al., 2012). It includes agricultural runoff and leakage. Figure 1.1 shows the pathways how pollutants discharged from the sources to nature. Through these various paths, micropollutants are present in the wastewater treatment systems and surface water (Table 1.2).

Wastewater treatment systems are recognized as the well-known point source of the micropollutants (Ternes 1998; Glassmeyer et al., 2005). Incomplete removal of micropollutants in the facilities is the main reason for the contaminants in natural aquatic environment. Some micropollutants are destructed easily, but most of the contaminants are persistent to decomposition. The behaviors of the micropollutants in wastewater treatment systems depend on the properties of the chemicals.

Table 1.3 shows the physical and chemical properties of the selected compounds. ACT, CFF, MTP, SMZ, and SMA are low in hydrophobicity ($\text{Log } K_{ow} < 2$), which dissolve in water at high concentrations. Therefore, hydrophilic pollutants such as

ACT, CFF, MTP, SMZ, and SMA are not mainly removed by absorbing on activated sludge (Dolar et al., 2012; Nguyen et al., 2013). They are mostly removed by microbial decomposition (Delgado et al., 2019; Lee et al., 2019; Gojkovic et al., 2019).

Conversely, hydrophobic compounds such as DCF, IBU, and BPA are relatively more adsorbed and removed from dissolved organic matter (DOM), particle, and sediment (Rogers 1996). DCF, IBU, NPX, SMA, and SMZ, which pK_a were lower than 7, maintain to negative charge state at a neutral. The ionized chemicals in water are more susceptible to direct photolysis than protonated form due to the influence of the substituent with unshared electrons (Lu et al., 2013). Other chemicals, on the other hand, need to change water pH in order to increase direct photodegradation efficiency.

Private sewage treatment systems in Korea

In populated areas, public wastewater treatment systems are provided. However, most rural areas are not connected to the systems. It is not affordable to install and operate the centralized public sewerage systems in sparsely populated areas. Therefore, private sewage treatment systems solutions are commonly preferred. Private sewage treatment systems are decentralized facilities installed in where public sewerage systems are unavailable. Private sewage treatment systems are usually installed in rural area of dormitories, apartments, and offices. There are

several types of technologies for private sewage treatment systems such as a private wastewater treatment facility (WTF) and a septic tank.

A private septic tank is installed where generates wastewater of up to two cubic meters per day, and a private WTF is installed where generates wastewater exceeding two cubic meters per day (Sewerage Act 2017). According to KMOE (2015), there were 381,932 of private WTFs and 535,337 of septic tanks in Korea.. Considering the discharge volume of private WTFs, the facilities will have more significant impact on surface water than septic tanks.

Private WTFs are considered to have a significant impact on small surface water because most water sources in that area originate from the effluent of the facilities (Li 2014). Therefore, micropollutants that have not been removed from private WTFs will have a significant negative effect on its receiving water. Recently, however, micropollutants have been detected in private WTFs and are attracting public attention. Godfrey et al. (2007) reported that 22 pharmaceuticals are detected in private sewage treatment systems. Other studies also found that the private WTFs in U.S. contain micropollutants such as ibuprofen, paracetamol, salicylic acid, and triclosan (Carrara et al., 2008; Conn et al., 2010).

In Korea, most of the monitoring research so far has been conducted on public wastewater treatment systems. Studies on the monitoring of micropollutants in private WTFs are mostly overseas cases. Lifestyle and eating habits of Koreans are different from those of other countries. In addition, the efficiency of private WTFs

can be different due to the difference of climate, operation methods. Therefore, the monitoring research on private WTFs in Korea is necessary. Moreover, Schaidler et al. (2017) demonstrated that the monitoring study of alternate onsite wastewater treatment systems such as private WTFs needs more information in a recent review.

Table 1.3 Chemical properties of the target micropollutants.

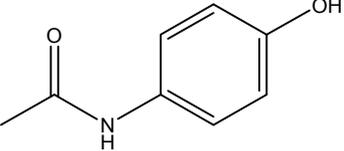
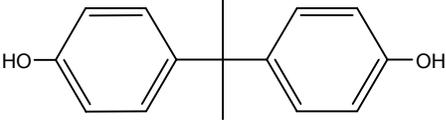
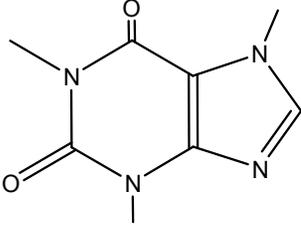
Target compound (chemical formula)	CAS-No.	M.W.	Water solubility (mg/L) ^a	pK _a	Log L _{ow}	Chemical structure
Acetaminophen (C ₈ H ₉ NO ₂)	103-90-2	151.06	14,000	9.38	0.46 ^b	
Bisphenol-A (C ₁₅ H ₁₆ O ₂)	80-05-7	228.12	300	10.2	3.4 ^c	
affeine (C ₈ H ₁₀ N ₄ O ₂)	58-08-2	194.08	21,600	14	-0.5 ^d	

Table 1.3 Continued.

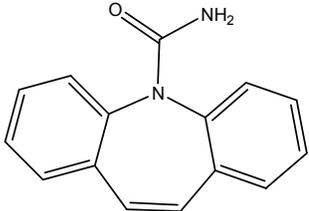
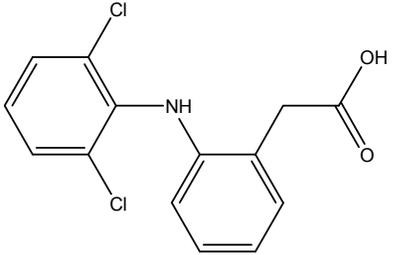
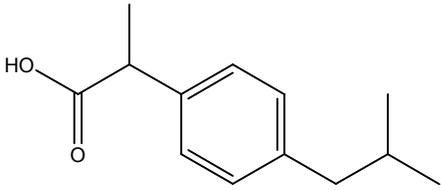
Target compound (chemical formula)	CAS-No.	M.W.	Water solubility (mg/L) ^a	pK _a	Log L _{ow}	Chemical structure
Carbamazepine (C ₁₅ H ₁₂ N ₂ O)	298-46-4	236.09	17.7	7	2.47 ^c	
Diclofenac (C ₁₄ H ₁₁ Cl ₂ NO ₂)	15307-79-6	295.02	2.37	4.15	3.91 ^d	
Ibuprofen (C ₁₃ H ₁₈ O ₂)	15687-27-1	206.13	21	4.51	3.64 ^d	

Table 1.3 Continued.

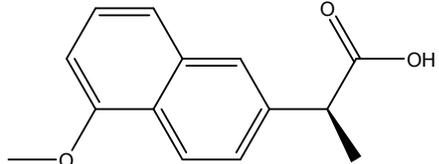
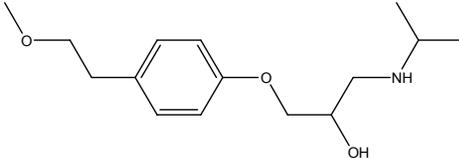
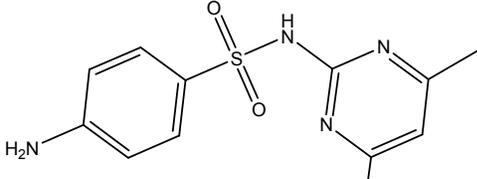
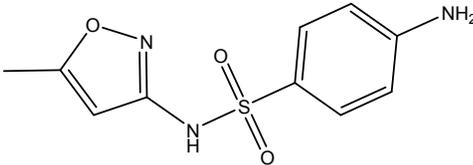
Target compound (chemical formula)	CAS-No.	M.W.	Water solubility (mg/L) ^a	pK _a	Log L _{ow}	Chemical structure
Naproxen (C ₁₄ H ₁₄ O ₃)	22204-53-1	230.09	15.9	4.2	2.84 ^d	
Metoprolol (C ₁₅ H ₂₅ NO ₃)	56392-17-7	267.18	1,000	9.68	1.88 ^e	
Sulfamethazine (C ₁₂ H ₁₄ N ₄ O ₂ S)	57-68-1	278.08	1,500	2.6/7.7 (pK _{a1} /pK _{a2})	0.62 ^f	

Table 1.3 Continued.

Target compound (chemical formula)	CAS-No.	M.W.	Water solubility (mg/L) ^a	pK _a	Log L _{ow}	Chemical structure
Sulfamethoxazole (C ₁₀ H ₁₁ N ₃ O ₃ S)	723-46-6	253.05	610	5.7	0.68 ^d	

a: HSDB 2011; b: Stackelberg et al., 2007; c: Staples et al., 1998; d: Bones et al., 2006; e: Gros et al., 2006; f: Henry et al., 1976.

1.3. Advanced oxidation processes

1.3.1. AOPs for contaminant removal in water

Advantages of AOPs in non-biodegradable micropollutants removal

In recent years, micropollutants level that can affect human health are continuously detected in the aquatic environment (Huerta-Fontela et al., 2010). STPs, WWTPs, and overflow are considered to be the major source of micropollutants in surface water (Lim 2008; Gros et al., 2010). Micropollutants are continuously discharged into surface waters, since conventional physical and biological wastewater treatments can only partially remove these substances (Zhang et al., 2008; Luo et al., 2014).

Over the past decade, many studies have devoted much effort to mineralize recalcitrant micropollutants such as pharmaceuticals and EDCs. There are various technologies such as membrane separation, disinfection, and AOPs. They can destroy the resistant contaminants in water. The technologies aim at the destruction of contaminants or, at least, at their transformation into harmless products.

Among them, a number of studies have been conducted on AOPs due to their many advantages. If adequately developed, AOPs have advantages to abate pollutions in points of those producing fewer by-products than disinfection, and requiring no final disposal which mandatory in filtration. Bolton et al. (1996)

defined that AOPs are based on the in situ generation of strong oxidants for the oxidation of organic compounds. This includes processes based on OH radicals ($\cdot\text{OH}$), which constitute the majority of available AOPs, and other oxidizing species such as sulfate or chlorine radicals.

All AOPs consist of two steps, the in situ formation of reactive oxidative species and the reaction of oxidants with target contaminants. Mechanisms of radical formation depend on system design, water quality, and water matrix (Villegas-Guzman et al., 2017; Acero et al., 2018). Besides radical scavengers such as nitrate, carbonate and bicarbonate play an important role for contaminant destruction (Chuang et al., 2017; Kralj et al., 2018).

AOPs are very different degrees of implementation ranging from research to practical application. The overview and classification of different AOPs are given in Figure 1.2 (Miklos et al., 2018). UV-based AOP, ozone-based AOP, and catalytic AOP have already established at field-scale of water treatment plants. On the other hand, electrochemical AOP and physical AOP are investigated at lab-scale. It is noteworthy, however, that this classification scheme should not be viewed as rigorous. Different processes can be assigned to different categories, including different technologies.

Applicability of AOP in private sewage treatment systems

There are few cases where AOPs have been applied in wastewater treatment facilities compared to the chlorination and the membrane processes. This is because AOPs are greatly affected by radical scavengers in water (Miklos et al., 2018). However, if used appropriately, AOPs have many advantages over other facilities. Chlorination should continuously adjust the injection concentration according to the influent water quality in order to comply with the residual chlorine concentration of the effluent (Zeng et al., 2012; Li et al., 2015). Membrane separation processes also require continuous management such as fouling prevention and backflushing (Srijaroonrat et al., 1999). Therefore, in chlorination and membrane processes, full-time operators have to manage the facilities. Public STPs and WWTPs have a large number of users (> 10,000 people), and the capacity of the facilities are large, so full-time operators can be hired to manage chlorination and membrane processes at all times.

However, the economic burden is enormous for hiring regular operators in private sewage treatment systems which are used by 50-100 people. In private sewage treatment systems, economic considerations have to be taken into account. High quality discharge standards without economic considerations may have negative consequences such as unauthorized discharge or abandonment of facility operations. There are 917,269 private sewage treatment systems in Korea (KMOE 2015). It is virtually impossible to manage them through crackdowns. Therefore, private sewage treatment systems have to rely in part on the conscience and honesty

of the users. For these reasons, in order to remove non-biodegradable micropollutants by applying additional treatment processes in private sewage treatment systems, the technology must be affordable.

Recently, AOPs have been increasing attention, as shown by a large number of fundamental and applied research works (Parsons 2004; Oturan and Aaron 2014). Indeed, the process is considered as a promising, efficient and environmental-friendly technology to remove persistent micropollutants in waters. However, there is a limit using AOPs alone to remove contaminants in wastewater treatment systems. When used in conjunction with biological and physical processes, AOPs have many advantages in removing non-biodegradable micropollutants (Kruithof et al., 2007; Audenaert et al., 2011).

AOPs are based on the in situ generation of powerful oxidizing agents, such as hydroxyl radicals ($\bullet\text{OH}$). The oxidant agents generated during reactions have highly active with a redox potential ($E^\circ = 0.5 - 2.9 \text{ V}$) and short half-life ($t_{1/2} = 10^{-3} \mu\text{s}$) (Olmez-Hanci and Arslan-Alaton 2013; Armstrong et al., 2015). Since radicals have a short half-life unlike chlorine disinfection, it is not necessary to consider the negative effects of radicals on the ecosystem of receiving water. In addition, the AOPs can be operated automatically as set conditions, so they do not require periodic facility management like membrane.

Based on the results of the review so far, AOPs can be a good complement to improve the treatment efficiency. Nevertheless, AOPs have not yet been applied in

private sewage treatment systems (Miklos et al., 2018). Although AOPs are less efficient than chlorination and membrane separations in public STP and WWTPs, the processes have many advantages in private sewage treatment systems. However, the treatment efficiency of AOP is greatly affected by the scavenging capacity of secondary treated wastewater effluents (Bennedsen et al., 2012). Natural water components such as nitrate, carbonate/bicarbonate, and humic acid react with the radicals and slow down the decomposition rate of pollutants. Therefore, it is necessary to study the effect of natural water compounds at environmentally relevant concentrations on AOPs as a basic study of the applicability of AOPs in private sewage treatment systems.

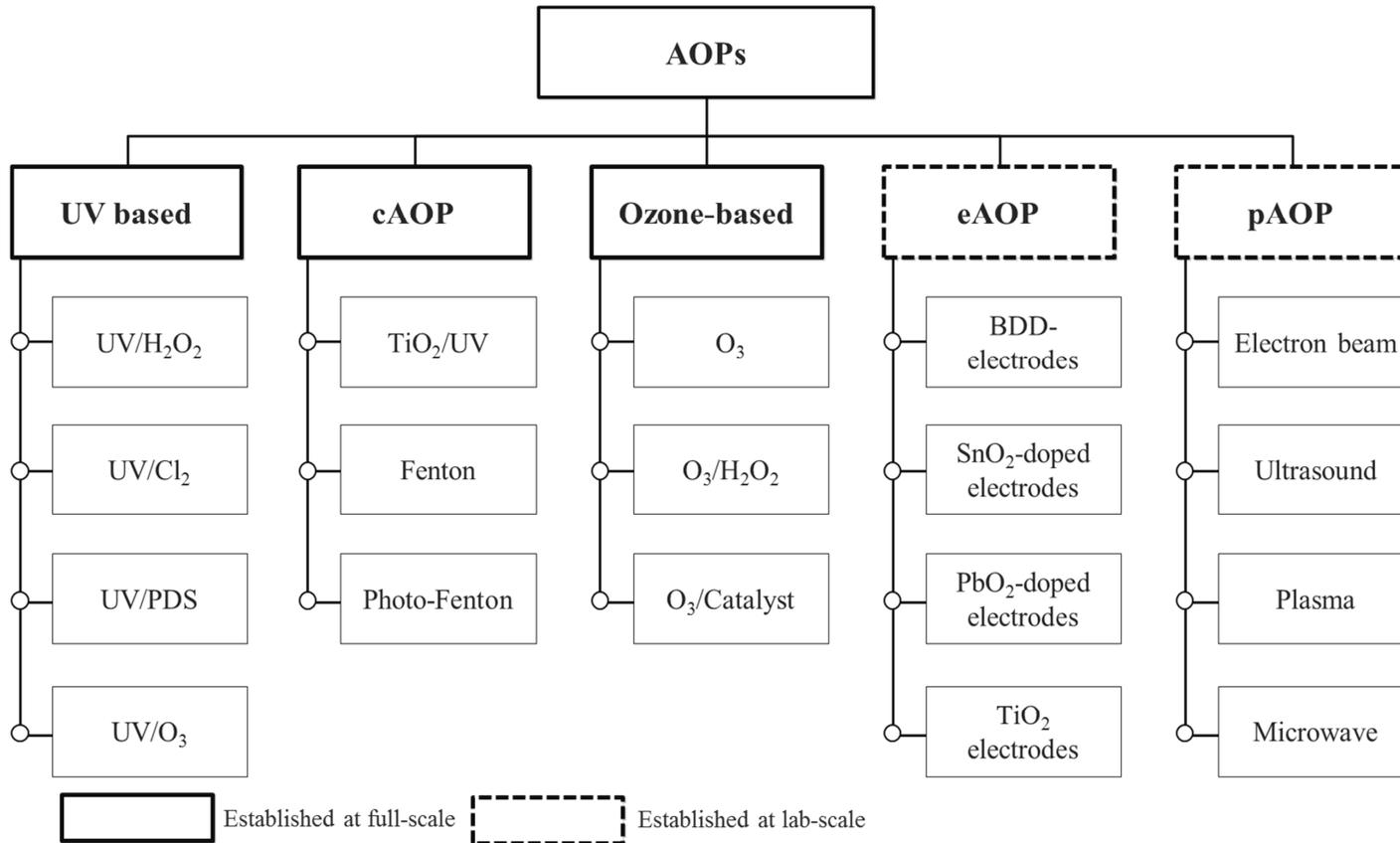


Figure 1.2 An overview and classification of different AOPs (Miklos et al., 2018).

1.3.2. H₂O₂/UV process

H₂O₂ (Hydrogen peroxide) is a well-known oxidant in AOPs, which produces OH radical on UV irradiation (Keen et al., 2016; Somathilake et al., 2019). The oxidant produces highly active with a redox potential ($E^\circ = 1.8 - 2.7$ V) and half-life ($t_{1/2} = 10^{-3}$ μ s) (Olmez-Hanci and Arslan-Alaton 2013). The combination of UV irradiation and H₂O₂ creates the photolytic cleavage of H₂O₂ into two OH radicals. Eqs. (1.1) – (1.7) show several successive and competitive reaction steps. Eq. (1.1) corresponds to the initiation step, Eqs. (1.2) – (1.4) to the propagation steps, and Eqs. (1.5) – (1.7) to the termination steps.



The molar absorption coefficient of H₂O₂ is relatively low ($\epsilon = 18.6 \text{ M}^{-1} \text{ cm}^{-1}$) at 254 nm. This property makes only 10 % of H₂O₂ convert to OH radicals. Therefore, high concentrations of H₂O₂ are required to generate sufficient OH radicals. However, excessive amounts of H₂O₂ can slow the reaction rate.

Figure 1.3 shows a general degradation pathway of contaminants under OH radical attack. Decomposition by OH radicals, known as electrophilic in nature, is considered to follow hydroxylation path predominantly. As depicted in Figure 1.3, the OH radicals are added to the aromatic ring of the target pollutants. The addition of OH radicals to substrate and the reaction of radical cation with water further generate hydroxylated derivatives of the target organic compounds (Hildenbrand et al., 1989).

The progressive attack of reactive radicals leads to the ring opening of the aromatic target compound through cleavage of C-C bond, and various elimination and oxidation reactions (Subagio et al., 2010; Zhang et al., 2014b). The ring opened structure, on further degradation, leads to the formation of acids such as formic and oxalic acids. The mineralization of acidic compounds ultimately leads to the formation of H₂O and CO₂ (although under ideal conditions).

The H₂O₂/UV has already been applied for the first time in potable water reuse and surface water treatment applications (Kruithof et al., 2007; Audenaert et al., 2011). However, low UV-transmittance and high scavenging capacity of secondary or tertiary treated wastewater effluents is still a challenge.

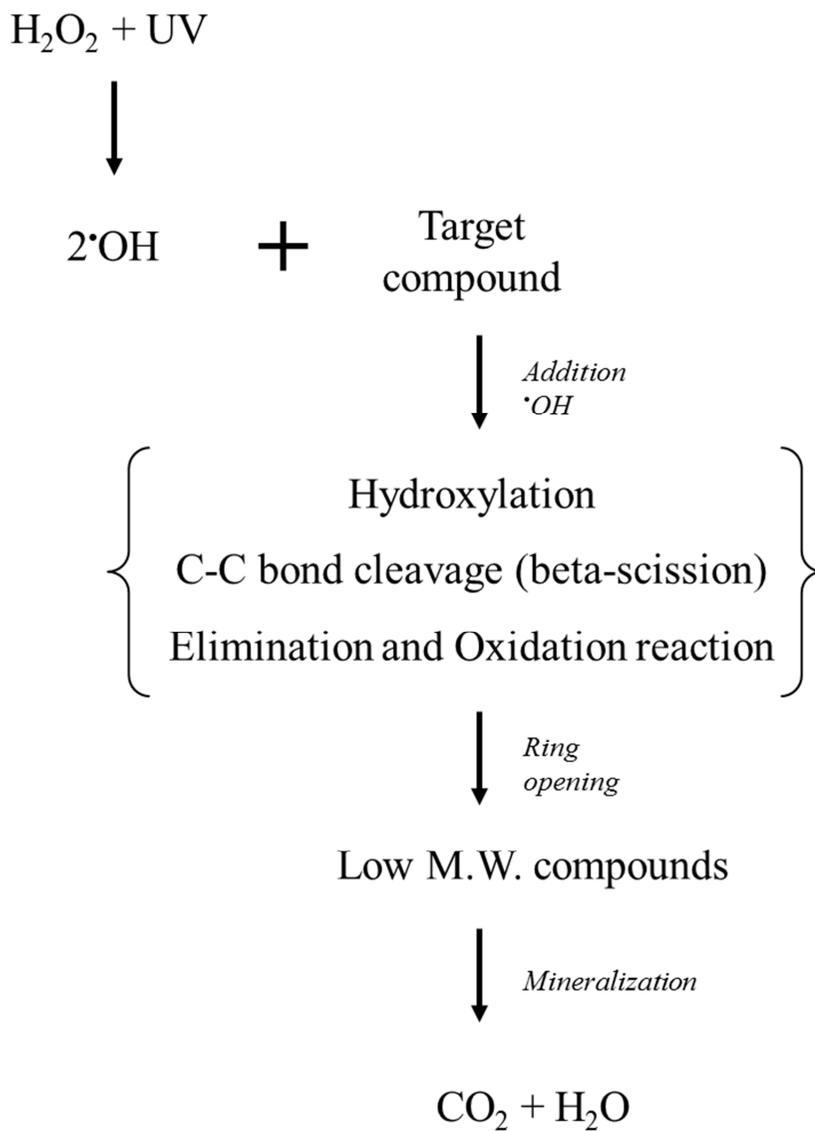
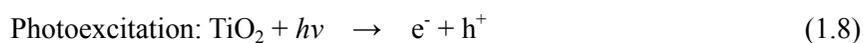


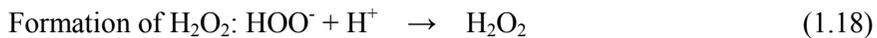
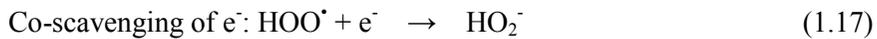
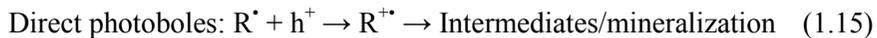
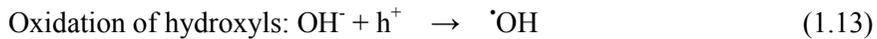
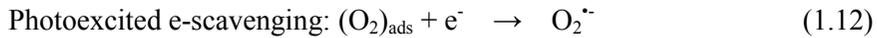
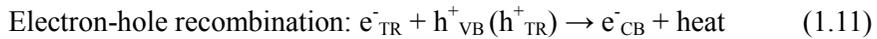
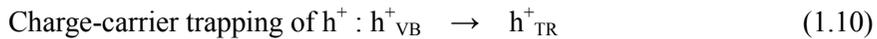
Figure 1.3 General mechanistic approach of OH radical toward a contaminant.

1.3.3. TiO₂/UV process

Titanium is the ninth most abundant element, and the fourth most abundant metal (Parr et al., 1985; Li and Shih 2006). TiO₂ material has been intensively reported in many literatures. The material are generally considered to be the most practical semiconductor photocatalysis for water treatment applications, since it is considered non-toxic, inexpensive, and chemically stable in aqueous solubility (Hoffmann et al., 1995; Fujishima et al., 2000; Gaya and Abdullah 2008). UV light with energy exceeding the semiconductor band gap energy of TiO₂ excites electrons from the filled valence band to an empty conduction band. This leads to charge separation and formation of strongly oxidizing valence band holes (h^+_{VB}) and strongly reducing conduction band electrons (e^-_{CB}).

Figure 1.4 illustrates the mechanism of the electron-hole pair formation under UV-irradiation of TiO₂ particle. The light wavelength for such photon energy usually corresponds to $\lambda < 385$ nm. The photonic excitation creates the electron hole pair ($e^- - h^+$). The sequence of chain oxidative reductive reactions is shown in Eqs. (1.8) – (1.18) (Chong et al., 2010). The series occur at the photon activated surface.





At the photocatalysis process, micropollutants in water will be eliminated to its corresponding intermediates and further mineralized to CO₂ and H₂O (although under ideal conditions). The overall photocatalysis reaction can be divided into five independent steps (Herrmann 1999).

- (1) Mass transfer of micropollutants in the liquid phase to the TiO₂ surface.
- (2) Adsorption of the micropollutants onto the photon activated TiO₂ surface.
(i.e. surface activation by photon energy occurs simultaneously in this step).
- (3) Photocatalysis reaction for the adsorbed phase on the TiO₂ surface.

(4) Desorption of intermediates from the TiO_2 surface.

(5) Mass transfer of intermediates from the interface region to the bulk fluid.

When the mass transfer steps (1 and 5) are very fast compared with the reaction steps (2, 3, and 4), the organic concentrations in the immediate vicinity of the active sites are indistinguishable from those in the bulk liquid phase.

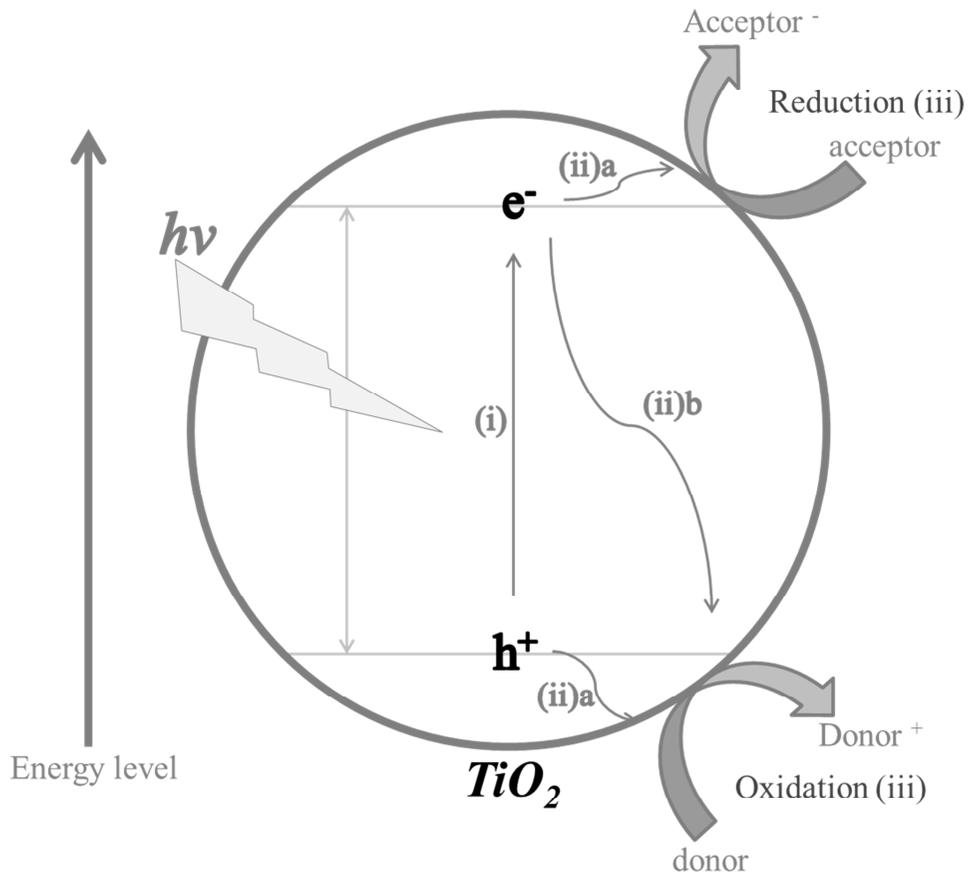


Figure 1.4 Main processes in semiconductor photocatalysis (i) photon absorption and electron-hole pair generation; (ii) charge separation and migration (ii)a: to surface reaction sites or (ii)b: to recombination sites; (iii) surface chemical reaction at active sites (Leary and Westwood 2011).

1.3.4. Ozonation process

Ozone is generated when oxygen molecules are stressed to high-voltage electric discharge. Physicochemical properties of ozone are closely related to its efficacy. Table 1.4 shows physico-chemical properties of ozone. The gas has a pungent odor and strong oxidizing properties (Guzel-Seydim et al., 2004). Because the gas is a strong oxidizing agent, it is becoming to apply for WWTPs as a clarifying and disinfecting agent (Wojtenko et al., 2001).

Micropollutants are oxidized through direct reaction of ozone or through indirect reactions such as $\cdot\text{OH}$, $\text{O}_2\cdot^-$, $\text{HO}_2\cdot$ produced by the decomposition of ozone (Rokhina and Virkutyte 2010). The ozone reacts selectively with compounds containing C=C bonds, anions (N, P, O, S), and certain functional groups (OH, CH₃, OCH₃) (Völker et al., 2019). Direct reaction predominates under acidic conditions and in the presence of radical. On the other hand, the indirect reaction occurs under alkaline conditions, or in the presence of radical promoting solutes because of the radical-type chain reaction and $\cdot\text{OH}$ formation (Irmak et al., 2005; Ning et al., 2007). However, due to the presence of several types of radical scavengers in wastewater (i.e. carbonate and bicarbonate), direct reaction of ozone is generally the predominant mechanism, especially at lower ozone concentration in water (Nakada et al., 2007).

The decomposition is chain reactions which include initiation, propagation, and termination steps (Staehelin and Hoigne 1985). Chain reaction steps are given below and Figure 1.5.

(1)Initiation: the reaction between OH⁻ ions and O₃ results in the formation of hydroperoxide ion (HO₂⁻) and is considered as the first reaction of the mechanism Eqs. (1.19) - (1.20).



(2)Propagation: further decomposition of ozone occurs because of its reaction with O₂^{•-}. It results in the formation of ozonide ion (Eq. (1.21)). The ozonide ion ultimately decomposes to form HO₃[•] (Eq. (1.22)) and then converted to [•]OH (Eq. (1.23)). The [•]OH also can react with O₃ to form HO₄[•] (Eq. (1.24)) and decomposes to form HO₂[•] and O (Eq. (1.25)).



(3) Termination: this step involves any recombination of $\cdot\text{OH}$, $\text{HO}_2\cdot$ and O_2 .

Ozone is relatively unstable in aqueous solutions. The gas decomposes continuously to oxygen according to a pseudo first-order reaction (Tomiyasu et al., 1985). The stability of ozone in aqueous solutions is largely affected by the source of water. Wastewater contains organic and inorganic substances that can easily be oxidized. These substances may react rapidly with ozone and lead to decrease considerably its half-life.

$$\frac{d[\text{O}_3]}{dt} = k[\text{O}_3][\text{OH}^-] \quad (1.26)$$

Recently, UV-C and H_2O_2 are applied for the ozonation process in order to enhance ozone performance. UV-C radiation to ozone results in photodecomposition of ozone and formation of H_2O_2 . This application leads to the formation of the $\cdot\text{OH}$, which is an extremely reactive specie.

Table 1.4 Physical and chemical properties of ozone.

Property	Value ^d
Melting point, °C	-251
Boiling point, °C	-112
Critical pressure, atm	54.62
Critical temperature, °C	-12.1
Specific gravity	1.658 higher than air 1.71 gcm ⁻³ at -183 °C
Critical density, kgm ⁻³	436
Heat of vaporization, calmol ^{-1a}	2,980
Heat of formation, calmol ^{-1b}	33,880
Free energy of formation, calmol ^{-1b}	38,860
Oxidation potential, V ^c	2.07

a: at the boiling point temperature; b: at 1 atm and 25 oC, c: at pH = 0; d: Green and Perry 1997 .

1.4. Greenhouse gas emissions

1.4.1. Global climate change issues

A certain amount of greenhouse gases (GHGs) is essential to maintain the Earth at constant temperature (Mitchell 1989). However, over the past 100 years, anthropogenic GHGs such as carbon dioxide (CO₂), methane (CH₄), nitrous oxide (N₂O), hydrofluorocarbons (HFCs), perfluorocarbons (PFCs), and sulfur hexafluoride (SF₆) have been excessively released into the atmosphere (El-Fadel and Massoud 2001). A considerable increase in concentrations of the anthropogenic GHGs in the atmosphere resulted in the global climate change. Anthropogenic GHG concentrations in atmosphere are the highest in history. Showstack et al. (2013) reported that before the pre-industrial revolution, the CO₂ level was 280 ppm in the atmosphere, but nowadays it exceeded 400 ppm. Human being has been suffering from climate change phenomenon caused, and even some species are threatened to survive.

The climate change caused many negative impacts. The global temperature data show warming of 0.65 to 1.06 °C over the period from 1880 to 2012 (Pachauri et al., 2014). Also, during the last 20th century, sea levels have risen by an average of 10 to 20 cm. Table 1.5 shows that there are numerous other negative impacts on climate change. The intergovernmental panel on climate change (IPCC) also disclosed that

the global surface temperature is likely to rise a further 0.3 to 1.7 °C for the lowest emission scenario and 2.6 to 4.8 °C for the highest emission scenario at its fifth Assessment Report.

Unlike many other environmental problems, the issue of climate change requires a global response because GHGs can affect from a region to other regions. International response to climate change began with the adoption of United Nations Framework Convention on Climate Change (UNFCCC) at the 1992 United Nations Conference on Environment and Development (UNCED) in Rio. Since then, the movement to respond to climate change has begun in earnest. UNFCCC called the world to jointly respond to the problem of increasing GHG concentrations in atmosphere. Thus, every year, conference of the parties (COP) discusses and decides on specific implementation measures to mitigate climate change.

The first COP was held in Berlin, Germany in 1995. Later, the Kyoto Protocol was adopted in 1997 at the third COP in Kyoto, Japan, which set a GHG reduction target for developed countries (Annex I). As the Kyoto Protocol entered into force in February 2005, Annex I countries were forced to reduce GHG emissions during the first commitment period from 2008 to 2012 (Grubb et al., 1997). The 2011 Durban COP agreed to establish the post-2020 in which all countries had to reduce GHG emissions, regardless of advanced or developing countries. The 2012 Doha COP decided to extend the Kyoto Protocol by 2020. In December 2015, the Paris Agreement was adopted, which delegates from 195 countries consented to reduce

GHG emissions. Accordingly, the countries have established the intended nationally determined contribution (INDC) and announced their GHG reduction target through the UNFCCC homepage (Table 1.6).

Korea is a country with the significantly high GHG emissions and the per capita GHG emissions among OECD member countries (Figure 1.6). Therefore, Korea is considered that has great global climate change mitigation effect by reducing GHG emissions. In August 2008, Korea government declared 'low-carbon, green growth' to cope with the international concern about climate change and future regulatory pressures. In January 2010, the framework act on low-carbon, green growth was enacted to implement policies for reducing GHG emissions. The act includes the implementation of green management systems across all areas of industry and the establishment of low-carbon culture for green growth. In June 2015, Korea submitted the INDC, which reduces GHG emissions by 37% (BAU) by 2030. Therefore, Korea should implement various research and activities to achieve the GHG reduction target promised to the international community.

Table 1.5 Observed changes in climate system with the increase of anthropogenic GHG concentrations in the atmosphere.

Media	Changes ^a	Likelihood
Atmosphere		
	The period from 1983 to 2012 was likely to be the warmest 30 years of the past 800 in the northern hemisphere.	High confidence
	The period from 1983 to 2012 was likely to be the warmest 30 years of the past 1400 in the northern hemisphere.	Medium confidence
	The globally averaged combined land and ocean surface temperature warmed to 0.85 (0.65 - 1.06) °C over the period 1880 to 2012.	90% likelihood
	Precipitation is likely to increase since 1951.	High confidence
	Precipitation is likely to increase since 1901.	Medium confidence
Ocean		
	Regions of high surface salinity, where evaporation dominates, have become more saline since the 1950s.	Medium confidence
	Regions of low salinity, where precipitation dominates, have become fresher since the 1950s.	Medium confidence
	The pH of ocean surface water has decreased by 0.1 (26% increase in acidity).	High confidence
	Oxygen concentrations have decreased in coastal waters and in the open ocean thermocline in many ocean regions since the 1960s.	Medium confidence

Table 1.5 Continued.

Media	Changes ^a	Likelihood
Cryosphere	Arctic sea ice extent decreased in range from 3.5 to 4.1 % per decade over the period 1979 to 2012.	High confidence
	Antarctic sea ice extent increased in the range of 1.2 to 1.8% per decade (extent increasing in some regions and decreasing in others).	High confidence
	The extent of Northern Hemisphere snow cover has decreased by 1.6 % per decade for March and April, and 11.7% per decade for June since the mid-20th century.	High confidence
	Permafrost temperatures have increased in most regions of the Northern Hemisphere since the early 1980s.	High confidence
Sea level	The mean rate of global averaged sea level rise was 1.7 (1.5 - 1.9) mm/yr from 1901 to 2010.	High confidence
	The mean rate of global averaged sea level rise was 3.2 (2.8 - 3.6) mm/yr from 1993 to 2010.	High confidence
	Glacier mass loss and ocean thermal expansion from warming contribute about 75% of the observed global mean sea level rise since the early 1970s.	High confidence
	The maximum global mean sea level during the last interglacial period (129,000 to 116,000 years ago) was at least 5 m higher than present.	High confidence

a: Pachauri et al., 2014.

Table 1.6 Nationally determined contribution submitted to UNFCCC^a.

Country	Target (%)	Type	Base year	Target year
Australia	-26~28%	Absolute target	2005	2030
Austria ^b	-40%	Absolute target	1990	2030
Belgium ^b	-40%	Absolute target	1990	2030
Canada	-30%	Absolute target	2005	2030
Chile	-30%	Emissions per GDP	2007	2030
Czech Republic ^b	-40%	Absolute target	1990	2030
Denmark ^b	-40%	Absolute target	1990	2030
Estonia ^b	-40%	Absolute target	1990	2030
Finland ^b	-40%	Absolute target	1990	2030
France ^b	-40%	Absolute target	1990	2030
Germany ^b	-40%	Absolute target	1990	2030
Greece ^b	-40%	Absolute target	1990	2030
Hungary ^b	-40%	Absolute target	1990	2030
Iceland	-40%	Absolute target	1990	2030
Ireland ^b	-40%	Absolute target	1990	2030
Israel	-26%	Absolute target	2005	2030
Italy ^b	-40%	Absolute target	1990	2030
Japan	-26%	Absolute target	2013	2030
Korea	-37%	Business as usual	-	2030
Latvia ^b	-40%	Absolute target	1990	2030
Lithuania ^b	-40%	Absolute target	1990	2030
Luxembourg ^b	-40%	Absolute target	1990	2030
Mexico	-25%	Business as usual	-	2030
Netherlands ^b	-40%	Absolute target	1990	2030
NewZealand	-30%	Absolute target	2005	2030
Norway	-40%	Absolute target	1990	2030
Poland ^b	-40%	Absolute target	1990	2030
Portugal ^b	-40%	Absolute target	1990	2030
Slovak Republic ^b	-40%	Absolute target	1990	2030
Slovenia ^b	-40%	Absolute target	1990	2030
Spain ^b	-40%	Absolute target	1990	2030
Sweden ^b	-40%	Absolute target	1990	2030
Switzerland	-50%	Absolute target	1990	2030
Turkey	-21%	Business as usual	-	2030
United Kingdom ^b	-40%	Absolute target	1990	2030
United States	-26~28%	Absolute target	2005	2025

a: UNFCCC 2018; b: EU NDC

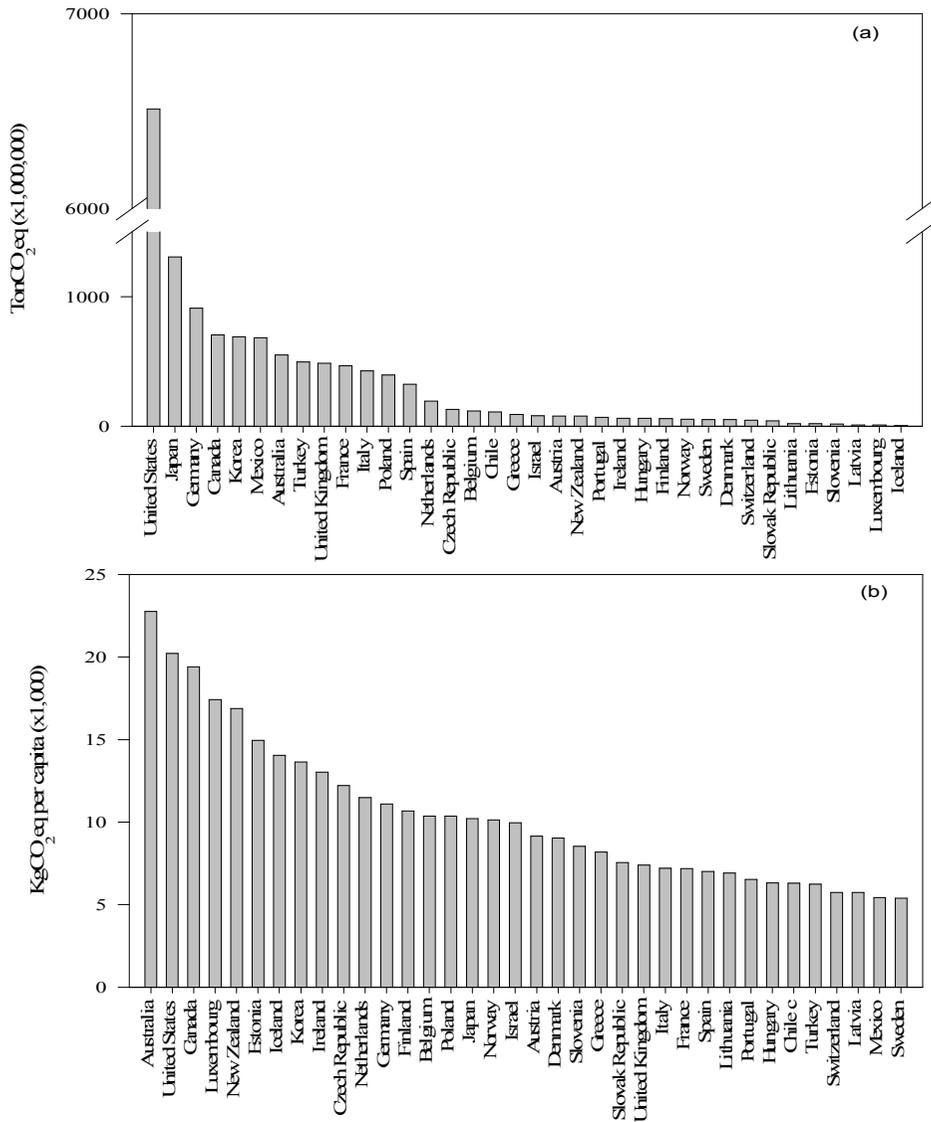


Figure 1.6 Greenhouse gas emissions of OECD (Chile: GHG emissions in 2013, Korea and Mexico: GHG emissions in 2015, Other Countries: GHG emissions in 2016) (OECD 2014).

1.4.2. GHG emissions from wastewater treatment systems

GHGs are emitted from the variety of fields. The national inventory report submitted to UNFCCC distinguishes GHG emissions fields in five sectors (i.e. energy, industrial processes and product use, agriculture, land use land-use change and forestry (LULUCF), and waste). The wastewater treatment systems are included in the waste sector. As shown in Table 1.7, which shows the amount of GHG emissions in Korea, the wastewater treatment systems account for 9 % of the GHG emissions in the waste section (KMOE 2015). It does not seem to be large. However, this ratio includes only the facilities registered as the wastewater treatment servicers, excluding the amount of GHGs emitted from wastewater treatment systems belonged to the energy and industrial processes and product use sectors. Considering the fact that most of the industries operate a wastewater treatment system, the emissions would be significant. Indeed, many studies reported that WWTPs are one of the major sources of GHG emissions and an important topic of a GHG emission study (Yan et al., 2014; Gu et al., 2016).

In general, wastewater treatment systems consist of pre-treatment, primary treatment, secondary treatment, tertiary treatment, and sludge treatment. A pre-treatment is the physical treatment process removing particles such as cans, sticks and other materials using grit clarifiers. In a primary treatment, pollutants are removed by settling and rising. Contaminants with a heavier specific gravity than

water precipitate, and substances with a lower specific gravity than water rise. The precipitated and raised contaminants are physically easily removed. Secondary treatment is very important process to eliminate pollutants using biological processes. Tertiary treatment is used to remove nutrients contaminants such as nitrogen and phosphorus. Sludge is produced in the primary, secondary, and tertiary processes. Sludge treatments reduce the volume using anaerobic digestion, aerobic digestion, and composting.

GHGs such as carbon dioxide (CO₂), methane (CH₄), and nitrous oxide (N₂O) are emitted from all processes of wastewater treatment facilities. The gases occur during decomposing contaminants and operating of the facilities. The decomposition of contaminants includes direct emission of CO₂, CH₄, and N₂O (Scope I). GHG emissions during the operation of the facilities come from the use of fossil fuel (scope I), electricity (scope II), and all other indirect emissions in value chains (scope III).

Direct emission of CO₂ (scope I) is generated from the decomposition of contaminants. The abiotic and biogenic CO₂ emissions during decomposition of contaminants are excluded from the anthropogenic GHG emissions, whereas direct emission of CH₄ and N₂O are contained in the direct emission of wastewater treatment system inventory (Griffith et al., 2009; Masuda et al., 2018).

Direct emission of CH₄ (scope I) occur mainly from anaerobic decomposition by activating methanogens, as well as from the anaerobic digestion of the wastewater

sludge. As showed in Table 1.8, the amounts of CH₄ emissions during wastewater treatments can be calculated using emission factors. BOD and COD are the most commonly used direct emission factors of CH₄ in wastewater treatment. On the other hand, Wang et al. (2011b) studied the direct emission factor of CH₄ using number of persons using wastewater treatments.

Direct emission of N₂O (scope I) can be produced by nitrifying and denitrifying bacteria under aerobic or anaerobic conditions in wastewater treatment (Wunderlin et al., 2012). During nitrification, ammonia is converted into nitrite or nitrate, which is subsequently reduced to nitrogen gas during denitrification. Both processes can lead to emission of nitrogen oxides (Kampschreur et al., 2009). As presented in Table 1.8, the amounts of N₂O emissions during wastewater treatments can be calculated using emission factors. The general parameter of direct emission of N₂O is the TN.

Fossil fuel produces CO₂, CH₄, and N₂O gases by oxidation with air during combustion (scope I). Electricity does not generate GHGs at the usage stage, but GHGs are generated during the process of electricity production. Thus, electricity is classified as the scope II. The chemicals and materials purchased also do not produce GHGs in the process of usage, but in the process of manufacturing and disposal (sometime in the usage stage). Although GHGs are not generated during the usage stage, the user can select and use the low-carbon product. Therefore, goods

purchased in the value chains are classified as the scope III and can be included in the user's boundary.

Direct and indirect GHG emissions in wastewater treatments are usually calculated using emission factors. Many studies have been conducted on emissions factors. However, most of the studies have focused on the direct emission in biological treatments (Table 1.8). Recently, new treatment technologies such as AOPs have been used to treat non-biodegradable micropollutants in water. They require large amounts of energy and chemicals to remove non-biodegradable micropollutants in water. Therefore, it is assumed that a large amount of GHGs will be released into the atmosphere during the processes.

However, most of the recent advanced treatment studies have focused on the degradation kinetics and byproducts. As the problem of increasing anthropogenic GHG concentrations in the atmosphere has emerged as a sustainable ecological issue in the world, sustainable development in terms of GHG emissions from wastewater treatment systems has now become just as an important issue for us as the degradation kinetics and byproducts. If some wastewater treatment processes have similar decomposition rates and byproducts, it is necessary to consider using the process with lower GHG emissions.

However, until now, research to assess GHG emissions are relatively limited compare to biological processes. To our best knowledge, study of GHG emissions from the advanced processes has not been conducted. In order to reduce GHG

emissions, assessment of GHG emissions must be studied to clearly understand the mechanism of GHG generation. Therefore, it is necessary to study GHG emission factors for new technologies such as AOPs.

Table 1.7 Annual greenhouse gas emissions (tCO₂eq x 1,000,000) in Korea.

Sectors		2014	2015	2016
Energy	Fuel combustion	594.7	598.6	600.9
	Omission	4.1	3.8	3.9
Industrial processes and product use	Mineral Industry	33.6	34.2	34.8
	Chemical Industry	0.9	0.8	0.9
	Metal Industry	0.4	0.2	0.3
	Halocarbons and hexafluoride consumption	21.1	18.0	15.5
Agriculture	Intestinal fermentation	4.2	4.1	4.0
	Treatment of livestock manure	4.6	5.0	5.4
	Rice cultivation	6.3	6.2	6.1
	Agricultural soil	5.7	5.6	5.7
	Incineration of crop residues	0.0	0.0	0.0
Land use land-use change and forestry	Forest land maintained as forest	-47.3	-47.0	-48.5
	Agricultural land maintained as agricultural land	4.3	3.8	3.7
	Grassland maintained as grassland	-0.1	-0.1	-0.1
	Wetlands maintained as wetlands	0.3	0.4	0.4
Waste	Waste landfill	7.3	7.7	7.6
	Wastewater treatment	1.4	1.4	1.4
	Waste incineration	6.3	6.9	7.1
	Other	0.3	0.3	0.4
Total		648.3	650.1	649.6

Table 1.8 Emission factors of CH₄ and N₂O for wastewater treatments.

GHGs	Treatment processes	Emission factors	Unit	References
CH ₄	WWTP	3.734	g CH ₄ /kg BOD ₅	Hwang et al., 2016
	WWTP	11.000	g CH ₄ /kg COD	Daelman et al., 2013
	A ² O	4.022	g CH ₄ /kg BOD ₅	Hwang et al., 2016
	A ² O	0.900	g CH ₄ /kg COD	Yan et al., 2014
	A ² O	11.300	g CH ₄ /person/yr	Wang et al., 2011b
	Bardenpho process	277.300	g CH ₄ /kg BOD	Kyung et al., 2015
	Sludge digestion	509.000	mg/m ³ -influent	Oshita et al., 2014
	Orbal oxidation ditch	3.300	g CH ₄ /kg COD	Yan et al., 2014
N ₂ O	WWTP	1.256	g N ₂ O/kg TN	Hwang et al., 2016
	WWTP	28.000	g N ₂ O/kg TKN	Daelman et al., 2013
	A ² O	1.605	g N ₂ O/kg TN	Hwang et al., 2016
	A ² O	0.800	g N ₂ O/kg TN	Yan et al., 2014
	Bardenpho process	715.000	g N ₂ O/kg TN	Kyung et al., 2015
	BNR	0.035	kg N ₂ O/kg N	Foley et al., 2010
	Sludge digestion	7.100	mg/m ³ -influent	Oshita et al., 2014
	Orbal oxidation ditch	3.600	g N ₂ O/kg TN	Yan et al., 2014

1.5. Objectives and dissertation structure

Ten micropollutants (ACT, BPA, CBM, CFF, DCF, IBU, NPX, MPT, SMA, and SMZ) were selected as target compounds in monitoring study. BPA was chosen as a pollutant for the AOP degradation and the GHG emissions studies. The main objectives of the study are (1) to monitor the fate of the ten selected micropollutants in small-scale wastewater treatment facilities, (2) and to investigate the applicability of AOPs in wastewater treatment facilities by studying the impact of natural water components on the AOPs, (3) and to calculate and compare GHG emissions in AOPs for the sustainable development.

Specific studies are:

In Chapter 2, (1) to investigate the occurrence, removal, and discharge of ten selected micropollutants from private WTFs. (2) To investigate the effect of WTFs on its receiving water by examination of changes in concentrations of micropollutants at upstream and downstream. (3) To estimate the annual release of these micropollutants from the private wastewater treatment facilities in eight provinces of Korea.

In Chapter 3, (1) To investigate the effects of environmentally relevant concentrations of pH, NO_3^- , $\text{CO}_3^{2-}/\text{HCO}_3^-$, and humic acid on the degradation kinetics of BPA during UV photolysis and $\text{H}_2\text{O}_2/\text{UV}$ process. (2) To propose the degradation mechanisms of BPA during UV photolysis and $\text{H}_2\text{O}_2/\text{UV}$ process in the presence of NO_3^- , $\text{CO}_3^{2-}/\text{HCO}_3^-$ and both ions together using the identified byproducts.

In Chapter 4, (1) To estimate GHG emissions and degradation kinetics during degradation of BPA in AOPs using experimental scale processes ($\text{H}_2\text{O}_2/\text{UV}$, TiO_2/UV , and O_3 processes). (2) To calculate carbon footprints of AOPs under experimental conditions that emits the lowest GHG to remove BPA. (3) To compare the carbon footprint values in the manufacturing, usage, and disposal phases.

This dissertation composes five chapters (Figure 1.7). Chapter 1 presents the background information and the literature review. Chapter 2 focuses on the behavior and effects of ten target micropollutants in small-scale wastewater treatment facilities and its receiving water, providing its low removal efficiency for some micropollutants. Chapter 4 presents on the effects of environmentally relevant

concentrations of pH, NO_3^- , $\text{CO}_3^{2-}/\text{HCO}_3^-$, and humic acid on UV photolysis and $\text{H}_2\text{O}_2/\text{UV}$ process, implying applicability of AOPs in the small-scale wastewater treatment facility. Chapter 4 shows GHG emissions during degradation of BPA in AOPs (i.e. $\text{H}_2\text{O}_2/\text{UV-C}$, $\text{TiO}_2/\text{UV-C}$, and ozonation processes), providing the comparison of AOPs in terms of sustainability. Lastly, Chapter 5 presents the conclusions and future study.

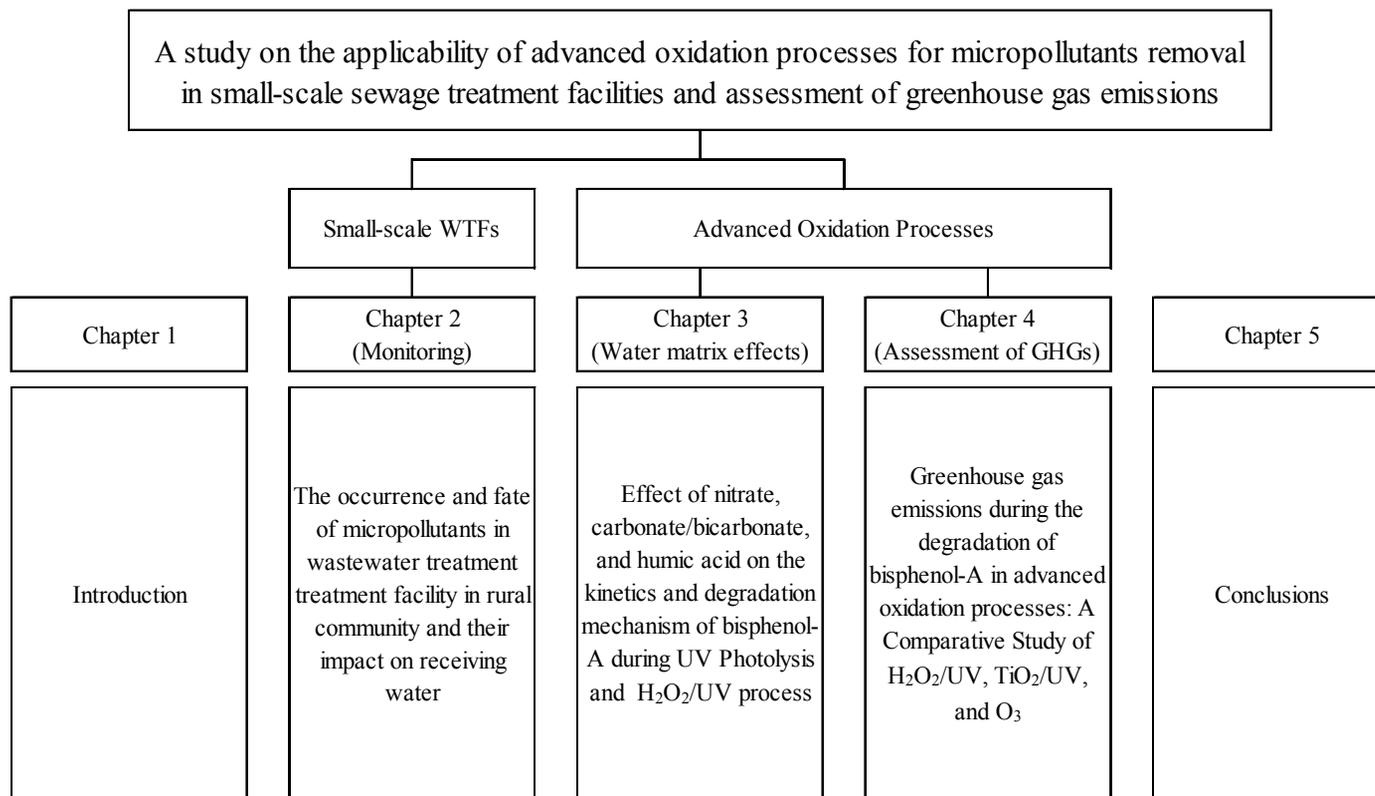


Figure 1.7 Schematic diagram of the overall composition in the dissertation.

Chapter 2.

The occurrence and fate of micropollutants in small-scale wastewater treatment facilities in rural community and their impact on receiving water

2.1. Introduction

Micropollutants such as pharmaceuticals and endocrine disrupting compounds (EDCs) are a group of emerging micropollutants that are increasingly of concern because of adverse health effects to human and potential risk to aquatic environments (Ying et al., 2009; Staniszewska et al., 2015; K'oreje et al., 2016). These micropollutants can be introduced into sewage treatment plants (STPs), wastewater treatment plants (WWTPs), and other types of wastewater treatment systems via human excreta (Guerra et al., 2014; Kim et al., 2017; Kosma et al., 2017; Rivera-Jaimes et al., 2018). The micropollutants that have not been removed in wastewater treatment facilities can enter surface aquatic ecosystems (Kim et al., 2016; Kay et al., 2017).

Approximately 7% of the population in Korea lives in rural areas, where public sewage treatment facilities are unavailable (KMOE 2015). Since it is economically unfeasible to build and operate centralized STPs in poorly populated rural areas, a private sewage treatment facility should be installed to comply with sewage discharge guidelines in such areas (Sewerage Act 2017). There are two types of private sewage treatment facilities such as a private septic tank and a private wastewater treatment facility (WTF) in Korea. A private septic tank is installed where generates wastewater of up to two cubic meters per day, and a private WTF is installed where generates wastewater exceeding two cubic meters per day (Sewerage

Act 2017). Septic tanks mainly use anaerobic conditions and drainfields (Du et al., 2014). WTFs, on the other hand, mainly remove pollutants under aerobic conditions and discharge treated water to into small surface waters, such as streams and creeks (Schaidler et al., 2017). Unlike the septic tanks, the volume of water discharged from private WTFs is too large to drain into the soil.

Several types of treatment technologies have been developed and adopted to private WTFs such as conventional biological treatments, trickling filters, membranes, and bio-filters. WTFs with activated sludge process are among the most popular private facility (> 80%) in Korea (Kwun et al., 2005; Park and Kim 2005). The activated sludge is not difficult to manage after the microorganisms are properly cultured in the treatment tank. However, since WTF largely relies on an automated process and focuses on removing conventional wastewater pollutants such as BOD and SS, the facility may not be sufficient to treat non-biodegradable micropollutants.

Recently, several studies investigated occurrence and fate of micropollutants in wastewater treatment systems. Most of studies, however, have focused on fate of micropollutants in STP or WWTP systems that are used in urban areas and private septic tanks since public STPs have a large treatment capacity and septic tanks are prevalent in rural areas of the U.S. and developed countries (Conn et al., 2010; Du et al., 2014; McEneff et al., 2014; Lolić et al., 2015; Park et al., 2017; Yang et al., 2017; Guyader et al., 2018). In Korea, there were 381,932 of private WTFs and 535,337 of septic tanks (KMOE 2015). Considering the discharge volume of private WTFs, the

facilities will have a more significant impact on the environment compared to septic tanks. However, few studies have investigated the occurrence and fate of micropollutants in private WTFs used in rural areas, and the impact on receiving water. A recent review on the behavior of micropollutants in onsite wastewater treatment systems also noted that the study of alternate onsite wastewater treatment systems (e.g., aerobic treatment units) is very limited and further research is required (Schaidler et al., 2017).

Therefore, the objectives of this study were to investigate the occurrence, removal, and discharge of selected micropollutants from private WTFs. In addition, the effect of WTFs on its receiving water was investigated by examination of changes in concentrations of micropollutants at upstream and downstream. Lastly, based on the per capita discharge loads of selected micropollutants in WTFs which were derived from this study, we estimated the annual release of these micropollutants from private WTFs in eight provinces of Korea.

2.2. Materials and methods

2.2.1. Chemicals

Acetaminophen (ACT), bisphenol-A (BPA), carbamazepine (CBM), caffeine (CFF), diclofenac (DCF), ibuprofen (IBU), naproxen (NPX), metoprolol (MPT), sulfamethazine (SMA), and sulfamethoxazole (SMZ) were purchased from Sigma-Aldrich (St. Louis, MO, USA) and Fluka (St. Louis, MO, USA). $^{13}\text{C}_6$ -sulfamethoxazole and $^{13}\text{C}_6$ -naproxen were used as internal standards to compensate for matrix effects. Ammonium formate (Sigma-Aldrich Co. Ltd., USA), ammonium acetate (Sigma-Aldrich Co. Ltd., USA), and formic acid (Fluka, Buchs, Switzerland) were purchased as the mobile phase buffers in LC-MS-MS.

2.2.2. Selection of micropollutants

Ten micropollutants (ACT, BPA, CFF, CBM, DCF, IBU, MPT, NPX, SMA, and SMZ) were selected based on the annual production in Korea and the concentration observed in surface water and wastewater. According to European Commission (2003), it is reported that the pharmaceutical producing annually more than 600 kg can affect environment. Table 1.1 showed the annual productions in Korea and occurrences of selected micropollutants in water. The selected pharmaceuticals have been produced more than 800 kg/yr in Korea, and previous monitoring of these micropollutants showed significant concentrations in surface water and wastewater (Table 1.1).

2.2.3. Sampling site and collection

South Korea is divided into eight provinces on the mainland (excluding Jeju Island); Gyeonggi (GG), Gangwon (GW), Chungcheongbuk (CB), Chungcheongnam (CN), Jeollabuk (JB), Jeollanam (JN), Gyeongsangbuk (GB), and Gyeongsangnam (GN). 92% of Korea's private WTFs are located in these eight provinces (KMOE 2015). Therefore, in order to assess and compare regional variation of private WTFs in Korea, it is appropriate to select the sampling sites at these eight provinces excluding Jeju island. Private WTFs belonging to some metropolitan cities were included in the provinces where the cities were belonged to the past.

Three WTFs were selected from each province (for a total of 24 WTFs) to compare the selected micropollutant levels (Figure 2.1). In each WTF, four points, the influent and effluent of the WTFs as well as the areas upstream and downstream of the receiving water, were sampled in June 2017 (Figure 2.2). A total of 96 samples were collected at the 24 WTFs, with 24 samples taken from each influent, effluent, upstream, and downstream point. During the sampling, five day composition samples were collected, and stored in a refrigerator at 4°C until analysis.

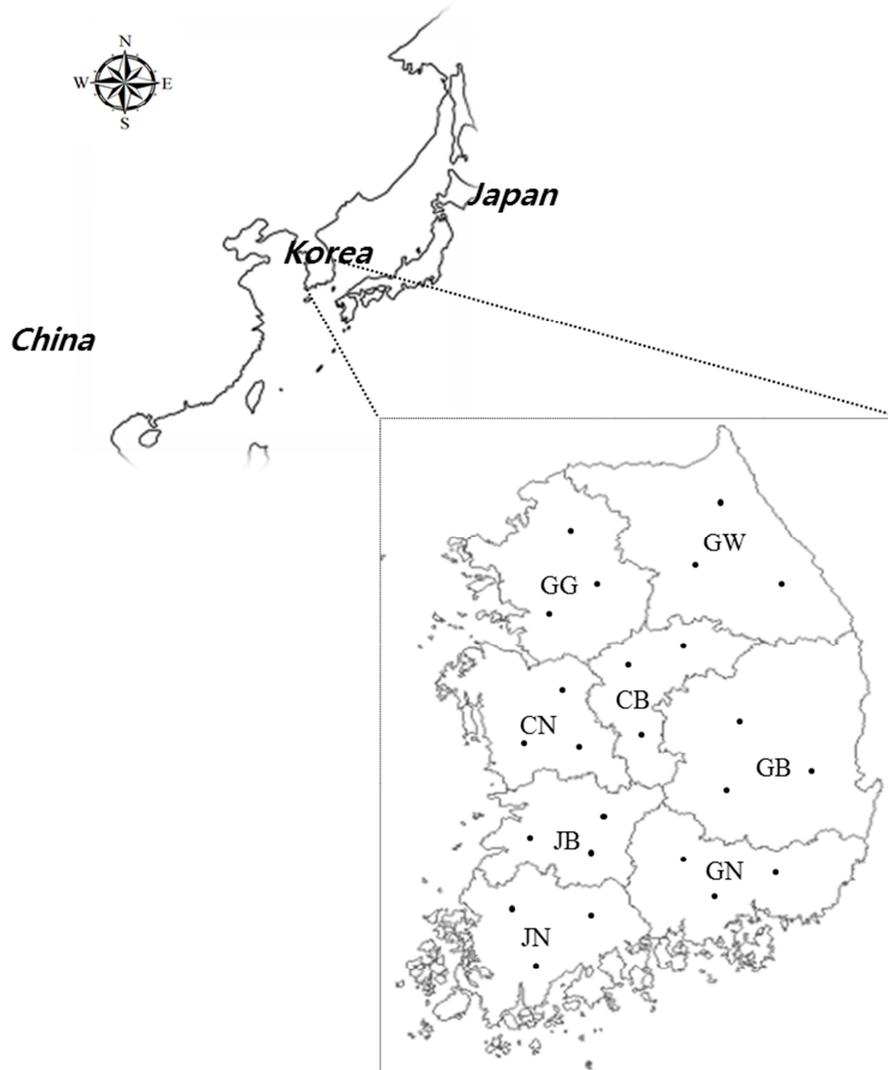


Figure 2.1 Sampling locations (●) of wastewater treatment facilities in each province of South Korea (Province; Gyeonggi (GG), Gangwon (GW), Chungcheongbuk (CB), Chungcheongnam (CN), Jeollabuk (JB), Jeollanam (JN), Gyeongsangbuk (GB), Gyeongsangnam (GN)).

2.2.4. Description of WTFs

All selected WTFs were designed to treat less than 50 m³/day of sewage water via an activated sludge process. The effluent levels of biological oxygen demand (BOD) and suspended solid (SS) during the sampling period ranged from 5 to 30 mg/L (provided from the WTF operating agencies). Table 2.1 presents detailed information on the WTFs, such as flow rate (m³/day), population served, hydraulic retention time (HRT), BOD (mg/L), and SS (mg/L).

As illustrated by Figure 2.2, a WTF consists of an equalization tank that stores and separates sewage, a biological treatment tank, and a sedimentation tank that transports the precipitated activated sludge to the equalization tank and then discharges the supernatants. The biological treatment tank has an air generator to promote aerobic degradation. The WTFs are buried or installed underground, and a cap is installed on the upper part to operate and maintain a facility. WTFs are based on a technology that relies largely on an automated process. The purified water is then directly discharged into small surface waters, such as streams and creeks.

Table 2.1 Water quantity and quality parameters in WTFs (Province; Gyeonggi (GG), Gangwon (GW), Chungcheongbuk (CB), Chungcheongnam (CN), Jeollabuk (JB), Jeollanam (JN), Gyeongsangbuk (GB), Gyeongsangnam (GN)).

WTF i.d.	Flow rate (m ³ /day)	Population served	HRT (hr)	BOD (mg/L)	SS (mg/L)
GG 1	50	93	29	8	10
GG 2	35	65	19	9	11
GG 3	49	70	25	10	10
GW 1	36	67	18	12	15
GW 2	50	93	24	8	11
GW 3	30	60	18	15	10
CB 1	35	65	19	15	12
CB 2	50	93	24	18	22
CB 3	35	60	19	25	20
CN 1	30	56	14	22	15
CN 2	35	65	19	28	20
CN 3	40	65	20	17	15

Table 2.1 Continued.

WTF i.d.	Flow rate (m ³ /day)	Population served	HRT (hr)	BOD (mg/L)	SS (mg/L)
JB 1	30	56	18	21	20
JB 2	35	65	18	10	15
JB 3	30	40	18	10	9
JN 1	49	91	28	15	12
JN 2	35	65	18	14	15
JN 3	30	45	18	15	11
GB 1	30	56	14	16	17
GB 2	50	93	24	18	12
GB 3	30	45	18	10	13
GN 1	30	56	18	25	20
GN 2	24	45	17	17	20
GN 3	49	50	18	20	12

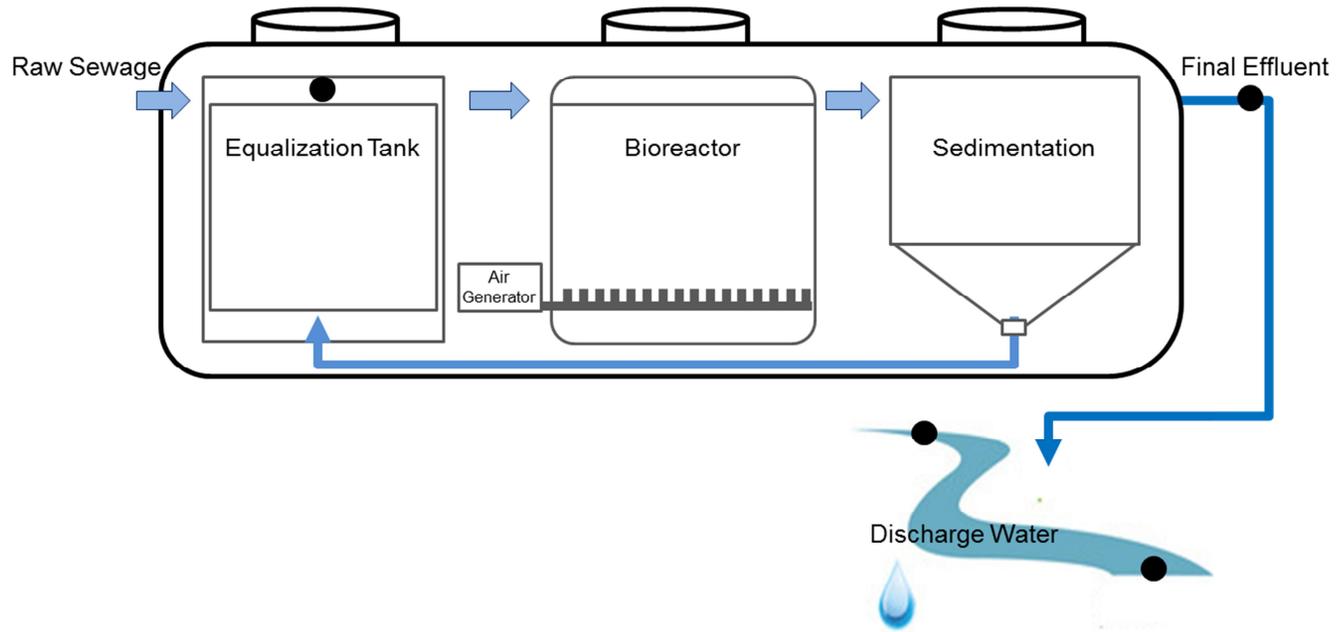


Figure 2.2 Schematic diagram of the treatment process in the wastewater treatment facility and sampling points (●).

2.2.5. Analytical methods

Samples collected from the WTFs and their receiving waters were filtered consecutively through a 1.2 μm GF/C filter (Whatman, Little Chalfont, UK) and a 0.45 μm MEC filter (Whatman, Little Chalfont, UK). A sample volume of 200 mL was spiked with 10 ng of the internal standards. Hydrophile-lipophile balance cartridges (Oasis HLB; Waters, Milford, MA, USA) were conditioned with 5 mL of methanol and 5 mL of Milli-Q water. The spiked samples were then loaded into the previously conditioned cartridges at a flow rate of 1.5 mL/min. Thereafter, the cartridges were dried for 5 min and eluted with 6 mL of methanol. The eluted samples were adjusted to 1 mL using a nitrogen evaporator (CVE-3100; EYELA, Tokyo, Japan) and then reconstituted with 1 mL of methanol.

All samples were analyzed using ultra performance liquid chromatography (UPLC; Nexera; Shimadzu, Kyoto, Japan) equipped with a triple quadrupole mass spectrometer (ABI-4000; Applied Biosystems, Foster City, CA, USA) and operated in both positive and negative modes. Separation was performed using a reverse phase C18 column (Luna 3 μm ; 150 \times 20 mm; Phenomenex, Torrance, CA, USA; 10 μL injection volume). The mobile phase used in the UPLC separation was 95:5 (v/v, %) methanol to water containing 10 mM ammonium formate and 0.3% formic acid in the positive mode, and 98:2 (v/v, %) methanol to water with 5 mM ammonium acetate (v/v, %) in the negative mode. The column oven temperature and

flow rate were set at 40°C and at 0.2 mL/min, respectively.

ACT, BPA, NPX, IBU, and DCF were detected in negative mode and MPT, SMZ, SMA, CFF, and CBM were detected in positive mode. The average recoveries of the internal standards were in the range of 75–121% for influent and effluent and 87–111% for receiving water. The limit of detection (LOD) and the limit of quantification (LOQ) were determined from signal-to-noise ratios of 3 and 10, respectively. The LODs ranged from 0.81 to 3.62 ng/L and the LOQs ranged from 2.70 to 12.06 ng/L. Detailed information of the optimization conditions and detection limits of the ten micropollutants are presented in Table 2.2.

Table 2.2 LC-MS/MS micropollutants analysis conditions.

Compounds	Detection mode	Retention time (min)	LOD (ng/L)	LOQ (ng/L)	Precursor ion (m/z)	Product ion (m/z)	Declustering potential (mV)	Collision energy (mV)	Collision cell exit potential (mV)
Acetaminophen	Negative	1.78	2.54	8.48	149.942	106.9	-65	-24	-5
						108	-65	-20	-5
Bisphenol-A	Negative	1.88	1.99	6.65	226.923	211.9	-70	-26	-15
						211	-70	-26	-11
Naproxen	Negative	3.31	1.51	5.05	228.928	185	-30	-10	-11
						168.9	-30	-36	-11
Ibuprofen	Negative	3.51	1.63	5.43	205.227	158.8	-45	-10	-9
						160.8	-45	-10	-9
Diclofenac	Negative	4.14	3.62	12.06	293.794	249.9	-45	-14	-17
						214	-45	-28	-15

Table 2.2 Continued.

Compounds	Detection mode	Retention time (min)	LOD (ng/L)	LOQ (ng/L)	Precursor ion (m/z)	Product ion (m/z)	Declustering potential (mV)	Collision energy (mV)	Collision cell exit potential (mV)
Metoprolol	Positive	1.26	1.58	5.28	268.087	116.1	81	25	12
						121.1	81	31	12
Sulfamethoxazole	Positive	1.77	0.81	2.7	254.011	156	61	21	16
						92.1	61	37	10
Sulfamethazine	Positive	1.80	1.23	4.11	279.001	186	61	23	16
Caffeine	Positive	1.97	2.14	7.14	194.99	137.9	56	25	14
						137.7	56	25	12
Carbamazepine	Positive	2.02	1.37	4.56	237.134	194.1	61	25	18
						191.8	61	31	20

2.3. Results and discussion

2.3.1. Occurrence of micropollutants in WTFs

The selected micropollutants were detected in WTFs influent at nanogram-to-microgram per liter concentrations (Table 2.3). Generally, the concentrations of micropollutants in the influent were similar or slightly lower than those reported in public STPs in Korea (Choi et al., 2008; Sim et al., 2010; Behera et al., 2011). CFF (13,346 ng/L), ACT (11,331 ng/L), IBU (1,440 ng/L), and NPX (1,313 ng/L) were the dominant pollutants in the WTF influents. In all samples, CFF was the micropollutant present at the highest concentration, possibly due to its frequent use in products such as coffee, tea, cola, and chocolate (Sim et al., 2010; Behera et al., 2011). Disposal of caffeinated beverages directly into drain pipes may also have caused the high concentrations of CFF in the WTFs. The order of the detected pharmaceuticals (ACT > IBU > NPX) in the WTF influents was in agreement with the amounts produced annually, as reported by the KMOE. For instance, 765 730 kg/year of ACT, 145 849 kg/year of IBU, and 69 274 kg/year of NPX were produced in Korea (KMOE 2011).

Figure 2.3(a) compares the measured concentrations of the micropollutants in the WTF influents. The micropollutant composition profiles did not differ significantly among the provinces. Sewage influent depends on inhabitant behavior;

therefore the result implies that the intake and exposure patterns of rural populations for selected micropollutants did not differ by province in Korea. Sun et al. (2016) also observed the same result that the influent compositions of two STPs, which consisted mainly of domestic wastewater, were similar in southeast of China.

In the WTF effluents, the selected micropollutants were detected at concentrations of several to thousand nanograms per liter (Table 2.3). Among the selected micropollutants, only CFF and ACT were detected in all WTF effluent samples. The concentrations of micropollutants in the effluents showed a different order and ration (Table 2.3 and Figure 2.3). The discrepancy between the influent and effluent concentrations may have been due to the different degradation efficiencies and adsorption capabilities of micropollutants in WTFs (Chen et al., 2016; Li et al., 2016; Papageorgiou et al., 2016; Kay et al., 2017). For instance, CFF and ACT are readily removed by STPs through both microbial degradation and adsorption mechanisms (Behera et al., 2011). However, micropollutants present at high concentrations in the influent (i.e., 10 times higher than the other pollutants studied) remained as the pollutants present at the highest concentrations in the effluent. The main removal mechanism of IBU (the third highest concentration in influent) is aerobic biodegradation (Matamoros and Bayona 2006; Chen et al., 2016). The aerobic condition of the WTFs examined in this study may have led to lower concentrations of IBU in the effluent of the WTFs. NPX was detected at higher concentrations in the effluent due to its lower degradation efficiency compared to

IBU (Table 2.3). In fact, the low removal efficiency of NPX compared to IBU has been reported in previous studies (Carballa et al., 2004; Radjenović et al., 2009; Chen et al., 2016). In addition, microorganisms that would have been cultured differently in each WTF would have differed in biodegradation.

Generally, the effluent levels of the selected micropollutants in the WTFs examined in this study were higher than in the effluents of public STPs in Korea. For example, Choi et al. (2008) and Sim et al. (2010) reported concentrations of IBU, ACT, DCF, NPX, and CFF to be < LOD, 9, 23, 128, and 688 ng/L in conventional STP effluents, respectively. However, as shown in Table 2.3, the levels of the selected micropollutants were more than one order higher in the effluents of WTFs. These results may be due to the lower removal efficiencies of the selected micropollutants in WTFs.

Table 2.3 Concentrations (ng/L) of ten micropollutants in wastewater treatment facilities.

Compound	Influent		Effluent	
	Mean	NOD ^a	Mean	NOD ^a
CFF	13,346	24	1,912	24
ACT	11,331	24	1,586	24
IBU	1,440	21	389	22
NPX	1,313	16	475	16
BPA	185	19	96	19
DCF	121	19	73	19
SMZ	115	16	52	17
CBM	101	22	89	23
SMA	45	11	36	12
MTP	11	15	9	15

a: Number of samples detected among 24 total samples with concentrations greater than LOD

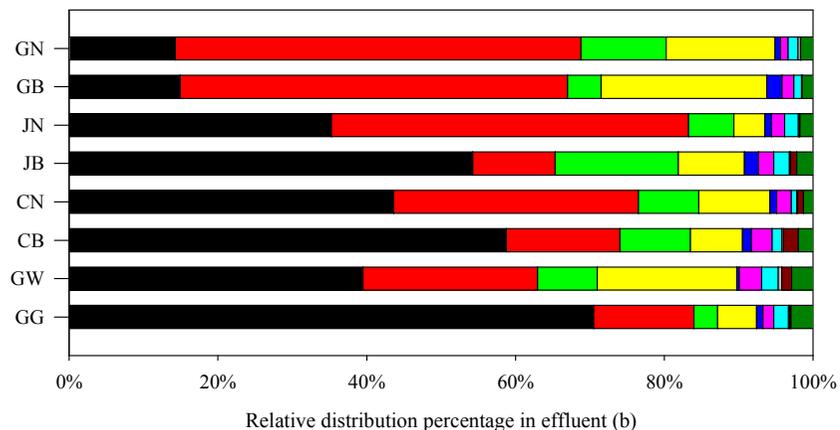
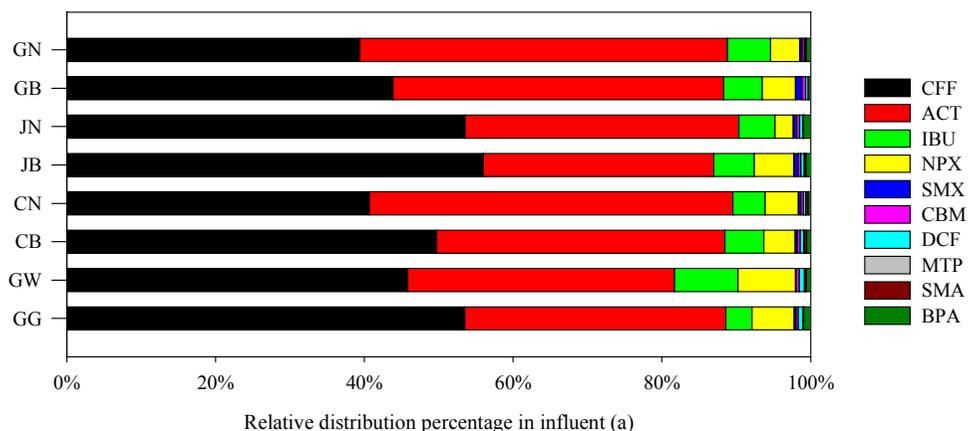


Figure 2.3 Composition profiles of the selected micropollutants collected from (a) influent and (b) effluent of WTFs in each province (Province; Gyeonggi (GG), Gangwon (GW), Chungcheongbuk (CB), Chungcheongnam (CN), Jeollabuk (JB), Jeollanam (JN), Gyeongsangbuk (GB), Gyeongsangnam (GN)).

2.3.2. Removal efficiency of micropollutants during WTFs

The removal efficiencies of the selected micropollutants in WTF are outlined in Figure 2.4. Although in some cases the micropollutants showed negative removal after WTF processing, the average removal efficiencies of almost all micropollutants were positive. ACT, CFF, IBU, and NPX were the only micropollutants with removals higher than 60% (88, 86, 74, and 62%, respectively). On the other hand, SMZ, BPA, DCF, SMA, MTP, and CBM showed low-to-moderate removal efficiencies (53, 38, 38, 21, 16, and 12%, respectively).

The removal efficiencies of the selected micropollutants examined in this study were lower than those reported for STPs and WWTPs. In previous studies, STPs and WWTPs demonstrated removal rates of 99% for CFF, 89% for IBU, 92% for NPX (Matamoros et al., 2009), 99% for ACT, 63% for BPA, and 60% for SMA (Luo et al., 2014; Sun et al., 2014). The lower removal rates in WTFs compared to STPs and WWTPs may be due to the harsh conditions employed by WTFs to reduce the concentrations of micropollutants compared to those used in STPs and WWTPs. WTFs usually operate automatically with a part-time operator; therefore, they are limited in their ability to reduce contaminant concentrations. In other words, WTFs cannot adjust operating conditions immediately upon the entry of pollutants that reduce the removal efficiency of the treatment process. Chen et al. (2016) and Verlicchi et al. (2012) demonstrated that conditions that reduced the removal

efficiency of conventional water quality parameters (e.g., low temperature, low pH, and low dissolved oxygen) in influent were correlated with the low removal efficiency of pharmaceuticals such as ketoprofen, DCF, and MTP. The limitations of WTFs described above may not be reflected in the various operating conditions of WTFs, and may have a negative impact on the elimination of the selected micropollutants.

Tertiary treatment facilities such as denitrification, ultraviolet disinfection, sand filtration, and chlorination can also help to increase the removal of micropollutants in STPs or WWTPs. No tertiary treatment processes were used in the WTFs selected for this study, whereas most WWTPs and STPs that have been studied employ tertiary treatment processes such as disinfection, sand filters, and membranes (Sim et al., 2010; Sun et al., 2014; Xu et al., 2014; Chen et al., 2016). Even though large portions of micropollutants are removed during biological treatment and absorption, tertiary treatment can help eliminate chemicals with low removal efficiencies (Vieno et al., 2005; Sim et al., 2010).

However, the removal efficiencies of micropollutants in WTFs were higher than the septic tanks without drainfields (Conn et al., 2010; Du et al., 2014). In the septic tank, ACT, CFF, CBM, DCF, and SMZ were removed 65, 52, 6, 43, and 48%, respectively, showing lower removal than WTFs (Du et al., 2014). Schaidler et al. (2017) also showed that the removal efficiencies of micropollutants in septic tanks were 8% for CBM, and 54% for NPX, which are lower than WTFs. Many organic

wastewater contaminants (OWCs) prefer to decompose under aerobic conditions rather than anaerobic conditions. Therefore, the aerobic condition of WTF may have led to a higher removal of micropollutants than septic tanks. In contrast, conventional septic tanks treat contaminants with drainfields to compensate for low removal efficiencies. Septic tank effluent (STE) is distributed to drainfields using gravity or pressure from pipes or pits into well-draining vadose zone soils (Guyader et al., 2018). OWCs not degraded during septic tanks systems can be removed by sorption, volatilization, and aerobic degradation in drainfields. Micropollutant removal in septic tank with drainfields was comparable to conventional WWTPs (Schaidler et al., 2017).

WTFs have streamlined facilities and operations to handle sewage from small communities with minimal installation and operational costs; however, the low throughput of micropollutants is likely to increase in future WTFs. In other words, WTFs can treat sewage water generated from small-scale communities inexpensively, but the low removal efficiencies for micropollutants implies that further research is needed to improve the treatment of micropollutants by WTFs.

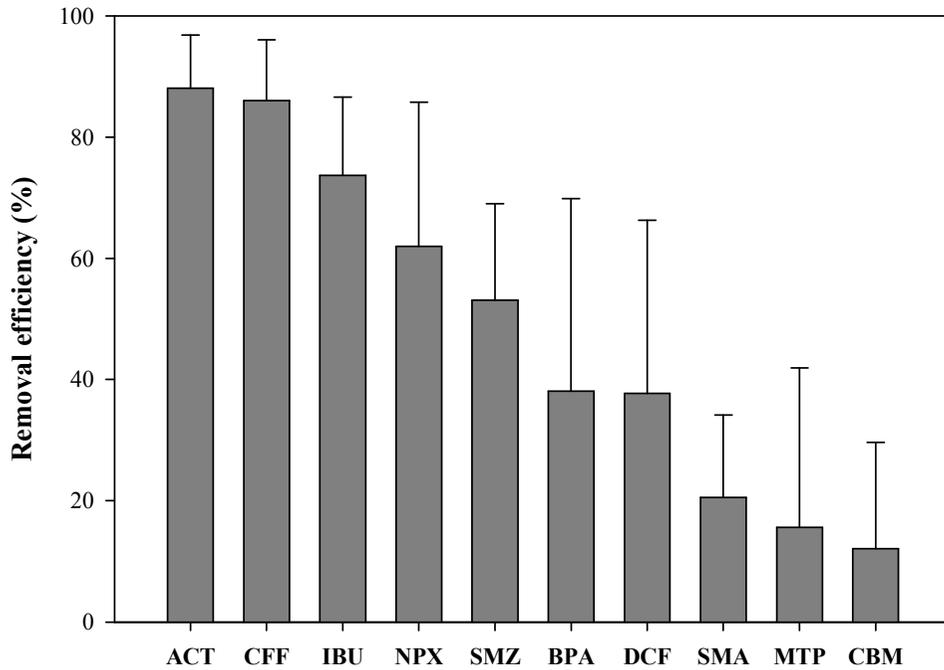


Figure 2.4 Mean removal efficiencies for selected micropollutants during WTFs process.

2.3.3. Occurrence of micropollutants in receiving waters

Because sewage treatment plants cannot remove all micropollutants, they are released into nearby rivers and streams (Cespedes et al., 2008; Pothitou and Voutsas 2008; Gracia-Lor et al., 2012). In this study, to examine the effect of WTF effluent on receiving water, the concentrations of the selected micropollutants were measured at points 50 m upstream and downstream of the WTF effluent discharge point. Table 2.4 presents the concentrations of the selected micropollutants in the upstream and downstream surface water samples. The concentrations detected in the streams followed the same order as those from other studies of micropollutant concentrations in Korean rivers. Yoon et al. (2010) reported a concentration of 94 ng/L for CFF, 57 ng/L for NPX, 31 ng/L for SMZ, 27 ng/L for BPA, 23 ng/L for IBU, and 15 ng/L for DCF in Han River, Korea. Sim et al. (2010) found similar levels (ACT: 47 ng/L, CBM: 37 ng/L, NPX: 12 ng/L) in Nakdong River, Korea.

At the upstream points, micropollutants such as CFF (48 ng/L) and BPA (59 ng/L) were frequently detected in high concentrations, possibly due to recreational activity and dumping of trash. Major sources of BPA in water are plastic products and cans discarded during water recreation activities (Staniszewska et al., 2015). In fact, beverages containing CFF are often flowed in the stream during water activities or from nearby households (Buerge et al., 2003).

Figure 2.5(a) shows the composition profiles measured upstream of the receiving water of the WTFs. Unlike the profiles observed in the influent samples, the composition profiles of micropollutants in the upstream samples showed variation. The concentrations of micropollutants in natural waters are greatly influenced by the presence of contamination sources (Cho et al., 2014). The presence of various nonpoint pollution sources in the upstream area probably played a role in the regional variation observed. For example, there were cattle sheds and pigsties upstream of the WTFs in JB, CB, and GW, where SMA levels were high. Differences in the conditions that can affect the degradation of micropollutants in each stream may have also resulted in regional differences in the distribution of the selected micropollutants (Andreozzi et al., 2003; Li et al., 2004; Vieno et al., 2005; Staniszewska et al., 2015; Kay et al., 2017).

The composition profiles have changed in the downstream (Figure 2.5 (b)). In the upstream, the dominant micropollutant was BPA. However, after passing WTFs effluent, CFF became the dominant micropollutant. In addition, the concentration of some micropollutants showed higher than those observed upstream. As seen in Figure 2.6, most micropollutant concentrations were higher downstream than upstream. In particular, the average concentrations of ACT, IBU, and CFF downstream increased by approximately 408, 367, and 344%, respectively. Moreover, the average concentrations of NPX, SMZ, CBM, DCF, and MTP were located above the trendline of Figure 2.6. The results of the Mann–Whitney U test

comparing the upstream and downstream concentrations of eight micropollutants showed a significant difference ($p < 0.05$) between upstream and downstream concentrations. This result indicated that the effluent from WTF affected the level of the selected micropollutants downstream. Previous research has also demonstrated the relationship of STPs effluents and its receiving water (Yoon et al., 2010; Wu et al., 2016). Using a cluster analysis, Sim et al. (2010) demonstrated that the presence of pharmaceuticals in the river was associated with the inflow from WWTPs. Li et al. (2004) also demonstrated that STP effluents were a major source of nonylphenol in rivers based on results monitoring the increasing downstream concentrations of nonylphenol. WTFs also have a negative impact on their receiving streams. Considering that most stream water sources originate from the effluent of WTFs, especially during the dry season, likely exert a greater effect on stream ecosystems compared to the effects of STPs and WWTPs on their receiving waters.

In contrast, BPA and SMA were located slightly below the trendline in Figure 2.6. This result indicated that the concentrations of both micropollutants in the streams were not significantly affected by WTF effluents. The results of the Mann–Whitney U test also showed that the upstream and downstream concentrations of the two micropollutants did not differ significantly ($p > 0.05$). SMA is a drug commonly used in veterinary medicine to prevent and control diseases in cattle, as well as for promoting the growth of dairy cows (Zhang et al., 2014c). Since WTF influent originates from human usage, SMA present in receiving stream water mainly

originates from nonpoint sources, such as livestock wastewater, rather than from WTF effluent.

In case of BPA, BPA concentration in the upstream (59 ng/L) was higher in downstream (50 ng/L), implying that WTF effluent was not the major source in the receiving stream. Generally, STPs are a well-known source of BPA (Sun et al., 2017), thus we expected that BPA concentrations in the WTFs would be higher than in the stream. This is probably because of that most STPs in Korea treat significant amounts of industrial wastewater together with sewage water (Kim et al., 2012). In contrast, WTFs only purify domestic sewage water. Therefore, the contribution of BPA of the WTFs on its receiving water can be relatively small compared to STPs. Instead, cans and plastics left behind after leisure activities and from dumping of waste probably have enough contributed to upstream BPA pollution.

Table 2.4 Concentrations (ng/L) of ten micropollutants in receiving waters.

Compound	Upstream		Downstream	
	Mean	NOD ^a	Mean	NOD ^a
CFF	48	19	164	24
ACT	28	14	115	24
IBU	17	10	61	21
NPX	41	10	92	20
BPA	59	17	50	19
DCF	17	8	36	17
SMZ	10	16	28	21
CBM	14	12	40	19
SMA	33	17	21	17
MTP	2	5	5	15

a: Number of samples detected among 24 total samples with concentrations greater than LOD

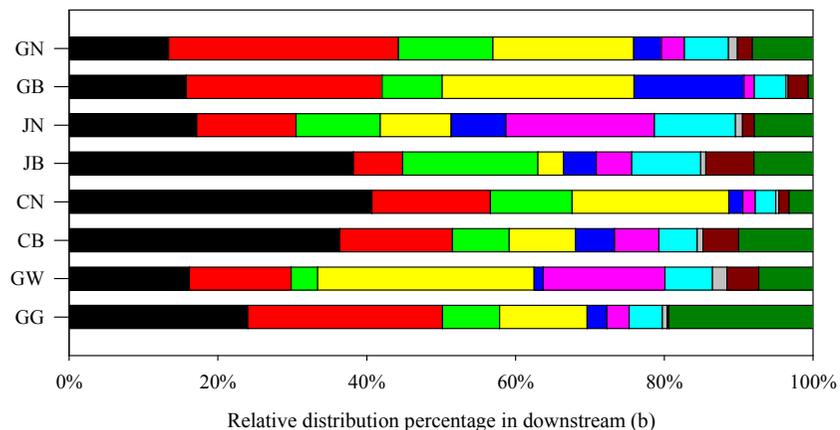
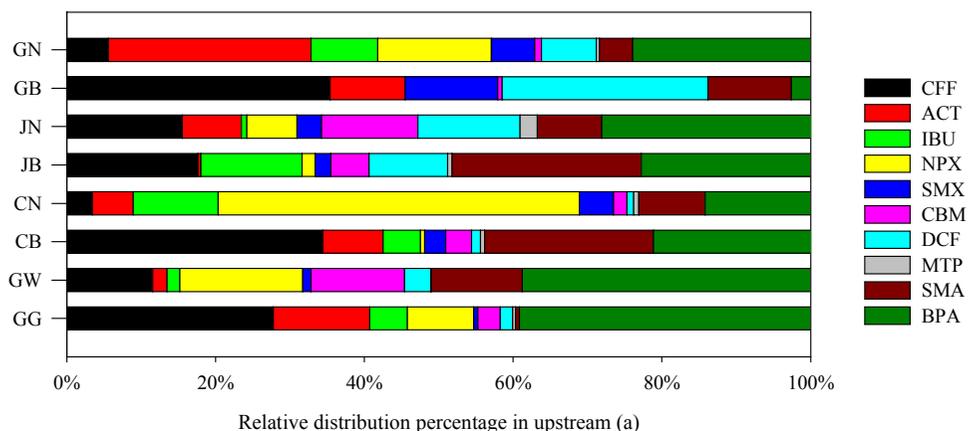


Figure 2.5 Composition profiles of the selected micropollutants collected from (a) upstream and (b) downstream of receiving water of WTFs in each province (Province; Gyeonggi (GG), Gangwon (GW), Chungcheongbuk (CB), Chungcheongnam (CN), Jeollabuk (JB), Jeollanam (JN), Gyeongsangbuk (GB), Gyeongsangnam (GN)).

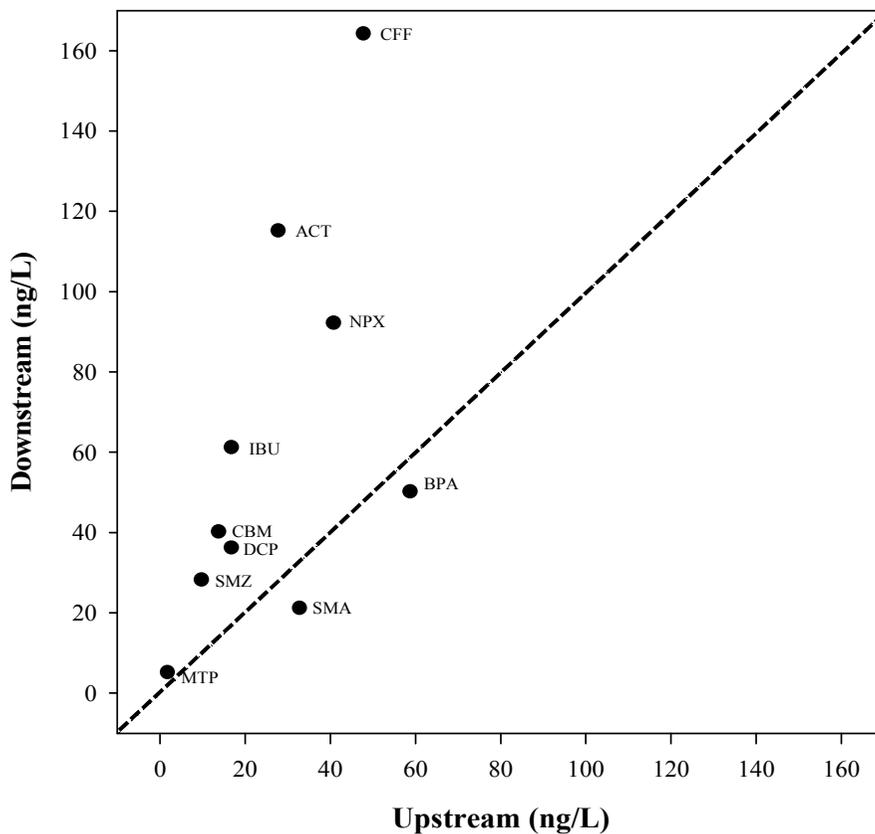


Figure 2.6 Mean concentrations of selected micropollutants in upstream and downstream (dotted line represents 1:1 concentration between upstream and downstream samples).

2.3.4. Discharge loads of target micropollutants from WTFs in Korea

The per capita discharge loads of the selected micropollutants were derived from the daily discharge loads of WTFs (mg/day) divided by the population served by each WTF (Table 2.1). As shown in Table 2.5, the results for the emission factors associated with CFF, ACT, NPX, IBU, BPA, CBM, DCF, SMZ, SMA, and MTP were 1098, 911, 272, 223, 55, 51, 42, 30, 20, and 5 mg/d/1000 inhabitants, respectively.

The per capita discharge loads of the WTFs differed from those of conventional STPs. The discharge loads of CFF and ACT from STPs were reported to be 31 and 10 mg/d/1000 inhabitants, respectively, 100 times lower than values observed in this study (Zorita et al., 2009; Verlicchi et al., 2012). Also, the per capita discharge loads of NPX, CBM, DCF, and SMZ in STPs of 146, 3.24, 18, and 0.53 mg/d/1000 inhabitants, as observed by other researchers, were lower than the values for WTFs observed in this study (Subedi et al., 2015; Papageorgiou et al., 2016; Lin et al., 2018). The higher removal efficiencies at STPs probably led to the lower per capita discharge loads of STPs.

We derived the annual emissions (kg/year) of ten selected micropollutants from private WTFs in Korea. Since more than 80% of Korea's WTFs have adopted an activated sludge process (Park and Kim 2005; KMOE 2015), it is reasonable to use the per capita discharge loads calculated from this study to evaluate the annual

emissions of micropollutants from private WTFs in Korea. The annual emissions were calculated by multiplying the capita discharge loads and the population using regional private WTFs (Tables 2.5 and 2.6 present the values used in the calculation). As illustrated by Figure 2.7, the total amount of the selected micropollutants discharged from annual private WTFs was 1,030 kg/year. Among the provinces, GG province discharged the highest amount followed by GB, GN and CN. This result might be due to that the population using private WTF was more than twice as many as in other provinces (Table 2.6). Since most stream waters are affected by the water released from private WTFs (Ying et al., 2009); thus, the impact of private WTFs on the receiving aquatic ecosystem cannot be neglected.

Finally, the actual emission of micropollutants especially pharmaceuticals can be higher than emission derived from this study because the sampling period in this study was a summer season and in summer, as the water usage increases, the concentration of micropollutants in the influent can be diluted (Sun et al., 2014). In addition, the higher consumption of pharmaceuticals in the cold seasons can cause the increased concentration of especially pharmaceuticals in the WTF influent (Davey et al., 2008). Therefore, considering the low removal efficiency of WTFs and its effect on its receiving water, additional process to treat micropollutants at WTF is necessary.

Table 2.5 The per capital discharge loads (mg/d/1000 inhabitants) of ten micropollutants in wastewater treatment facilities.

Compound	Per capital discharge load
CFE	1,098
ACT	911
IBU	223
NPX	272
BPA	55
DCF	42
SMZ	30
CBM	51
SMA	20
MTP	5

Table 2.6 Summary of private wastewater treatment facilities in Korea^a.

Province	Population	Private WTFs
Gyeonggi (GG)	391,439	143,939
Gangwon (GW)	83,568	26,012
Chungcheongbuk (CB)	95,804	27,196
Chungcheongnam (CN)	109,276	50,871
Jeollabuk (JB)	23,939	16,209
Jeollanam (JN)	74,442	28,041
Gyeongsangbuk (GB)	138,796	44,084
Gyeongsangnam (GN)	124,825	39,977

a: KMOE 2015

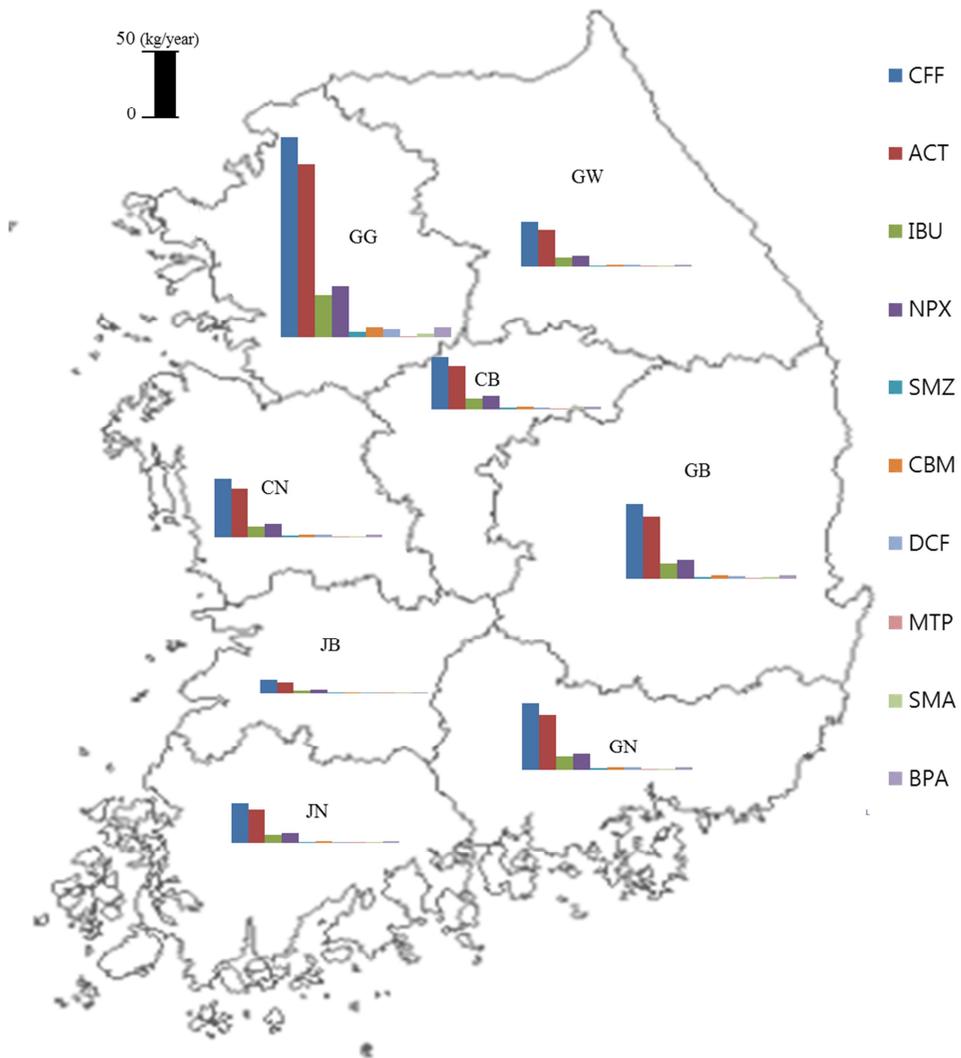


Figure 2.7 Discharge rates (kg/year) of target micropollutants from private wastewater treatment facilities in eight provinces of Korea (Province; Gyeonggi (GG), Gangwon (GW), Chungcheongbuk (CB), Chungcheongnam (CN), Jeollabuk (JB), Jeollanam (JN), Gyeongsangbuk (GB), Gyeongsangnam (GN)).

2.4 Conclusions

In this work, we investigated the occurrence and removals of 10 micropollutants in WTFs and their impact on its receiving waters. CFF (13,346 ng/L), ACT (11,331 ng/L), and IBU (1,440 ng/L) were observed in the highest concentrations in WTF influent, whereas CFF (1,912 ng/L), ACT (1,586 ng/L), and NPX (475 ng/L) were present in higher concentrations in effluent. The composition profile of selected micropollutants in WTF influents showed little regional variation, suggesting that the consumption pattern of rural residents in Korea do not differ from region to region. In contrast, the composition profiles of micropollutants in streams showed variation. The removal efficiencies of micropollutants by WTFs were lower than those of conventional STPs and the septic tanks with drainfields, suggesting the need for improved treatment processes in WTFs. However, the removal efficiencies of micropollutants during WTFs were higher than the septic tanks without drainfields. Upstream, CFF (48 ng/L) and BPA (59 ng/L) were frequently detected in high concentrations. The changes in the concentrations of micropollutants between upstream and downstream water verified that WTF effluent is a major source of pollutants in stream water. The per capita discharge loads of pollutants were higher in WTFs than STPs. The annual emission of 10 micropollutants from private WTFs in Korea calculated in this study was 1,030 kg/yr.

Chapter 3.

Effect of natural water components on the kinetics and degradation mechanism of bisphenol-A during UV photolysis and H₂O₂/UV process

3.1. Introduction

Endocrine disrupting compounds (EDCs) cause an adverse health effect by mimicking a hormone or blocking humoral effects. EDCs have attracted increased attention as they are suspected of contributing to breast and testicular cancer, hypospadias, and a progressive fall in the sperm count (Komesli et al., 2015; Omar et al., 2016). Bisphenol-A (BPA) is one of the well-known EDCs due to its widespread use globally (Dekant and Völkel 2008; Seachrist et al., 2016). BPA is used as a raw material for polycarbonate plastics and epoxy resins, which are used in food cans, drink packages, bottle tops, and water supply pipes. Every year, a million tons of BPA is produced and discharged into aquatic systems by way of sewage and wastewater treatment plants (Lyons 1997; Tran et al., 2015). Due to the poor removal efficiency in the treatment processes, BPA has been detected in various aqueous environments in the range of 8.8 - 1000 ng/L in surface water (Vethaak et al., 2005) and up to 930 ng/L in ground water (Hohenblum et al., 2004).

Based on the best available data, Minnesota Department of Health (MDH 2015) developed a guidance value of 20 µg/L. A person drinking water at or below these levels would have little or no risk of any health effects from BPA. According to EPA (1993), the intake limit of BPA for human health assessment is reported as 0.05 mg/kg/day. Willhite et al. (2008) also reported that the application of US EPA uncertainty factor guidance and the threefold database uncertainty factor to the no

observed adverse effect level (NOAEL) results in an oral reference dose (RfD) of 0.016 mg/kg/day.

Ultraviolet (UV) photolysis can decompose organic pollutants via either direct photolysis in which photons destroy chemicals, or indirect reactions in which reactive molecules such as hydroxyl radicals ($\cdot\text{OH}$), singlet oxygen ($^1\text{O}^{\cdot}$), or bi/carbonate ($\cdot\text{CO}_3^-/\cdot\text{HCO}$) radicals can attack the pollutants (Wang et al., 2017). UV photolysis can treat micropollutants, such as tolfenamic acid (de Melo et al., 2016), pharmaceuticals and personal care products (Carlson et al., 2015), and lampricides (McConville et al., 2016). UV can also effectively removal contaminants in combination with Cl_2 , O_3 , and TiO_2 (Reisz et al., 2003; Von Sonntag 2008; Simonsen et al., 2010; Fang et al., 2014; Pouran et al., 2015). In particular, $\text{H}_2\text{O}_2/\text{UV}$ process has been studied for a long time because of its high OH radical production capacity.

The investigation of BPA degradation mechanism during applied treatment, da Silva et al. (2014) examined the photodegradation of BPA, and they found the seven byproducts such as hydroxylated compounds, quinonic intermediates, and acyclic compounds. Moreover, they revealed that the byproducts showed a higher toxicity than that measured for BPA. Poerschmann et al. (2010) also reported the generation of ring opening products during the oxidative degradation of BPA including lactic, acetic, and dicarboxylic acids. However, most research conducted the experiments using deionized water, and the results obtained using deionized water cannot exactly predict the removal efficiency in the natural water environment.

Nitrate (NO_3^-), carbonate/bicarbonate ($\text{CO}_3^{2-}/\text{HCO}_3^-$), pH, and humic acid are ubiquitous in various water environments. They are found in natural waters in the range of 0.04 - 0.4 mM for NO_3^- , 0.4 - 4 mM for $\text{CO}_3^{2-}/\text{HCO}_3^-$, 4 - 11 for pH, and 1 - 30 mg C/L for humic acid (Lam et al., 2003; KMOE 2016). These compounds can either promote photodegradation by generating reactive species (e.g., OH , NO_2 , $\text{CO}_3^-/\text{HCO}_3^-$, and O^- radicals) or inhibit the degradation of pollutants by reacting with OH radicals, depending on the AOPs conditions (Mack and Bolton 1999; Bennedsen et al., 2012; Sharma et al., 2015a; Orellana-García et al., 2015). However, the effects of these components and the combinations of these compounds on the degradation mechanism especially byproduct formation during $\text{H}_2\text{O}_2/\text{UV}$ process and UV photolysis were not comprehensively studied.

The treatment efficiency of AOP is greatly affected by the scavengers in water (Bennedsen et al., 2012). Therefore, the applicability of AOPs in private sewage treatment systems can be identified by studying the effect of natural water compounds on AOPs. In this study, we examined the effects of NO_3^- , $\text{CO}_3^{2-}/\text{HCO}_3^-$, pH, and humic acid on the kinetics and degradation mechanisms of BPA at $\text{H}_2\text{O}_2/\text{UV}$ process and UV photolysis. Especially, the degradation byproducts were identified using liquid chromatography-tandem mass spectroscopy (LC/MS/MS) in the presence of NO_3^- , $\text{CO}_3^{2-}/\text{HCO}_3^-$ and both ions together. Finally, the degradation mechanisms of BPA during UV photolysis and $\text{H}_2\text{O}_2/\text{UV}$ process were proposed using the identified byproducts.

3.2. Materials and methods

3.2.1. Chemicals

Bisphenol-A (BPA, $C_{15}H_{16}O_2$, 99%), potassium nitrate (KNO_3 , 99%), sodium carbonate (Na_2CO_3 , 99%), and humic acid were purchased from Sigma-Aldrich (St. Louis, MO, USA). To adjust initial pH, hydrochloric acid (HCl, 37 %, v/v), sodium hydroxide (NaOH, 98%) were purchased from Sigma Aldrich (St. Louis, MO, USA). Hydrogen peroxide (H_2O_2 , 50%) was also purchased from Sigma-Aldrich (St. Louis, MO, USA) as a radical promoter. Stock solutions were prepared in deionized water ($R = 18.2 M\Omega cm^{-1}$, Milli-Q). All chemicals used in this study were of reagent grade and used as received.

The degradation constant is affected by the removal efficiency of the pollutant, but also by the initial concentration of the pollutant (Luo et al., 2014; Sharma et al., 2015a). Therefore, BPA was selected based on its highest concentration in WTF effluent among the micropollutants with decomposition rate of less than 60% in WTF (from the results of chapter 2).

3.2.2. Photo-reactor

The BPA degradation was performed in a circulating photo-reactor system consisting of a stirred reservoir, six UV lamps (Sanko Denki, Tokyo, Japan), a photo-reaction chamber, and a peristaltic pump (Master Flex model 7518-00, Cole-Parmer, Vernon Hills, IL, USA) for circulating the solution (Figure 3.1). The reaction solutions were recirculated continuously with a rotary pump at a flow rate of 1 L/min. The distance from the UV lamp to the quartz column was 20 mm. A Teflon tube was used for connecting the quartz columns (10 mm diameter, 650 mm length). The reactor around the quartz columns was covered with aluminum foil for UV safety and energy considerations (Figure 3.1).

The UV intensity, measured by a radiometer (VLX-3W Radiometer 9811-50; Cole-Parmer) at a distance of 20 mm, was 21.36 mW/cm². The initial pH was adjusted using trace amounts of 0.5 N HCl and NaOH with a pH meter (Model 52A, Orion, Reno, NV, USA).

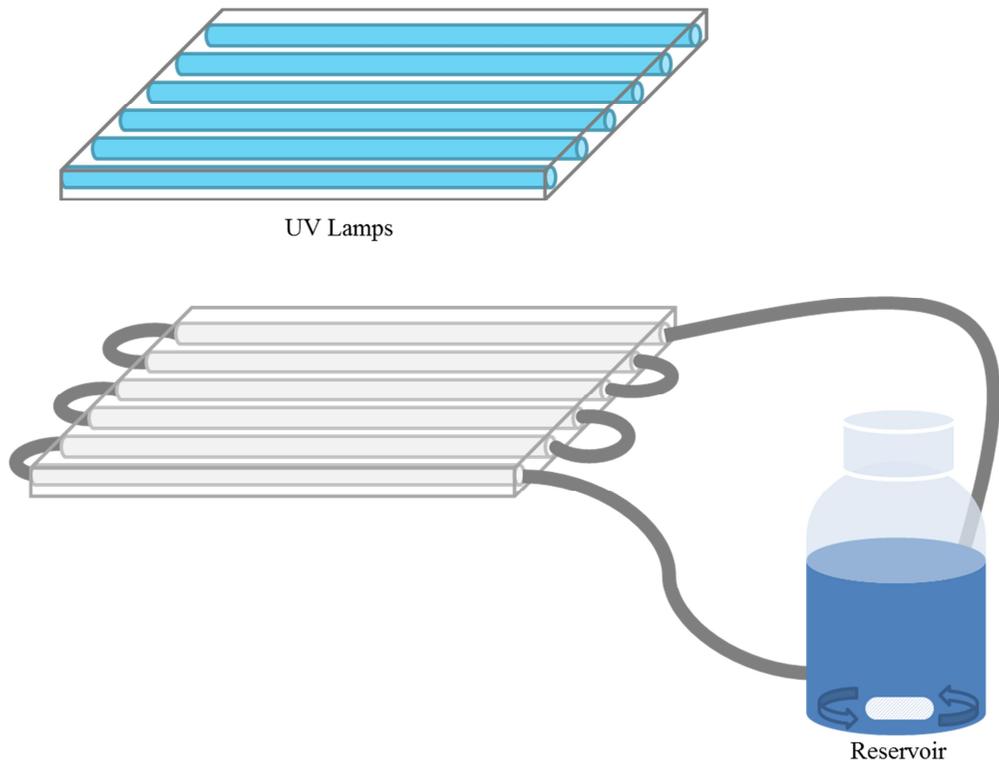


Figure 3.1 Schematic diagram of the reactor.

3.2.3. Experimental design

Experiments were conducted at pH 4, 7, and 11 using UV-C lamps to examine the effects of pH. Environmentally relevant concentrations of NO_3^- (0.04 - 0.4 mM), $\text{CO}_3^{2-}/\text{HCO}_3^-$ (0.4 - 4.0 mM), and humic acid (1 - 30 mg/L) on the degradation of BPA during UV-C photolysis and $\text{H}_2\text{O}_2/\text{UV-C}$ process were examined to know the effects of natural water constituents (Huang and Mabury 2000; KMOE 2016). To identify byproducts, 0.4 mM NO_3^- and 4 mM $\text{CO}_3^{2-}/\text{HCO}_3^-$ were used during UV-C photolysis and $\text{H}_2\text{O}_2/\text{UV-C}$ process. Samples were taken at each designated time using the sampling port. All experiments were conducted in triplicate to remove experiment and analysis errors.

The $\text{H}_2\text{O}_2/\text{UV-C}$ process, among AOPs, was selected due to its high OH radical production capacity and high scavenging effects. The UV-C photolysis was studied together to clearly understand the kinetic and degradation mechanism in the $\text{H}_2\text{O}_2/\text{UV-C}$ process.

3.2.4. Analysis

All samples taken at the selected times were filtered through a 0.45- μm polytetrafluoroethylene (PTFE) filter (Advantec, Dublin, CA, USA) to remove any suspended material before analysis. The concentration of BPA was determined using ultra-performance liquid chromatography (UPLC; Nexera, Shimadzu, Kyoto, Japan) equipped with an API-4000 mass spectrometer (AB Sciex, Concord, Ontario, Canada). The mobile phase was methanol and water (98:2, volume %) at a flow rate of 0.2 mL/min with a Luna C18 (2) column (150 mm \times 20 mm i.d., 3- μm particles; Phenomenex, Torrance, CA, USA) and the mass spectrometer was operated in negative ion mode [M-H]. The recovery of BPA was in the range of 95–108 % with stock solutions. The limits of detection (LOD) and quantification (LOQ) were determined using signal-to-noise (S/N) ratios with 3 and 10 was 1.99 ng/L and 6.65 ng/L, respectively.

OH radical concentrations were measured using an aminophenyl fluorescence (APF) probe, which is recognized as one of the most useful fluorescence probes for OH radical measurements due to its sensitivity and selectivity (Cohn et al., 2008). The concentration of the APF probe in each sample was 10 μM , and the fluorescence was measured by fluorescence spectroscopy (Infinite M200, TECAN, Männedorf, Switzerland) using a 96-well microplate (ViewPlateTM, Perkin-Elmer, Waltham, USA). Excitation and emission wavelengths were 490 and 515 nm, respectively.

3.2.5. Byproduct identification

Byproducts of BPA were identified with a triple quadrupole mass spectrometer (API-4000, AB Sciex). The sample was scanned fully to identify precursor ions and fragmentation of the identified precursor ions was conducted to examine the product ions using collisions with high-purity nitrogen gas.

ACD/MS Fragmenter software ver. 2015 (Advanced Chemistry Development, Inc., Toronto, Canada) was used to predict possible chemical structures and proposed byproduct formation pathways.

3.3. Results and discussion

3.3.1. Effects of pH on UV-C photolysis and H₂O₂/UV-C process

First, to examine the effects of the pH during UV-C photolysis and H₂O₂/UV-C process, experiments were conducted at pH 4, 7, and 11. The pH conditions were selected by considering the pK_a of BPA (pK_a = 10.2) and the environmentally reported levels because the pH of a solution can shift the molar absorption coefficients of a compound by changing the charge of the compound (Lu et al., 2013). Figure 3.2 shows the photodegradation of BPA under different pH.

Figure 3.2 (a) showed that a significant increase in BPA degradation during UV-C photolysis was obtained at pH 11 which is higher than the pK_a of BPA. The rate constants were 0.0019 min⁻¹ and 0.0027 min⁻¹ at pH 4 and 7, respectively, but the value became to be 0.0095 min⁻¹ at pH 11. This result can be explained by the change in the absorption coefficient of BPA at higher pH. Direct photodegradation occurs when a compound absorbs photons. Figure 3.3 shows the molar absorption coefficients of BPA according to pH values. Since the molar absorption coefficient of BPA is high at pH 11, direct photolysis of BPA is more effectively at the pH value. It was reported that the significant increase in the molar absorption coefficient at pH exceeding the pK_a of the compound is due to the effect of the substituent with unshared electrons where the length of the π -system increases via non-bonding

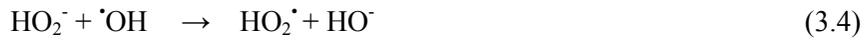
electrons through resonance (Lee and Von Gunten 2012; Adak et al., 2019).

The H₂O₂/UV-C process is one of the advanced oxidation processes (AOPs) via the generation of OH radicals by Eq. (3.1). Compared to UV-C photolysis, BPA removal efficiency increased from 24% to 96% in the presence of 0.05 mM H₂O₂ (at pH 7) during 120 min of reaction.



During the H₂O₂/UV-C process, degradation of BPA was more efficient in acid medium (pH 4). The rate constant was 0.0388 min⁻¹ at pH 4. It was at least two times faster than pH 11 values. Competing processes between the production of the hydroxyl radicals and the scavenging of hydroxyl radicals may cause the decrease in BPA removal with an increase in pH values. In alkaline medium, hydroperoxide anion (HO₂⁻) is produced and can improve the formation of OH radical via Eqs. (3.2) – (3.3). However, hydroperoxide anion also reacts with OH radical (as a scavenger) and H₂O₂ via Eqs. (3.4) - (3.5). Therefore, H₂O₂ loses its properties as an oxidant in neutral to basic medium via Eqs (3.1) – (3.4).





It should note that in $\text{H}_2\text{O}_2/\text{UV-C}$ process, alkaline condition also increases the direct decomposition rate of BPA. But OH radical generation is a critical factor to remove BPA in the indirect decomposition, the condition producing more OH radical determines the entire decomposition mechanism.

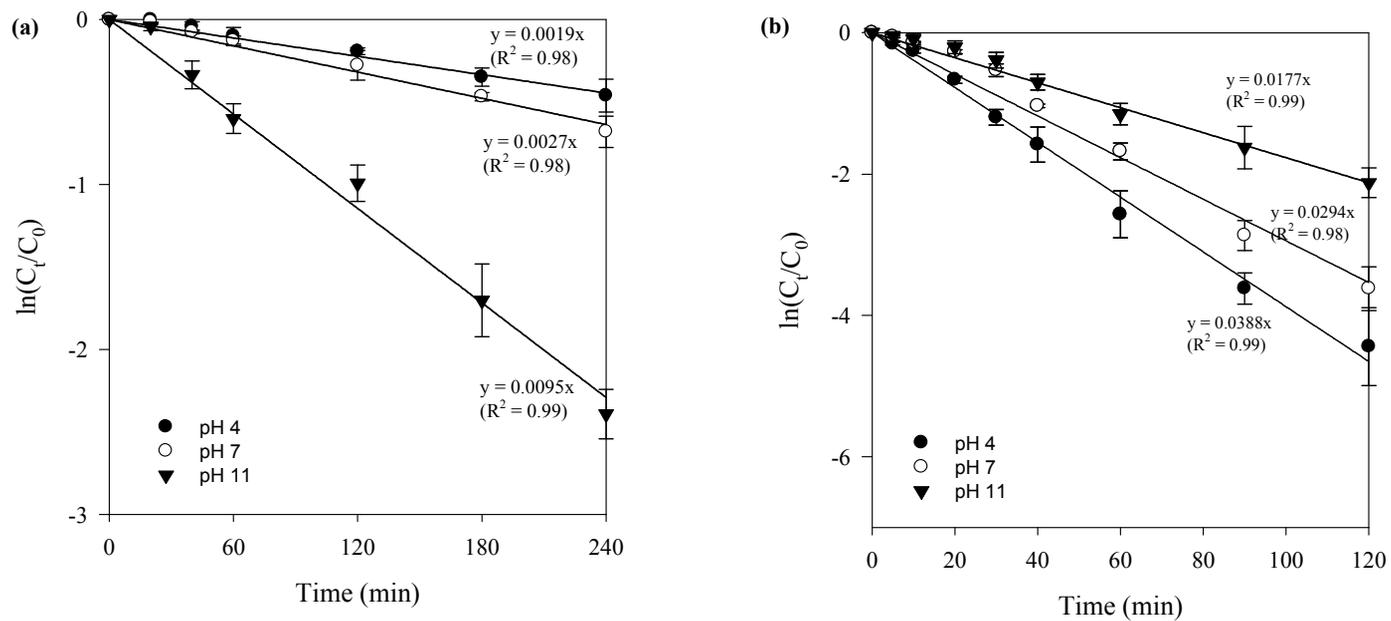


Figure 3.2 The photodegradation kinetics of BPA under (a) UV-C photolysis and (b) H_2O_2 /UV-C process at various pH values ($[BPA]_0 = 0.02$ mM, $[H_2O_2]_0 = 0.05$ mM, UV intensity = 21.36 mW/cm², Error bars represent the standard deviation of triplicate experiments).

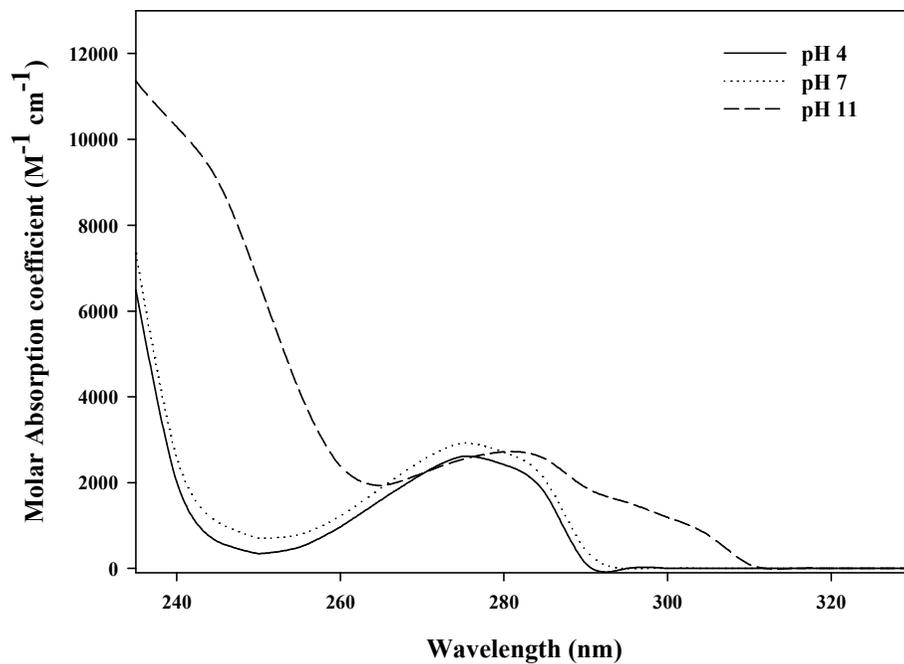


Figure 3.3 Molar absorption coefficient of BPA at pH 4, 7, and 11.

3.3.2. Effects of natural water components on UV-C photolysis and H₂O₂

/UV-C process

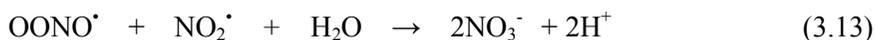
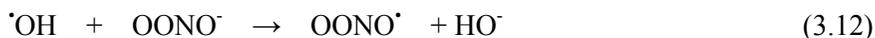
The effects of natural water constituents, such as NO₃⁻, CO₃²⁻/HCO₃⁻, and humic acid, on the degradation of BPA during UV-C photolysis and H₂O₂/UV-C process were examined using environmentally relevant concentrations (0.04 - 0.4 mM NO₃⁻ ions; 0.4 - 4.0 mM CO₃²⁻/HCO₃⁻ ions, and 1 - 30 mg/L humic acid) (Huang and Mabury 2000; KMOE 2016).

First, Figure 3.4(a) showed that the removal efficiency of BPA during UV-C photolysis increased in the presence of NO₃⁻ ions. All of the degradation rates were fitted into the pseudo-first-order kinetics ($R^2 > 0.98$). This result implies that, at higher NO₃⁻ concentrations, NO₃⁻ ion was used to induce radicals such as OH radical via Eqs. (3.6) - (3.9) (Mack and Bolton 1999).



Recent studies also suggested that many inducers can have negative effects by scavenging via Eqs. (3.10) to (3.13) (Mack and Bolton 1999; Boucheloukh et al.,

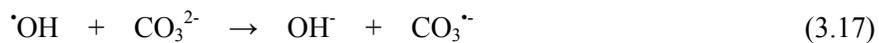
2012; Sharma et al., 2015b). However, the concentrations of NO_3^- ions used in the study did not have a negative effect on UV photolysis of BPA.



However, Figure 3.4(b) shows that nitrate reduced the BPA degradation during $\text{H}_2\text{O}_2/\text{UV-C}$ process. The rate constant of the $\text{H}_2\text{O}_2/\text{UV-C}$ system was 0.154 min^{-1} , but it was reduced to 0.1024 , 0.0556 , and 0.0432 min^{-1} as the concentration of NO_3^- increased. Due to the OH radical scavenging effect of NO_3^- , the removal efficiency of BPA consequently decreased with increase in the NO_3^- concentrations. As shown in Eq. (3.14), NO_3^- can react with OH radical and produces NO_3 radical (Gonzalez and Braun 1995; Park et al., 2014). The radical is able to also diminish BPA concentration but slower than OH radical (Parsons 2004). The oxidation potential of the radical ($E^\circ = 2.46 \text{ V}$) is lower than that of OH radical ($E^\circ = 2.8 \text{ V}$) (Armstrong et al., 2015). In addition, the reaction from the Eqs. (3.10) to (3.12) prevents OH radical to react with BPA.



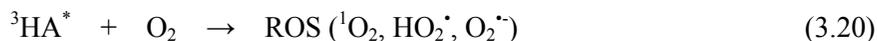
Next, Figure 3.5(a) shows that the direct photodegradation of BPA increased with $\text{CO}_3^{2-}/\text{HCO}_3^-$ and kinetics fit a pseudo-first-order reaction ($R^2 > 0.98$). The $\text{CO}_3^{2-}/\text{HCO}_3^-$ ions can enhance UV photolysis by producing hydroxide ion at alkaline pH by Eqs. (3.15) to (3.18) (Sánchez-Polo et al., 2013; Orellana-García et al., 2015), implying that $\text{CO}_3^{2-}/\text{HCO}_3^-$ ions at environmental levels have a positive effect on UV photolysis of BPA



On the other hand, $\text{CO}_3^{2-}/\text{HCO}_3^-$ reduced the BPA degradation during $\text{H}_2\text{O}_2/\text{UV-C}$ process (Figure 3.5(b)). The rate constant of the $\text{H}_2\text{O}_2/\text{UV-C}$ process was 0.154 min^{-1} , but it was decreased to 0.0585 , 0.0365 , and 0.0282 min^{-1} as the concentration

of $\text{CO}_3^{2-}/\text{HCO}_3^-$ increased. The presence of $\text{CO}_3^{2-}/\text{HCO}_3^-$ prevents OH radical from reacting with BPA (Park et al., 2015). The reaction of $\text{CO}_3^{2-}/\text{HCO}_3^-$ with OH radical is present in Eqs. (3.16) and (3.17). $\text{CO}_3^{\cdot-}/\text{HCO}_3^{\cdot-}$ can also degrade BPA, but oxidation potential of the radicals ($E^\circ = 1.78 \text{ V}$) are much lower than that of OH radical ($E^\circ = 2.8 \text{ V}$) (Parsons 2004; Merouani et al., 2010). In other words, $\text{CO}_3^{2-}/\text{HCO}_3^-$ in UV-C photolysis facilitated the decomposition of BPA by creating a production condition of OH radicals and $\text{CO}_3^{\cdot-}/\text{HCO}_3^{\cdot-}$ radicals. However, in the $\text{H}_2\text{O}_2/\text{UV-C}$ system, $\text{CO}_3^{2-}/\text{HCO}_3^-$ acted as a scavenger of OH radical.

The BPA solutions containing humic acid (1 to 30 mg/L) were also irradiated with UV-C light. As shown in Figure 3.6(a), less than 3 mg/L humic acid improved the BPA removal, while concentrations of higher than 3 mg/L inhibited the degradation of BPA. The enhanced photodegradation of BPA by humic acid at lower levels can occur because photons excite humic acid into a triplet state, which generates various reactive oxygen species (ROS) such as singlet oxygen ($^1\text{O}_2$), hydroperoxyl radicals (HO_2^{\cdot}), superoxide anions ($\text{O}_2^{\cdot-}$) (Zepp et al., 1985; Zhang et al., 2012; Zhang et al., 2014a). The ROS can attack and decompose BPA. The reactions are presented in Eqs. (3.19) to (3.20). However, higher levels of humic acid can lower the penetration of UV light, which lower removal efficiency of BPA during UV-C photolysis. Other studies have also reported that humic acid both promoted and inhibited photodegradation (Stangroom et al., 1998).



Humic acid was also added to the H₂O₂/UV-C reaction of BPA. Zhang et al. (2013) reported that HA can react as a photosensitizer even in the presence of permanganate (KMnO₄). In our study, HA is, however, found to adversely affect the degradation of BPA during the H₂O₂/UV-C reaction (Figure 3.6(b)). The rate constants of the H₂O₂/UV-C process in the presence of 1, 15, and 30 mg/L HA were 0.0195, 0.0138, and 0.0065 min⁻¹ as compared to 0.154 min⁻¹ without HA. HA clearly acted as OH radical scavenger and as inner filter. At high concentration, the HA may in competition with BPA for OH radical, which reduces the amount of OH radical for BPA degradation. Because HA contains a large amount of organic matter. The increase of HA also lowers the transparency, which inhibits the photons to pass the water solution.

Compared with 0.4 mM of NO₃⁻, 4 mM of CO₃²⁻/HCO₃⁻, and 3 mg/L of humic acid which showed the highest rate constants during the UV-C photolysis, NO₃⁻ showed the greatest promoter of the degradation of BPA followed by CO₃²⁻/HCO₃⁻ and HA (Figure 3.7(a)). As in Eq. (3.6), NO₃⁻ reacted directly with photons to produce radicals. On the other hand, CO₃²⁻/HCO₃⁻ destructed BPA in two steps. First, the reaction of UV-C and OH⁻ produced OH radical. After the reaction, the

secondary products such as $\text{CO}_3^{\cdot-}/\text{HCO}_3^{\cdot}$ generated by the OH radical attacked BPA. In addition, the amount of OH radicals produced during UV-C photolysis was higher at UV-C photolysis with NO_3^- than UV-C photolysis with $\text{CO}_3^{2-}/\text{HCO}_3^-$ (Figure 3.8). HA degraded BPA by generating ROS, but HA, brownish substance, inhibited UV-C irradiation to pass through the reaction mixture from the point of time when it was put into the water.

When 0.4 mM of NO_3^- , 4 mM of $\text{CO}_3^{2-}/\text{HCO}_3^-$, and 3 mg/L of humic acid were used during the $\text{H}_2\text{O}_2/\text{UV-C}$ reaction, humic acid showed the greatest inhibition of the degradation of BPA followed by $\text{CO}_3^{2-}/\text{HCO}_3^-$ and NO_3^- ions (Figure 3.7(b)). The highest inhibition in the presence of humic acid during the $\text{H}_2\text{O}_2/\text{UV}$ reaction can be due to the inhibition of photon penetration through the solution by humic acid (Gao and Zepp 1998). When humic acid was added to the solution, the solution became brown; suggesting that humic acid in solution reduces the penetration of photons produced by UV photolysis. In addition, HA contains a large amount of organic matter. The HA may in competition with BPA for OH radical. The next strongest inhibitor was $\text{CO}_3^{2-}/\text{HCO}_3^-$ ions. This can be explained by the rate constant of the OH radical and its concentration in water. The reported rate constants between the OH radical and water component are $1.0 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ for NO_3^- , $3 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ for CO_3^{2-} , and $8.5 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ for HCO_3^- , respectively (Buxton et al., 1988; Gonzalez and Braun 1995). This result indicates that the OH radical can be scavenged by $\text{CO}_3^{2-}/\text{HCO}_3^-$ ions much faster than by NO_3^- ion. In addition, natural water typically

contains almost 10 times more $\text{CO}_3^{2-}/\text{HCO}_3^-$ than NO_3^- ion (Huang and Mabury 2000).

To verify the presence of these radicals, particularly OH radical, we measured OH radical using APF (3'-p-(aminophenyl) fluorescein) probe during UV photolysis in the presence of NO_3^- , $\text{CO}_3^{2-}/\text{HCO}_3^-$, and $\text{NO}_3^-/\text{CO}_3^{2-}/\text{HCO}_3^-$, respectively. APF is recognized as one of the most useful fluorescence probes for OH radical due to its sensitivity and selectivity. The APF probe emits strong fluorescence after reaction with OH, while its reactions with H_2O_2 and O_2^- radical are negligible (Inagaki et al., 2016). As shown in Figure 3.8, we observed that OH radicals are produced during UV-C photolysis in the presence of NO_3^- , $\text{CO}_3^{2-}/\text{HCO}_3^-$, and $\text{NO}_3^-/\text{CO}_3^{2-}/\text{HCO}_3^-$ during UV-C photolysis.

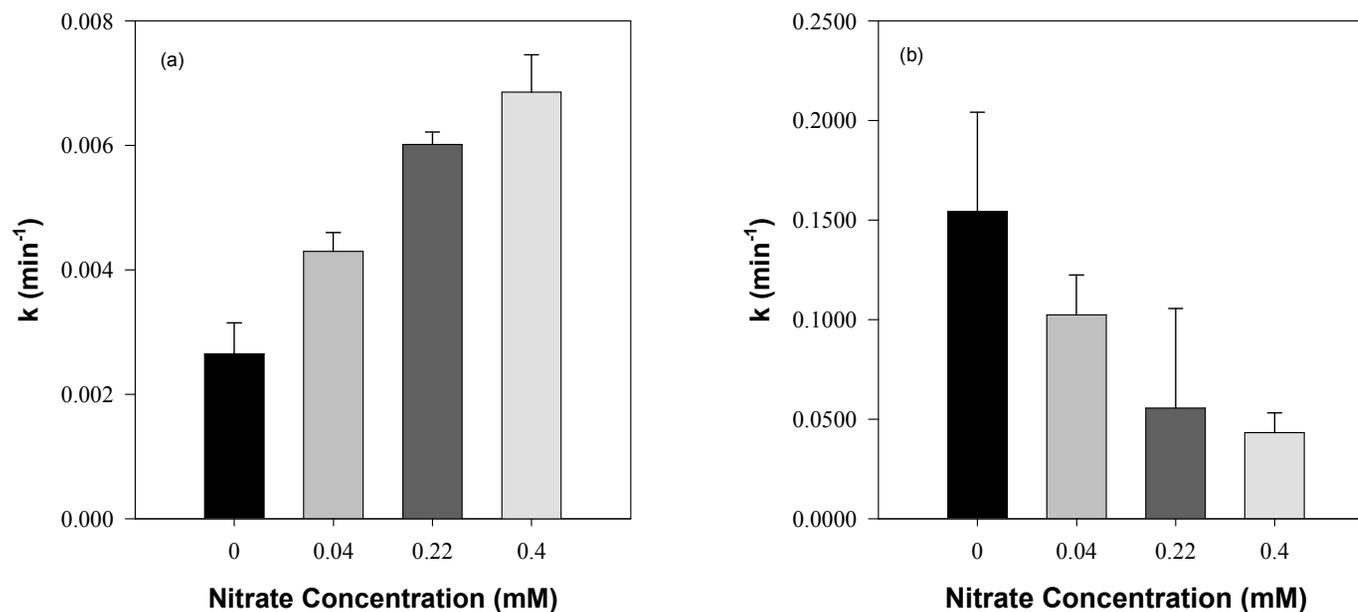


Figure 3.4 Effect of nitrate on BPA degradation during (a) UV-C photolysis and (b) H₂O₂/UV-C process ([BPA]₀ = 0.02 mM, [H₂O₂]₀ = 0.2 mM, UV-C intensity = 21.36 mW/cm², pH = 6.8 - 7.4, Reaction time = 4 h for UV-C photolysis, 2 h for H₂O₂/UV-C process, Error bars represent the standard deviation of triplicate experiments).

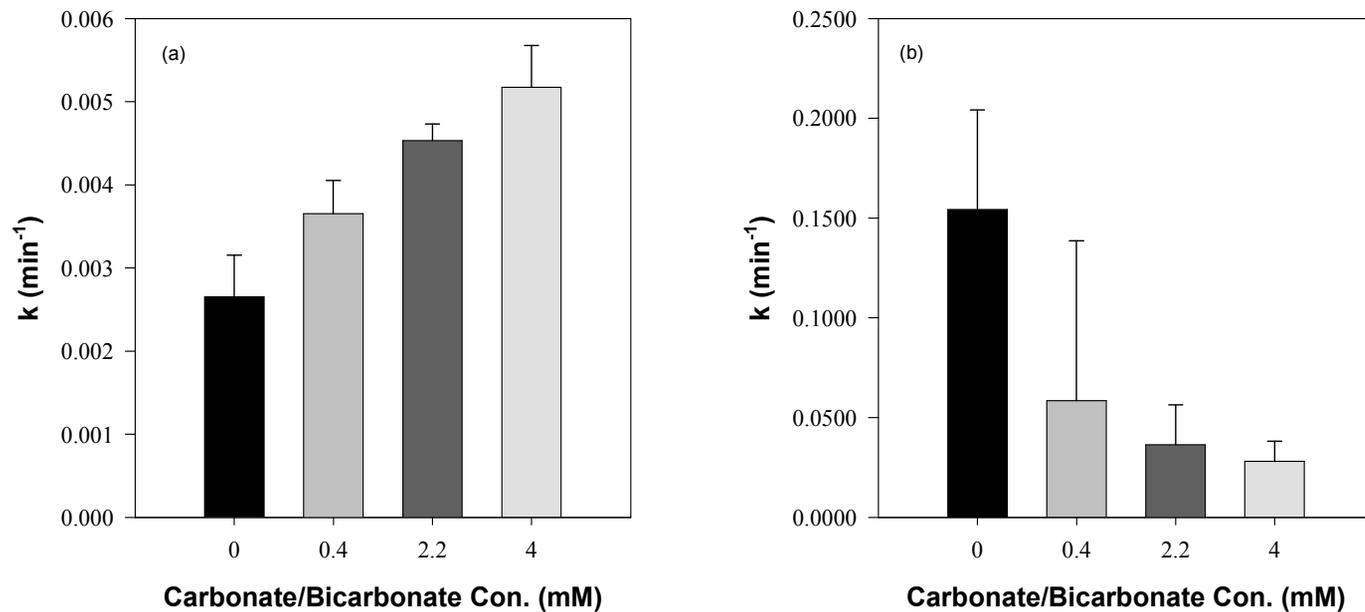


Figure 3.5 Effect of carbonate/bicarbonate on BPA degradation during (a) UV-C photolysis and (b) H₂O₂/UV-C process ([BPA]₀ = 0.02 mM, [H₂O₂]₀ = 0.2 mM, UV-C intensity = 21.36 mW/cm², pH = 6.8 - 9.3, Reaction time = 4 h for UV-C photolysis, 2 h for H₂O₂/UV-C process, Error bars represent the standard deviation of triplicate experiments).

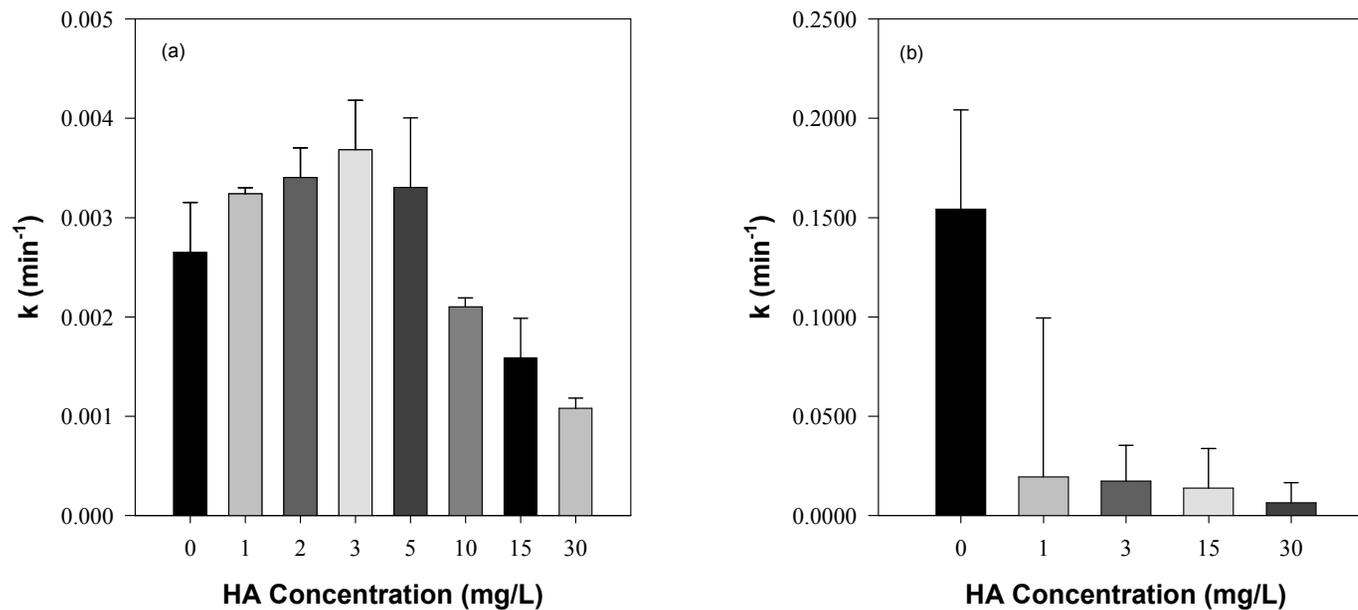


Figure 3.6 Effect of humic acid on BPA degradation during (a) UV-C photolysis and (b) H₂O₂/UV-C process ([BPA]₀ = 0.02 mM, [H₂O₂]₀ = 0.2 mM, UV-C intensity = 21.36 mW/cm², pH = 6.8 - 8.1, Reaction time = 4 h for UV-C photolysis, 2 h for H₂O₂/UV-C process, Error bars represent the standard deviation of triplicate experiments).

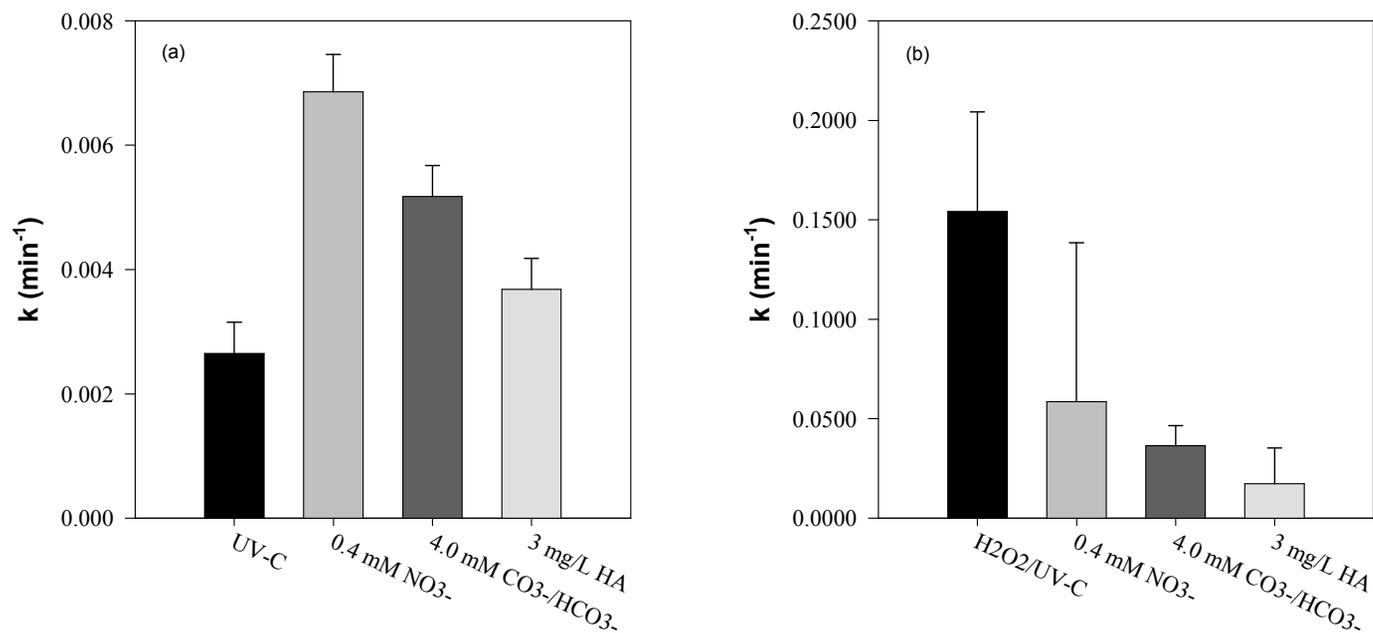


Figure 3.7 Comparison of nitrate, carbonate/bicarbonate, and humic acid on BPA degradation during (a) UV-C photolysis and (b) H₂O₂/UV-C process ([BPA]₀ = 0.02 mM, [H₂O₂]₀ = 0.2 mM, UV-C intensity = 21.36 mW/cm², pH = 6.8 - 8.1, Reaction time = 4 h for UV-C photolysis, 2 h for H₂O₂/UV-C process, Error bars represent the standard deviation of triplicate experiments).

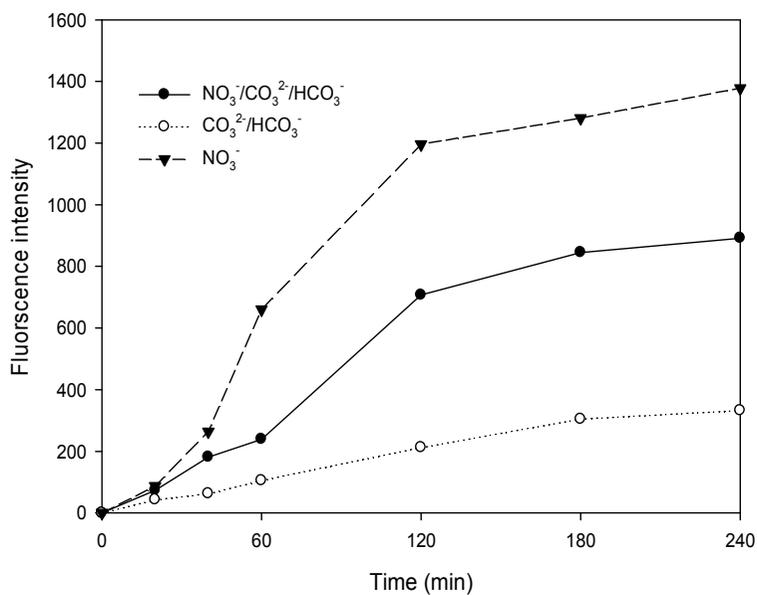


Figure 3.8 OH radical produced during UV-C photolysis in the presence of NO_3^- , $\text{CO}_3^{2-}/\text{HCO}_3^-$, and $\text{NO}_3^-/\text{CO}_3^{2-}/\text{HCO}_3^-$.

3.3.3. Byproducts identification during UV photolysis and H₂O₂/UV-C process in the presence of water components

Since different byproducts are formed depending on the oxidant type and reaction conditions (Liu et al., 2010; Sharma et al., 2015b; Sharma et al., 2016), the byproducts of BPA generated during UV-C photolysis and H₂O₂/UV-C process in the presence of NO₃⁻, CO₃²⁻/HCO₃⁻, and both ions together, were identified using LC-MS/MS. UV-C photolysis and H₂O₂/UV-C reaction were conducted for 10 h and 4 h in the presence of 0.4 mM NO₃⁻ or 4 mM CO₃²⁻/HCO₃⁻ to identify byproducts generated from BPA. Table 3.1 and 3.2 summarized the identified byproducts of BPA with the retention time and ions, using LC-MS/MS analysis and the ACD/MS Fragmenter program. For example, the program identified peak 1 of Table 3.1 as 4-nitrophenol with fragment ion peaks at m/z 122 (M-1-16) and 92 (M-1-46), resulting from the losses of O and NO₂, respectively. Peak 1 of Table 3.2 was identified as 2-(4-hydroxyphenyl)-2-methylpropanal, with a parent peak at m/z 163 (M-1) and fragments at m/z 147 (M-1-16), m/z 134 (M-1-29), and 92 (M-1-71), indicating the loss of O, CHO, and CCH₃CH₃CHO functional groups, respectively.

The number and magnitude of the peaks in the chromatograms initially increased as the reactions proceeded, and then decreased. This result indicates that produced byproducts were generated and then decomposed with further reaction. However, the generation and decomposition times of each peak differed. In addition,

the peaks in the chromatograms differed depending on the ions added.

As presented in Table 3.1, the UV-C photolysis with NO_3^- produced the greatest number of peaks (eight byproducts), followed by UV-C photolysis with $\text{NO}_3^-/\text{CO}_3^{2-}/\text{HCO}_3^-$ (four peaks) and UV-C photolysis with $\text{CO}_3^{2-}/\text{HCO}_3^-$ (three peaks). It was reported that nitration and hydroxylation have been observed due to NO_2 and OH radicals during the UV photolysis in the presence of NO_3^- ions (Shankar et al., 2007; Sharma et al., 2016). This implies that NO_2 and OH radicals are the main cause for the larger number of byproducts during UV-C/ NO_3^- photolysis, resulting in the generation of nitrogenated- and hydrogenated- byproducts.

In comparison, no nitrogenated byproducts were observed during UV-C photolysis of BPA in the presence of $\text{NO}_3^-/\text{CO}_3^{2-}/\text{HCO}_3^-$ ions. This result can be explained by the small amount of NO_2 radicals produced due to the low quantum yield of NO_2 radical ($\Phi=0.09$), and reactions of the produced NO_2 radical with $\text{CO}_3^{2-}/\text{HCO}_3^-$ ions (Denicola et al., 1996; Mark et al., 1996; Ninomiya et al., 2000; Wu and Linden 2010). However, only hydrogenated byproducts were formed during UV-C/ $\text{NO}_3^-/\text{CO}_3^{2-}/\text{HCO}_3^-$ photolysis, indicating that the OH radical is produced in sufficient amounts to be the main cause during the UV-C photolysis of BPA in the presence of $\text{NO}_3^-/\text{CO}_3^{2-}/\text{HCO}_3^-$.

Interestingly, no hydrogenated byproducts or adducts (addition products) were detected during the UV-C photolysis of BPA in the presence of $\text{CO}_3^{2-}/\text{HCO}_3^-$ ions. It was reported that $\text{CO}_3^-/\text{HCO}_3$ radicals are generated during UV photolysis in the

presence of $\text{CO}_3^{2-}/\text{HCO}_3^-$ ions and these radicals can promote the degradation of pollutants (Sánchez-Polo et al., 2013; Orellana-García et al., 2015). In our study, BPA was broken down into smaller molecules without producing an adduct during UV-C/ $\text{CO}_3^{2-}/\text{HCO}_3^-$ photolysis, indicating that $\text{CO}_3^{2-}/\text{HCO}_3^-$ ions inhibited OH radical addition into BPA to produce hydroxylated byproducts and $\text{CO}_3^{\cdot-}/\text{HCO}_3^{\cdot-}$ were the predominant radicals to destroy BPA.

In the $\text{H}_2\text{O}_2/\text{UV-C}$ process, four byproducts were detected regardless of input ions (Table 3.2). During the all $\text{H}_2\text{O}_2/\text{UV-C}$ reactions with ions, hydrogenated byproducts were detected, but nitrogenated byproducts were not found. Compared to UV-C photolysis, $\text{H}_2\text{O}_2/\text{UV-C}$ system produces enormous amount of OH radical (Bali et al., 2004). Therefore, in the $\text{H}_2\text{O}_2/\text{UV-C}$ reaction, OH radical would have decomposed BPA as a predominant radical. This would result in the same byproducts, regardless of the presence of water matrix. For example, during $\text{H}_2\text{O}_2/\text{UV-C}$ with NO_3^- reaction, NO_2 radical could be generated, but much smaller amount than OH radical and have limited reaction with BPA. The same mechanism also observed during UV-C/ $\text{NO}_3^-/\text{CO}_3^{2-}/\text{HCO}_3^-$ photolysis, which sufficient amount of OH radicals inhibited generation of nitrogenated byproducts.

Table 3.1 Structure and mass spectra data for the byproducts during UV-C photolysis in the present of natural water components, as determined from LC/MS/MS.

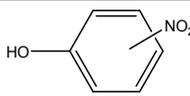
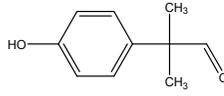
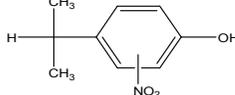
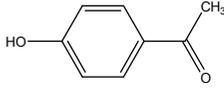
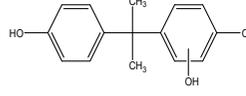
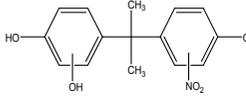
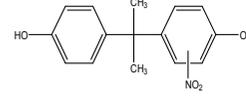
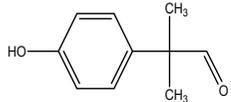
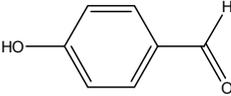
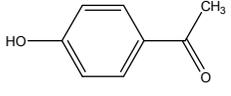
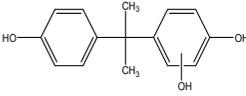
Peak (byproduct #)	Retention time (min)	Detected ions (m/z)		Possible byproducts	Water matrix		
		MS	MS/MS		NO ₃ ⁻	NO ₃ ⁻ /CO ₃ ²⁻ /HCO ₃ ⁻	CO ₃ ²⁻ /HCO ₃ ⁻
1	1.11	138	122, 92, 76		○		
2	2.17	163	147, 134, 92		○	○	○
3	2.31	121	105, 92, 93		○	○	○
4	2.65	180	165, 137, 134		○		
5	2.99	135	119, 93, 92, 76		○	○	○
6	3.08	243	226, 228, 150		○	○	
7	3.31	288	273, 271, 242, 179, 150		○		
8	4.04	272	257, 226, 179, 134		○		

Table 3.2 Structure and mass spectra data for the byproducts during H₂O₂/UV-C process in the present of natural water components, as determined from LC/MS/MS.

Peak (byproduct #)	Retention time (min)	Detected ions (m/z)		Possible byproducts	Water matrix		
		MS	MS/MS		NO ₃ ⁻	NO ₃ ⁻ /CO ₃ ²⁻ /HCO ₃ ⁻	CO ₃ ²⁻ /HCO ₃ ⁻
1	2.17	163	147, 134, 92		○	○	○
2	2.31	121	105, 92, 93		○	○	○
3	2.99	135	119, 93, 92, 76		○	○	○
4	3.08	243	226, 228, 150		○	○	○

3.3.4. Proposed mechanism of BPA degradation

The mechanism of pollutant degradation depends on the water matrix during UV photolysis because different radicals are generated (Sánchez-Polo et al., 2013; Sharma et al., 2015b; Sharma et al., 2016). However, the water matrix does not affect the formation of byproducts in H₂O₂/UV-C process due to predominant of OH radical.

The BPA byproducts generated during the UV photolysis with NO₃⁻ and NO₃⁻/CO₃²⁻/HCO₃⁻ and H₂O₂/UV-C with ions can be classified into two groups; the first group appeared in the early stage of reactions, while the second groups were generated in the middle of reactions. In the early stage of degradation, the electrophilic OH and NO₂ radicals can attack electron-rich positions (*i.e.*, the phenyl ring), resulting in the addition of these radicals to BPA and the formation of hydrogenated and nitrogenated byproducts (Nélieu et al., 2008; Torres et al., 2008). This reaction can lead to the formation of byproducts 6 to 8 in UV-C/NO₃⁻ photolysis (Table 3.1), and byproduct 6 in UV-C/NO₃⁻/CO₃²⁻/HCO₃⁻ photolysis (Table 3.1), and byproduct 4 in H₂O₂/UV-C process with ions (Table 3.2).

As UV-C photolysis and H₂O₂/UV-C process progresses, the byproducts generated in the early stages decreased as the number of new byproducts increased. The β-scission (C–C bond) of the isopropyl group of BPA by radical attack can break BPA into smaller byproducts (Cui et al., 2009; Zhang et al., 2013). This

reaction can result in the formation of byproduct 1 through 5 during UV-C/NO₃⁻ photolysis (Table 3.1), byproduct 2, 3, and 5 during UV-C/NO₃⁻/CO₃²⁻/HCO₃⁻ photolysis (Table 3.1), and byproduct 1, 2, and 3 during H₂O₂/UV-C process with water matrix (Table 3.2).

However, during UV-C/CO₃²⁻/HCO₃⁻ photolysis, hydrogenated or nitrogenated byproducts or other adduct products were not observed (Table 3.1). This result implies that, instead of producing adduct product by OH and NO₂ radicals, BPA can be degraded directly into smaller byproducts during UV-C/NO₃⁻/CO₃²⁻/HCO₃⁻ photolysis. The methyl group of BPA can be attacked directly by CO₃⁻/HCO₃ radicals, resulting in the production of byproduct 2, 3, and 5 by β-scission of the C–C bond of the isopropyl group (Table 3.1).

Based on the identification of byproducts, and the generation and decomposition of the byproduct, we proposed the mechanisms of BPA degradation during UV-C photolysis and H₂O₂/UV-C process when ions were presented (Figure 3.9). As illustrated in Figure 3.9, UV-C/NO₃⁻ photolysis of BPA produced nitrogenated byproducts. It is reported that nitrogenated byproducts are more toxic than the mother compound (Zhan et al., 2006). The acute toxicity of the byproduct (peak 1 of Table 3.1) based on the dermal LD₅₀ is reported as 16 times higher than that of BPA (Kitajima et al., 2006; Guo et al., 2014). However, UV-C/CO₃²⁻/HCO₃⁻ photolysis and H₂O₂/UV-C process inhibited the generation of nitrogenated byproducts (Figure 3.9). This result implied that the production of nitrogenated

byproducts of BPA can be inhibited by $\text{CO}_3^{2-}/\text{HCO}_3^-$ ions and OH radical.

Thus our results clearly show that fewer nitrogenated byproducts can be produced during $\text{H}_2\text{O}_2/\text{UV-C}$ process and $\text{UV}/\text{CO}_3^{2-}/\text{HCO}_3^-$ photolysis. $\text{CO}_3^{2-}/\text{HCO}_3^-$ ions can be supplied into surface waters by CO_2 from the atmosphere. These ions exists with much higher levels than NO_3^- ion in surface waters, fewer nitrogenated byproducts can be produced during UV photolysis of BPA under natural water environment.

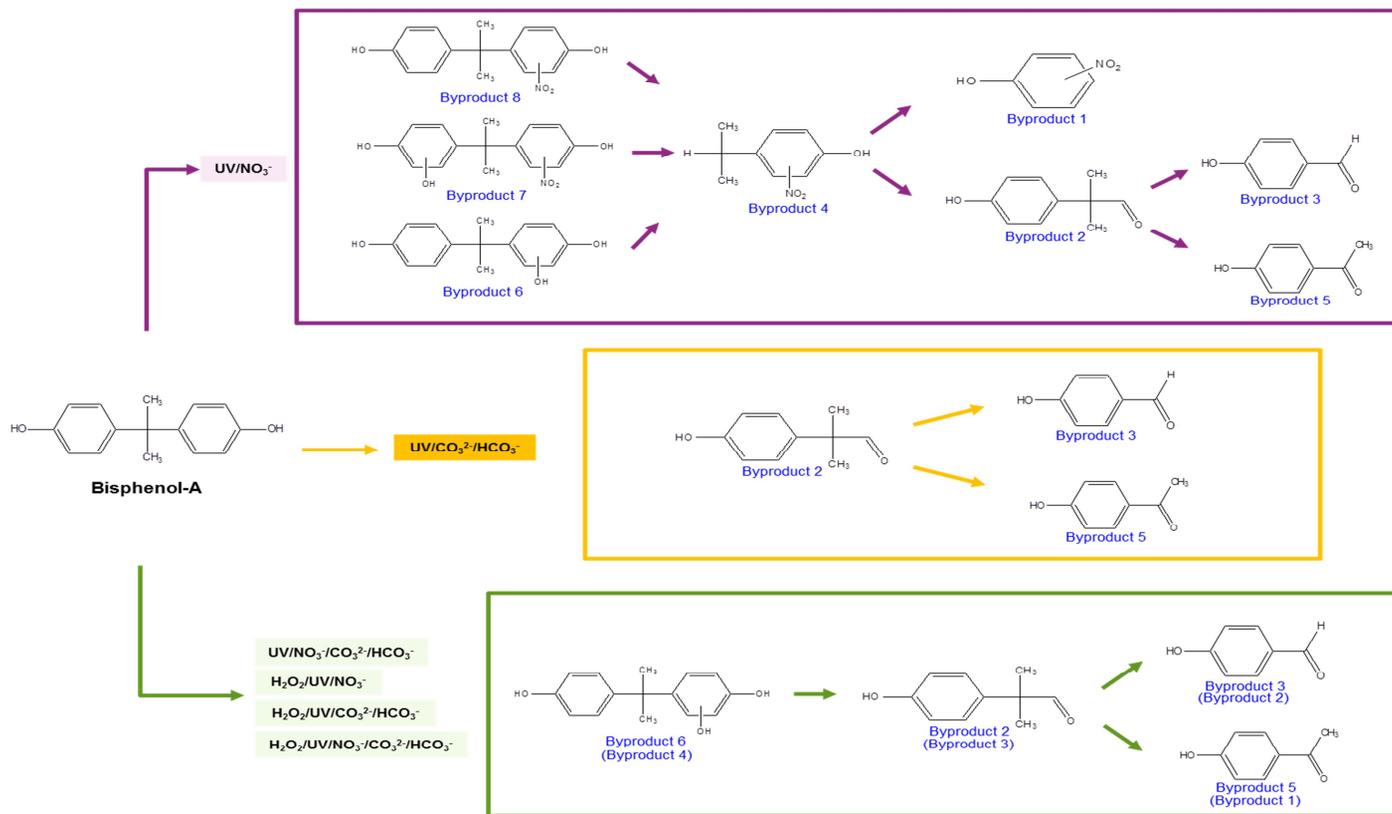


Figure 3.9 The proposed degradation pathway of BPA during UV-C photolysis and H₂O₂/UV-C process on water component present (the parentheses represent the detected peak numbers at H₂O₂/UV-C process).

3.4 Conclusion

We examined BPA degradation mechanisms in the presence of natural compounds during UV photolysis and the H₂O₂/UV process. BPA removal efficiency was increased dramatically when the solution pH was higher than the pK_a of BPA, due to the increased molar absorption coefficient of BPA at higher pH during UV-C photolysis. However, during the H₂O₂/UV-C process, degradation of BPA was more efficient in acid condition (pH 4) due to low productivities of hydroxyl radicals in alkaline medium. BPA degradation was more effective during the H₂O₂/UV reaction. NO₃⁻ and CO₃²⁻/HCO₃⁻ ions at environmentally reported concentration promoted BPA degradation during UV-C photolysis because these ions can produce NO₂ and CO₃⁻/HCO₃ radicals under UV photolysis. Humic acid acted as a promoter at concentrations less than 3 mg/L humic acid, but as a radical scavenger when exceeding 5 mg/L. NO₃⁻, CO₃²⁻/HCO₃⁻ ions, and humic acid, however, inhibited the BPA degradation during H₂O₂/UV-C process, in the order humic acid > CO₃²⁻/HCO₃⁻ > NO₃⁻.

The byproducts identified during UV-C photolysis were different depending on water component present. Nitrogenated- and hydrogenated byproducts of BPA were identified during the UV-C/NO₃⁻ photolysis, while only hydrogenated byproducts of BPA were detected in the UV-C/NO₃⁻/CO₃²⁻/HCO₃⁻ photolysis, implying that CO₃²⁻

HCO_3^- ions prevented generation of nitrogenated byproducts. No hydrogenated byproduct was detected during the UV-C/ CO_3^{2-} / HCO_3^- photolysis. In the ions/ H_2O_2 /UV-C process, four byproducts were detected regardless of input ions. During the all ions/ H_2O_2 /UV-C reactions, hydrogenated byproducts were detected, but nitrogenated byproducts were not found. Due to enormous amount of OH radical produced during H_2O_2 /UV-C process, ions seem to have no affect to byproducts.

The number and magnitude of the peaks in the chromatograms initially increased as the reactions proceeded, and then decreased. This result indicates that produced byproducts were generated and then decomposed into smaller compounds during the UV-C/ NO_3^- , UV-C/ $\text{NO}_3^-/\text{CO}_3^{2-}/\text{HCO}_3^-$, and ions/ H_2O_2 /UV-C reactions. In comparison, BPA was decomposed into smaller compounds via β -scission of the isopropyl group by radical attacks during UV-C/ $\text{CO}_3^{2-}/\text{HCO}_3^-$ photolysis reaction.

Chapter 4.

Greenhouse gas emissions during the degradation of bisphenol-A in advanced oxidation processes: A Comparative Study of H₂O₂/UV, TiO₂/UV, and O₃

4.1. Introduction

Bisphenol-A (BPA) is an endocrine-disrupting compound (EDC) that is used as a raw material in polycarbonate and epoxy resins. It can accumulate in natural waters and cause reproductive damage to aquatic organisms due to its low elimination efficiency in wastewater treatment plants (WWTPs) (Vethaak et al., 2005; Tran et al., 2015). In recent decades, there has been much interest in the development of effective treatment processes to decompose BPA in contaminated water sources.

Anthropogenic emissions of greenhouse gases (GHG) have been attracting public attention due to the considerable increase in the concentration of these gases in the atmosphere over the past 100 years and their role in global climate change (El-Fadel and Massoud, 2001). The United Nations Framework Convention on Climate Change (UNFCCC) is the global platform for collective action aimed at reducing GHG emissions. Since the adoption of the Paris Agreement, in which delegates from 195 countries agreed to reduce GHG emissions according to their intended nationally determined contribution (INDC), the UNFCCC has had an impact on the reduction of global GHG emissions (Geden, 2016).

Advanced oxidation processes (AOPs) can oxidize non-biodegradable organics, such as dyes, EDCs, and pharmaceuticals and personal care products (PPCPs) through the in situ generation of strong oxidants (Bolton et al., 2001). Several

processes have been studied to determine their potential as AOPs. Some AOPs, such as ozonation- and UV-based processes, have been investigated extensively and applied in water treatment plants (WTPs) and water reuse facilities (Meneses et al., 2010; Drewes and Khan 2015). Emerging AOPs, such as photo catalysts, have been studied by various researchers (Kanakaraju et al., 2018).

WTPs and WWTPs are well known sources of GHG emissions, and there have been many attempts to estimate the amount of GHG emissions that they release (Gu et al., 2016). However, most investigations have estimated the GHG emissions from physical and biological treatment processes (Shahabadi et al., 2009; Mander et al., 2014; Mannina et al., 2016; Parravicini et al., 2016). Recently, many AOPs have been used in WTPs and WWTPs to treat emerging micropollutants. However, AOPs require enormous amounts of energy and chemicals for effective treatment. Therefore, AOPs may emit large amounts of GHGs from scope II and III. Nevertheless, there have been few studies of GHG emissions during the operation of AOPs, and only a few studies have estimated and compared GHG emissions during AOPs such as ozonation, and UV photolysis (Munoz et al., 2009; Pasqualino et al., 2011).

Therefore, the aim of this study was to estimate and compare the GHG emissions from AOPs using three laboratory scale processes: $\text{H}_2\text{O}_2/\text{UV}$, TiO_2/UV , and ozonation processes. To analyze GHG emissions in AOPs, BPA was selected due to its high production, utilization, health effects, and the low removal efficiency

and the high concentration in the discharge of private WTF (the result of chapter II). We compared the degradation efficiency of BPA and GHG emissions during three AOPs. The amount of GHG emissions was calculated during manufacturing, usage, and disposal in terms of the life cycle to provide basic data for GHG reduction. Lastly, the optimum process for the treatment of BPA in terms of GHG emissions was determined.

4.2. Materials and methods

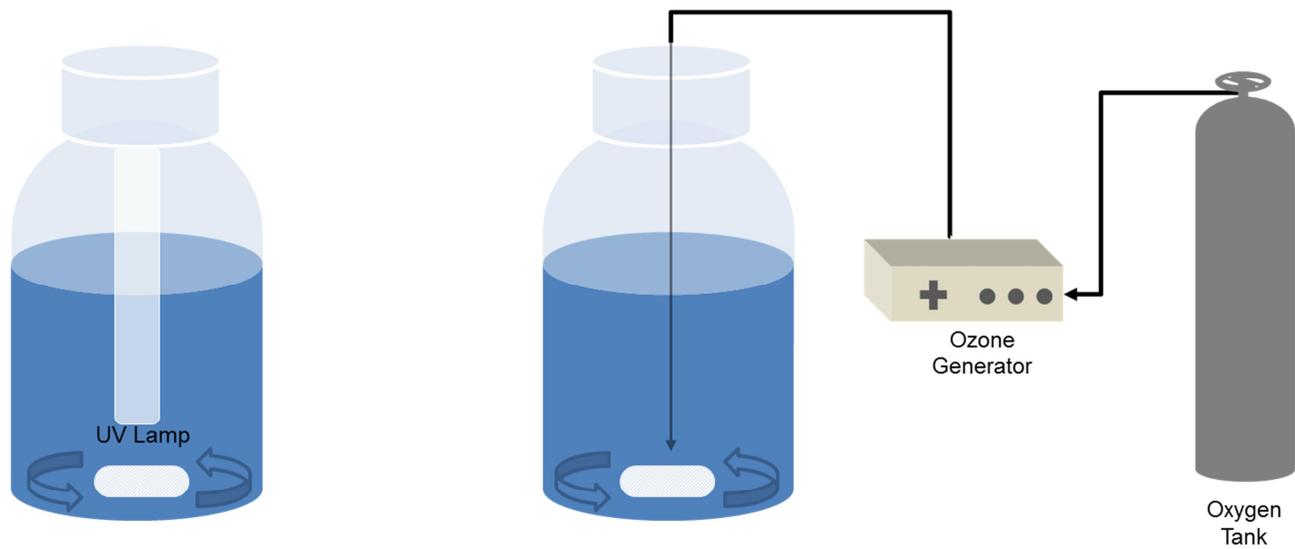
4.2.1. Chemicals

Bisphenol-A (BPA, $C_{15}H_{16}O_2$, 99%) was purchased from Sigma-Aldrich (St. Louis, MO, USA). BPA was selected because of its highest concentration in WTF effluent among the micropollutants with decomposition rate of less than 60% in WTF (from the results of chapter 2). However, BPA has limitations that cannot represent nitrogen-containing substances. To prepare the stock solution, BPA was dissolved in deionized water obtained with a Milli-Q Water Purification System (Millipore, Burlington, MA, USA) to make a concentration of 0.04 mM. Hydrogen peroxide (H_2O_2 , 50%) was purchased from Sigma-Aldrich (St. Louis, MO, USA) as a radical promoter. Titanium dioxide (P25; Degussa Co., Augsburg, Germany), with an average particle size of 30 nm and Brunauer–Emmett–Teller (adsorption isotherm) surface areas of $50 \pm 15 \text{ m}^2/\text{g}$, was used as a photocatalyst. Sodium thiosulfate ($Na_2S_2O_3$, 99%) was purchased from Sigma-Aldrich and used as a residual ozone quencher.

4.2.2. Experimental design

The BPA degradation was performed in a batch-type photo-reactor equipped with a UV lamp (4W, Sankyo Electronics Co., Ltd., Inazawa, Japan) for H₂O₂/UV and TiO₂/UV reactions. For the ozonation experiment, a batch-type ozone-reactor equipped with an ozone generator (140W, OZONIZER, Model GEA-C020, Korea) was used. The reactor system consists of a stirred 2-L glass bottle with a sampling valve. The reactor around was covered with aluminum foil for UV safety and energy considerations. A schematic illustration of the reactors is shown in Figure 4.1.

Before conducting the photo-experiments, a UV lamp was turned on for 30 min to stabilize. The UV intensity, measured by a radiometer (VLX-3W Radiometer 9811-50; Cole-Parmer) at a distance of 20 mm, was 3.8 mW/cm². For the ozone experiment, gaseous ozone was continuously injected by an ozone generator using oxygen (>99.9% purity) as the feed gas. The ozone concentrations were adjusted by changing the oxygen flow rate from 0.5 to 1.4 L/min. A 24 mM sodium sulfite solution (98%, ACS reagent, Sigma-Aldrich) was used to quench residual ozone in the sample. All experiments were carried out in a thermostatic chamber with a temperature of 24 ± 1 °C.



(a) $\text{H}_2\text{O}_2/\text{UV}$ and TiO_2/UV Reactor

(b) Ozone Reactor

Figure 4.1 Schematic diagrams of (a) $\text{H}_2\text{O}_2/\text{UV}$ and TiO_2/UV reactor and (b) Ozone reactor.

4.2.3. Analysis

During the photoreaction, a 6 mL sample was taken at various time points and filtered through a 0.45-mm polytetrafluoroethylene (PTFE) filter (Advantec, Dublin, CA, USA) to remove the catalyst or particle suspensions before analysis. The BPA concentration was determined using ultra-performance liquid chromatography (UPLC; Nexera, Shimadzu, Kyoto, Japan) equipped with an API-4000 mass spectrometer (AB Sciex, Concord, Ontario, Canada) and a Luna C18 (2) column (150mm × 20mm i.d., 3-µm particles; Phenomenex, Torrance, CA, USA). The mass spectrometer was operated in negative ion mode [M - H] and the mobile phase was methanol:water (98:2, V/V) with 5 mM ammonium at a flow rate of 0.2 mL/min.

4.2.4. Degradation kinetic parameters

The pseudo-first order kinetics of BPA degradation during H₂O₂/UV and ozonation processes were described by Eqs. (4.1) – (4.2) (Gultekin et al., 2009; Umar et al., 2013; Kang et al., 2018).

$$-\frac{dC}{dt} = k \cdot C \quad (4.1)$$

$$\ln \frac{C}{C_0} = -k_{obs} \cdot t \quad (4.2)$$

where C_0 and C are the BPA concentration at times zero and t , k is the BPA degradation rate constant, and k_{obs} is the observed or apparent first-order rate constant.

For TiO₂/UV-C process, the Langmuir–Hinshelwood kinetic model was used as shown in Eq. (4.3) (Im et al., 2012).

$$-\frac{dC}{dt} = \frac{k \cdot K \cdot C}{1 + K \cdot C} \quad (4.3)$$

At low solute concentrations (i.e., $C \ll 1$), Eq. (4.3) can be transformed into Eqs. (4.4) – (4.5) (Tsai et al., 2009; Wang et al., 2009).

$$-\frac{dC}{dt} = k \cdot K \cdot C = k_{obs} \cdot C \quad (4.4)$$

$$\ln \frac{C}{C_0} = -k_{obs} \cdot t \quad (4.5)$$

where C_0 and C are the BPA concentration at times zero and t , k is the BPA degradation rate constant, and K represents adsorption equilibrium constant, and k_{obs} is the observed or apparent first-order rate constant.

At the Eqs. (4.2) and (4.5), the kinetic parameters k_{obs} were investigated in order to compare the effects of various factors on BPA degradation efficiency.

4.2.5. Greenhouse gases calculation

The GHG emissions in this study were confined to the manufacturing, usage, and disposal of H₂O₂, TiO₂, and O₂ (O₂ is used to make O₃), UV lamp, and ozone generator (referred to as scope II and III emissions). Direct emissions (scope I) were excluded from the calculated values. Because direct emissions of methane (CH₄) is produced during anaerobic digestion, and direct emissions of nitrous oxide (N₂O) is produced during the denitrification process, these GHGs were not generated as direct emissions in this study (Mannina et al., 2016). Although CO₂ is generated during reactions as a direct emission, abiotic and biogenic CO₂ was excluded from the calculation of direct emissions during water treatment (Griffith et al., 2009; Hwang et al., 2016; Masuda et al., 2018).

The life cycle inventory (LCI) value of H₂O₂ was obtained using the ecoinvent database (version 2.0) (Frischknecht et al., 2007), and the LCI values of TiO₂ and O₂ were obtained from the LCI DB (database) of the Korea Environmental Industry and Technology Institute (KEITI, 2003). The LCI values of the UV lamp and ozone generator were provided by the product producers.

For the calculation of GHG emissions from electricity use, the average value for 2007 and 2008 in Korea was used (0.4663 kg CO₂ eq/kWh). The global warming potential (GWP), which is a measure of how much heat GHGs trap in the

atmosphere at a specific time relative to CO₂, was also used; a GWP of 21 kg CO₂ eq/kg was applied for CH₄ and a value of 310 kg CO₂ eq/kg was applied for N₂O (Eggleston et al., 2006).

In WWTPs, the carbon footprint is defined according to the life cycle assessment (LCA) of the GHG emissions resulting from the treatment of 1 m³ of wastewater (kg CO₂ eq/m³). This value can be used to make a comparison among different processes (Singh et al., 2016; Robescu and Presură, 2017).

The carbon footprint was estimated using Eq. (4.6):

$$\text{Carbon footprint (kgCO}_2\text{eq/m}^3\text{)} = \frac{G_{\text{manufacturing}} + G_{\text{usage}} + G_{\text{disposal}}}{Q} \quad (4.6)$$

where $G_{\text{manufacturing}}$ is the GHG emission during the manufacturing stage (kg CO₂ eq) (scope III), G_{usage} is the GHG emission during the usage phase (kg CO₂ eq) (scope II), G_{disposal} is the GHG emission during the disposal stage (kg CO₂ eq) (scope III), and Q is the treatment capacity of a UV lamp or ozone generator during their lifespan (m³).

The GHG emission sources in each step are represented by the following equations:

$$G_{\text{manufacturing}} = G_{\text{ch}} + G_{\text{manufac. of mt}} \quad (4.7)$$

$$G_{\text{usage}} = G_{\text{electricity}} \quad (4.8)$$

$$G_{\text{diposal}} = G_{\text{disposal of mt}} \quad (4.9)$$

where G_{ch} is the GHG emission from the manufacturing of chemicals (kg CO₂ eq), $G_{\text{manufacturing of mt}}$ is the GHG emission from the manufacturing of a UV lamp or an ozone generator (kg CO₂ eq), $G_{\text{electricity}}$ is the GHG emission from electricity use (kg CO₂ eq), and $G_{\text{disposal of mt}}$ is the GHG emission during the disposal of a UV lamp or an ozone generator (kg CO₂ eq).

The specific calculation methods for GHG emission are:

$$G_{\text{ch}} = \text{Ch}_i \times \text{EF}_i \quad (4.10)$$

$$G_{\text{electricity}} = E_{\text{required}} \times \text{EF}_{\text{electricity}} \quad (4.11)$$

where Ch_i is the quantity of chemical i used during reactions (mg), EF_i is the GHG emission factor of chemical i (kg CO₂ eq/mg), E_{required} is the amount of electricity used during reactions (kWh), $\text{EF}_{\text{electricity}}$ is the GHG emission factor of electricity (kg CO₂ eq/kWh). The values of $G_{\text{manufacturing of mt}}$ and $G_{\text{disposal of mt}}$ are provided by the product producers.

4.3 Results and discussion

4.3.1. Kinetic and GHG emissions during H₂O₂/UV-C process

Hydroxyl radicals ($\cdot\text{OH}$), which are strong oxidants, can be generated during the H₂O₂/UV process. When H₂O₂ is subjected to UV-C irradiation ($\epsilon = 18.6 \text{ M}^{-1}\text{cm}^{-1}$) two OH radicals are produced via Eq. (4.12) (Kang et al., 2018). As the amount of H₂O₂ increases, the rate of OH radical formation increases and the decomposition rate of BPA increases. As can be seen in Figure 4.2, the rate constant (k_{obs}) was 0.090 min^{-1} in the 1 mM H₂O₂/UV-C reaction. The rate constants increased continuously from 0.152 to 0.353 min^{-1} as H₂O₂ increased from 2 to 4 mM in the H₂O₂/UV-C reaction. However, the rate constant was slightly reduced to 0.304 min^{-1} in the 5 mM H₂O₂/UV-C reaction.

As shown in Eq. (4.13), when excessive amounts of H₂O₂ are added, OH radicals can react with H₂O₂, slowing down the decomposition rate of compounds (Muruganandham and Swaminathan, 2004; Park et al., 2014; Sharma et al., 2015). In this study, the rate constant was also lowered by reacting H₂O₂ with OH radicals when H₂O₂ was added at 5 mM.





The GHG emissions during the H₂O₂/UV-C process were mainly due to H₂O₂ usage (mM) and UV lamp power consumption (Watt-hour). Figure 4.2 shows the change in GHG emissions due to the increase in H₂O₂ concentration. The GHG emissions decreased until 3 mM H₂O₂ was reached. This was because the reduced GHG emissions from electricity use were greater than those from H₂O₂ additions. While it took 44 minutes to remove 0.04 mM BPA in UV-C with the 1 mM H₂O₂ reaction, it took 34 min at 2 mM H₂O₂ and 20 min at 3 mM H₂O₂. The GHG emissions increased by 0.1×10^{-3} kg CO₂ eq. with addition of 1 mM H₂O₂. However, by reducing the reaction time, the GHG emissions decreased by at least 0.3×10^{-3} kg CO₂ eq. As a result, the total GHG emissions in the 1, 2, and 3 mM H₂O₂/UV-C reactions decreased to 1.5×10^{-3} , 1.4×10^{-3} , and 1.1×10^{-3} kg CO₂ eq, respectively.

The time required to remove BPA in the 4 mM H₂O₂/UV-C reaction was only 18 min. However, the GHG emissions increased to 1.2×10^{-3} kg CO₂ eq. This was because, even though GHG emissions were decreased by reducing the reaction time, this was negated by the increase in GHG emissions caused by the much greater use of H₂O₂ (4 mM). In other words, the increase in GHG emissions from H₂O₂ inputs (4 mM) was greater than the reduction in GHG emissions achieved by reducing power consumption. The reaction time for UV-C photolysis with 5 mM H₂O₂ was increased to 20 min, which was longer than when H₂O₂ was added at 4 mM. Thus,

the increases in both the amount of H₂O₂ and electricity consumption resulted in a large increase in GHG emissions.

We also estimated the cost effectiveness according to H₂O₂ concentrations (table 4.1). The cost of using H₂O₂ (US\$ 0.1953 per H₂O₂ mL) was comparable to the cost of electric charge (US\$ 0.1441 per kWh). The lowest cost point in the H₂O₂/UV process was shown at 3 mM H₂O₂.

It should be noted that the reaction conditions under which the decomposition rate was fastest (4 mM H₂O₂), and the conditions under which the GHG emissions were minimized (3 mM H₂O₂), were different. Many studies have focused on increasing the rate of degradation of pollutants. However, from the perspective of GHG emissions, the removal of pollutants and the amount of GHG emissions should be considered together.

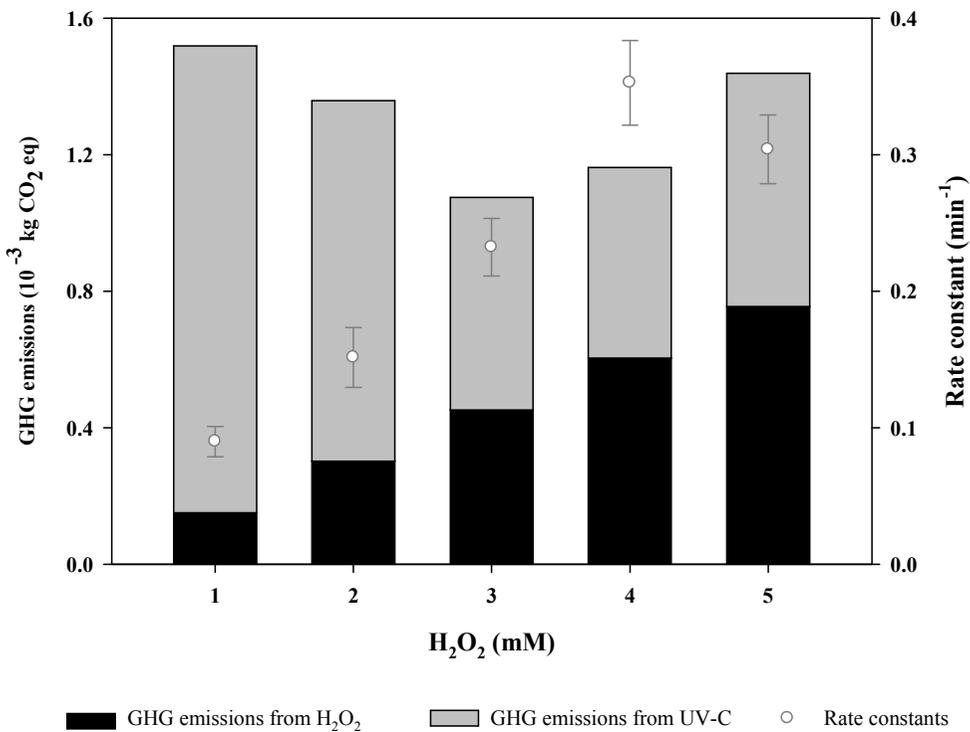


Figure 4.2 Rate constants (scatter plot) and greenhouse gas (GHG) emissions (bar chart) of bisphenol-A (BPA) during the H₂O₂/UV-C process at various H₂O₂ concentrations ([BPA]₀ = 0.04 mM, UV intensity = 3.8 mW/cm², n = 3).

Table 4.1 The cost effectiveness according to oxidant concentrations.

(a) H ₂ O ₂ /UV process									
[unit: US\$]									
Concentration (mM)	1	2	3	4	5	-	-	-	-
Cost of using H ₂ O ₂	0.03	0.05	0.08	0.11	0.13	-	-	-	-
Electric charge	0.42	0.33	0.19	0.17	0.19	-	-	-	-
Total	0.45	0.38	0.27	0.28	0.32	-	-	-	-

(b) TiO ₂ /UV process									
Concentration (mg/L)	100	200	300	400	500	1000	1500	2000	2500
Cost of using TiO ₂	0.43	0.85	1.28	1.70	2.13	4.26	6.39	8.52	10.65
Electric charge	2.31	1.82	1.49	1.30	1.15	0.86	0.58	0.48	0.49
Total	2.73	2.68	2.77	3.00	3.28	5.12	6.97	9.00	11.14

(c) O ₃ process									
Concentration (mg/L)	1	2	3	4	5	6	7	-	-
Cost of using O ₂	10.17	8.39	6.23	5.08	5.15	6.06	7.42	-	-
Electric charge	5.38	3.70	2.35	1.68	1.51	1.46	1.40	-	-
total	15.55	12.09	8.58	6.77	6.66	7.52	8.82	-	-

Electric charge = US\$0.1441 per kWh, H₂O₂ = US\$0.1953 per mL, TiO₂ = US\$2.1297 per g, O₂ = US\$1.2712 per L

4.3.2. Kinetic and GHG emissions during TiO₂/UV-C process

The TiO₂/UV process involves complicated reactions with OH radicals and the organic solutes adsorbed on the surface of the TiO₂ (Tsai et al., 2009; Wang et al., 2009). However, BPA degradation during the TiO₂/UV-C process is predominantly achieved by OH radicals that are produced via Eqs. (4.14) – (4.16) (Reddy et al., 2018).



The rate constants (k_{obs}) of BPA decomposition during the TiO₂/UV-C process are shown in Figure 4.3. The rate constant was 0.022 min⁻¹ at 100 mg/L of TiO₂ with UV-C. As the concentration of TiO₂ increased from 200 to 2,000 mg/L, the rate constant increased from 0.024 to 0.126 min⁻¹, respectively. However, when TiO₂ was 2500 mg/L, the rate constant decreased to 0.115 min⁻¹. Generally, higher amounts of TiO₂ promote BPA degradation. However, with very high TiO₂ concentrations, the number of active sites on the surface of TiO₂ particles that are available for

photocatalytic reaction may be reduced due to the reduction of light penetration and the increased scattering of UV light (Wong and Chu, 2003; Kaneco et al., 2004).

The GHG emissions during the TiO₂/UV-C process are mainly from TiO₂ (mg/L) usage and UV lamp power consumption (Watt-hour). As can be seen in Figure 4.3, GHG emissions were minimal in areas with low concentrations of TiO₂. GHG emissions were 8.0×10^{-3} kg CO₂ eq at 100 mg/L TiO₂, but it was decreased to 6.5×10^{-3} kg CO₂ eq at 400 mg/L TiO₂. Thereafter, as the concentration of TiO₂ increased from 500 to 2,500 mg/L, GHG emissions continued to increase from 6.6×10^{-3} to 16.1×10^{-3} kg CO₂ eq.

This is because, during the TiO₂/UV-C process, a significant proportion of the GHG emissions arose from the use of TiO₂. Although the GHG emissions decreased in the low TiO₂ concentration range (100 - 400 mg/L), the GHG emissions increased sharply with increasing TiO₂ concentrations (500 - 2,500 mg/L). In the low TiO₂ concentrations, the reduced GHG emissions (power consumption) were higher than the increased GHG emissions (TiO₂). However, in the high concentrations, as the TiO₂ concentration increased by 500 mg/L, GHG emissions increased by 2.9×10^{-3} kg CO₂ eq. However, the reduction in GHG emissions due to the reduced reaction time was only 0.9×10^{-3} kg CO₂ eq. In other words, although GHG emissions from electricity consumption were reduced by decreasing the reaction time, an increase in the TiO₂ concentration, which was responsible for a significant proportion of the GHG emissions, led to an overall increase in the total GHG emissions. However,

GHG emissions were reduced in low TiO₂ concentrations (100-400 mg / L). Therefore, in order to find the operating conditions in terms of the lowest GHG emission in the TiO₂/UV process, experiments should be carried out in the low TiO₂ concentration range. The reaction time required to remove BPA from the 2,500 mg/L TiO₂/UV-C reaction was 51 min, which was longer than when TiO₂ was added at 2,000 mg/L. Therefore, the GHG emissions increase was largely due to the addition of TiO₂ and the increase in reaction time.

The cost effectiveness during TiO₂/UV process is shown in Table 4.1. The lowest cost was at 200 mg/L TiO₂. The price of TiO₂ (US\$ 2.1297 per TiO₂ g) is relatively expensive compared to the price of electricity (US\$ 0.1441 per kWh). Therefore, costs were low in the low concentration range of TiO₂ during TiO₂/UV process.

From the experimental results obtained during the TiO₂/UV-C process, it was found that adding small amount of TiO₂ was critical for reducing GHG emissions. The increase in GHG emissions due to the addition of TiO₂ was greater than the reduction in GHG emissions due to the reduction in electricity consumption. The rate of BPA degradation during the TiO₂/UV-C process was almost inversely proportional to the GHG reduction.

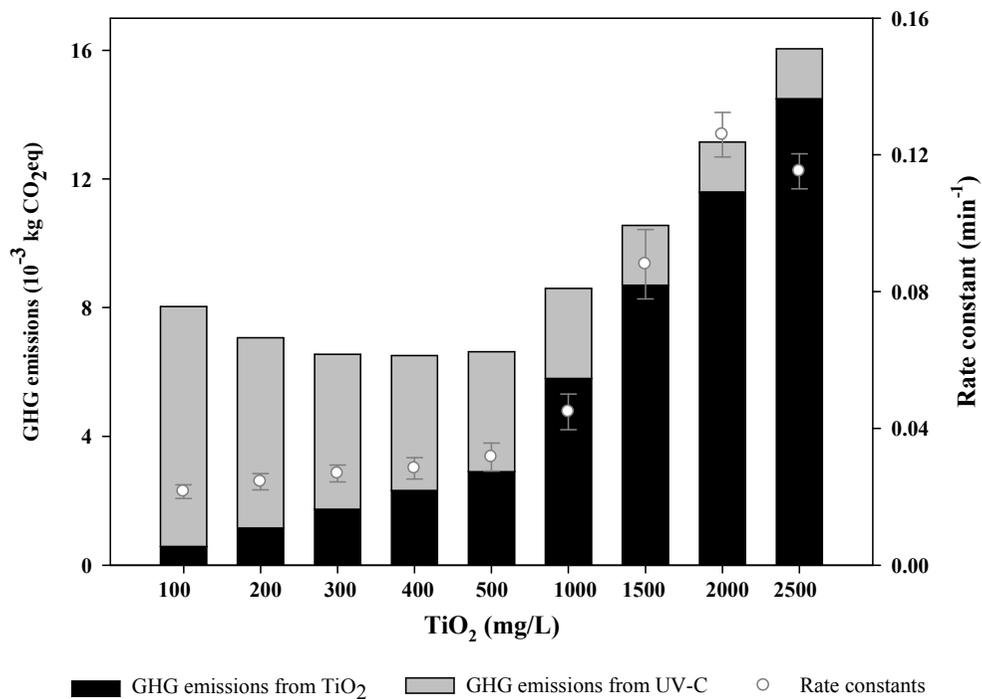
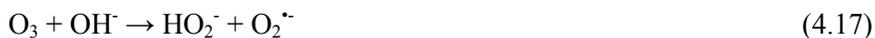


Figure 4.3 Rate constants (scatter plot) and GHG emissions (bar chart) of BPA during the TiO₂/UV-C process at various TiO₂ concentrations ([BPA]₀ = 0.04 mM, UV intensity = 3.8 mW/cm², n = 3).

4.3.3. Kinetic and GHG emissions during ozonation process

The ozonation process has long been recognized as an effective oxidation process to treat contaminated water (Mohapatra et al., 2010; Umar et al., 2013). During the ozonation process, the main mechanism of BPA removal is direct reaction with O₃ (Garoma and Matsumoto, 2009). In addition, pollutants can be eliminated by indirect reactions with OH and HO₂ radicals produced by O₃, as shown in Eqs. (4.17) – (4.21) (Beltran, 2003; Broséus et al., 2009).



The rate constants (k_{obs}) of BPA degradation with increasing ozone concentration are shown in Figure 4.4. The ozonation process resulted in a rapid BPA decomposition rate because ozone was continuously supplied during the reaction. As the ozone concentration increased from 1 to 7 mg/L, the rate constants of BPA degradation also increased from 0.269 to 1.467 min⁻¹, respectively. The

increase in ozone concentration did not adversely affect the BPA degradation rate.

The GHG emissions during ozonation are mainly produced by oxygen consumption (mg/L) and the power consumption of the ozone generator (Watt-hour). As ozone concentrations increased, GHG emissions continued to decline until ozone concentration was 5 mg/L (Figure 4.4). The GHG emission resulting from the elimination of 0.04 mM BPA was 23.1×10^{-3} kg CO₂ eq for the 1 mg/L ozone treatment. As the ozone concentrations increased to 2, 3, 4, and 5 mg/L, the GHG emissions decreased to 16.6×10^{-3} , 11.1×10^{-3} , 8.3×10^{-3} , and 7.8×10^{-3} kg CO₂ eq, respectively.

GHG emissions were significantly decreased until ozone concentration was 4 mg/L due to the reduction of the consumption of both the chemical inputs and electricity usage. The power consumption of the ozone generator accounts for 80% of the GHG emissions during the ozone generation process. Therefore, reducing electricity consumption can lead to a significant reduction in GHG emissions during the ozone treatment process. Furthermore, when the reaction time is shortened, the amount of oxygen supplied as a feed gas generating ozone can be reduced. This results in a minor reduction of GHG emissions arising from the ozone process. In other words, until ozone concentration was 4 mg/L, a decrease in reaction time can reduce GHG emissions by reducing the consumption of electricity and oxygen.

However, as ozone concentrations rose above 5 mg/L, GHG emissions due to oxygen use (ozone-generating gases) began to increase. At the ozone concentration

of 6 mg/L, the amount of the GHG emissions increased by oxygen use was bigger than the amount of the GHG reduction from a decrease in power consumption. In other words, GHG emissions during the ozone process began to increase from 6 mg/L ozone concentration.

The cost effectiveness according to O₃ concentrations is shown in Table 4.1. The costs were high at low concentrations of O₃. The consumed amount of oxidant and power were high at the low concentration due to the long reaction time. The cost of the O₃ process was minimal in ozone concentrations of 5 mg/L.

During the ozone generation reaction, GHG emissions from electricity consumption accounted for the majority of the total GHG emissions. Therefore, shortening the reaction time by increasing of the oxidant concentration reduces electricity consumption and GHG emissions. However, extremely high concentrations of oxidant offset the GHG reduction effects from reducing power consumption.

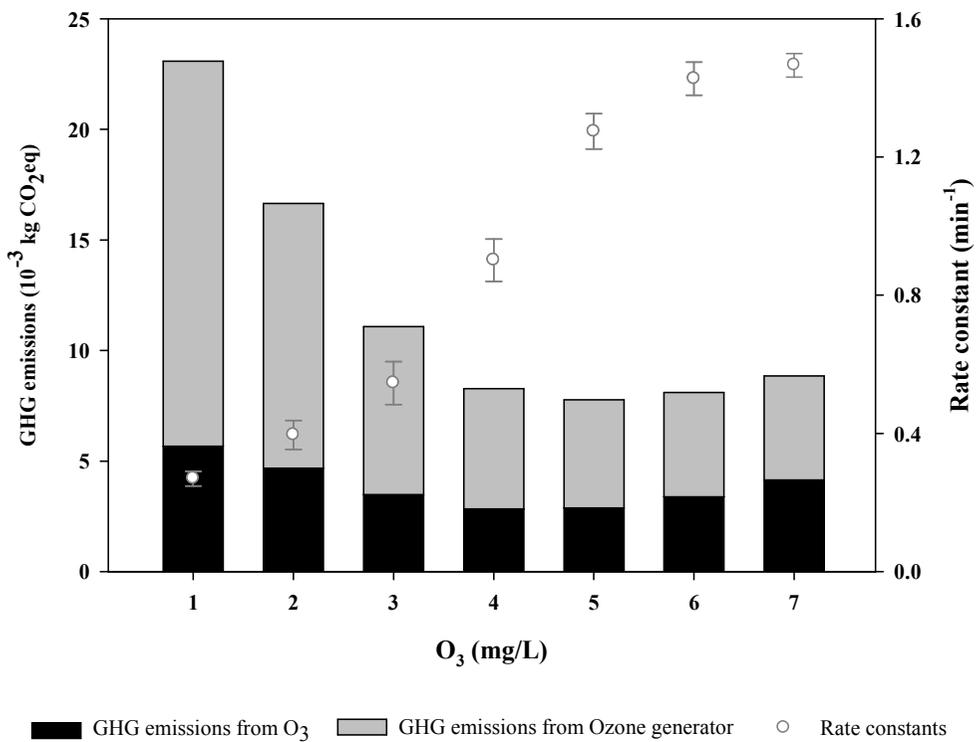


Figure 4.4 Rate constants (scatter plot) and GHG emissions (bar chart) of BPA during the ozonation process at various O₃ concentrations ([BPA]₀ = 0.04 mM, O₃ flow rate = 0.5 - 1.4 L/min, n = 3).

4.3.4. Comparison of kinetics and carbon footprints

The carbon footprint concept was used to compare the GHG emissions of different types of AOPs. The carbon footprints of the water treatment processes were determined by conducting an LCA of GHG emissions for the purification of 1 m³ of wastewater (Singh et al., 2016; Robescu and Presură, 2017). The values were used as a basis for comparison between the different processes. Carbon footprints were calculated and compared among processes at the point at which minimal GHG emissions were achieved during BPA removal. The conditions with the lowest GHG emissions were the 3 mM H₂O₂/UV-C process, the 400 mg/L TiO₂/UV-C process, and the 5 mg/L ozone treatment.

As shown in Table 4.2, ozone treatment was the fastest method for removing 0.04 mM BPA, with a first-order rate constant (k_{obs}) of 1.274 min⁻¹. The H₂O₂/UV-C process and the TiO₂/UV-C process followed, with k_{obs} values of 0.232 and 0.028 min⁻¹, respectively. Other studies have reported similar results. In the experiments conducted by Biń and Sobera-Madej (2012), the rate constant of an ozone treatment was three times higher than the rate constant of the H₂O₂/UV-C process. Riga et al. (2007) also compared degradation efficiency among AOPs. The slowest decomposition process was the TiO₂/UV-C process.

Electric energy consumption per order (EE/O) is an energy consumption parameter that can be applied to AOPs (Kim et al., 2018; Miklos et al., 2018). The

values for the processes in this study are given in Table 4.2. The most effective EE/O was obtained for the H₂O₂/UV-C process, with a value of 2.9 kWh/m³/order. The EE/O value of the ozonation process was 3.8 kWh/m³/order, while the value for the TiO₂/UV-C process was 159.0 kWh/m³/order. As shown in Figure 4.5, GHG emissions during the usage stage accounted for more than 50% of the total. However, there is a limit to the value of the EE/O because it can only be used to compare GHG emissions among processes during the usage stage.

The carbon footprint results are provided in Table 4.3. The H₂O₂/UV-C process produced 0.565 kg CO₂ eq/m³ of GHGs when treating 0.04 mM BPA. The GHG emissions from the TiO₂/UV-C and ozone treatment processes were 3.445 and 3.897 kg CO₂ eq/m³, respectively; this is because the H₂O₂/UV-C process can remove BPA by small amounts of radical promoter with low LCI value. The amount of GHG emissions from the chemicals used in the H₂O₂/UV-C process was at least three times less than that for the other AOPs. In addition, the GHG emissions from electricity consumption during the H₂O₂/UV-C process were at least six times lower than those during the other processes.

Compared to the TiO₂/UV-C process using the same UV lamp, the TiO₂/UV-C process needed six times more power consumption (Watt-hour) due to the longer reaction time when treating BPA. This resulted in a higher carbon footprint for the TiO₂/UV-C process than the H₂O₂/UV-C process at the manufacturing and disposal stages. In other words, due to the longer reaction time of the TiO₂/UV-C process,

despite using the same UV lamp, the amount of purified wastewater was smaller than for the H₂O₂/UV-C process over the lifespan of the UV lamp. Thus, the most effective process in terms of the carbon footprint was the H₂O₂/UV-C process.

A large amount of BPA-contaminated water could be treated over the lifetime of the ozone generator due to the short reaction time of the ozone treatment. However, by the end of its life, it will have consumed a lot of chemicals and power. The ozone process had lower GHG emissions at the disposal stages than the TiO₂/UV-C process, but had large GHG emissions at the manufacturing, usage stage. The total carbon footprint was slightly higher for the ozone treatment than for the other treatments. This was because the power consumption (Watt-hour) during ozone treatment was significantly higher than that during the TiO₂/UV-C process.

The experimental results showed that the manufacturing and usage stages were the most important in terms of reducing GHG emissions from AOPs. Several studies have been conducted to investigate GHG emission reduction at the usage stage. Raluy et al. (2005) used wind and photovoltaic energy in WTPs to reduce GHG emissions. Shahabadi et al. (2009) also confirmed that reusing fuel-generated biogas from anaerobic reactors can reduce the overall energy demand of a treatment facility. In addition, the use of low-carbon products in chemicals can reduce a large amount of GHG emissions from AOPs. Further studies should also be conducted on GHG emissions for various pollutants because degradation mechanisms during AOPs depend on the chemical properties. In addition, nitrogen-containing contaminants

may release the direct emission of N₂O into the atmosphere during the treatment process. Therefore, further studies of GHG emissions during the treatment of nitrogen-containing contaminants in the AOP should also be carried out.

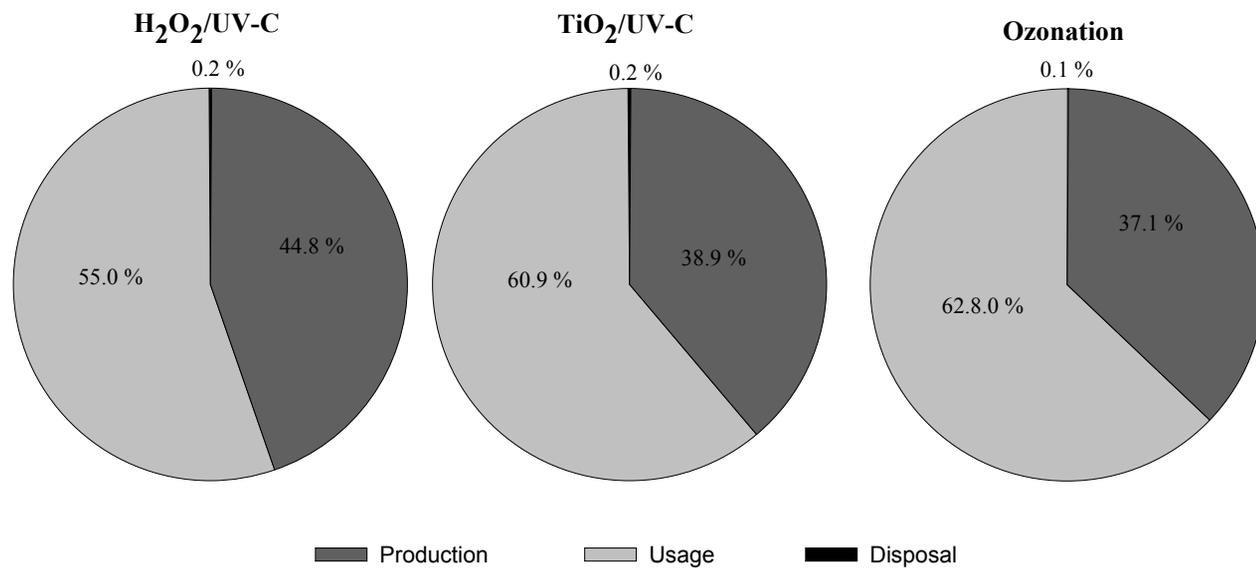


Figure 4.5 Carbon footprint associated with the manufacturing, usage, and disposal stages during BPA degradation processes (3 mM H₂O₂/UV-C, 400 mg/L TiO₂/UV-C, 5 mg/L ozonation).

Table 4.2 BPA degradation rate constants, EE/O values under the minimum GHG emissions conditions.

Processes	Experiment condition	k_{obs} (min^{-1})	EE/O ($\text{kWh/m}^3/\text{order}$)
H ₂ O ₂ /UV-C	H ₂ O ₂ 3mM	0.232	2.9
TiO ₂ /UV-C	TiO ₂ 400mg/L	0.028	159.0
Ozonation	O ₃ 5mg/L	1.274	3.8

Table 4.3 BPA carbon footprints under the minimum GHG emissions conditions.

Processes	Experiment condition	Carbon footprint (kgCO ₂ /m ³)			
		Total	Manufacture	usage	disposal
H ₂ O ₂ /UV-C	H ₂ O ₂ 3mM	0.565	0.253	0.311	0.001
TiO ₂ /UV-C	TiO ₂ 400mg/L	3.445	1.339	2.098	0.008
Ozonation	O ₃ 5mg/L	3.897	1.446	2.448	0.003

4.4. Conclusions

In this study, batch experiments were conducted to examine rate constants (k_{obs}) and GHG emissions during removal of BPA-contaminated water using three AOPs ($H_2O_2/UV-C$, $TiO_2/UV-C$, and ozonation processes). The highest degradation rate ($k_{obs} = 0.232 \text{ min}^{-1}$) was observed in the $H_2O_2/UV-C$ process with the 4 mM $H_2O_2/UV-C$ reaction, while the minimum GHG emission was observed with the 3 mM $H_2O_2/UV-C$ reaction. The fastest rate constant ($k_{obs} = 0.126 \text{ min}^{-1}$) during the $TiO_2/UV-C$ process was that for the 2,000 mg/L $TiO_2/UV-C$ reaction, while the minimum GHG emission was observed with the 400 mg/L $TiO_2/UV-C$ reaction. During the ozonation process, GHG emissions were minimized in the 5 mg/L ozonation process, which was different from the fastest rate constant.

The experimental results showed that there were three different types of GHG emissions during AOPs. First, electricity consumption accounted for most of the GHG emissions; therefore minimizing the reaction time by adding a high concentration of oxidant would reduce GHG emissions (e.g., ozonation process). Second, most GHGs can be emitted by chemicals (e.g., TiO_2/UV process). Therefore, conditions that minimize the input of chemicals will minimize GHG emissions. Finally, during some processes, the GHG emissions from chemical inputs and power consumption are similar (e.g., H_2O_2/UV process); therefore, when operating such processes, it is important to determine the appropriate reaction conditions.

Finally, the carbon footprints were calculated to compare GHG emissions among the selected AOPs ($\text{H}_2\text{O}_2/\text{UV}$, TiO_2/UV , and ozonation processes). The $\text{H}_2\text{O}_2/\text{UV}$ process had the smallest carbon footprint, generating $0.565 \text{ kg CO}_2 \text{ eq/m}^3$ when treating 0.04 mM of BPA. The TiO_2/UV process and the ozonation processes followed, with 3.445 and $3.897 \text{ kg CO}_2 \text{ eq/m}^3$, respectively. The manufacture and usage stage were the most important parts of the AOPs to reduce GHG emissions.

Chapter 5.

Conclusions

5.1 Conclusions

Research works on the occurrence and removal of micropollutants in small-scale wastewater treatment facilities (WTFs) have severally conducted. Therefore, this dissertation investigated the removal efficiency of micropollutants in small-scale private WTFs, and implemented a study to improve the treatment efficiency considering low-carbon development.

In the first study, the occurrence and removal of 10 micropollutants in WTFs and their impact on its receiving waters were investigated. CFF, ACT, and IBU were observed in the highest concentrations in WTF influent, whereas CFF, ACT, and NPX were present in higher concentrations in effluent. The composition profile of selected micropollutants in WTF influents showed little regional variation, suggesting that the consumption pattern of rural residents in Korea do not differ from region to region. The removal efficiencies of micropollutants by WTFs were higher than the septic tanks without drainfields, whereas lower than those of the conventional STPs and the septic tanks with drainfields. The changes in the concentrations of micropollutants between upstream and downstream waters verified that WTF effluent is a source of micropollutants in stream water. Based on the per capita discharge loads of micropollutants derived from this study, the annual total emissions of the ten micropollutants from all private WTFs in Korea was 1,030 kg.

According to the research results, the small-scale private WTFs cannot completely remove some micropollutants and contaminate its receding water. Therefore, it is necessary to increase the treatment efficiency of micropollutants in small-scale WTFs.

There are a variety of advanced treatment techniques to remove non-biodegradable micropollutants in water. Among them, advanced oxidation processes (AOPs), can be operated by a part-time worker. In addition, if adequately developed, AOPs have advantages to abate micropollutants in points of those producing fewer by-products, taking less time, and requiring no final disposal. Therefore, AOPs are the supplemental processes suitable for handling recalcitrant micropollutants entering small-scale private WTFs. However, the degradation efficiency is significantly affected by radical scavengers in water. Therefore, if the effects of radical influencers such as natural water components on the degradation of micropollutants are clarified, AOPs can be applied to small-scale private WTFs to efficiently remove micropollutants. In the second study, BPA degradation kinetics and byproducts in the presence of natural water components during UV photolysis and the $\text{H}_2\text{O}_2/\text{UV}$ reaction were examined to assess the applicability of AOPs in small-scale private WTFs. During UV photolysis, BPA removal efficiency was dramatically increased when the solution pH was higher than the pK_a of BPA, due to the increased molar absorption coefficient of BPA at higher pH. In the $\text{H}_2\text{O}_2/\text{UV}$ reaction, however, BPA degradation was more efficient in acid medium (pH 4)

because H_2O_2 changes in HO_2^- and scavenging of hydroxyl radicals in alkaline medium. NO_3^- and $\text{CO}_3^{2-}/\text{HCO}_3^-$ ions at environmentally reported concentration promoted BPA degradation during UV photolysis. Humic acid acted as a promoter at concentrations less than 3 mg/L humic acid, but as a radical scavenger when exceeding 5 mg/L. During $\text{H}_2\text{O}_2/\text{UV-C}$ reaction, however, NO_3^- , $\text{CO}_3^{2-}/\text{HCO}_3^-$ ions, and humic acid inhibited the BPA degradation, in the order humic acid > $\text{CO}_3^{2-}/\text{HCO}_3^-$ > NO_3^- . The byproducts identified during UV photolysis were different depending on water component present. Nitrogenated- and hydrogenated byproducts of BPA were identified during the NO_3^-/UV photolysis, while only hydrogenated byproducts of BPA were detected in the $\text{NO}_3^-/\text{CO}_3^{2-}/\text{HCO}_3^-/\text{UV}$ photolysis. Adducted form of byproduct was not detected during the $\text{CO}_3^{2-}/\text{HCO}_3^-/\text{UV}$ photolysis. During the ions/ $\text{H}_2\text{O}_2/\text{UV}$ reactions, identified byproducts were all the same regardless of the presence ions. Due to enormous amount of OH radical produced during $\text{H}_2\text{O}_2/\text{UV-C}$ process, ions seem to have no affect to degradation mechanism. Adduct forms of BPA byproducts were generated in the early stage of the reactions and then decomposed into smaller compounds during the $\text{UV-C}/\text{NO}_3^-$, $\text{UV-C}/\text{NO}_3^-/\text{CO}_3^{2-}/\text{HCO}_3^-$, and ions/ $\text{H}_2\text{O}_2/\text{UV-C}$ reactions. In comparison, BPA was decomposed into smaller compounds via β -scission of the isopropyl group by radical attacks during $\text{UV-C}/\text{CO}_3^{2-}/\text{HCO}_3^-$ photolysis. This study implies that natural water components affect the degradation kinetics and mechanisms of BPA during UV-C photolysis, However, the natural water components only affect degradation kinetic not

degradation byproducts in the H₂O₂/UV-C process. Therefore, the amount of oxidant input is a critical factor for the application of AOPs in small-scale WTFs. In addition, since AOPs are not affected in the degradation mechanisms by natural water components, their impact on the water ecosystem will be minimal when applied to small-scale WTFs.

However, it is assumed that the AOPs will emit a large amount of greenhouse gases (GHGs) into the atmosphere due to its huge chemicals used and power consumption. The considerable increase in the concentration of GHGs in the atmosphere has resulted in climate change. Therefore, even in the AOPs field, it is necessary to improve the treatment efficiency considering the low-carbon development. For the reasons, in the final study, BPA contaminated waters were purified using AOPs (H₂O₂/UV-C, TiO₂/UV-C, and ozone treatment) to investigate rate constants (k_{obs}) and GHG emissions. The results will provide fundamental data for the low-carbon development of AOPs. The experimental results showed that there were three different types of GHG emissions during AOPs. First, electricity consumption accounted for most of the GHG emissions; therefore minimizing the reaction time by adding a high concentration of oxidant would reduce GHG emissions (e.g., ozonation process). Second, most GHGs can be emitted by chemicals (e.g., TiO₂/UV process). Therefore, conditions that minimize the input of chemicals will minimize GHG emissions. Finally, during processes, the GHG

emissions from chemical inputs and power consumption are similar (e.g., H₂O₂/UV process); therefore, when operating such processes, it is important to determine the appropriate reaction conditions. The H₂O₂/UV-C process had the smallest carbon footprint, generating 0.565 kg CO₂ eq/m³ when treating 0.04 mM of BPA. The TiO₂/UV process and the ozonation processes followed, with 3.445 and 3.897 kg CO₂ eq/m³, respectively. The H₂O₂/UV had the smallest carbon footprint at all stages due to its low chemical use and low power consumption. It has been proved that the condition to increase the rate constant may not be optimal in terms of GHG emissions.

The comprehensive research results of this thesis are as follows. (1) The small-scale private WTFs are the main source of micropollutant contamination in its receiving water due to the limitation of the micropollutant removal in the facilities. Therefore, small-scale private WTFs need a supplementary treatment process to improve the treatment efficiency of micropollutants. (2) In the AOPs, the degradation kinetic was reduced by natural water components. However, natural water components did not affect byproduct formation. Therefore, a sufficient amount of oxidant should be added to apply AOP in small-scale private WTFs. (3) In the AOPs, the condition to increase the rate constant may not be optimal in terms of GHG emissions. Therefore, when operating AOPs, it is important to determine the appropriate reaction conditions to minimize GHG emissions. In addition, the use of

low-carbon oxidants and renewable power can reduce GHG emissions from AOPs. Based on the study results, policymakers and engineers can make prudent and accurate decisions. Moreover, it is expected that by applying the results of this research to small-scale WTFs in the future, a healthier aquatic ecosystem will be created.

5.2 Suggestions for future study

This dissertation carried out extensive research ranging from the behavior of micropollutants in small-scale wastewater treatment facilities to the natural water components effect and GHG emissions at AOPs. However, there are some areas that we have not implemented in this dissertation.

There are various technologies other than the WTF using biological treatment method for private wastewater treatment facilities. Therefore, the behavior of micropollutants in various private wastewater treatment facilities should be continuously monitored. In addition, the assessment of GHG emissions and effects of natural water components studies were conducted with lab scales. The results derived from this dissertation should be applied to field scale of small-scale wastewater treatment facilities to verify their effectiveness.

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국문초록

소규모 오수처리시설에서 미량오염물질 처리를 위한 고도산화공정 적용 가능성과 온실가스 발생량 평가에 관한 연구

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공공 하수처리시설이 제공되지 않는 지역에서는 개인 하수처리시설을 사용하여 하수를 정화해야 한다. 하지만, 의약품 (pharmaceuticals) 및 내분비계 교란물질 (endocrine disruptors)과 같은 미량오염물질은 생물학적 분해에 저항성을 가지고 있다. 따라서, 일반적인 소규모 개인 하수처리시설은 이들 물질을 완전히 제거하지 못하고 주변하천으로 방류하고 있을 것으로 추측된다. 하천에 유입된 미량오염물질은 자연 수생태계를 교란시키고, 나아가 정수시설에도 유입되어 인간에게 유해한 건강영향을 초래한다. 수중 난분해 미량오염물질을 제거하기 위해 다양한 처리방법이 연구 중이다. 이중 고도산화처리 (advanced oxidation processes)는 소규

모 하수처리시설시설과 같이 비상근 근로자가 운영하는 시설에 적용되기에 적합해 보인다. 하지만, 라디칼 (radical)을 소멸 시키는 방해요소로 인해 처리효과가 억제될 수 있다. 또한, 고도산화처리는 화학물질 사용량과 전력 소비량이 방대하여 대기오염으로 다량의 온실가스를 배출할 것으로 추측된다. 이와 같은 이유로, 소규모 오수처리시설에서 미량오염물질의 거동과 지속 가능한 저탄소 성장 (low-carbon growth) 측면에서 처리효율을 높이기 위한 연구의 필요성이 제기되고 있다.

따라서, 본 논문의 목적은 소규모 오수처리시설에서 미량오염물질의 제거효율을 점검하고, 저탄소 발전을 고려한 처리효율 향상 연구를 수행하는 것이다. 연구 (1)에서는 소규모 개인 오수처리시설에서 아세트아미노펜 (acetaminophen), 비스페놀-A (bisphenol-A), 카페인 (caffeine), 카바마제핀(carbamazepine), 디클로페낙 (diclofenac), 이부프로펜 (ibuprofen), 메토프로롤 (metoprolol), 나프록센 (naproxen), 설파메사진 (sulfamethazine), 설파메톡사졸 (sulfamethoxazole) 등 10 종 미량오염물질의 발생량 및 제거율을 점검하고, 방류수가 주변하천 미량오염물질 농도변화에 미치는 영향을 파악하였다. 연구 (2)에서는 자연 수중 성분 (natural water components)이 고도산화처리에서 비스페놀-A 분해속도 및 분해부산물에 미치는 영향을 파악하여 소규모 오수처리시설에서 고도산화

처리의 적용가능성을 확인하였다. 연구 (3)에서는 고도산화처리가 비스페놀-A를 제거하는 과정에서 배출하는 온실가스 량을 산정하고 비교하여 저탄소 발전을 위한 기초자료를 제공하였다. 구체적인 연구결과를 살펴보면 다음과 같다.

연구 (1)에서는 국내 8개도(道)를 대상으로 소규모 개인 오수처리시설에서 연구대상 미량오염물질의 유입농도와 방류농도를 측정하였다. 또한 방류지점을 기준으로 하천의 상류와 하류에서 미량오염물질의 농도변화를 확인하였다. 검출결과 미량오염물질의 농도는 오수처리시설에서 9 - 13 346 ng/L 범위로, 하천에서는 2 - 164 ng/L 범위로 존재하였다. 오수처리시설 유입수에서 미량오염물질 구성비율은 지역별로 차이가 없었다. 이 결과는 한국 외곽지역에 거주하는 주민의 의약품 소비패턴이 지역별로 차이가 없음을 보여준다. 개인 오수처리시설에서 미량오염물질의 제거효율은 12 % (카바마제핀) - 88 % (아세트아미노펜)로 공공 하수처리장 보다 낮았다. 하지만 혐기성처리를 사용하는 정화조보다는 높았다. 하천의 미량오염물질 농도는 오수처리시설의 방류수 영향으로 상류보다 하류에서 더 높았다. 따라서, 오수처리시설은 하천 미량오염물질 오염의 주요 원인이다. 또한, 10종의 미량오염물질을 대상으로 오수처리시설에서 인당 일일 오염물질 배출량 (per capita discharge loads)과 한국 개인 오수처리

리설에서 연간 배출하는 총 배출량을 산정하여 제시하였다. 연구결과를 종합적으로 살펴볼 때 소규모 오수처리시설은 미량오염물질을 적절하게 처리하지 못하고 주변하천으로 방류하고 있다.

연구 (2)는 UV 광분해 및 H_2O_2/UV 공정에서 pH, NO_3^- , CO_3^{2-}/HCO_3^- , 그리고 humic acid가 자연 수준 농도로 존재할 때 비스페놀-A 분해속도 및 분해부산물 생성에 미치는 영향 연구를 수행하였다. 실험결과 UV 광분해에서는 높은 pH에서 비스페놀-A 제거효율이 증가되었지만, H_2O_2/UV 공정에서는 낮은 pH에서 비스페놀-A의 분해가 더 효율적이었다. UV 광분해에서 NO_3^- (0.04 - 0.4 mM)와 CO_3^{2-}/HCO_3^- (0.4 - 4 mM)은 비스페놀-A의 분해속도를 증가시켰다. Humic acid (HA)는 비스페놀-A의 분해속도를 증가 시키기도 ($HA < 3$ mg/L), 저하시키기도 ($HA > 5$ mg/L)도 하였다. H_2O_2/UV 공정에서 NO_3^- , CO_3^{2-}/HCO_3^- , 그리고 humic acid는 모두 비스페놀-A의 분해속도를 감소시켰다. 특히 humic acid는 유기물을 다량 함유한 물질로 비스페놀-A의 분해속도 방해영향이 컸다. NO_3^- 가 첨가된 UV 광분해에서는 8개의 분해부산물 ($m/z = 122, 136, 139, 164, 181, 244, 273, 289$)이 확인되었지만, $NO_3^-/CO_3^{2-}/HCO_3^-$ 가 첨가된 UV 광분해와 CO_3^{2-}/HCO_3^- 가 첨가된 UV 광분해에서는 각각 4개 ($m/z = 122, 136, 164, 244$) 그리고 3개의 ($m/z = 122, 136, 164$) 분해부산물이 검출되었다. 하지만, H_2O_2/UV 공정에서는 첨가된

이온에 상관없이 모두 같은 분해부산물 ($m/z = 122, 136, 164, 244$)이 검출되었다. 검출된 분해부산물 결과로부터 UV 광분해 및 H_2O_2/UV 공정에서 이온 투입에 따른 분해 메커니즘을 제안하였다. 연구결과 NO_3^- 와 CO_3^{2-}/HCO_3^- 는 UV 광분해에서 비스페놀-A의 분해속도 및 분해부산물 생성에 영향을 미쳤지만, H_2O_2/UV 공정에서는 분해속도에만 영향을 주었고, 분해부산물 생성에는 영향을 미치지 못했다.

연구 (3)에서는 H_2O_2/UV , TiO_2/UV , 그리고 O_3 반응이 비스페놀-A를 제거하는 과정에서 배출하는 온실가스 배출량과 분해속도를 산정하여 저탄소 발전을 위한 기초자료를 제공하였다. 모든 실험은 실험실 규모로 진행되었다. H_2O_2/UV 공정에서 분해속도 ($k_{obs} = 0.353 \text{ min}^{-1}$)가 가장 빠른 실험조건은 H_2O_2 의 농도가 4 mM 이었지만, 온실가스 발생량이 최소인 실험조건은 H_2O_2 의 농도가 3 mM 에서였다. TiO_2/UV 공정에서는 TiO_2 의 농도가 2,000 mg/L 에서 가장 빠른 분해속도 ($k_{obs} = 0.126 \text{ min}^{-1}$)를 보였지만, 온실가스 배출량은 TiO_2 의 농도가 400 mg/L 에서 최소로 배출되었다. 오존공정에서 온실가스 발생이 최소인 조건은 오존의 농도가 5 mg/L 에서 였으며, 분해속도가 가장 빠른 실험조건과 달랐다. 탄소발자국 산정결과 비스페놀-A 0.04 mM 로 오염된 물 1 m³ 을 정화할 때 탄소발자국이 가장 낮은 고도산화처리는 H_2O_2/UV 공정 (0.565 kg CO₂ eq/m³)

이었다. 다음으로 TiO_2/UV 공정 ($3.445 \text{ kg CO}_2 \text{ eq/m}^3$)과 오존공정 ($3.897 \text{ kg CO}_2 \text{ eq/m}^3$)이 뒤를 이었다. 연구결과, 고도산화처리에서 분해속도가 가장 빠른 운전조건과 온실가스 발생량이 최소인 운전조건은 같지 않을 수 있음을 보여주었다. 또한, 고도산화처리에서는 생산과 사용과정에서 배출되는 온실가스 량이 온실가스 배출량의 대부분을 차지하고 있었다 (> 95%).

실험결과를 종합적으로 살펴보면 (1) 소규모 개인 오수처리시설에서 미량오염물질은 완전히 처리되지 못하고 주변하천으로 방류된다. 따라서, 소규모 오수처리시설에서 미량오염물질의 처리효율 향상을 위한 연구가 필요하다. (2) 고도산화처리는 자연 수중 성분에 의해 분해속도에는 영향을 받지만, 분해부산물에는 영향을 받지 않았다. 따라서, 소규모 오수처리시설에서 고도산화처리를 적용하여 난분해 미량오염물질을 제거하기 위해서는 충분한 양의 산화제를 투입해야 한다. (3) 고도산화처리시설에서 온실가스 배출량은 온실가스 배출량 최적화 운영으로 많은 양 감축할 수 있다. 또한, 저탄소 산화제와 신재생 에너지 사용은 고도산화처리에서 온실가스 감축의 핵심이 되는 부분이다. 앞으로 소규모 오수처리시설에 이 연구결과를 적용함으로써 자연과 인구집단에게 좀 더 건강한 수생태계가 조성될 수 있을 것으로 기대된다.

주요어: 미량오염물질, 개인오수처리시설, 고도산화처리, 온실가스 발생
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