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공학석사 학위논문

**Oxidation behaviors of microplastics
in water during UV photolysis and
ozonation**

UV 조사 및 오존 처리 중
수계 미세플라스틱의 산화 거동

2021 년 2 월

서울대학교 대학원

화학생물공학부

성 지 혜

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Abstract

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in water during UV photolysis and

ozonation

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In water treatment plants, microplastics undergo an oxidation process. However, studies on the effect of the oxidative behaviors of microplastics on the water environment in water treatment plants are still insufficient. This study was conducted to investigate the oxidation behaviors of microplastics during UV photolysis and ozonation in water treatment plants. In this study, changes in the physical/chemical properties of microplastics due to oxidation were observed and based on this, we predicted how the oxidation of microplastics would affect water quality. For this study, we produced five types of microplastics (i.e. PP, PE, PS, PVC and PET) stock suspensions with a particle size of about 1 μm by wet milling technique. The produced microplastics were exposed to the high concentration of ozone and

high intensity ultraviolet rays for 8 hours to observe changes in weight, dissolved organic carbon concentration, particle size distribution, zeta potential, and surface functional groups of the microplastics. As a result of the study, PVC showed the highest oxidative stability, and there was no change due to oxidation in most of the analyses. PP and PE had no weight loss due to oxidation, and the change in dissolved organic carbon concentration was insignificant, but functional groups containing oxygen on the surface increased and the dispersion stability decreased due to the change in the surface charge. This means that PP and PE have high oxidation stability, but when exposed to a strong oxidizing system, the surface is oxidized and has different particle properties than before. PS and PET showed the lowest oxidation stability, and as a result, weight reduction of about 30% (UV/PS, UV/PET, O₃/PET) and 100% (O₃/PS) depending on the oxidation system and type of plastic. This result most certainly shows that PS and PET are very vulnerable to UV and ozone oxidation, and at the same time, a clearly observed decrease in particle size also indicates the possibility of forming nanoplastics (NPs, <100 nm) due to oxidation. Through this study, microplastics can be oxidized during water treatment, resulting in a decrease in mass, dissolution of organic carbon, the decrease in particle size, the decrease in absolute surface charge, and the increase in oxygen-containing functional groups on the surface. These results show that there is a possibility that microplastics can be transformed into more threatening entities in the environment by the oxidation process of the water treatment plant. The oxidation stability found in this study is PVC>PE=PP>PET>PS, indicating that PVC is the most stable against oxidation and PS is the most unstable.

Keywords: microplastics, oxidation, UV photolysis, ozonation, water treatment plant

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Chapter 1.Introduction

Microplastics(MPs), generally defined as plastics with a particle diameter of less than 5 mm (Arthur et al., 2008), exist everywhere in the environment and have properties that are not easily degraded (Andrady, 2017). These have attracted more and more attention in recent decades as the emphasis has been placed on their potential to threaten human health and ecosystems (Sharma and Chatterjee, 2017; Y. Zhang et al., 2020). MPs are particularly concerning since they pose a substantial threat to the ecosystem and public health. Marine animals like seabirds and millions of mammals can ingest MPs (Moore, 2008), which can be toxic as MPs are known to adsorb and carry potentially harmful pollutants (Teuten et al., 2009). The intake of MPs might lead to the assimilation of chemicals in an organism's body (Chua et al., 2014), or a reduction in energy reserves in certain species (Wright et al., 2013). Another potential risk is the trophic transfer of MPs along the food web, with MPs playing a role as a vector of chemical contaminants (Santana et al., 2017), whereas other studies have shown that MPs do not play a key role in the movement of contaminants, but rather have the effect of being able to move contaminants out of the body in an organism (Devriese et al., 2017; Khan et al., 2015). However, as a contradictory result, studies have shown that chemicals such as polybrominated diphenyl ether added to plastics can migrate to the organism's gut tissue and inhibit feeding activity (Browne et al., 2013; Chua et al., 2014). Although there is little information available in literature about the potential toxicity of MPs to the human body, it is worth noting that MPs have already been detected in human ingested items, such as air (Gasperi et al., 2018), seafood (Cho et al., 2019), beer (Liebezeit and

Liebezeit, 2014) and salt (Yang et al., 2015). Therefore, more research is needed to clearly understand the role of MPs in the mechanism by which the transport of pollutants and additives moves into the organism.

Plastics can be decomposed or change their properties by ultraviolet (UV) irradiation, thermal decomposition, biodegradation and oxidation reactions. (Andrady, 2011; Jahnke et al., 2017). The energy delivered to the plastic in these ways changes the plastic's properties such as shape, mechanical strength, oxygen content, molecular weight, etc. (Gardette et al., 2013; Lv et al., 2017). Photochemical reactions are known to play the most important role in the oxidation of hydrocarbon (Andrady, 2015; Gewert et al., 2015). Numerous studies have revealed the mechanisms involved in the decomposition of hydrocarbon polymers under various environmental conditions (Gardette et al., 2013; Gewert et al., 2015; Rivaton and Gardette, 1998; Singh and Sharma, 2008). However, information on the oxidation behaviors of MPs in water treatment plants and their impact on the environment is limited. Therefore, it is important to observe changes in the physical/chemical properties of MPs due to oxidation and study their environmental impact. Several studies have conducted experiments on the oxidation of MPs under accelerated photolysis conditions, and as a result of them, cracks on the surface of MPs and the formation of oxygen-containing groups have been suggested (Luo et al., 2020; Mao et al., 2020; H. Zhang et al., 2020).

The objective of this study was to investigate the oxidation behaviors of polypropylene (PP), polyethylene (PE), polystyrene (PS) polyvinylchloride (PVC), Polyethylene terephthalate (PET) MPs by UV photolysis and ozonation.

These MPs are the five most frequently found in marine and freshwater environments.

Chapter 2. Literature Review

2.1. MPs in water treatment plants

2.1.1. Wastewater treatment plants (WWTPs)

Wastewater treatment plants (WWTPs) are considered one of the main routes for MPs into surface water (Xu et al., 2019). The overall MPs removal efficiencies of WWTPs at various locations in the final effluents range from 65% to 99.9% (Hou et al., 2021). Seven WWTPs in a coastal city of China displayed efficiencies of 79.88-97.84% (Long et al., 2019), and a secondary WWTP (population equivalent 650,000) in Scotland removed 98.41% of the MPs that entered in the influent (Murphy et al., 2016). The studies also investigated the performance of each unit in the plants, which are typically preliminary, primary, secondary, tertiary, and disinfection treatments, although the detailed configuration can vary in individual plants. Carr et al. (2016) identified primary skimming and settling processes as the most efficient, and in Murphy et al.'s (2016) study, preliminary and primary treatments removed 78.34% of the MPs and secondary treatment enhanced the efficiency by 20.1%. Three WWTPs in South Korea showed a removal rate of 75 - 91.9% after primary and secondary treatments, and tertiary treatments (ozone, membrane disc-filter, and rapid sand filtration) increased it to >98% (Hidayaturrahman and Lee, 2019). Tertiary treatments can be diverse with varying removal efficiencies (Hou et al., 2021; Talvitie et al., 2017a), which might have led to contradicting views on their effectiveness (Sun et al., 2019). Some studies did not observe a clear correlation between certain tertiary treatments and reduced MPs

discharge (Carr et al., 2016; Mason et al., 2016). However, in general, WWTPs with tertiary treatments displayed higher efficiencies than those without them (Sun et al., 2019).

Despite the high removal efficiencies of WWTPs, the sheer number of MPs emitted into aquatic and terrestrial environments is significant, implying that the WWTPs can work as a critical source of MPs. Even a WWTP with removal efficiency as high as 98.41% releases 65 million MPs via effluent every day (Murphy et al., 2016). 17 WWTPs in the U.S. with a low occurrence rate of 0.05 ± 0.024 MP/L discharge 50,000 to nearly 15 million particles each day, since even minor municipal WWTPs process millions of liters of wastewater each day (Mason et al., 2016). Further studies confirmed that the role of WWTPs cannot be overlooked, given the large volumes of daily discharge (Talvitie et al., 2017b; Ziajahromi et al., 2017), in line with a finding that 25% of ocean MPs come from the WWTPs (Boucher and Friot, 2017). WWTP effluents release 8 million microbeads into aquatic environments in the U.S. every day, which equals 2.9 trillion beads per year (Rochman et al., 2015). Moreover, MPs removed from the wastewater retain in sewage sludge (Gatidou et al., 2019), and accumulate in terrestrial environments through repeated sludge applications (Horton et al., 2017). The contribution of biosolids from WWTPs to the number of MPs transferred to agricultural solids is greater than the total amount of MPs present in ocean water (Nizzetto et al., 2016).

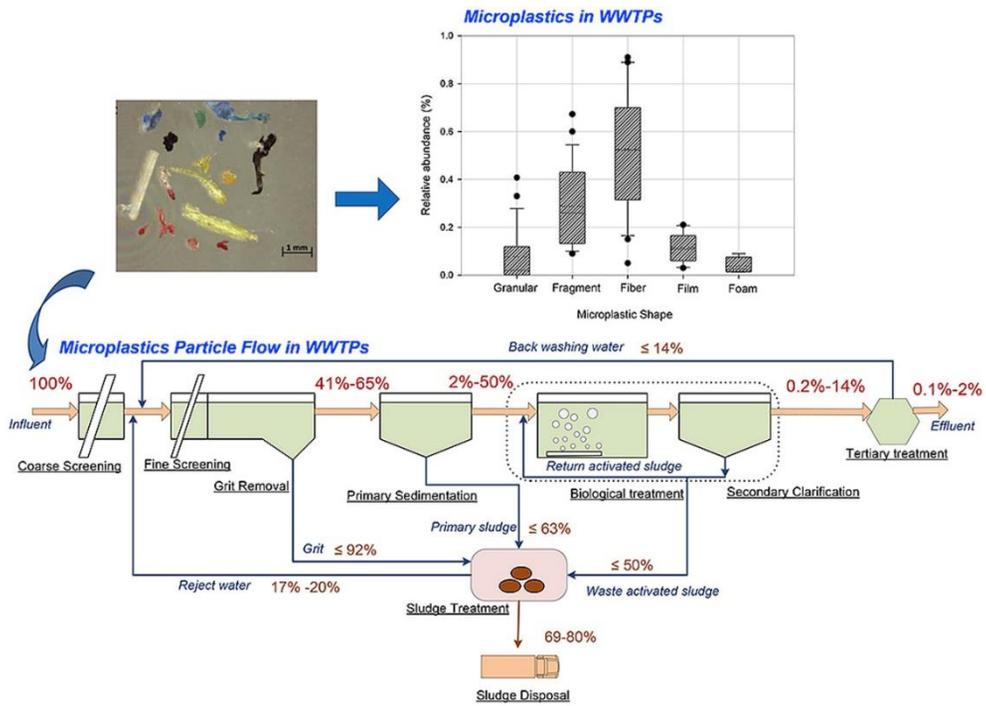


Figure 1. Schematic diagram showing the process sequence of WWTP and the efficiency of removing microplastics in a unit process (Sun et al., 2019).

2.1.2. Drinking water treatment plants (DWTPs)

Drinking water treatment plants (DWTPs) provide the safeguard for drinking water supply, thus it is urgent to explore the fates of MPs in DWTPs. However, there are few researches related to the removals of MPs in DWTPs and the information on the plastic contamination and removal effect in drinking water treatment processes is still limited. Mintenig et al. (2019) examined MPs as small as 20 μm in groundwater and its treated water from five DWTPs with $\mu\text{-FT-IR}$ to attain the highest concentration of 7 particles/ m^3 (size range 50–150 μm) in the raw water. As a result of examining the concentration of MPs in raw and treated water, it was reported that the concentration of MPs in treated water decreased by approximately 70-80% (Pivokonsky et al., 2018). However, it is not yet clear which unit process in DWTP has the greatest effect on removal, as there are still no available data on the removal efficiency of MPs by each treatment process. The relationship between microplastic features and their removal in DWTPs is still not clear (Novotna et al., 2019). In addition, the ozonation combined with granular activated carbon filtration (GAC) is widely used to remove some emerging pollutants (Fu et al., 2019; Li et al., 2018; Sbardella et al., 2018). So far, there is no report on the removals of MPs by this advanced process.

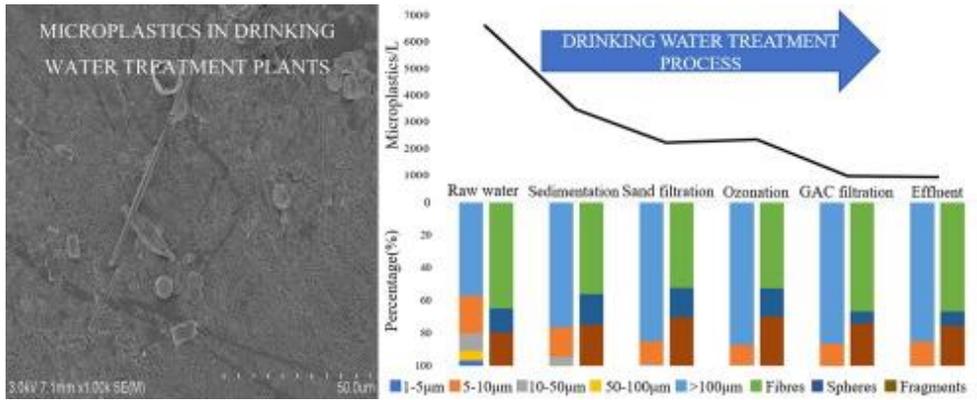


Figure 2. Plastic debris found in DWTP (left), profile of microplastics changing through WWTP treatment (right) (Wang et al., 2020).

2.2. Oxidation systems for MPs

2.2.1. Photochemical Processes

Advanced Oxidation Processes (AOPs) are water treatment processes capable of oxidizing the toxic contaminants in municipal, industrial, and agricultural wastewater effluents. Among the many AOPs, photochemical processes based on light irradiation such as UV/H₂O₂ are applied in tertiary treatments at WWTPs as they have high performance rates and low costs (Ameta and Ameta, 2018). They are often employed to serve disinfection purposes as well (Parsons, 2004). The primary mechanism of the photochemical oxidation is the formation of strong oxidizing species like hydroxyl radical ($\bullet\text{OH}$), either by direct photolysis of hydrogen peroxide (H₂O₂) or photocatalysis (Parsons, 2004).

Before addressing the impact of the photochemical processes on MPs, the initial interest in photo-oxidation of plastics should be discussed first. Since the UV light content in sunlight has been known to damage plastics (Brennan & Fedor, 1994), various researchers studied UV irradiation's effects on plastics to maximize their resistance and lifetime. Early studies analyzed the mechanism of the plastic photo-oxidation and emphasized the role of photostabilizers in preventing the oxidation (Andrady et al., 1998; Rånby, 1989). It was discovered that UV irradiation could result in the breaking of polymer chains, the formation of free radicals, and the reduction in molecular weight, eventually disintegrating the plastics into smaller fragments (Browne et al., 2007; Yousif and Haddad, 2013). MP samples collected from the oceans showed a high degree of oxidation on the surface due to sunlight exposure (ter Halle et al., 2017). The photo-oxidation rate is known to be influenced by temperature, oxygen level, and the presence of biofilm, water, and wet soil (Allen et al., 1994; Duis and Coors, 2016). Furthermore, K. Zhu et al. (2019) simulated the UV irradiation of PS MPs with the addition of H₂O₂ and discovered that the reactive oxygen species (ROS) such as O₂^{•-}, H₂O₂, ¹O₂, and $\bullet\text{OH}$ played a crucial role in photo-oxidizing the microplastics,

increasing their surface roughness and decreasing the particle sizes.

The photo-oxidized plastics commonly show an increase in their carbonyl and hydroxyl groups in their FTIR spectra (Yousif and Haddad, 2013). Photo-oxidation also affects the adsorption efficiencies of organic pollutants on MPs. The photo-oxidized PS MPs (UV/H₂O₂ treatment for 96 hours) displayed up to one order of magnitude lower adsorption capacities towards organic compounds relative to the pristine MPs, possibly due to a decrease in surface hydrophobicity (Hüffer et al., 2018). The release of dissolved organic carbon (DOC) is another effect of photo-oxidation of MPs, as L. Zhu et al. (2020) identified DOC as the main product of photo-oxidation of PP, PE, and Expanded PS (EPS) after 68 days of UV-A exposure. The UV-A treatment also induced a mass loss of 6.6%, one of the highest reported mass losses with the UV irradiation alone. Specific types of plastics can contribute to the release of different organic compounds. C. Chen et al. (2019) reported that photo-oxidized PVC MPs could release the organotin compounds after UV-Vis light irradiation for 56 hours.

Lin et al. (2020) simulated the UV-C and vacuum ultraviolet (VUV) treatments in WWTPs by limiting the irradiation dose according to the USEPA manual (~180 mJ cm⁻²), and it was noted that even low doses significantly decreased the surface hydrophobicity of PS, PE, PVC, and PET MPs. UV irradiation alone has limitations since the contaminant needs to absorb the irradiation and go through the oxidation from its excited state (Parsons, 2004), which might be one reason why mass losses are rarely detected after the UV irradiation treatments alone. Despite the limitations of UV irradiation as a sole method, its various photo-oxidative effects on MPs imply that the UV-based AOPs employed in WWTPs, including UV/O₃ and UV/H₂O₂, could photo-oxidize the MPs and alter their organic compound adsorption abilities, physical traits, and functional groups. Some studies investigated the effectiveness of different tertiary wastewater treatments in removing the MPs (Hidayaturrahman and Lee, 2019; Talvitie et al., 2017b). However, the research literature is

still sparse on the performances of existing photochemical processes employed in WWTPs in removing or oxidizing the MPs.

Photocatalysis refers to the phenomenon that photocatalysts change the rate of a chemical reaction when exposed to light, and generate an electron-hole pair on the semiconducting material (Ameta and Ameta, 2018). Heterogeneous photocatalysis (HPC) became an attractive topic for many researchers after the first accomplishment by Fujishima and Honda (1972) to split water using UV light-induced Titanium oxide (TiO_2) photo-anode. HPC using TiO_2 as a photocatalyst has been getting attention as a promising photo-oxidation process for MPs. One of the first attempts to apply this technology was to photo-oxidize the MPs using TiO_2/CuPc catalyst under the fluorescent light (Shang et al., 2003). In this study, PS-(TiO_2/CuPc) composite thin films were prepared by adding the photocatalyst nanopowder into the dissolved PS solution in tetrahydrofuran, and 200 hours of the light irradiation induced about 7% mass loss of the films (Shang et al., 2003). Nabi et al. (2020) achieved almost complete mineralization (98.4%) of PS MPs into CO_2 by volume with TiO_2 nanoparticle films upon 12 hours of UV light irradiation.

Various other novel TiO_2 -based photocatalysts showed notable efficiencies in photo-oxidizing the plastics. Carbon and nitrogen-doped TiO_2 under 50 hours of visible light irradiation induced 71.77 ± 1.88 % mass loss of HDPE MPs at 0°C and $\text{pH} = 3.0$ (Ariza-Tarazona et al., 2020). Thomas and Sandhyarani (2013) observed PE- TiO_2 nanocomposite films experiencing a 68% reduction in mass within 200 hours of solar irradiation. Other TiO_2 -based photocatalysts reported were mesoporous N- TiO_2 (Llorente-García et al., 2020), protein-based porous N- TiO_2 (Ariza-Tarazona et al., 2019), combination of TiO_2 and FeSt_3 (Fa et al., 2020), dye-sensitized titania nanotubes (Ali et al., 2016), nano- TiO_2 coating (Luo et al., 2020), and the Polypyrrole/ TiO_2 nanocomposites (Li et al., 2010). They all resulted in efficient photo-oxidation of plastics.

Tofa et al. (2019a) first identified Zinc Oxide (ZnO) nanorods as a promising photocatalyst for MPs, which increased the carbonyl index, brittleness, and wrinkles of Low Density Polyethylene (LDPE) MPs. Moreover, Platinum/Zinc Oxide (Pt/ZnO) successfully photo-oxidized the LDPE MPs with 78% enhanced light absorption and 15% enhanced photocatalytic activity (Tofa et al., 2019b). Goethite was also tested as a photocatalyst, and the PE-goethite composite films showed a 16% mass loss with 300 hours of UV irradiation (Liu et al., 2010).

The applications of HPC for photo-oxidation of MPs have both prospects and constraints. Most of the studies on HPC with MPs used two methods: composite film formation or HPC in water. While turning plastics and photocatalysts into composite films can significantly increase the light absorption and photocatalytic performance of the plastics (Thomas and Sandhyarani, 2013), it will not be easy to apply it in WTPs or WWTPs, as the MPs remain dispersed in the wastewater. Furthermore, HPC in water poses limitations since the adsorption of dispersed MPs on photocatalysts can be difficult due to their size difference (Llorente-García et al., 2020). To overcome this drawback, Llorente-García et al. (2020) suggested the use of mesoporous N-TiO₂ coating, which could allow the collision of dispersed MPs and interact with the ROS accumulated on the coating surface, leading to the diffusion of ROS in the medium for further oxidation. Moreover, HPC in the solid matrix instead of water can be applied in sludge treatments. Nabi et al. (2018) mentioned adding the TiO₂-based films onto the MP filters for HPC in the solid matrix. HPC offers a high efficiency in oxidizing the MPs and will be a promising solution to the MPs problem if applied with further investigation of the operating conditions.

2.2.2. Ozone-based treatments

Using Ozone (O_3) as a highly efficient oxidant, the ozone-based treatments can oxidize numerous organic and inorganic compounds with the ROS formed from the ozone decomposition, including the hydroxyl radical ($\bullet OH$) (Ikehata and Li, 2018). They have been globally used in WTPs and WWTPs for several decades, mainly for disinfection purposes (Loeb et al., 2012). Ozone residuals do not remain long in the water, and ozone can be generated on-site from the oxygen gas, but the main drawback is its high cost (Chen et al., 2018; Crini and Lichtfouse, 2019).

Many researchers have investigated ozone treatments and its effects on plastics for decades to enhance the plastics' functionalities or their endurance under atmospheric ozone exposure. One of the earliest reports on the plastic interaction with ozone is by Kefeli et al. (1971). The study discovered that the ozone in the air could oxidatively degrade the PE plastics in a solid matrix, forming functional groups such as ketones, acids, and hydroperoxides. Later, the ozone degradation has been tested on various plastic types such as polychloroprene rubber (Anachkov et al., 1993), PE pulp fiber (Chtourou et al., 1994), microporous PP (Gatenholm et al., 1997), polyamide films (Ozen et al., 2002), PVA (Cataldo and Angelini, 2006), and polybutadienes (Anachkov et al., 2007). The most common outcome of ozone-based treatments on plastics is the increase in oxygen-containing groups and the evidence of surface oxidation (Chtourou et al., 1994; Ozen et al., 2002; Tian et al., 2017; Zafar et al., 2020). Another main result is the increase in surface hydrophilicity (Gongjian et al., 1996; Kumagai et al., 2007; Kurose et al., 2008; Reddy et al., 2010). Using these changes in surface properties, researchers designed the separation of particular

plastics types from a plastics mixture. Okuda et al. (2007) coupled ozonation with froth floatation. In their study, 60 minutes of ozonation induced a remarkable decrease in PVC floatability and hydrophobicity, resulting in their separation from a mixture of plastics with similar densities. The following studies observed the same outcomes with the PVC separation (Kurose et al., 2008; Reddy et al., 2010)(Mallampati et al., 2010; Kurose et al., 2008).

In ozone-based processes, different doses and exposure times can induce varying effects on the plastics. Zafar et al. (2021) conducted surface modification experiments on PE MPs with a range of ozone doses and durations (4 to 7 mg/min for 60 to 180 minutes). The study noted that the results depended on the conditions; 7 mg/min of ozonation for 180 minutes yielded the maximum ozone uptake and increase in carbonyl and hydroxyl indices. Apart from the traditional ozonation processes, various ozone-based treatments and their interactions with plastics were studied. UV light/Ozone treatments enhanced the hydrophilicity, adhesion property, and dyeability of PE and PP MP films (Gongjian et al., 1996). Another novel process is the heterogeneous nano-Fe/Ca/CaO catalyzed ozonation. Mallampati et al. (2017) applied it to separate the brominated and chlorinated flame retardants (B/CFRs) added plastics found in automobile shredder residue. In their study, the B/CFRs containing plastics underwent a decrease in Cl/Br functional group ratio and an increase in hydrophilic groups, leading to a successful froth floatation separation. The combination of thermal and ozone treatment also showed synergy in modifying the surfaces of PE, PVC, PS MP films (Kumagai et al., 2007).

The ozone treatments' ability to oxidize plastics is well reported, but it is imperative to question how they are performing in WTPs and WWTPs in treating the MPs. Hidayaturrahman and Lee (2019) examined the MP removal efficiencies of three WWTPs with different tertiary treatments in South Korea. Among the three, the WWTP with ozone treatment removed 89.9% of MPs by number of particles, and it achieved a total removal of 99.2% in the final effluent, which is significantly high. Z. Wang et al. (2020) analyzed the MP removal efficiencies of different processes at an advanced drinking water treatment plant. In this study, the 1-5 μm sized MPs in the ozonation tank showed a negative removal efficiency, meaning that the particle number increased, possibly due to fragmentation of larger plastics induced by the shearing flow in the tank (Horton et al., 2017). However, the authors discovered that the combination of ozonation and granular activated carbon (GAC) filtration enhanced the removal by 17.2-22.2%. These reports indicate that the ozonation can be an efficient and necessary treatment for MPs in WTPs and WWTPs. Nevertheless, more research is needed to confirm the oxidative effects on MPs in WTPs and WWTPs since existing literature mainly focus on the removal efficiencies in terms of particle number. Moreover, early findings on the oxidative effects of ozonation on plastics are mostly on macroplastics (>5 mm). Future studies should be more directed towards MPs in line with the emerging concerns on MPs.

Chapter 3. Materials and Method

3.1. Preparation of MPs

In this study, polypropylene (PP) with M_w of $\sim 12,000$, polyethylene (PE) with M_w of $\sim 4,000$, polystyrene (PS) with M_w of $\sim 35,000$, poly(vinyl chloride) (PVC) with M_w of $43,000$ and poly(ethylene terephthalate) (PET) beads with granular form were used as source of MPs. These plastic beads were obtained from Sigma-Aldrich. For the experiment, plastic beads were pulverized by Fritsch's Planetary Micro Mill "Pulverisette 7" into MPs having a size of about $1 \mu\text{m}$ using a wet-milling technique. The water used in both wet milling and experiments is Milli-Q water ($>18.2 \text{ M}\Omega \text{ cm}$, Milli-Q Integral Water Purification System, Millipore Co.). Zirconium oxide was used for both the grinding bowl and the ball, and the size of the grinding bowl was 2 mm . For detailed wet milling conditions, see Table 1. After wet-milling is finished, filter the grinding bowl and plastic beads by sieves, and wash the MPs suspension 3 times using a centrifuge to remove DOC. After washing was completed, the concentration of the stock suspension was measured and stored in a lab bottle and refrigerated. The concentration was measured by the following method. Prepare in advance by weighing a filter (White Nylon Membrane Filter, Whatman) with a pore size of $0.2 \mu\text{m}$. And the stock suspension is strongly stirred at 700 rpm for perfect mixing. After that, 1 ml is aliquoted with a micropipette and filtered through a membrane filter. Next, dry it in an oven at 60°C for more than 12 hours to completely remove moisture. Weigh the

filter with MPs and subtract the filter weight. In this way, the weight of the MPs in 1 ml of the stock suspension can be obtained.

Table 1. Wet milling conditions. (Weight of plastics, DI water and Grinding ball, Rotating speed and Milling time)

	Plastic weight (g)	DI water weight (g)	Grinding ball weight (g)	Rotating speed (rpm)	Milling time (milling (min)/pause (min))*repetition
PP	50	100	150	500	(30/30)*48
PE	50	100	150	500	(30/30)*24
PS	50	100	150	100	(60/0)* 192
PVC	25	100	150	500	(30/30)*24
PET	25	100	150	300	(180/30)*40

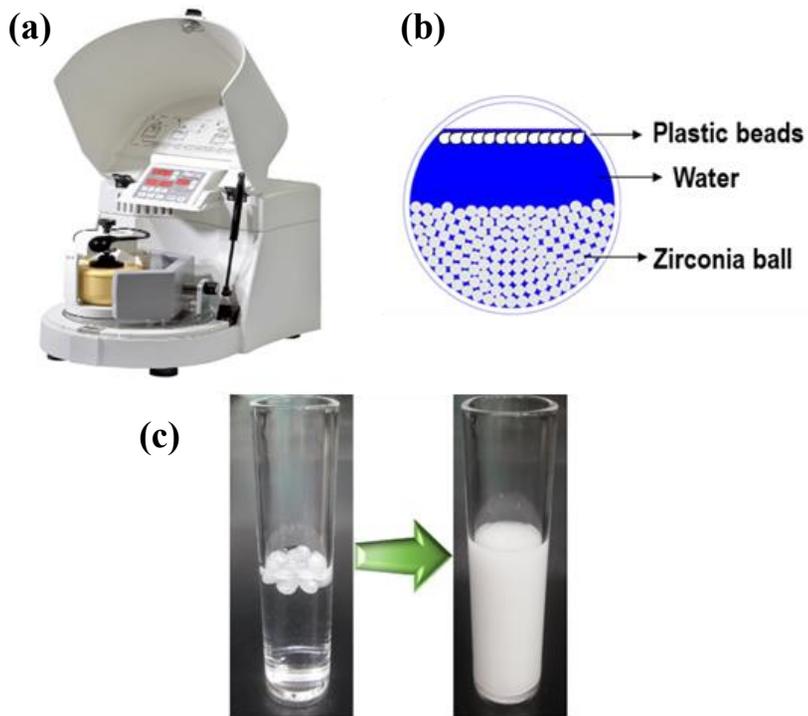


Figure 3. Wet Milling Technique. (a) Fritsch's Pulverisette 7, (b) Schematic diagram in a grinding bowl, (c) Before (left) and after (right) wet milling

3.2. Experiment

3.2.1. UV photolysis

The UV photolysis experiments of MPs were performed in a custom-made quartz reactor (diameter: 4.5 cm, height: 13.7 cm), exposing the MPs suspension to the UV from six 4-W low-pressure mercury vapor lamps (TUV 8W G8 T5 UVC Lamps, Philips Co.), which were placed equally on both sides of the reactor. All experiments related to UV photolysis were performed in the same manner under the same conditions, and the experimental procedure is as follows.

A reactor consisting of 100 mL of MPs suspension at a concentration of 100 ppm MPs was prepared by adding a calculated aliquot of the MPs stock suspension to distilled water. The photolysis reaction was initiated by exposing the reactor to UV. The reaction solution was vigorously mixed using a magnetic stirrer. The fan was operated during the reaction time to prevent heating of the reactor by heat generated from the lamps. Samples were collected at predetermined time intervals (0, 1, 2, 4, 8 h). A series of photolysis experiments were performed in duplicate and the average value and standard deviation of the experimental results were plotted on a graph.



Figure 4. A photograph of a black box consisting of 6 UV lamps and UV photolysis reaction of a MPs.

3.2.2. Ozonation

The ozonation system consists of an ozone generator and a reactor. The reactor consists of a 100 mL Pyrex flask, a rubber septum sealing the upside of the reactor, and a needle-type diffuser equipped to inject gas. (blue needle: diffuser, pink needle: vent, Figure 5.). One hour before the start of the reaction, the ozone generator is turned on to create ozone saturated water by bubbling ozone into DI water, and the reaction is started by adding an amount of MPs stock suspension to saturated ozone water. Ozone is supplied continuously until the reaction is over, maintaining a constant ozone concentration (~16ppm). All ozonation experiments were conducted in a fume hood. A series of ozonation experiments were performed in duplicate and the average value and standard deviation of the experimental results were plotted on a graph.

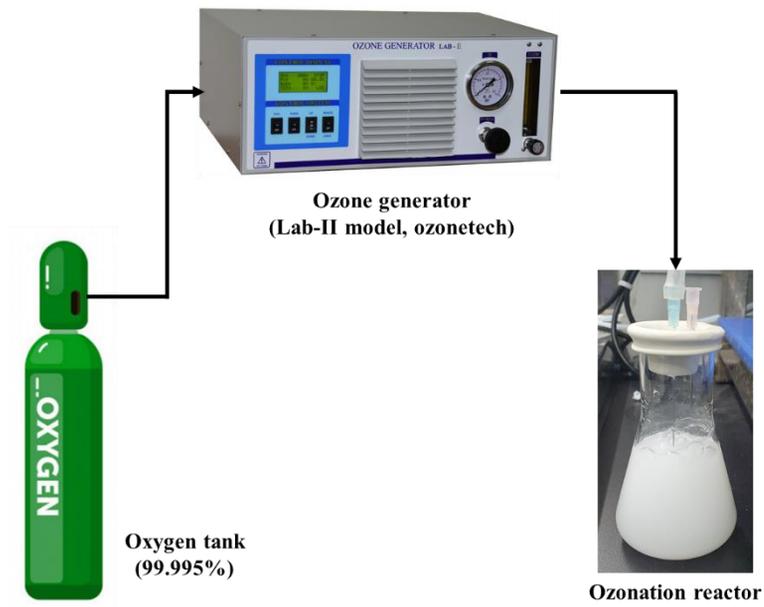


Figure 5. Schematic diagram of a reactor for the ozonation of MPs consisting of an ozone generator and a reactor.

3.3. Analytical methods

3.3.1. Mass loss

Prepare in advance by weighing a filter (White Nylon Membrane Filter, Whatman) with a pore size of 0.2 μm . After the reaction, the suspension of MPs is filtered using a vacuum filter. Next, dry it in an oven at 60°C for more than 12 hours to completely remove moisture. Weigh the filter with MPs and subtract the filter weight. By measuring the MPs mass according to the reaction time, the change in weight can be expressed as a graph.

3.3.2. DOC

10 mL samples were collected at predetermined time intervals. Filter the MPs using a syringe filter (HP 020AN, Adventec) and analyze the filtered solution with a TOC analyzer (Sievers M5310 C).

3.3.3. FT-IR analysis

Dry the MPs suspension to form a powder. Mix KBr powder (Sigma aldrich) and MPs in a ratio of 100:1 and grind with a mortar. A 13 mm pellet was made using Evacuable KBr Die (Perkin Elmer) and measured using an FT-IR spectrometer (Frontier, PerkinElmer) equipped with a slide holder.

3.3.4. Zeta potential and particle size distribution

Zeta potential (ZP) and particle size distribution (PSD) were both analyzed by Zetasizer Nano ZS (Malvern Panalytical). Disposable folded capillary cell was used to analyze and the The refractive index of MPs entered into the

program is Table 2. All absorption values were entered as 0.01 (Latex). ZP was measured according to the pH from 2 to 12, and NaOH and HClO₄ were used for pH adjustment. The calculated amount of MPs suspension was injected into 5 ml DI water with pH adjusted. Mix enough using a vortex, then put it into the cell for analysis. Three repeated measurements were performed to determine the average values and standard deviation.

Table 2. Refractive indices of MPs.

	Refractive index
PP	1.4920
PE	1.5190
PS	1.5717
PVC	1.5435
PET	1.5486

Chapter 4. Results and Discussion

4.1. Mass loss of MPs and DOC generation

MPs particles were oxidized by UV photolysis and ozonation, and as a result, the particles were dissolved and DOC was generated (Figure 6., Figure 7.). In Figure 6.(a), in the UV photolysis system, both PS and PET showed a mass loss of about 38%, but PP, PE, and PVC did not change in mass. Figure 6.(b) shows the mass change according to the MPs ozonation. PS showed 100% mass loss (no particles left) in 8 hours, and PET showed 32% mass loss. There seems to be a 11% change in the mass of PVC as well, but this is likely to be an error in the measurement process. PVC MPs easily fall off membrane filters because of their unique properties. Since mass loss occurred due to an experimenter's error in the process of weighing after drying the filter, re-experiments are necessary for accurate analysis. PP and PE did not lose weight by ozonation.

As mass loss occurs, the concentration of DOC also increases. However, DOC was measured at a concentration lower than that corresponding to the amount of reduced mass. This is because DOC is also oxidized and removed by UV and ozone. The decrease in the concentration of DOC means that organic carbon has been mineralized into CO₂ and water due to oxidation. Using the following equation, the amount of carbon mineralized can be obtained. PS was the most mineralized with about 59% by ozonation, and the rest was mineralized with about 10 to 16% (Table 3.).

Amount of mineralize carbon =

$$\text{(Mass loss (mg} \cdot \text{L}^{-1}\text{))} \times \text{(Carbon content)} - \text{(DOC (mg} \cdot \text{L}^{-1}\text{))}$$

These results show that when MPs are exposed to the oxidation system of a water treatment process over a long period of time, the particles can transform into DOC form and eventually become mineralized. The conditions used in this experiment were much harsher than the actual water treatment plant, so the mass change in the short term cannot be predicted. Plastics include a flame retardant called hexabromocyclododecane, plastic additives such as PAHs, DDTs, BPA, and phthalates, as well as persistent organic pollutants, so dissolution of DOC may lead to deterioration of water quality. We must continue to discuss how to solve this problem.

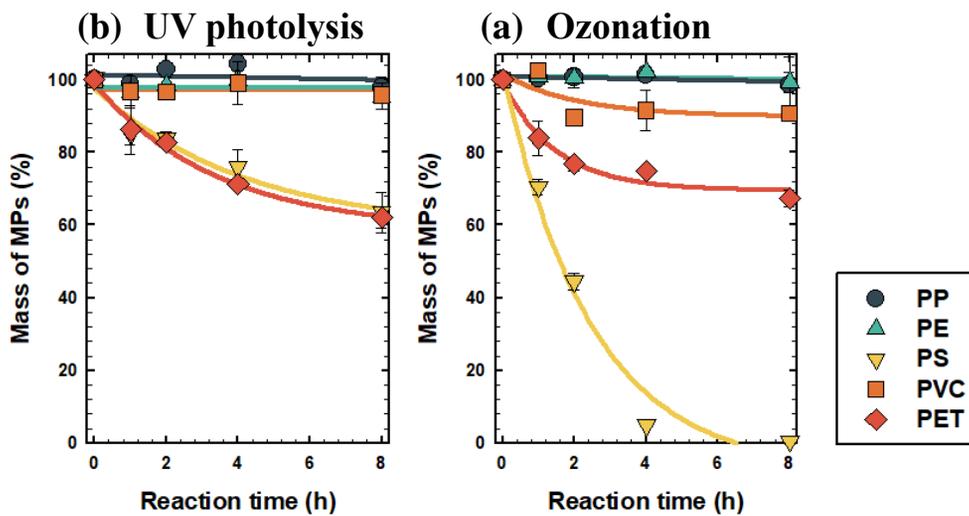


Figure 6. Mass loss of MPs by (a) UV photolysis and (b) ozonation.

$[PP]_0 = [PE]_0 = [PS]_0 = [PVC]_0 = [PET]_0 = 100$ ppm; $[O_3]_{avg.} = 16$ ppm.; UV lamp = 6 e.a.;

Reaction time = 8 h.

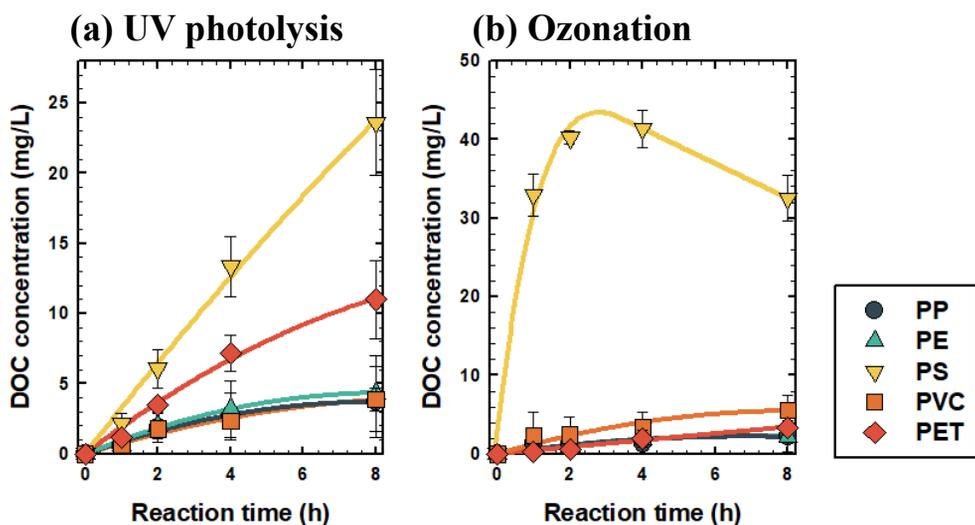


Figure 7. Dissolved organic carbons from MPs during (a) UV photolysis and (b) ozonation.

$[PP]_0 = [PE]_0 = [PS]_0 = [PVC]_0 = [PET]_0 = 100$ ppm; $[O_3]_{avg.} = 16$ ppm.; UV lamp = 6 e.a.;
Reaction time = 8 h.

Table 3. Calculated mineralized carbon from PS and PET.

	UV photolysis		Ozonation	
	PS	PET	PS	PET
Mineralized carbon (mg/L)	10.12	12.71	59.21	16.22

4.2. Changes in PSD of the MPs suspension

As MPs are oxidized, their size may decrease. These changes were also observed in our study. No significant size reduction was observed in PP, PE and PVC. In PS and PET, the size decreased significantly after oxidation. The size of PS decreased significantly after ozonation, whereas PET decreased significantly after UV photolysis. The size of the UV-treated PP seems to increase, but it does not actually increase, and because the dispersion stability decreased due to the change of the Zeta potential, aggregation occurred, the PSD peak shifted to the right. A detailed explanation is given in 4.3.

The reduction in the size of MPs has a negative impact on environmental aspects in three major ways. The first is the generation of nanoplastics (NPs <100 nm). Since NPs are very difficult to detect and analyze, few studies have been conducted to detect them in environmental samples. However, because of their very small size, it is easy for microorganisms such as plankton to be ingested. In addition to this, when it enters the body, it can travel through blood vessels without being excreted through the digestive tract. NPs traveling through blood vessels can attack other cells. The second is an increase in toxicity. MPs have high adsorption capacity for various contaminants, and the larger the specific surface area, the more contaminants can be adsorbed. As the size of MPs gets smaller, the surface-area-to-volume ratio increases exponentially, so it can be thought that the toxicity of MPs also increases. The third is the difficulty of detection. Until now, studies on detecting and analyzing MPs in environmental samples have been conducted on MPs with a

size of 10 μm or more. Despite the fact that MPs with a size of 1 to 10 μm reach 95% of the total, the reason there has been little research on them is that the time and economic cost required to detect small size MPs is much higher. The smaller the size of MPs, the more difficult it is to detect, and it becomes very difficult to separate or monitor MPs from the environment. For these three reasons, it can be said that the size reduction of microplastics can have a very negative impact on the environment.

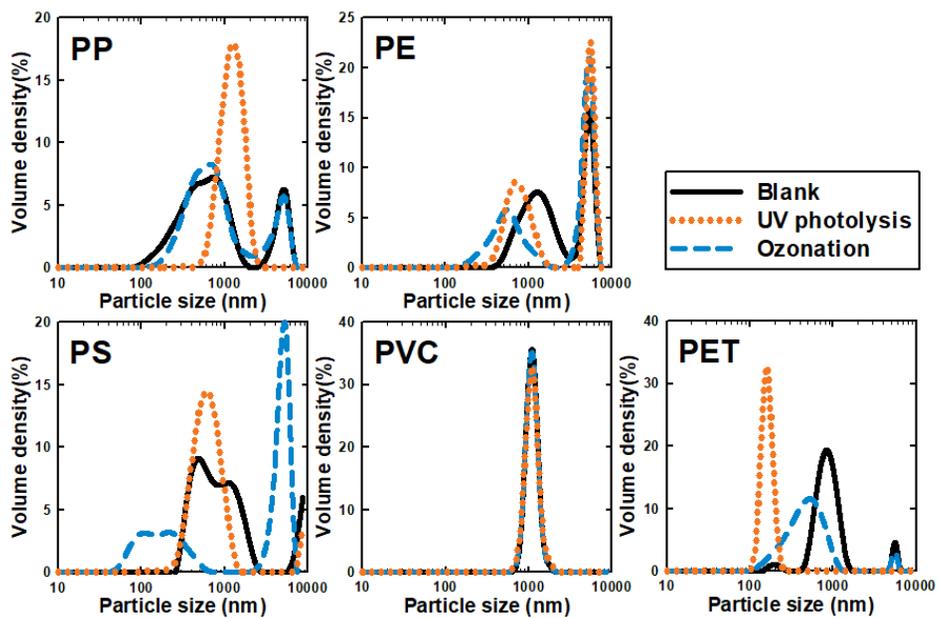


Figure 8. Particle size distributions of MPs suspensions before and after UV photolysis and ozonation.

$[PP]_0 = [PE]_0 = [PS]_0 = [PVC]_0 = [PET]_0 = 100 \text{ ppm}$; $[O_3]_{\text{avg.}} = 16 \text{ ppm}$.; UV lamp = 6 e.a.;

Reaction time = 8 h.

4.3. Reduced dispersion stability of MPs

The dispersion stability of MPs can be evaluated through the change of the Zeta potential (ZS). It can be said that the dispersion stability of MPs decreases as the absolute value of the slope of the graph when plotting ZS according to pH decreases. The higher the dispersion stability, the less aggregation between particles, and the lower the dispersion stability, the more likely to occur aggregation. The most significant change in the slope of the graph was PP, which was actually aggregated after UV photolysis (Figure 8.). PS and PVC also showed a large change in values, but after PS oxidation, the graph shifted in the overall negative direction. This means that the inert particle has become acidic. PVC is slightly different from PS. Both before and after oxidation are acidic, the degree of acidic decreases after oxidation and dispersion stability decreases at the same time. PE and PET also showed a slight decrease in slope, but the difference was very slight.

In other previous studies, pristine MPs were oxidized to increase dispersion stability. If so, the reason why this study is different from previous studies should be explained. Additional experiments and analysis are required for a more thorough explanation, but looking at the results so far, it can be explained as follows. Since MPs were made through wet milling, a large amount of alcohol functional groups were formed on the surface due to strong weathering, and MPs with increased hydrophilicity existed well dispersed in water. The dispersion stability may have decreased due to the disappearance or transformation of functional groups that

helped the dispersion through oxidation by UV and ozone. However, this is only conjecture and further study is needed to determine the exact cause.

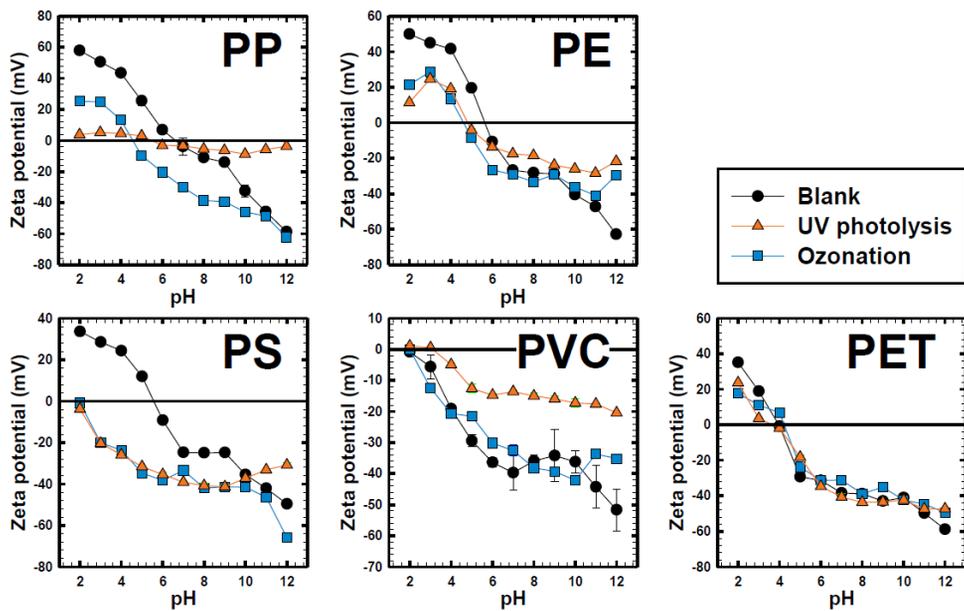


Figure 9. Zeta potential of MPs suspensions as a function of pH before and after UV photolysis and ozonation.

$[PP]_0 = [PE]_0 = [PS]_0 = [PVC]_0 = [PET]_0 = 100 \text{ ppm}$; $[O_3]_{\text{avg.}} = 16 \text{ ppm}$.; UV lamp = 6 e.a.;

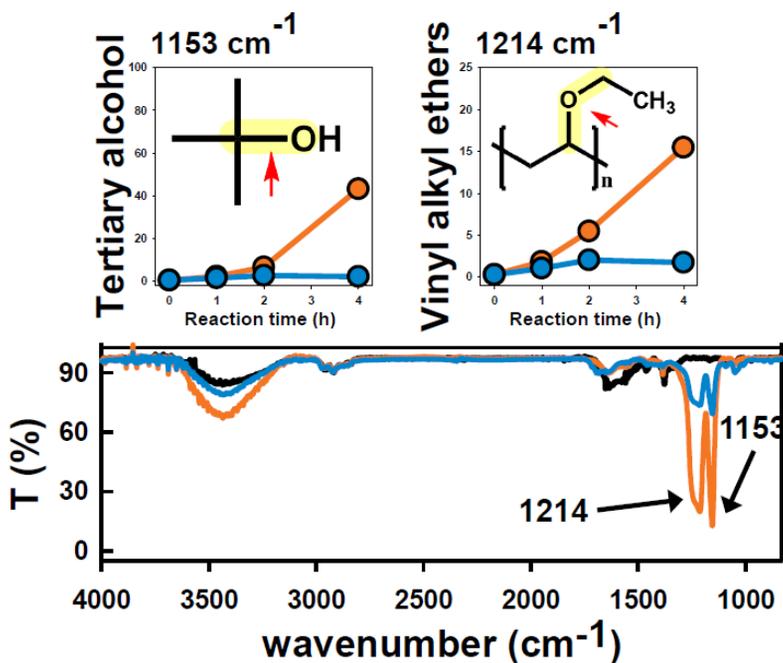
Reaction time = 8 h.

4.4. OCFG increase on the surface of MPs

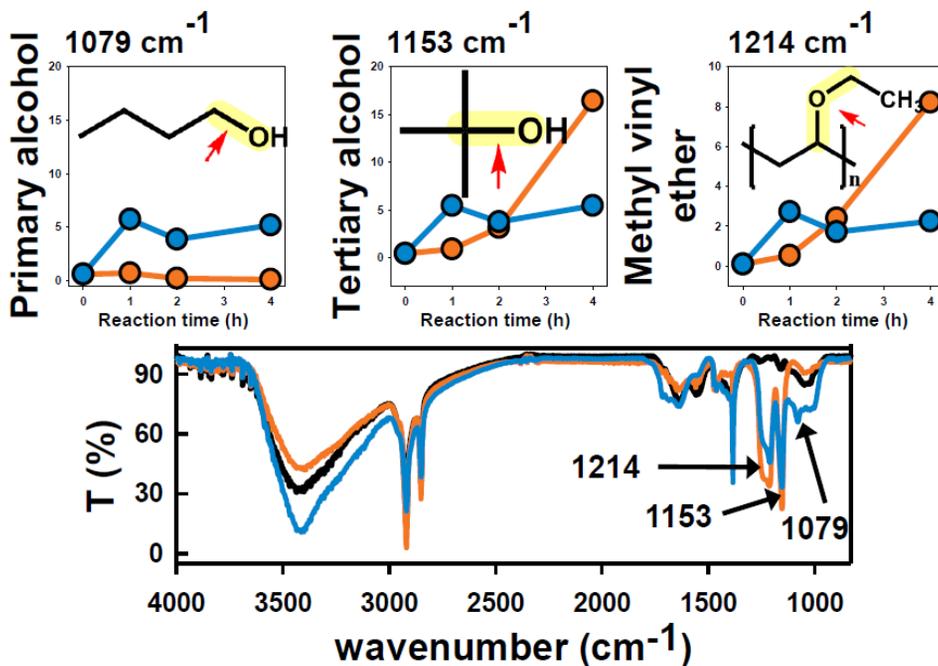
Oxygen-containing functional groups (OCFG) increase on the surface when MPs are oxidized. Our study also confirmed the result of an increase in OCFG after oxidation. Overall, the physical changes (mass loss, DOC, PSD) of MPs have changed significantly by ozonation, and the chemical changes (ZP, OCFG) seem to change significantly by UV photolysis. Looking at the FT-IR spectrum of Figure 10., it seems that the greatest change occurs when PS and PET are exposed to UV. In PS, an increase in alcohol (O-H, 3435 cm^{-1}), aliphatic aldehyde (C=O, 1731 cm^{-1}), and vinyl alkyl ethers (C-O-C, 1214 cm^{-1}) groups was observed. In PET, an increase in alkyl aryl ether (C-O-C, 1046 cm^{-1}), benzoate ester (C-O, 1269 cm^{-1}), benzoate ester (C=O, 1721 cm^{-1}), and alcohol groups was observed. PP and PE showed similar changes. In common, alcohol, vinyl alkyl ethers, and tertiary alcohol (C-O, 1153 cm^{-1}) groups increased, and primary alcohol increased only in PE. There was no change in FT-IR spectrum for PVC. In summary, it can be said that OCFG did not increase in PVC, PP and PE increased, but not as much as PS and PET.

Since OCFG acts as an active site for pollutants on the surface of MPs, there are studies that increase the adsorption capacity of pollutants when OCFG increases. It can be said that the oxidation of MPs certainly enhances the adsorption of pollutants to the surface. Oxidized MPs reduce particle size, resulting in an increase in surface area to volume ratio. This provides a larger surface area for contaminants to adhere to. At the same time, OCFG is also increased, providing more active sites for contaminants to adhere to.

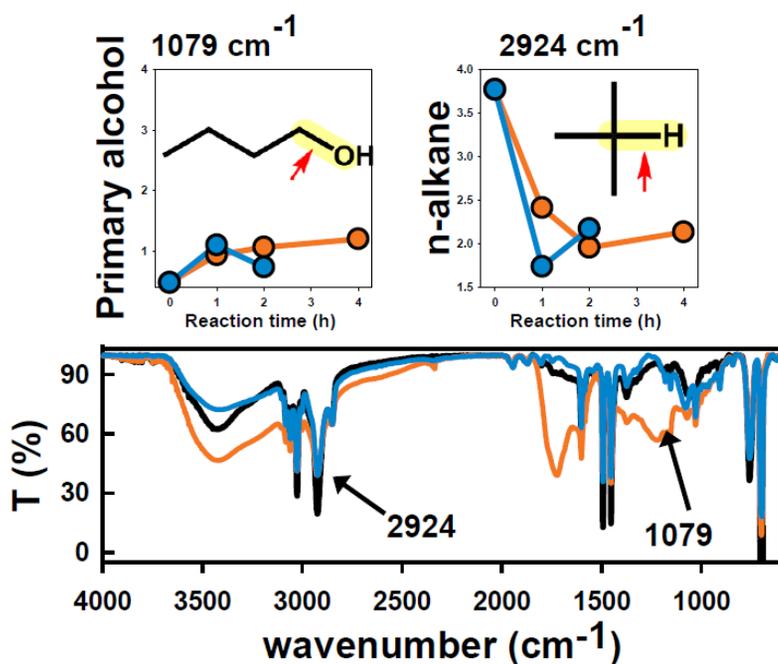
(a) PP



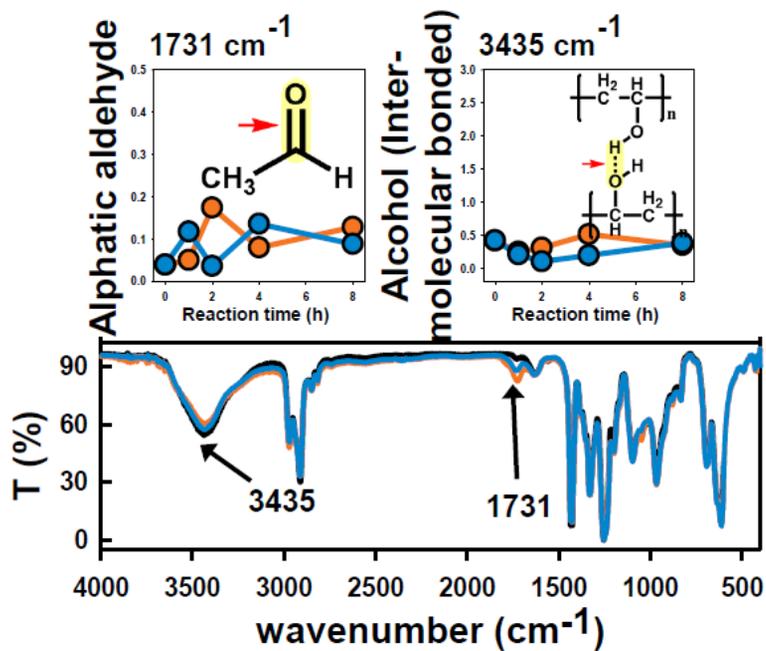
(b) PE



(c) PS



(d) PVC



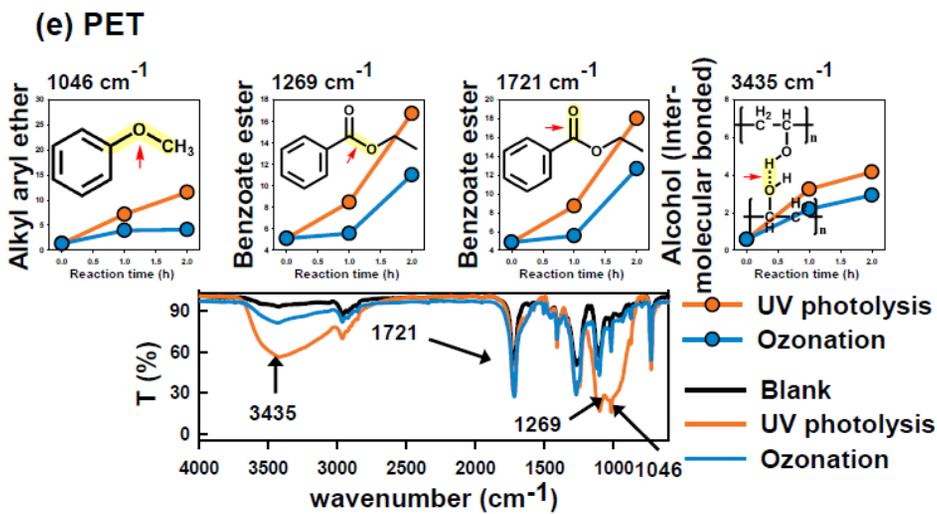


Figure 10. Changes in the FT-IR spectrum and peak height of the functional groups were observed during UV photolysis and ozonation.

[PP]₀ = [PE]₀ = [PS]₀ = [PVC]₀ = [PET]₀ = 100 ppm; [O₃]_{avg.} = 16 ppm.; UV lamp = 6 e.a.;

Reaction time = 8 h.

Chapter 5. Conclusions

This study investigated the oxidation behavior of MPs by two oxidation systems (i.e. UV photolysis and ozonation). The results from this study provide the following: MPs are oxidized to change to DOC form and at the same time the particle mass decreases. Also, the size decreases, dispersion stability decreases, and OCFG increases. To compare the oxidation stability of the five MPs investigated, PVC>PP=PE>PET>PS. PS and PET showed distinct changes in almost all analyses, whereas PVC was the most unchanged MPs.

As a result of the study, it seems that the oxidized MPs in the water treatment plant will worsen the water quality. As the plastic dissolves, the concentration of POPs in the water increases. In addition, due to the decrease in particle size, toxicity increases, and water quality management becomes difficult as it is not detected. In addition, the contaminant adsorption capacity increases due to the increase in the surface-area-to-volume ratio and the increase in OCFG. These problems are the parts that we must study, consider, and solve together in the future.

WTP needs to develop technology to quickly detect and isolate MPs over 1 μ m. After that, they have to develop a system that can collect and process MPs larger than 1 μ m and mineralize smaller MPs via AOPs.

The laboratory should develop a technology that can monitor NPs in the

environment and come up with a plan to manage MPs, which are getting smaller over time.

Plastics production plants need to develop and use environmentally friendly additives that can replace PAHs, DDTs, BPA, and phthalates.

This study was conducted under conditions that are much harsher than the actual water treatment plant conditions. As a follow-up study, it may be necessary to check the oxidation change of MPs by experimenting similarly to the conditions of the actual water treatment plant.

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국문 초록

지구의 유비쿼터스 오염 물질인 미세플라스틱(MPs, <5 mm)은 인류의 건강과 생태계에 심각한 잠재적 위협을 가하고 있다. MPs의 위해성은 주로 입자의 크기, 입자에서 용출된 유기물의 독성, 입자의 오염물질 흡착 능력 등에 의해 결정된다. MPs의 위해성은 입자가 산화됨에 따라 변화될 수 있는데, 지금까지 수행된 대부분의 연구는 해양환경에서 일어나는 산화 거동에만 집중하였다. 하지만 많은 양의 MPs가 하수처리장과 정수처리장 내에서 검출되었고 이에 따라 수처리장 내 MPs의 산화 거동 연구의 필요성이 새롭게 제기되었다. 그러나 현재까지 수행된 관련 연구의 수가 매우 적고, 각 연구에서 제공하는 정보가 매우 제한적이므로 수처리장 내 MPs의 산화 거동을 종합적으로 예측하는 데에 많은 어려움이 있다.

이 연구는 수처리 공정 중 UV 광분해 및 오존 공정에서 일어나는 MPs의 산화 거동을 환경에서 가장 많이 발견되는 다섯 종류의 MPs (즉, PP, PE, PS, PVC 및 PET)를 대상으로 조사하였다. 산화에 의한 MPs의 물리적/화학적 특성 변화를 종합적으로 분석하고, 이를 바탕으로 MPs의 산화가 수질에 미치는 영향을 예측하였다. 실험을 위해 습식분쇄기법으로 입자 크기가 약 1 μm 인 MPs 현탁액을 제조한 후에 8시간 동안 고농도의 오존과 고강도의 자외선에 지속적으로 노출시킨 후 MPs의 중량, 용존 유기 탄소 농도, 입도 분포, 제타 전위, 표면 작용기의 변화를 관찰했다. 연구 결과 PVC가 가장 높은 산화 안정성을 보였으며 대부분의 분석 결과에서 산화 전후의 차이를 보이지 않았다. PP와 PE의 경우 산화에 의한 중량 손실이 없고, 용존 유기 탄소 농도의 변화 또한 미미하였으나 표면에 산소 함유 작용기가 증가하였고 표면 전하의 변화로 분산 안정성이 감소하였다. 이는 PP와 PE가 산화 안정성이 높지만 강한 산화 환경에 노출되면 표면이 산화되어 이전과는 다른 입자적 특성을 갖게 됨을 의미한다. PS와 PET는 가장 낮은 산화 안정성을 보였으며 그 결과 산화 시스템 및 플라스틱의 종류에 따라 약 30%(UV/PS, UV/PET,

O₃/PET) 및 100% (O₃/PS)의 중량 손실이 나타났다. 이 결과는 PS와 PET가 UV 및 오존 산화에 매우 취약함을 보여주며 산화로 인해 입자 크기가 감소한 결과는 초미세플라스틱(NPs, <100 nm)의 발생 가능성을 의미하기도 한다. 이 연구를 통해 MPs가 수처리 공정에서 산화되어 질량 감소, 용존 유기 탄소의 용출, 입자 크기 감소, 표면 전하의 절댓값 감소 및 표면의 산소 함유 작용기 증가와 같은 물리적/화학적 특성 변화가 일어나는 사실이 밝혀졌다. 이러한 결과는 수처리 공정에 의해 MPs가 수질 환경에 더 위협적인 존재로 변화될 가능성이 있음을 보여준다. 또한, 다양한 분석을 통해 PVC>PE=PP>PET>PS 순서로 MPs가 UV와 오존에 대하여 강한 산화 안정성을 가지고 있음을 밝혔다.

주요어 : 미세플라스틱, 산화, UV 광분해, 오존 공정, 수처리장

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