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Changes in Organics and Nitrogen during Ozonation of Anaerobic Digester Effluent

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Abstract: The objective of this study is to investigate the consequence of ozone dosage rate on the qualitative change in organic compounds and nitrogen in anaerobic digester effluent during the ozone process. Therefore, ozonation improves the biodegradability of recalcitrant organic compounds, quickly oxidizes the unsaturated bond, and forms radicals that continue to deteriorate other organic matter. In this study, ozonation was performed in a microbubble column reactor; the use of microbubble ozone improves the status of chemical oxygen demand (COD) and changes of organic nitrogen to inorganic compounds. The ozone injection rates were 1.0, 3.2, and 6.2 mg/L/min. The samples obtained during the ozone treatments were monitored for COD_{Mn}, COD_{Cr}, TOC, NO_2^--N, NO_3^--N, NH_4^+-N, T-N, and Org-N. The ozone dose increased 1.0 to 6.2 mg/L and it increased the degradation ratio 40% and the total organic carbon 20% during 20 min of reaction time. During the ozonation, the COD_{Cr} and COD_{Mn} values were increased per unit of ozone consumption. The ozone treatment showed organic nitrogen mineralization and degradation of organic compounds with the contribution of the microbubble ozone oxidation process and is a good option for removing non-biodegradable organic compounds. The original application of the microbubble ozone process, with the degradation of organic compounds from a domestic wastewater treatment plant, was investigated.

Keywords: anaerobic digester effluent; biodegradability; nitrogen; ozone; organic compound

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1. Introduction

Millions of tons of organic waste are produced by humans every day, a significant portion of which is dumped into domestic wastewater. In domestic wastewater treatment plants, the principal treatment system is mostly biological [1]. The conventional biological wastewater treatment process employs a group of various microorganisms to degrade organic wastewater compounds aerobically [2]. Effluent from anaerobic digestion tank and composting processes effluent is more specific type of wastewater, the properties primarily rely on the oxygenation and moisture of the treated substance. Recalcitrant organic compounds are compounds that resist the atmosphere and are especially conducive to the treatment of aerobic microbial wastewater [3]. Recalcitrant compounds consistently emerge from biological treatment processes, and they create a potential problem for water reuse [4–7]. Anaerobic digestion is a possible technique for processing many types of recalcitrant organic matter. In anaerobic digesters, nitrogenous substances are converted to ammonium nitrogen (NH_4^+-N) by a biodegradation process [8]. Therefore, the dissolved oxygen level in the anaerobic digester effluent is not sufficient, due to the anaerobic process. The high concentrations of nutrients and low oxygen availability in the anaerobic digester effluent can affect aquatic organisms that receive the natural water, reducing biodiversity. However, wastewater from anaerobic digesters requires further treatment to protect the aquatic environment [9].

Currently, ozonation is a popular technology for the neutralization of fluid process residues. Most commonly, ozone reduces the number of organic pollutants or the toxicity

of wastewater. In addition, organic compounds can be oxidized and become degradable by ozonation [10]. Ozone has been successfully used for the disinfection and decomposition of dissolved organic pollutants [11–16]. Ozone is a strong oxidant that reacts as molecular ozone or through the formation of secondary oxidants, such as free radicals [17]. The principle of the ozone process is based on the release of hydroxyl radicals, which accelerate the degradation of organic compounds in an aquatic environment. The main factors affecting ozonation performance were pH, the nature and concentration of oxidizable organics, ozone dose, the presence of oxidant scavengers, and the efficiency of ozone mass transfer. Ozone pretreatment, to improve biodegradation via partial oxidation, is a potential solution for recalcitrance.

Therefore, it is possible to use the ozone oxidation system for preliminary preparation of the digestion tank effluent from the composting procedure for neutralization in a professional wastewater treatment plant. Ozonation is among the most effective technologies to oxidize recalcitrant and non-degradable substances converted to a biodegradable form [1], and is also considered a good treatment option, as ozone is a strong oxidant that converts organic and inorganic pollutants into non-toxic by-products [18,19]. Ozone has been used in potable water treatment for disinfection, odor treatment, and color removal [20]. The ozonation of organic compounds involves a stepwise process, where the oxygen particles are gradually integrated into the compound [2]. Therefore, ozone treatment shows a strong positive impact on digestion wastewater, due to the high content of aerobic bacteria and non-degraded organic matter. The objective of this study is to investigate the change in recalcitrant organic carbons and nitrogen in effluent from an anaerobic digestion tank. Anaerobic digestion has been used for decades to treat leachate from municipal solid waste landfills, and leachate is well known for its high COD and ammonium concentration and low biodegradability [21]. Due to the characteristics of this kind of effluent, the improvement in organic characteristics by the ozone process is the focus of this study. This study aimed to develop a more effective and economic ozone treatment process for sewage water, with a significant component of non-biodegradable substances, to establish an ozone dosage rate for improving organic removal and conditions for the ozone operation. However, the experimental results also efficiently evaluate the ozone dosage's performance to enhance the biodegradability of effluent from the organic waste digestion tank at a laboratory scale.

2. Materials and Methods

2.1. Experimental Setup

The experimental devices shown in Figure 1 are installed at the domestic sewage treatment plant (STP), located in South Korea. In this experiment, the effluent from the anerobic digestion tank was used as the target water for treatment. The influents used in this experiment, from the anaerobic digestion tank composting process effluents, depended mainly on the oxygenation and moisture of the processed material.

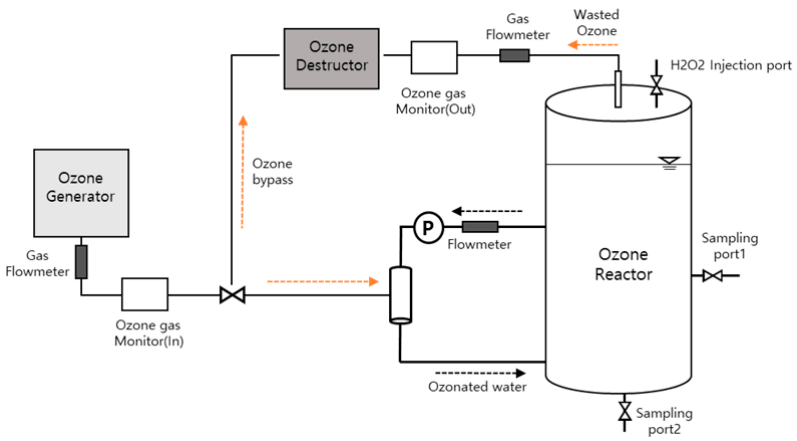

Figure 1. Schematic diagram of experimental setup.

2.2. Operational Condition

The batch test was conducted with 3 different ozone feed rate and with 1 L/min fixed ozone flow rate. The raw water volume and water flow rate were fixed at 20 L and 25 L/min, respectively, for all conditions. Operating conditions are listed in Table 1.

Table 1. Operational conditions.

Operating Conditions	Unit	Ozone Feed Rate (mg/L/min)		
		1.0	**3.2**	**6.2**
Oxygen flow rate	L/min	1.0	1.0	1.0
Oxygen tank flow rate	L/min	3.5	4.0	4.0
Pressure	(Kgf/cm^2)	0.7	0.7	0.7

2.3. Characteristics of Wastewater

The STP anerobic digestion tank effluent contained a high COD concentration and low biodegradability. This wastewater composition was consistent with the pollutant characteristic of domestic sewage. Water temperature (T) and pH were measured in the process of sampling. Detailed properties are shown in Table 2.

Table 2. Characteristics of influent.

Parameter	Concentration	Parameter	Concentration
pH	7.80	T-N (mg/L)	350–355
Temp	30–35 °C	NH_4^+-N (mg/L)	270–280
COD_{Cr} (mg/L)	180–280	NO_3^--N (mg/L)	0.007–0.009
COD_{Mn} (mg/L)	95–105	NO_2^--N (mg/L)	3.0–8.0
TOC (mg/L)	130–140	SS (mg/L)	40–45

2.4. Experimental Procedure

The ozone system consists of an ozone generator, ozone reaction column (effective volume 20 L), sampling port, residual ozone meter (electrode method, measuring range 0.5 ppm), flowmeter (20 LPM), ejector, ozone gas monitor, gas flow meter, and ozone destructor. Ozone was generated from oxygen conversion in the ozone generator and simultaneously entered the ozonation reaction column.

The ozone process was fed domestic wastewater from the anaerobic digestion tank effluent and contained a high COD concentration and had low biodegradability. This wastewater composition was consistent with the pollutant characteristics of domestic sewage. Water temperature (T) and pH were measured in the process of sampling.

2.5. Analytical Methods

The ozonation process was performed in a reactor and was fixed with a microbubble generator. Samples were collected at 2–5 min intervals after starting the ozonation using 1 L plastic bottles from sampling ports of the reactor. Temperature and pH were measured using a pH meter (S-610H) immediately after sampling. Soluble COD_{Cr}, COD_{Mn}, NO_2^--N, and NO_3^--N were measured after filtration using 47 mm microfiber filter paper. Total COD_{Cr}, COD_{Mn} and T-N were measured using the CMAC standard method by the HACH DR-5000 spectrophotometer. Dissolved ozone concentration gas was captured from the ozone gas monitor by electrode method; the measuring range was 0.5 ppm. For the analysis of TOC, the total organic high-temperature carbon combustion oxidation method (ES 04311.1b) was applied among the water pollution process test standards. The instrument used for the analysis was a TOC-V CPH (SHIMADZU), and the combustion temperature was 680 °C. The amount of sample used for the analysis was 40 mL, filtered once using a 0.45 μm syringe filter, transferred to a vial, mounted on an auto-sampler, and measured

by the non-purifying organic carbon method (NPOC method) at 680 °C, and the pH was controlled by 85% H_3PO_4 (automatic injection of the instrument).

3. Results

3.1. Changes in Organic Compounds

The chemical oxygen demand potassium dichromate index (COD_{Cr}) measures the oxygen equivalent of the amount of organic matter oxidizable by potassium dichromate in a 50% sulfuric acid solution. The chemical oxygen demand potassium permanganate index (COD_{Mn}) measurement of a sample is an alternative method for measuring the oxygen requirement and is an indication of the oxidative degradation potential of wastewater [2]. The COD_{Mn} measurement requires a shorter oxidation time, simpler apparatus, and produces no hazardous chromium waste. Due to its high reproduction potential and reactivity, ozone reacts with both organic and inorganic compounds [22–24]. In addition, ozone is a strong oxidant that is capable of causing cell lysis and disinfection and increasing the content of soluble COD [17,25–27].

Figure 2a shows that when the ozone dosage was 1.0 mg/L/min, the efficiency of improving organic compounds increased slowly, and the soluble COD_{Cr} value increased from 190 to 275 mg/L. This results occurred due to dissolved ozone was present, organic matter was decomposed by the ozone, and the degradation performance of the ozone process was enhanced [28,29]. However, under the different ozone conditions, the feed rate had an almost similar efficiency in improving organic compounds with increasing reaction time. Here, mainly in the ozone system, ozone oxidized the organics directly [28]. Ozone utilization is more effective at lower ozone concentrations, but longer retention times are required for optimal efficiency [30]. When the dosage of ozone was increased from 3.2 to 6.2 mg/L/min (Figure 2b), the soluble COD_{Cr} changed only slightly after 10 to 20 min. This phenomenon happened because the O_3 solubility in water is constant; therefore, an overly excessive dose of O_3 cannot improve its oxidation performance. The COD_{Mn} determination of wastewater is the amount of oxidizing organic matter in the sample [31] and indicates the potential extent of biological oxidation. An increase in the COD_{Mn} of a sample would indicate its higher amenability to biodegradation.

Figure 2b indicates that during the ozone dosing from 1.0 to 6.2 mg/L/min, the efficiency of improving organic compounds increased from 32 to 51%. On the other hand, when the ozone dosage increased from 3.2 to 6.2 mg/L/min (Figure 2b), the soluble COD_{Mn} did not increase compared to the ozone dosage rate. The graph indicates that the 3.2 mg/L/min O_3 feed rate has the maximum increment, and increased rapidly between 10 min and 20 min. In this stage, the O_3 solubility in water is increased; therefore, a 3.2 mg/L/min dose of O_3 can improve its oxidation performance. However, in all conditions of ozone feed rate, the conversion of material into biodegradable matter enhanced after 10 min of ozone reaction time. Comparatively, in low O_3, the feed rate had better efficiency in improving organic compounds with increasing reaction time.

The total organic carbon (TOC) content of a sample is the amount of organic matter potentially available for microbial mineralization. The COD/TOC ratio is an indication of biodegradability. An increase in the proportion after ozone treatment indicates better biodegradability because of an increase in the COD and TOC proportions, which can be modified by biological mineralization [2]. From Figure 2d, it can be observed that the ozone experiments decreased the recalcitrant organic load of the anaerobic digestion tank effluent and increased the COD_{Mn}/TOC ratio. These results show that inorganic compounds were changed into organic substances; therefore, it could easily be biologically degraded. Although there is a crucial improvement of COD_{Mn}/TOC ratio which is higher than 0.4 and this is the minimum value considered apposite for the efficient implementation of a biological treatment [32].

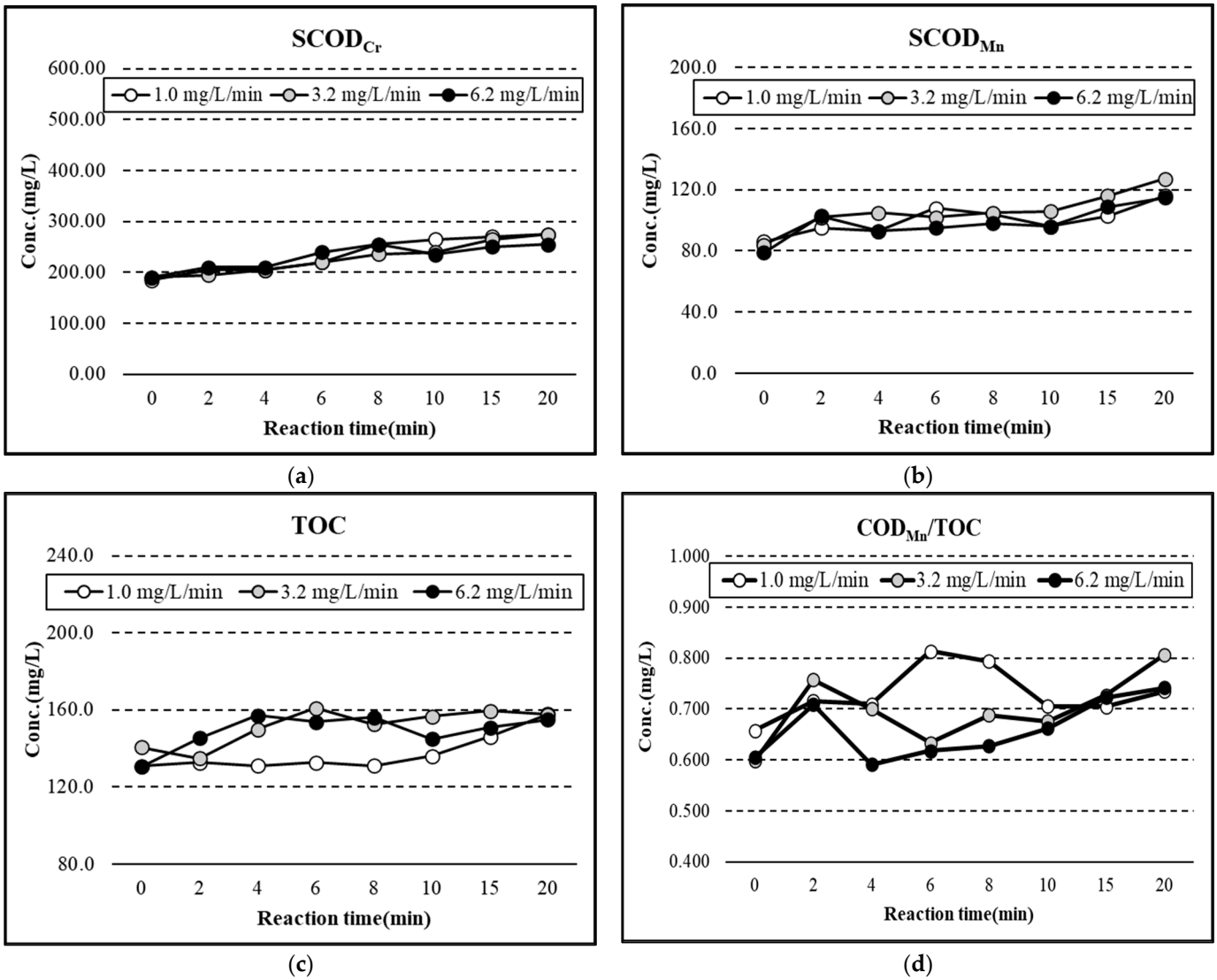

Figure 2. Effect of ozone feed rate on (a) $SCOD_{Cr}$, (**b**) COD_{Mn}, (**c**) TOC, and (**d**) COD_{Mn}/TOC.

3.2. Changes in Nitrogen

To demonstrate the transformation of nitrogen in the ozonation process, the anaerobic digestion tank effluent was exposed by ozone at feed rates of 1.0, 3.2, and 6.2 mg/L/min, and the total reaction time of each experiment was 20 min. Figure 3 presents NO_2^--N, NO_3^--N, NH_4^+-N, and T-N variations at three different feed rates. Due to the inhibitory characteristics of ammonium nitrogen, during 20 min of reaction, the NH_4^+-N concentration was nearly similar compared to all the feed rates of ozone oxidation. This indicated that the ozone could hardly convert the NH_4^+-N into NO_3^--N or NO_2^--N in this case. In contrast, ozone may be more involved in the oxidation of nitrite, nitrate, and organic nitrogen. Hence, the ozone had minimal effect on T-N removal and changes in NH_4^+-N. During 20 min of ozone reaction, the variation in the T-N concentration was inconspicuous, which indicated that the effect of ozone on nitrogen removal was not significant. However, the nitrate and nitrite concentrations of the anaerobic digestion tank effluent were below than 0.5 mg/L and, when ozone applied the values were increased per unit of ozone consumption. This showed that the pre-ozone treatment mainly had a significant changing effect on organic nitrogen in wastewater.

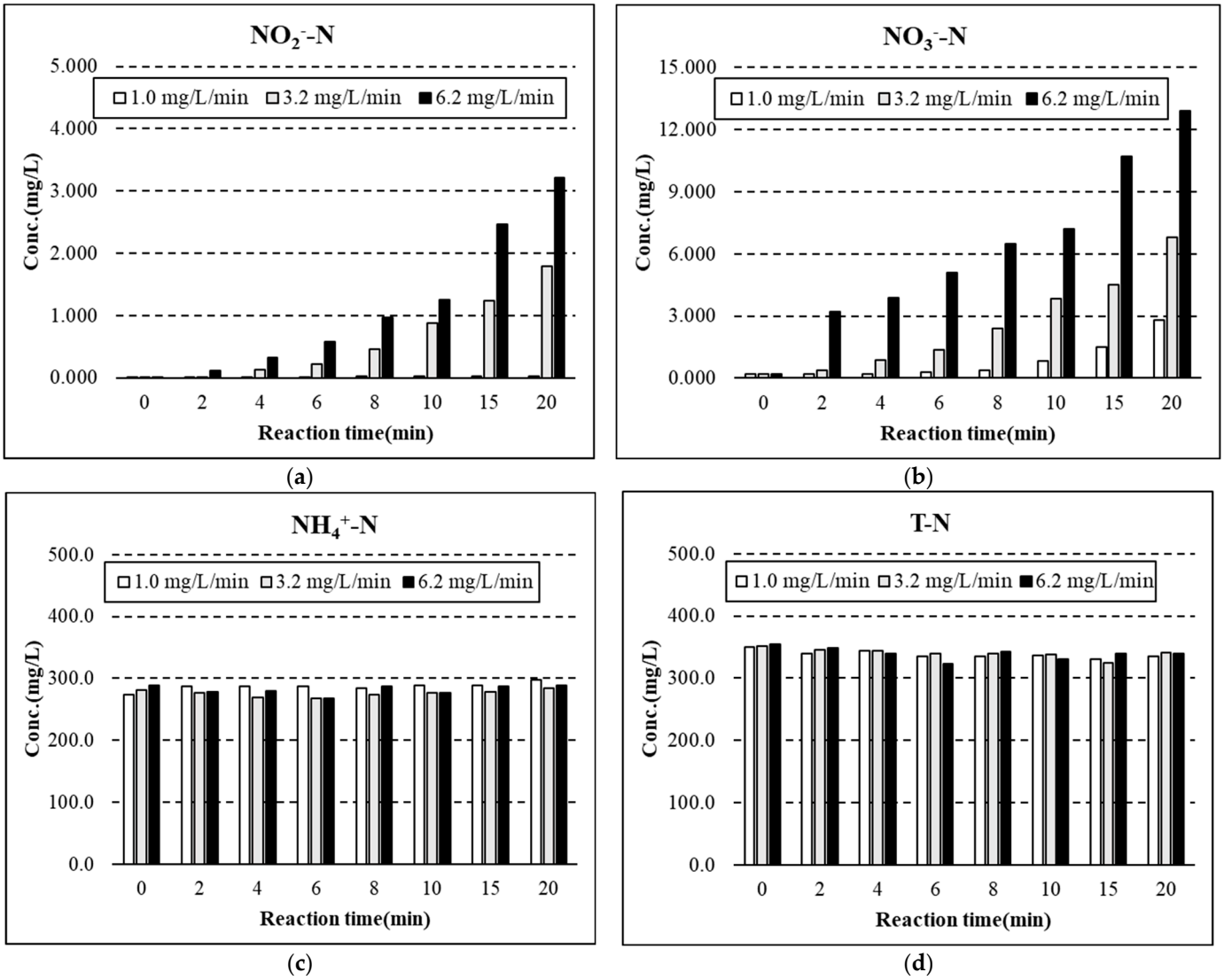

Figure 3. Nitrogen changes by ozone: (**a**) NO_2^--N, (**b**) NO_3^--N, (**c**) NH_4^+-N, and (**d**) T-N.

3.3. Effect of Ozone Dosage on Nitrogen

From Figure 3, the changes in NO_2^--N, NO_3^--N, T-N, and NH_4^+-N can be observed, and the values were monitored to investigate the effect of ozone treatment. The average changes according to the total composition of NH_4^+-N, NO_3^--N, NO_2^--N, and T-N during the ozonation treatment process are shown in Figure 4. After ozone treatment, the results present increasing NO_3^--N and NO_2^--N, slightly decreasing NH_4^+-N, and almost consistent T-N. In the process of this treatment, a small amount of ammonia nitrogen can be oxidized to nitrogen nitrate. The radicals produced by ozone treatment potentially resist ammonification from organic nitrogen, a small amount of ammonia nitrogen can be oxidized to nitrogen, and the combination of the two will reduce the concentration of ammonia nitrogen, so the amount of ammonia nitrogen declined slightly [33,34]. The ozone process could not remove nitrogen directly, which led to an almost similar concentration of T-N, and [35] also reported that nitrate formation is enhanced by the direct oxidation of ammonium by ozone.

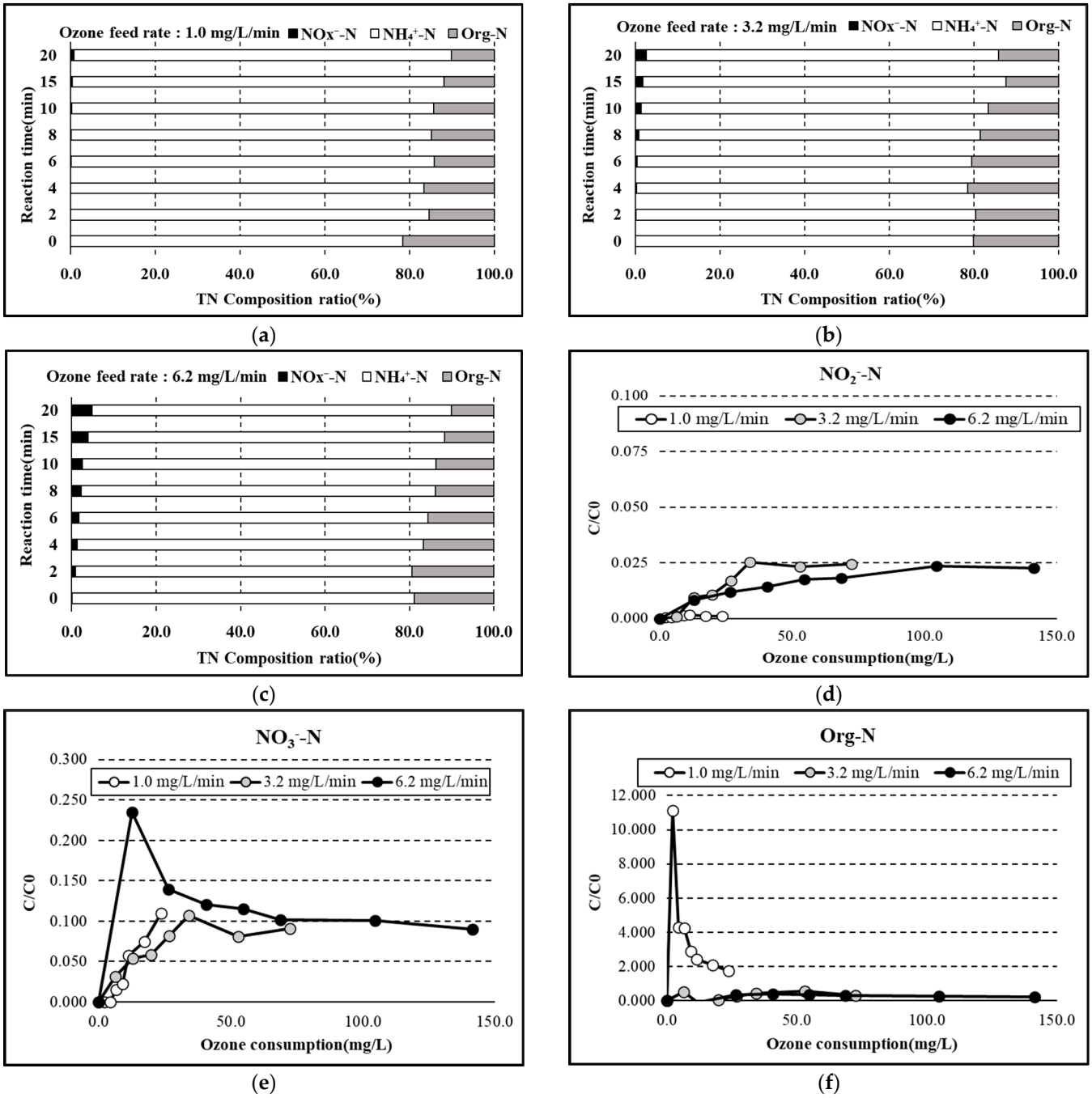

Figure 4. Effect of ozone feed rates on (**a**) NO_2^--N, (**b**) NO_3^-N, and (**c**) Org-N, and ozone consumption vs. generated (**d**) NO_2^--N, (**e**) NO_3^-N, and (**f**) Org-N.

3.4. Effect of Ozone Dosage on COD_{Cr}, COD_{Mn}, and TOC

To demonstrate the effect of ozone dosage and reaction time, the anaerobic digestion tank effluent was exposed to ozone dosage at 6.2, 3.2, and 1.0 mg/L/min, respectively, for 20 min of reaction time. Figure 5 shows that when the ozone dosage increased from 1.0 to 6.2 mg/L/min, the ozone consumption also increased from 2.1 to 141.4 mg/l. With the increase in ozone consumption, the soluble COD_{Cr} and COD_{Mn} concentrations also increased. Consequently, the effect of low ozone dosage can achieve high degradation of organic compounds. The result shows that ozonation is more effective at degrading organic pollutants in under 20 min of reaction time. In these experimental conditions, ozonation allowed direct oxidation by microbubble ozone; the pH value was around 7.8

and there was almost zero sludge production. The applied ozone dosage was determined upon TOC and COD content in the effluent. The result shows the effectivity of direct ozone reactions on TOC increment efficiency. Studying the COD and TOC variations helped to better understand the effect of ozonation. The increase in COD was insignificant when the ozone dose of 6.2 mg/L/min was introduced. An excess ozone dosage lowered the total process utilization efficiency.

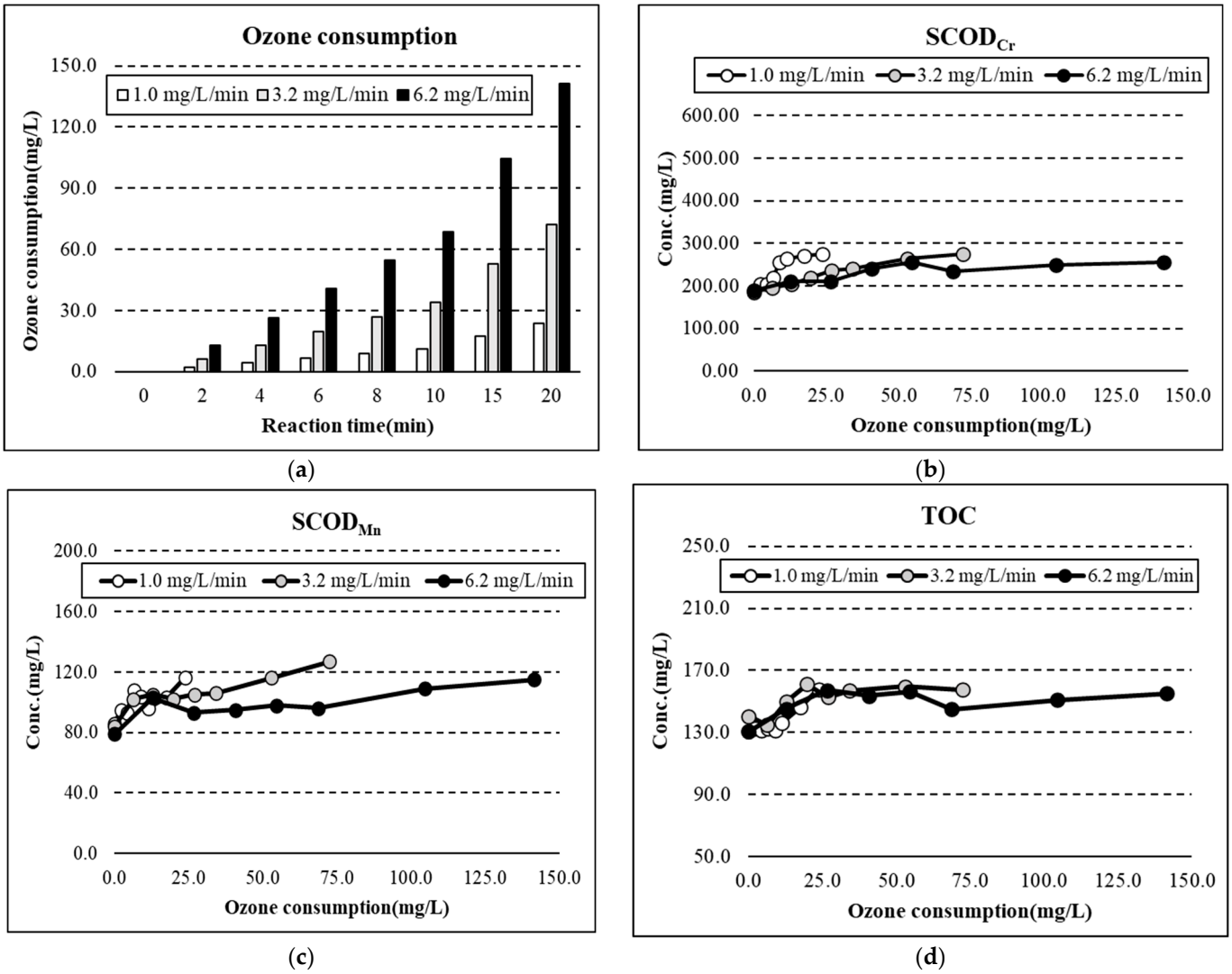

Figure 5. Effect of (**a**) ozone consumption and feed rate on (**b**) COD_{Cr}, (**c**) COD_{Mn}, and (**d**) TOC.

3.5. Ozone Dosage on Ozone Consumption and Reaction Time Effects on Biodegradability

Figure 6 indicates that when the reaction time of ozonation was 60 min, the efficiencies of improving the biodegradability COD_{Mn}/COD_{Cr} ratios were 1.08%, 0.85%, and 0.72%, respectively, but at 20 min of reaction time, the COD_{Mn}/COD_{Cr} ratios were high (0.99%, 0.92%, and 0.81%), and from this, the ratios declined to 0.83%, 0.84%, and 0.72%, respectively. With the high ozone feed rate, the efficiency of improvement was comparably high, and the high ozone concentration may have promoted the degradation of organic matter. Therefore, at a low feed rate of ozone gas, the reaction time was a maximum of 180 min and the ratio of COD_{Mn}/COD_{Cr} was increased from 0.39 to 0.77, but the maximum value of 96 appeared at 120 min of reaction time. When the initial ozone concentration was 3.4 mg/L/min, the COD_{Mn}/COD_{Cr} ratios were increasing up to 60 min, and then became stable, and, thus, difficult to decompose organic matter. In this situation, the total COD_{Cr} and COD_{Mn} values were also decreased. In opposition, at a high ozone concentration, the ratio increases from

0.79 to 1.29, which shows high biodegradability compared to the other feed rate of ozone gas. In other cases, the biodegradability parameters are estimated as a function of ozone dosage and show the optimum ozone dose for maximum biodegradability improvement [2].

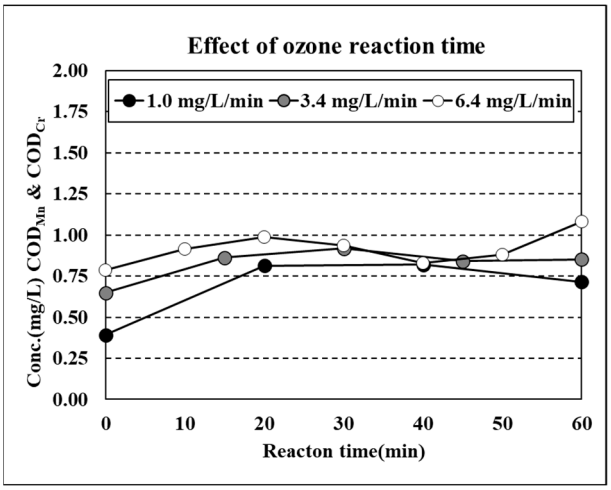

Figure 6. Ozone dosage and reaction time effects.

4. Discussion

Ozone-based oxidation processes are currently being assessed and increasingly applied for strengthened treatment of domestic wastewater effluents [36]. Initially, reduction or conversion of the parent compound was the only goal of such treatment, but micropollutants do not usually mineralize and less transformation products arise during the reaction with ozone [36,37]. Previous studies have shown that the formed transformation products have less biological activity, compared to the original compounds [38]. However, some literature showed enhanced toxicity after ozonation [39,40], and in these observations, it is unknown which transformation products from micropollutants, or by-products were formed during oxidation [36,38,41–44]. Additionally, the increased ozonation-induced toxicity is often mitigated by biological after-treatment [40].

The results of the present study confirm that ozone can effectively degrade the organic compounds from the anaerobic digestion tank and assist in biodegradability. Moreover, the results showed the significant changing effect on organic nitrogen during the ozone process. Microbubble ozone technology was chosen for ozonation because of the reliability and efficiency; the use of the microbubble type of ozone also overcomes the limitation of solubility, which leads to low utilization efficiency during wastewater treatment. During ozonation, an appropriate ozone flow rate selection for the decomposition of organic pollutants is very important for optimizing ozone utilization. An increase in ozone dose enhances the driving force for ozone to move into wastewater, which increases the production of hydroxyl groups that ultimately improve the decomposition efficiency and mineralization rate of organic matter [45,46]. In this experiment, ozonation was used to improve the characteristics of organic pollutants from non-degradable to biodegradable, by changing the biological properties during the oxidation process. The ozone feed rate and ozone reaction time affect the change of organics [2] and the ratio of organics increases over time [22]. In previous studies of wastewater treatment, various parameters have been used to measure improved biodegradability ratios (BOD/COD, BOD/TOC, and BOD/DOC) [2]. In addition, the biodegradability parameters identify the optimum ozone conditions for the removal of recalcitrance. Overall, the COD_{Cr}, COD_{Mn}, and TOC rates increased after the main experiment, to 30%, 40%, and 20%, respectively. However, the initial concentration levels of COD and TOC were higher during the main experiment, compared to the preliminary experiment, due to the different sampling times.

To demonstrate the ozone dosage effect on ozone consumption and reaction time on the improvement of biodegradability, the anaerobic digestion tank effluent was subjected

to ozonation at 1.0, 3.2, and 6.2 mg/L for 20 min of reaction time. The results indicate that ozonation is more effective at degrading the non-degradable pollutants under 20 min of reaction time. However, the ozone concentration increasing because of the ozonation utilization rate decreasing is a sign of a suitable situation at which to stop ozonation and commence biodegradation. In these experimental conditions, ozonation allows direct oxidation by microbubble ozone; the pH value was around 7.8 and there was much less sludge production.

However, there are also a few limitations for the ozone treatment, such as the application of excessive ozone dosage to compensate for the low ozone solubility. This leads to the high cost of the ozonation process. Ozonation may form toxic by-products and the partial oxidation of biodegradable matter may form recalcitrant compounds [2].

5. Conclusions

The effect of ozone dose on organic compound and nitrogen changes has been investigated by using anaerobic digester effluent. Under the appropriate parameter conditions (ozone gas flow of 1.0 L/min and ozone dosage of 1.0–6.2 mg/L), the effluent soluble COD_{Cr}, COD_{Mn}, and TOC values were increasing, which indicated that the system improved the biodegradability of organic substances. The ozone dose of 6.2 mg/L increased the degradation ratio by 40% and increased the total organic carbon by 20% over 20 min of reaction time. Therefore, the COD_{Cr} and COD_{Mn} values will increase per unit of ozone consumption with the increase in reaction time. On the other hand, the new findings of this study were that the appropriate ozone feed rate confirms to change the nitrite and nitrate ions under ozonation. The ozone treatment showed organic nitrogen mineralization and degradation of organic compounds, with the contribution of the microbubble ozone oxidation process, and is a good option for removing non-biodegradable organic compounds. The application of the microbubble ozone process, with the degradation of organic compounds from a domestic wastewater treatment plant, was investigated. It is well known that ozonation can oxidize non-degradable organic compounds to degradable by-products. In addition, ozone promotes the partial oxidation of pollutants, and by partial oxidation, wastewater organic pollutants improve their characteristics. Finally, the above-mentioned results indicated that the process was more suitable for the pre-treatment of anaerobic digester effluent to treat refractory organics of domestic wastewater. Further studies should be focused on the cost effectiveness and optimization of ozone in the following treatment process. Further, it is necessary to carry out more pilot plant-scale experiments with actual domestic wastewater implementations of scale-up parameters.

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Abbreviations

COD	Chemical oxygen demand
COD_{Cr}	Chemical oxygen demand by dichromate
COD_{Mn}	Chemical oxygen demand by permanganate
TOC	Total organic carbon
NO_2^--N	Nitrite nitrogen
NO_3^--N	Nitrate nitrogen
T-N	Total nitrogen
NH_4^+-N	Ammonia nitrogen
Org-N	Organic nitrogen
SS	Suspended solids
BOD	Biochemical oxygen demand
DOC	Dissolved organic carbon

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