Enhanced removal of dichloroacetonitrile from drinking water by the combination of solar-photocatalysis and ozonation

Donghoon Shin a, Min Jang c,*, Mingcan Cui a,b, Seungmin Na a, Jehee Yong Khim a,*

a School of Civil, Environmental and Architectural Engineering, Korea University, 5 Anam-dong, Seoul 136-701, Republic of Korea
b Jilin Institute of Chemical Technology, 5 Cheng De Jie, Jilin 132022, China
c Department of Civil Engineering, Faculty of Engineering, University of Malaya, Kuala Lumpur 50603, Malaysia

Abstract

In this study, the photocatalytic ozonation process using either UV lamps with a wavelength close to a solar wavelength (UVsolar) or natural solar light was established to study the effects of the major operating parameters on the removal of a toxic disinfection by-product (DBP), dichloroacetonitrile (DCAN), from drinking water. Based on the test results of a bench system, the UVsolar/TiO2/O3 process had the highest DCAN-removal rate among the advanced oxidation processes (AOPs). The optimal TiO2 and ozone doses were 1 g L−1 and 1.13 g L−1 h−1, respectively, while room temperature (20 °C) produced the highest rate constant in the kinetic tests. The kinetic rate constants linearly increased when the UVsolar intensity increased in the range 4.6–25 W m−2; however, it increased less at intensities higher than 25 W m−2. The test results of the outdoor system showed that the solar/TiO2/O3 process provided complete removal of DCAN that was two times faster and had about 4.6 times higher energy efficiency than with solar/TiO2.

As a green oxidation technique, solar photocatalytic ozonation could be a good alternative for treating recalcitrant and toxic organic pollutants, because it has high oxidation potential and low energy consumption compared to conventional AOPs.

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1. Introduction

Although disinfection by-products (DBPs) can be controlled through removing natural organic matters (NOMs) in the drinking water treatment process, it is not only difficult to remove NOMs completely, but DBPs are inevitably produced when the remaining chlorine is released to rivers and reacts with NOMs. As a representative DBP, dichloroacetonitrile (DCAN, a type of haloacetonitrile) is produced by the reaction between NOMs and chlorine in the drinking water treatment process. According to the World Health Organization (WHO), the provisional guideline value of DCAN is 0.02 mg L−1 (WHO, 2011), and the Ministry of Environment, South Korea, mandates it to be at 0.09 mg L−1. In the water-treatment plants of South Korea, concentrations higher than 0.04 mg L−1 have frequently been detected since 2009, while those of Florida, USA, have a concentration higher than 0.02 mg L−1 (Reckhow et al., 2001). When taken orally for a long time, DCAN forms and accumulates thiocyanate (SCN−) in the liver, blood, skin, and muscles, causing fetal malformations, respiratory disorders, and skin cancer (Nikolau et al., 1999). Thus, it is necessary to completely remove this toxic chemical through an effective oxidation technique. Because of the strong oxidation capacity of advanced oxidation processes (AOPs), extensive studies have been conducted on using ultrasound (US), the Fenton process, UV/H2O2, ozone, US/UV, UV/TiO2, and solar/Fenton processes to treat recalcitrant organic compounds such as trihalomethane (THM), chloroform, and dichloroacetic acid (Tang and Tasso, 1997; Mohamadin, 2001; Bahnemann et al., 2002; Nogueira and Mode, 2002; Shemer and Narkis, 2005; Guo et al., 2006; Rice, 2008; Jo et al., 2011; Park et al., 2011). However, in the case of DCAN, only a few studies...
related to AOPs, especially those using ozone and activated carbon, have been reported (Chu et al., 2012). Nowadays, an important trend is to focus on green oxidation, which can reduce the use of energy and consumable chemicals. Photocatalysis using sunlight, a type of green oxidation process, has been recognized as an energy-saving and environmental-friendly process. However, the oxidation ability of sunlight photocatalysis in degrading DBPs is lower than with the other chemical processes. As a strong oxidative chemical, ozone also has low reactivity on compounds bearing single carbon bonds, such as DCAN (Bryant et al., 1992). Hence, it is difficult to degrade DCAN below the permissible limit (0.02 or 0.09 mg L\(^{-1}\)) when ozone alone is used.

The photocatalytic ozonation process using sunlight can be considered an important tool in the removal of recalcitrant organic compounds, because it is energy efficient and can accelerate oxidative reactions by generating additional hydroxyl radicals. Despite these advantages, detailed studies on this process have not been reported so far. In particular, there is no study on the factors influencing the removal of DCAN by photocatalysis or/and ozone process. One of the important parameters, pH, can affect the removal kinetics by governing the surface charges of the catalyst and the pollutant, as well as the ozone reaction (Wang et al., 1999). Therefore, the optimum pH should be determined for obtaining the highest rate of target pollutant removal. Second, the catalyst and ozone doses should also be optimized because of their effect on the removal kinetics. Due to their close interaction, the optimum ratio should also be defined in the treatment process. In addition, UV intensity has an important role in enhancing the ozone mass transfer. Although some reports have shown that the efficient UV intensity range for degrading organic pollutants is 20–30 W m\(^{-2}\) (Herrmann, 1999; Malato et al., 2009), there is no study on the optimal UV intensity in photocatalytic ozonation. Temperature, another significant factor, could affect the adsorption, reaction activity, and ozone concentration. For example, as temperature increases, entropy increases, which reduces the adsorption capacity of the contaminant on the catalyst surface, as well as ozone dissolution, whereas the ozone decomposition rate can increase to enhance the radical reaction.

In this research, the major operating parameters such as pH, catalyst (i.e., TiO\(_2\)) and ozone doses, temperature, and UV intensity, were investigated in the removal of DCAN by photocatalytic ozonation. Through operating bench and outdoor systems using UV lamps and solar light, respectively, the energy efficiency for each process was also estimated on the basis of DCAN-removal kinetics and efficiency. In particular, the authors attempted to use the most efficient concentrator geometry (i.e., compound parabolic concentrator, CPC) in the oxidation process of DCAN (Bahnemann, 2004).

2. Materials and methods

2.1. Materials

DCAN and methyl tert-butyl ether (MTBE) were purchased from Sigma Aldrich (99.5% pure grade) and J.T. Baker, respectively. Titanium dioxide (Degussa, P-25, anatase/rutile = 75/25%) was used as a catalyst in the process. The molecular formula of DCAN is C\(_2\)H\(_4\)Cl\(_2\)N (109.94 g mol\(^{-1}\)) and Henry's law constant is 3.79 \times 10^{-6} \text{atm m}^3\text{mol}^{-1}. DCAN has a neutral charge in the aqueous phase, DCAN was extracted by a liquid extraction method using a gas chromatography–mass spectrometry (GC–MS) system (Agilent 7890A/5975C), equipped with a DB-5MS column (YW Scientific, length: 30 m, inner diameter: 0.25 mm, film thickness: 0.25 μm). MS was set at electron impact-GC–MS scan mode (70 eV) with specific retention time (4.678 min), confirmation ion (m/z 74), and quantitative ion (m/z 82).

2.2. Setup of bench and outdoor photocatalytic ozonation systems

Bench and outdoor photocatalytic ozonation systems mainly consisted of the combination of CPC and ozone reactor (Fig. 1). CPC contained three quartz tubes (length: 40 cm, diameter: 3 cm, thickness: 1.5 mm) and three stainless modules with reflectors made of polished aluminum. A cylindrical ozone reactor with a cooling system was made of stainless steel (length: 110 cm, diameter: 10.5 cm, and total volume: 9.5 L). For the bench system, UV radiations were obtained from three metal halide lamps of different powers (100, 250 and 400 W), purchased from Osram (Munich, Germany) which were placed 60 cm above the CPC reactor at the top of the chamber as artificial solar light. The UV intensity in the sunlight wavelength range was measured using a spectroradiometer (PS-200, Apogee Instruments). The irradiation wavelengths of the metal halide lamps (designated as UV\(_{\text{solar}}\), 300–800 nm) and solar light (>300 nm) were similar in terms of the light spectrum.

Meanwhile, all devices and operation conditions for the outdoor system were the same as for the bench system, except that natural solar light was used instead of UV\(_{\text{solar}}\) lamps. As shown in Fig. 1b, the angle of CPC modules was set at 38° (Malato et al., 2002). For both systems, deionized water (5 L) containing 1 mg L\(^{-1}\) of DCAN (initial concentration) was circulated using a magnetic centrifugal pump (MD-40, Iwaki) from circulation reservoirs to CPC chambers. To improve the utilization of the catalyst, the Reynolds number should be between 4000 and 10000 for creating turbulence (Fernandez-ibanez et al., 2009; Malato et al., 2009). In this study, the flow was maintained at 14 L min\(^{-1}\), which is more than 10000 Reynolds number. Temperature was controlled at 20 ± 1 °C using a cooling system. Ozone was injected into the reservoir from an ozone generator (Trigen) using glass diffusers (pore size: 20 μm). Ozone generation was controlled in the range 1.00–1.38 g L\(^{-1}\) h\(^{-1}\). A gas phase ozone analyzer (IN USA) was installed at the top of the reservoir to measure ozone in the gas phase.

2.3. Degradation

To measure the DCAN oxidation rate in each treatment process with various parameters, a pseudo-first-order kinetic model was adopted to obtain the kinetic rate constant.

2.4. Analytical methods

In the aqueous phase, DCAN was extracted by a liquid extraction method (APHA, 1998). During the 4 h reaction, three samples (10 mL) at predetermined times were taken, filtered using a 0.45 μm filter, and then extracted with 2 mL MTBE with constant shaking for 4 h at 200 rpm. The extracted amount of DCAN was analyzed using a gas chromatography–mass spectrometry (GC–MS) system (Agilent 7890A/5975C), equipped with a DB-5MS column (YW Scientific, length: 30 m, inner diameter: 0.25 mm, film thickness: 0.25 μm). MS was at electron impact-GC–MS scan mode (70 eV) with specific retention time (4.678 min), confirmation ion (m/z 74), and quantitative ion (m/z 82).

3. Results and discussion

3.1. Kinetics of DCAN removal by various processes

Fig. 2 shows the kinetic result of DCAN removal by several processes, including UV\(_{\text{solar}}\)/TiO\(_2\), O\(_3\)/TiO\(_2\), UV\(_{\text{solar}}\)/O\(_3\), and UV\(_{\text{solar}}\)/TiO\(_2\)/O\(_3\). The applied pH and temperature were 6.5 and 20 ± 1 °C, respectively. The TiO\(_2\) and ozone doses were 0.4 g L\(^{-1}\) and 1 g L\(^{-1}\) h\(^{-1}\), respectively, while the UV\(_{\text{solar}}\) intensity was 33.8 W m\(^{-2}\).

The kinetic rate constant (0.98 \times 10^{-3} \text{min}^{-1}) of DCAN removal by UV\(_{\text{solar}}\)/TiO\(_2\) system was relatively low, and only 20% was removed in 4 h.

Through ozone oxidation, the kinetic rate constant of DCAN removal was 1.9 \times 10^{-3} \text{min}^{-1} and approximately 40% of DCAN was
removed within 4 h. The degradation mechanism of the ozone process was divided into direct and indirect reactions. At a pH lower than 4, the direct reaction is dominant, while above a pH of 8, the indirect reaction dominates (Tomiyasu et al., 1985; Ershov and Morozov, 2008).

Similar to the simple ozone process, ozone/TiO₂ has direct and indirect reactions occurring in between a pH of 4 and 8. OH can also be produced following Eqs. (1) and (2) (Lin et al., 2002; Tong et al., 2010). In this result, the kinetic rate constant (2.1 × 10⁻¹⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻㈸

\[
\begin{align*}
O_3 & \xrightarrow{TiO_2} O + O_2 \\
O + H_2O & \xrightarrow{} \cdot OH + OH^-
\end{align*}
\]

Meanwhile, the photolytic ozonation (UV_{solar}/O₃) process had a kinetic rate constant higher than that of UV_{solar}/TiO₂/C₅, O₃/C₅, or O₃/TiO₂. The UV_{solar}/O₃ process had a kinetic rate constant of

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Fig. 1. (A) Bench system consisting of compound parabolic concentrator (CPC) and ozone generation system and (B) actual photo of outdoor photocatalytic ozonation system.

DCAN has been known to self-decompose at alkaline pH (Reckhow et al., 2001). In this test, phosphate buffer chemicals were not used to adjust pH because they can enhance the hydrolysis of DCAN. These can also be decomposed to dichloroacetamide by reacting with OH•. Reckhow et al. (2001) observed that the decomposition rate of DCAN linearly increased by approximately 10 and 100 times at pH 7.5 and 9, respectively; however, at a pH lower than 7.5, the decomposition rate was quite slow, 0.001 h⁻¹, similar to this study. In this study, at pH 10, approximately 57% of DCAN was decomposed in 2 h (k = 7.4 × 10⁻³ min⁻¹). However, at a pH of 3, approximately 7% of DCAN was removed, which did not occur at pH 6.5. Presumably, the removal of DCAN at a low pH occurs through the reaction with chloride ions. When H₂SO₄ is used to obtain a lower pH, no reduction in the DCAN concentration was observed. As a hypothetical reaction with HCl, DCAN might be transformed to trichloroacetonitrile in the aerobic environment.

In the oxidation process using UVsolar/TiO₂/O₃, the kinetic rate constant was the highest at a pH 10 (2.1 × 10⁻² min⁻¹), followed by pH 6.5 (1.1 × 10⁻² min⁻¹) and pH 3 (1.5 × 10⁻² min⁻¹). The reason that oxidation rate was the highest at a high pH can be explained as follows. A radical reaction actively occurs when the concentration of OH⁻ increases. As described in Section 3.1, the direct reaction (oxidizing agent: ozone) is dominant at <pH 4, while indirect reaction (oxidizing agent: hydroxyl radicals) is significant at >pH 8 (Tomiyasu et al., 1985; Ershov and Morozov, 2008). In terms of oxidation potential, however, a hydroxyl radical (OH, E₀ = 2.80 V) is stronger than ozone (O₃, E₀ = 2.07 V) (Rodriguez et al., 2008).

On excluding the self-decomposition rate, the kinetic rate constant obtained at pH 6.5 (1.1 × 10⁻² min⁻¹) was comparable to that at pH 10 (1.36 × 10⁻² min⁻¹). Approximately 62% of DCAN was removed within 1 h at pH 6.5. The zero point charge (ZPC) of TiO₂ has been reported in the pH range 6.2–6.6 (Wang et al., 1999; Doong et al., 2001). As shown in Eqs. (22) and (23), the

\[
\text{Synergetic index } = \frac{k_{\text{UVsolar/TiO}_2/O_3}}{k_{\text{UVsolar/TiO}_2} + k_{O_3}}
\]

Where k is the kinetic rate constant.

3.2. Effect of pH

An important parameter, pH, has been known to significantly affect the rate of the oxidation process, because the surface charge of the catalyst can vary with pH (Wang et al., 2000). In addition, different pH values can provide different ozone activation rates. Fig. 3 shows the self-decomposition of DCAN and removal kinetics by the UVsolar/TiO₂/O₃ process according to different pH values.

Fig. 3. Kinetics of (A) self-decomposition and (B) removal of dichloroacetonitrile (DCAN) in UVsolar/TiO₂/O₃ process at various pH values (20 ± 1 °C, TiO₂ dose 0.4 g L⁻¹, ozone dose g (L h)⁻¹, UV intensity 33.8 W m⁻²).
surface of the catalyst has predominantly positive charges at a pH lower than 2PC and negative charges at a pH higher than 2PC.

Depending on the target organic compound, the optimal pH conditions may vary in the photocatalytic process (Inel and Okte, 1996; Chu and Choy, 2007). This is because of the relationship between the pollutant adsorption on the catalyst surface and the electrostatic charge balance. The optimal pH for removing phenol (pK_a = 9.9) was 7 in the photocatalytic process, while for 2-isopropyl-6-methyl-4-pyrindinol (IMP, pK_a = 1.8 and 6.8), it was 6.3 (Lee et al., 2003; Ciou et al., 2008). As shown in the cases of phenol and IMP, the interaction between DCAN and the catalyst might be also the highest at a neutral pH.

Although the DCAN-removal rate is highest at pH 10, a neutral pH is more effective because no pH adjustment is needed.

3.3. Effects of catalyst and ozone dose

In order to optimize the amounts of catalyst and ozone, the kinetic rate constant of the photocatalytic ozonation of DCAN was measured with various doses of TiO_2 (0.2–2.5 g L\(^{-1}\)) and ozone (1.00–1.38 g L\(^{-1}\) h\(^{-1}\)) (Fig. 4). At a 0.4 g L\(^{-1}\) TiO_2 dose, the kinetic constant increased with the ozone dose. However, regarding the catalyst dose, 1 g L\(^{-1}\) of TiO_2 injection in photocatalytic ozonation had the highest rate constant (0.032 min\(^{-1}\)) with either 1.13 or 1.38 g (L h\(^{-1}\)) of ozone.

This might be explained by the following hypothesis. As the catalyst dose increases, the rate constant increases owing to a higher reactive area; however, simultaneously the solution turbidity also increases, leading to a decrease in the UV penetration. Higher turbidity decreases the efficiency of the photonic reaction. Thus, there is an optimal catalyst concentration. This trend is similar to other studies (Gimeno et al., 2007; Beltran et al., 2009), in which the optimal catalyst dose was 1.5 g L\(^{-1}\) for removing sulfamethoxazole and purifying winery wastewater by photocatalytic ozonation.

In terms of effectiveness, the optimum ozone dose was found to be 1.13 g L\(^{-1}\) h\(^{-1}\). Ozone dose affects the concentration of dissolved ozone in the solution. The kinetic rate constants of DCAN removal increased with an increase in ozone concentration. In general, however, the utilization efficiency of ozone gradually decreased, because the dissolution of ozone is limited (Alaton et al., 2002). Interestingly, the kinetic rate constants of the UV_{solar}/TiO_2/O_3 process increased with increasing ozone doses while they did not change with an increase of ozone dose for the UV_{solar}/O_3 process.

These results are similar to the results of Giri et al. (2007), in which the increase in ozone dose in the photolytic ozonation process had a lower efficiency than the photocatalytic ozonation process in the removal of 2,4-dichlorophenoxyacetic acid. As the ozone dose increased, the kinetic rate constant of the UV_{solar}/TiO_2/O_3 process also significantly increased to 0.032 min\(^{-1}\), which was approximately 11 times higher than that of photolytic ozonation (approximately 0.003 min\(^{-1}\)). This was because the catalyst effect can increase the mass transfer of ozone. The decomposition of ozone by UV_{solar} can be limited in the UV_{solar}/O_3 process, while in the UV_{solar}/TiO_2/O_3 process, ozone can be actively decomposed not only by UV_{solar} but also by the reaction with electrons produced by TiO_2.

3.4. Effect of temperature

The effect of the temperature on DCAN removal by the UV_{solar}/TiO_2/O_3 process was observed (Fig. 5). In the range 10–40 °C, the highest rate constant (0.033 min\(^{-1}\)) was obtained at 20 °C. As the temperature is changed, the major parameters affecting the kinetic rate constants in the UV_{solar}/TiO_2 process and UV_{solar}/TiO_2/O_3 process are: (1) Ozone decomposition and dissolution rates, (2) adsorption of pollutants, and (3) changes in the catalyst particle size. Thus, the photocatalytic ozonation process is too complex to cancel out the temperature effect. To distinguish the temperature effect on each mechanism, we additionally conducted the batch tests of the sole ozone process and measured particle size distribution of TiO_2 according to temperature. In the sole ozone process of our study, more DCAN was removed when the temperature was increased (e.g., ~65% DCAN remained at 10 °C, while only ~35% remained at 40 °C (Supplementary Material (SM), Fig. SM-1). Beltran et al. (1999) also showed that the removal rates of organic pollutants increase proportionally with temperature. Presumably, as the temperature increases, the decomposition rate of ozone increases to enhance the radical production and reaction even though the dissolution rate of ozone decreases. Meanwhile, the UV/TiO_2 process is known to follow the Langmuir–Hinshelwood model, assuming that the oxidation reaction occurs on the surface of the catalyst (Inel and Okte, 1996). Giri et al. (2007) reported that photocatalytic ozonation decomposed 2,4-dichlorophenoxyacetic acid with the highest rate at 20 °C. However, depending on the target element, the optimal temperature can differ. Thus, the reaction rate is strongly related to the adsorption of pollutant on the surface of the catalyst, and an increase in temperature reduces the adsorption capacity of the catalyst and dissolution of ozone (Herrmann, 1999), whereas it increases the activity of ozone as shown above (Mehrjouie et al., 2011). In addition to the effects of temperature, another effect is the particle size of the catalyst. In this study, the size distribution of TiO_2 at each applied temperature was analyzed by a particle-size analyzer (Malvern instrument, Micro-P model) using the laser diffraction method in a wet process (Fig. SM-2). As a result, it was found that TiO_2 had bimodal-size distribution, and the average particle sizes increased with increasing temperature. In particular, the particle volumes in the fractions between 0.08–0.5 and 1–50 μm gradually increased. Accordingly, as the particle sizes of TiO_2 increased, the available surface areas of TiO_2 for adsorbing DCAN could be reduced to affect the oxidation kinetics. Overall, temperatures higher than 20 °C negatively affected the DCAN oxidation kinetics because of the dominant effect of TiO_2-activity reduction by the increase of particle sizes.

3.5. Effect of UV intensity

UV intensity is expected to be one of the rate-controlling parameters (Laoufi et al., 2008). Fig. 6 shows the kinetics of DCAN removal by photocatalytic ozonation at various UV_{solar}.
intensities (4.6–33.8 W m\(^{-2}\)). Approximately 53% of DCAN was removed in 2 h with UV\(_{\text{solar}}\) intensity of 4.6 W m\(^{-2}\), while more than 97% of DCAN was removed when intensities higher than 19.8 W m\(^{-2}\) were used (Fig. 6a). The kinetic rate constants increased linearly when the UV\(_{\text{solar}}\) intensity increased in the range 4.6–25 W m\(^{-2}\); however, the increasing trend of rate constants was gradually reduced at the UV\(_{\text{solar}}\) intensity of 25 W m\(^{-2}\) (Fig. 6b). Most photocatalytic reactions have shown a proportionally increasing rate with an increasing UV intensity, but above a certain reaction rate, the rate becomes proportional to the square-root of UV intensity (Herrmann et al., 1983; Malato et al., 2009). The surface of the catalyst can be activated more by increasing the UV intensity. An activated catalyst increases the concentrations of the produced h\(^{+}\) and e\(^{-}\), thus increasing the removal rate. However, when the concentrations of h\(^{+}\) and e\(^{-}\) increase, h\(^{+}\) and e\(^{-}\) tend to recombine, decreasing the catalytic effect. Also, in other studies, the efficiency of UV intensity gradually decreased above a certain value, even though the applied UV intensities were different (Ollis et al., 1991; Liu et al., 2006; Benabbou et al., 2007; Chu et al., 2009).

3.6. Results of outdoor photocatalytic ozonation system

Based on the results of the bench tests, outdoor photocatalytic ozonation tests using natural solar light were set and conducted to determine the DCAN-removal efficiency. For 5 months (May to September in 2012), the system was operated with the optimal conditions determined at bench tests: 20 °C, pH 6.5, 1 g L\(^{-1}\) TiO\(_2\) dose, and a 1.13 g L\(^{-1}\) h\(^{-1}\) ozone dose. Fig. 7 shows the UV intensities measured at each time and the time dependence of the rate constants of DCAN removal by the solar/TiO\(_2\)/O\(_3\) and solar/TiO\(_2\) processes. The UV intensity of solar light was measured to be 8.2–61.1 W m\(^{-2}\) from 8 am to 7 pm. The highest intensities were obtained between 10 am and 2 pm. Depending on the UV intensity, approximately 8–36% of DCAN was removed in 2 h by the solar/TiO\(_2\) process with a kinetic rate constant of 8.5 × 10\(^{-4}\)–3.2 × 10\(^{-3}\) min\(^{-1}\). Meanwhile, the solar/TiO\(_2\)/O\(_3\) process removed approximately 95.2–99.7% of DCAN and had a rate constant between 0.038 and 0.17 min\(^{-1}\), which is almost 100 times higher than that of solar/TiO\(_2\).

3.7. Implications of treatment efficiency based on energy consumption

The energy consumption needed for operating the UV lamp in the UV\(_{\text{solar}}$/TiO\(_2\)$ process, including the pump operation, was 1750 W (average), while those for the UV\(_{\text{solar}}$/TiO\(_2\)/O\(_3\) and O\(_3\) processes were 1654 and 154 W, respectively. Thus, it should be noted that UV lamps consumed a significant amount of energy. Because no energy was required for the outdoor system (natural solar radiation), the energy consumption for the solar/TiO\(_2\) (96 W) and solar/ TiO\(_2\)/O\(_3\) (154 W) processes was much smaller than that of the bench system. Although the energy input for TiO\(_2\) manufacture should be considered, we did not include it because the concentration (1 g L\(^{-1}\)) of TiO\(_2\) applied is small. Based on the energy consumption required for each process, the electrical energy per mass (EE/M) value (Bolton et al., 1995) was calculated to determine the treatment efficiency:

$$
EE/M = \frac{P \times t \times 1000}{V \times M \times 60 \times (C_i - C_f)}
$$

Where $P$ is consumption power (kW), $t$ is time (min), $V$ is solution volume (L), $M$ is molecular weight, $C_p$ and $C_i$ are the initial and final concentrations of contaminant. Because the EE/M value is defined as power consumption per removed contaminant mass, a lower value is more efficient. In the bench tests, the O$_3$ process had a lower EE/M value ($\approx$300 kW h kg$^{-1}$ of DCAN) than the UV$_{solar}$/TiO$_2$/O$_3$ ($\approx$835 kW h kg$^{-1}$) or UV$_{solar}$/TiO$_2$ ($\approx$4550 kW h kg$^{-1}$) processes. This result could be explained by the fact that the energy consumption of the UV lamp was much higher than that of ozone generation, even though the removal efficiency and rate by O$_3$ were much lower than by UV$_{solar}$/TiO$_2$/O$_3$. The solar/TiO$_2$/O$_3$ process was more efficient than the other processes in the outdoor system. The EE/M value of solar/TiO$_2$/O$_3$ process was approximately 62 kW h kg$^{-1}$, while that of solar/TiO$_2$ was 284 kW h kg$^{-1}$. Accordingly, the solar/TiO$_2$/O$_3$ process had approximately 4.6 times higher energy efficiency than solar/TiO$_2$.

4. Conclusions

Compared to the single process, the UV$_{solar}$/TiO$_2$/O$_3$ process had the highest DCAN-removal rate, because it can induce additional OH production by the reaction of ozone with the electrons of the conduction band in the catalyst. The UV$_{solar}$/TiO$_2$/O$_3$ system showed an enhanced DCAN-removal rate, and the synergistic index calculated for a single process was 3.8. The optimum pH for DCAN removal by UV$_{solar}$/TiO$_2$/O$_3$ was found to be neutral because of the maximum interaction between TiO$_2$ and DCAN. According to the results of TiO$_2$ and ozone-dose tests, 1 g L$^{-1}$ TiO$_2$ and 1.13 g L$^{-1}$ h$^{-1}$ ozone in photocatalytic ozonation were optimal to provide the highest rate constant. From the temperature variation test results, the highest rate constant (0.033 min$^{-1}$) was obtained at 20 °C. Temperature simultaneously affected several parameters such as DCAN adsorption and particle-size change of TiO$_2$, as well as the decomposition and dissolution rates of ozone. However, temperatures higher than 20 °C negatively affected the DCAN-removal kinetics, because the negative effect of temperature on TiO$_2$ activity might be higher than the positive effect on ozone activity. In the tests regarding the UV$_{solar}$ intensity, the kinetic rate constants increased linearly when the UV$_{solar}$ intensity increased in the range 4.6–25 W m$^{-2}$; however, the increasing trend of rate constants were gradually reduced above 25 W m$^{-2}$. The test results of the outdoor system indicated that the solar/TiO$_2$/O$_3$ process showed complete removal with rates that are two orders greater than those obtained with solar/TiO$_2$. In particular, irrespective of UV intensity, the complete removal of DCAN was obtained within 2 h by the solar/TiO$_2$/O$_3$ process. In addition, calculation of EE/M showed that the solar/TiO$_2$/O$_3$ process had about 4.6 times higher energy efficiency than solar/TiO$_2$. Although 2 h was needed for solar/TiO$_2$/O$_3$ to remove a high level of DCAN (1 mg L$^{-1}$) in synthetic solution completely, a shorter retention time can be expected in actual application for wastewater containing a low concentration of DCAN. As a green oxidation technique, solar photocatalytic ozonation could be a good alternative for treating recalcitrant and toxic organic pollutants, because it has a high oxidation potential and low energy consumption compared to conventional AOPs.

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Appendix A. Supplementary material

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References


