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Original Article

Study on the Removal Technology of Trichloramine from Drinking Water Using Ultraviolet Light

Ayumi Hashiguchi [a], Shiho Yoshida [b], Shinya Echigo [c], Ryohei Takanami [d], Hideaki Nagare [a]

[a] *Faculty of Environmental, Life, Natural Science and Technology, Okayama University, Okayama, Japan*
[b] *Graduate School of Natural Science and Technology, Shimane University, Matsue, Japan*
[c] *Graduate School of Global Environmental Studies, Kyoto University, Kyoto, Japan*
[d] *Faculty of Design Technology, Osaka Sangyo University, Daito, Japan*

ABSTRACT

Trichloramine (NCl_3) is an inorganic chloramine that causes a pungent chlorine-like odor, and it is difficult to remove its precursors (nitrogen organic compounds and/or ammonia) completely from water. Powdered activated carbon, ozonation, and UV treatment have been applied for decomposing NCl_3, but free chlorine was also decomposed. So, it is necessary to develop a technique that can selectively control NCl_3 without losing free chlorine. UV light-emitting diodes (265, 280, and 300 nm) and plasma emission UV sheet (347 ± 52 nm, hereafter 350 nm) were compared to find the optimal wavelengths that decompose NCl_3 but not free chlorine. As a result, 90.6, 96.7, 92.5, and 77.8% of NCl_3 were removed at 265, 280, 300 (3,600 mJ/cm^2), and 350 nm (14,400 mJ/cm^2), respectively. On the other hand, free chlorine at neutral pH (hypochlorous acid is dominant) and slightly alkaline pH (hypochlorite ion is dominant) was not decomposed at 350 nm, but at other wavelengths (*i.e.*, 265, 280, and 300 nm) the removals were more than 64%. Therefore, UV radiation at 350 nm can be candidates to remove NCl_3 while maintaining free chlorine. However, this method requires high input energy, and further study is needed for evaluating the practical applicability of this method by considering optimal reactor design.

Keywords: trichloramine, disinfection byproducts, drinking water, ultraviolet light

INTRODUCTION

Trichloramine (NCl_3) is one of the inorganic chloramines that cause a pungent chlorine-like odor. This compound is recognized as one of the major factors determining tap water's comfortableness. NCl_3 has been produced during chlorination through the reactions of chlorine and nitrogen organic compounds and/or ammonia, so NCl_3 can be considered a disinfection byproduct in a broad sense. However, the control of the precursors is not easy because the threshold of the chlorine-like odor to humans is quite low, and people easily perceive the odor of NCl_3 even if the removal percentage of nitrogen precursors is relatively high. Therefore, it is necessary to develop a technique that can remove NCl_3 without degrading free chlorine. Examples of this approach include increasing pH and water temperature, two-step chlorination, and ion exchange [1–3]. However, each of these methods requires the use of additional chemicals, which leads to higher cost and risk of different disinfection byproducts, and/or the installation of new equipment to raise the water temperature. For example, ion exchange is one method for removing NCl_3 precursors, but its performance is highly dependent on the quality of raw water, and it is difficult to completely remove the precursors. Although powdered activated carbon [4], UV-ozonation [3], and UV treatment at 254 nm have been applied for the decomposition of NCl_3 from water, free chlorine is also decomposed in these treatments, and the residual disinfection effect is lost [5].

Corresponding author: Ayumi Hashiguchi, E-mail: hashiguchi-a@okayama-u.ac.jp
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NCl_3, hypochlorous acid (HOCl), and hypochlorite ion (OCl^-) show high UV absorption at a wavelength of 340–350 nm, 230 nm, and about 300 nm, respectively. Using these differences in UV absorption, it may be possible to search for conditions under which only NCl_3 can be decomposed while maintaining free chlorine concentration in water. So far, there was no attempt to decompose NCl_3 without free chlorine decomposition and, in most of the cases researchers used low- or medium-pressure UV lamps, which can emit 254 nm monochromatic UV and 200–400 nm polychromatic UV, respectively, since there were less choices for the UV emitting source. Currently, many types of UV emitting sources are significantly developed. Mercury-free UV light-emitting diodes (UV-LEDs) that can selectively irradiate the UV from the rage in 255–400 nm, and plasma emission UV sheet (UV-SHiPLA) are one of the safe, flexible, and long-life services. All UV-LEDs 265, 280, and 300 nm can be absorbed by NCl_3 with different absorption ratio and also absorbed by free chlorine, and 350 nm can be absorbed with less abruption by any free chlorine species (HOCl and OCl^-).

This study focused on the UV absorption characteristics of free chlorine (HOCl and OCl^-) and NCl_3 and attempted to select a specific UV wavelength that can decompose NCl_3 without losing free chlorine. These mercury-free UV-LEDs (265, 280, and 300 nm) and UV-SHiPLA (350 nm) were selected for the optimal decomposition conditions (*i.e.*, wavelengths that decompose NCl_3 but not free chlorine).

To decide the wavelength that can selectively decompose NCl_3 while maintaining free chlorine (HOCl and/or OCl^-) in water, decomposition experiments of NCl_3 were conducted at 265, 280, 300, and 350 nm UV. In these experiments, the decomposition of free chlorine (HOCl and OCl^-) was also monitored. In addition, to confirm whether they are produced after NCl_3 decomposition, the decomposition constant (k) of free chlorine in NCl_3 solution and those obtained in the UV irradiation experiments of HOCl and OCl^- alone (*i.e.*, without NCl_3) at pH 7 (HOCl dominant) and pH 9 (OCl^- dominant) were compared.

MATERIALS AND METHODS

Chemicals and reagents

All the chemicals used in this study were of analytical grade or better and purchased from Fujifilm Wako (Osaka, Japan) unless otherwise noted. Special grade *N*,*N*-diethyl-*p*-phenylenediamine sulfate, 98% ethylenediaminetetraacetic acid disodium salt (EDTA 2Na), and disodium hydrogen phosphate (Na_2HPO_4) were purchased from Sigma-Ardrich (St. Louis, USA), BLD pharmatech (Shanghai, China), and Nacalai Tesque (Kyoto, Japan), respectively. Also, the grade of sodium hypochlorite (Fujifilm Wako) was practical grade (*i.e.*, for general chemistry experiments). Milli-Q water (*i.e.*, the water produced by a Milli-Q® EQ7000 system (Merck Millipore, Burlington, USA)) was used for washing glassware and preparation of the aqueous solutions used in this study.

Preparation of NCl_3 solution

We essentially followed the procedure by Kosaka *et al.* [6]. In brief, 55 mL of phosphate buffer (24 g of Na_2HPO_4 and 46 g of KH_2PO_4 dissolved in 1 L Milli-Q water) was added to Milli-Q water (1,045 mL), and 0.55 mL of NH_4Cl (appox. 30 mM) and 1.925 mL of NaOCl was added at a molar ratio for 1:3.15 while mixing the solution in a 1 L amber glass bottle for 30 min. This daily prepared solution was kept in a water bath for 2.5 h, and the obtained solution was used as the NCl_3 standard solution for the decomposition experiments.

UV irradiation sources and experimental setup for the decomposition experiments

The UV light sources used in this study were three types of UV-LED devices (265, 280, and 300 nm chip-type light-emitting devices with a side of 1.87 mm and an area of 3.5 mm^2, manufactured by Nikkiso Giken, Hakusan, Japan). Irradiation at 350 nm wavelength was performed with a UV-SHiPLA device (SK-BUVA-0806, length: 7.5 mm, width: 2.0 mm, area: 15 mm^2 plasma light-emitting lamp, manufactured by Shikoh Giken, Awaji, Japan), which has a main wavelength of 350 nm and broad spectrum in the range of 300 and 400 nm.

The UV-LED UV irradiation apparatus is shown in **Fig. 1**. This device consists of three components: the UV-LED substrate, a Peltier cooling unit, and jigs for adjusting the distance between the UV-LED and the sample water surface (1.5 cm). On the UV-LED substrate, nine UV-LED elements, three each for wavelengths of 265, 280, and 300 nm, are installed in a regular circle, and the three LED elements of the same wavelength are arranged at intervals of 120 degrees to avoid uneven irradiation. The height of the sample surface can be adjusted by fixing the glass Petri dish at a position directly under the UV-LED substrate and changing the height of the bottom plate. Each wavelength UV LED element (set of three) is connected to a separate power supply (compact DC stabilized power supply PMX35-1A by Kikusui Electronics, Yokohama, Japan), and each power supply can be

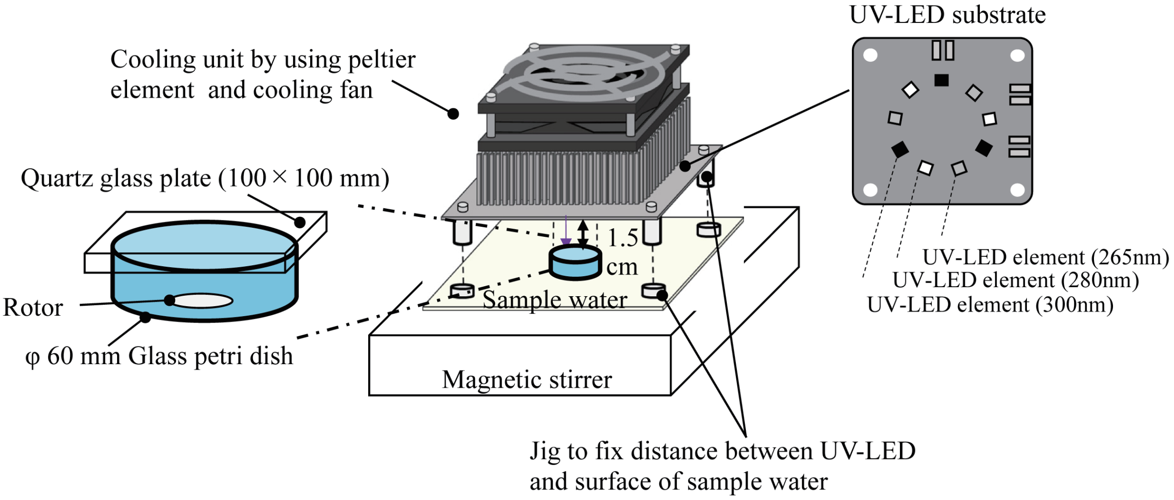

Fig. 1 Experimental setup for the UV irradiation experiment with UV-LEDs (265, 280, and 300 nm).

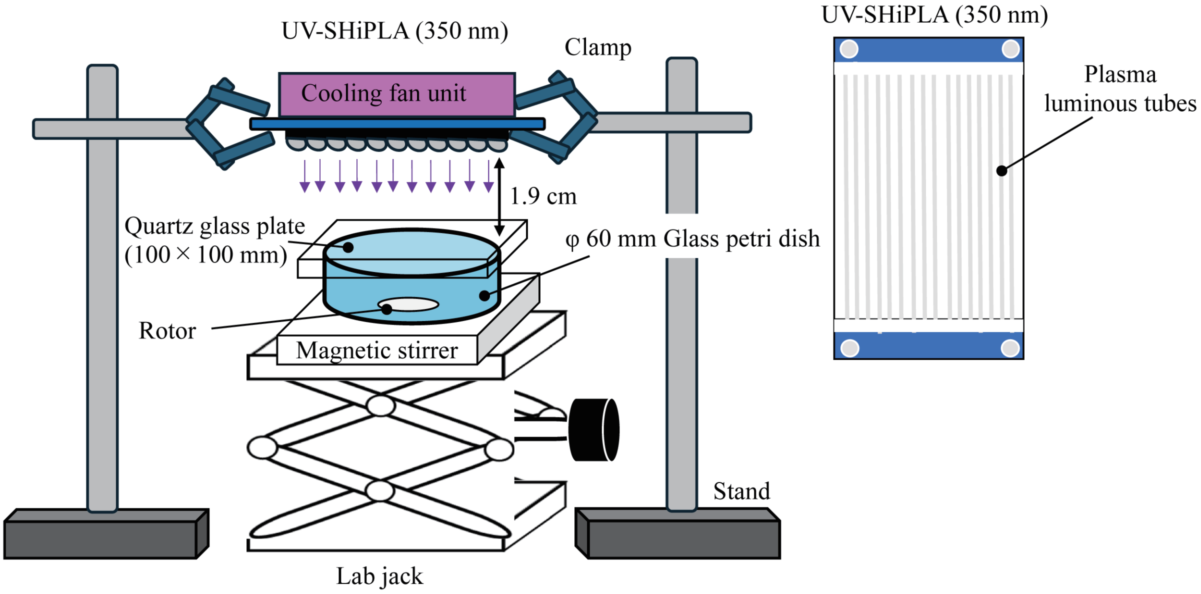

Fig. 2 Experimental setup for the UV irradiation experiment with UV-SHiPLA (350 nm).

turned on and off to irradiate each wavelength and adjust the irradiation energy level.

The UV irradiation device for UV-SHiPLA is shown in **Fig. 2**. This device is an integrated module consisting of a UV-SHiPLA substrate, a cooling fan attached to the top of the substrate, and a switch directly connected to the power supply to turn the power supply on and off. Twenty-three UV-SHiPLA plasma emitting lamps are placed on the substrate. The distance between the base and the sample water surface was adjusted by clamping both sides of the base frame between clamps attached to the stand (1.9 cm). The UV wavelengths of the UV-LEDs (265, 280, and 300 nm) and UV-SHiPLA (350 nm), and their relative intensity and full width at half maximum (FWHM) are shown in **Fig. 3**. FWHW were 21 nm for 265 nm UV-LED, 14 nm for 280 nm UV-LED, 14 nm for 300 nm UV-LED and 52 nm for 350 nm UV-SHiPLA, respectively.

Irradiance of the emitted UV were measured by an irradiance meter (USR-45DA, USHIO Inc., Tokyo, Japan). UV-SHiPLA emits ultraviolet rays of other wavelengths broadly (**Fig. 3**), thus the integrated irradiance was measured in the wavelength range of 250 and 380 nm.

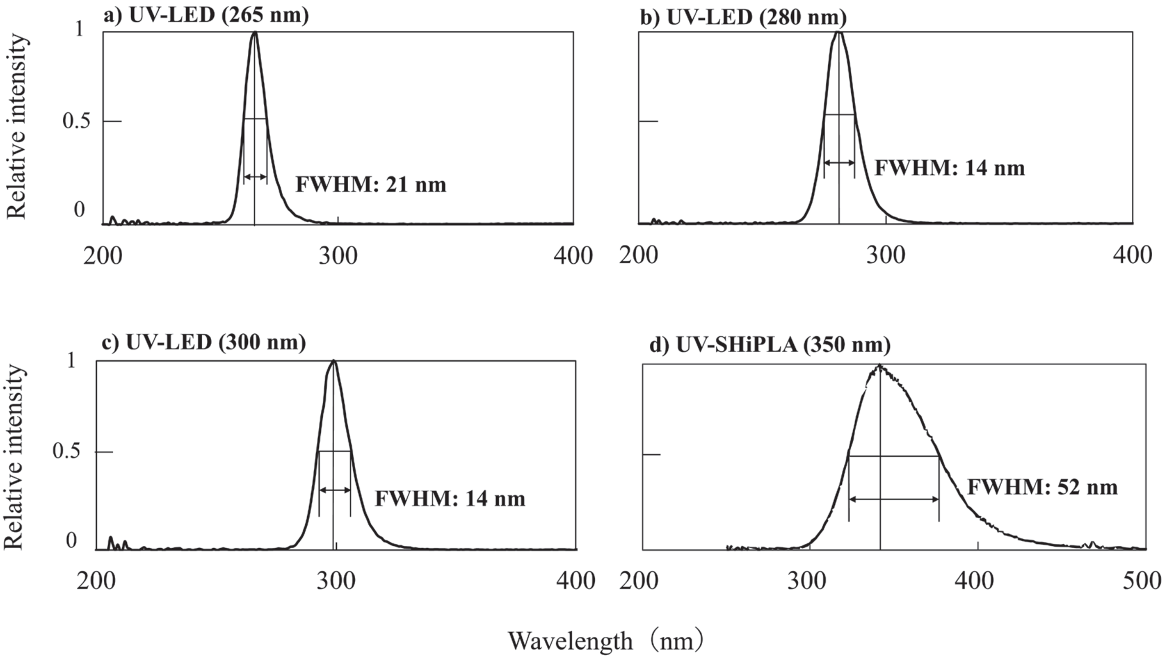

Fig. 3 Relative spectral intensity of a) 265, b) 280, c) 300, and d) 350 nm.

Table 1 Irradiation conditions for the decomposition experiment.

Conditions	NCl_3	Free chlorine
pH range	6.66–7.15	6.69–6.79 (HOCl dominant), 8.02–9.40 (OCl^- dominant)
Wavelengths (nm)	265, 280, 300, and 350	
Irradiance (mW/cm^2)	1.0 (265, 280, and 300 nm) 2.0 (350 nm)	
Irradiation time (min)	0, 1, 10, 30, and 60 (265, 280, and 300 nm) 0, 10, 30, 60, and 120 (350 nm)	
Fluence (mJ/cm^2)	0–3,600 (265, 280, and 300 nm) 0–14,400 (350 nm)	

Decomposition experiments of NCl_3 and free chlorine (HOCl and OCl^-) under different pH conditions

The irradiance of UV radiation emitted by the UV-LEDs was adjusted by increasing or decreasing the applied current to the power supply connected to the UV-LED elements to achieve 1.0 mW/cm^2 at wavelengths of 265, 280, and 300 nm, respectively. The irradiation time was changed by turning the power supply on and off for each wavelength to adjust the amount of irradiation energy. The irradiation time was set to 0, 1, 10, 30, and 60 min. For the irradiation experiments, a glass Petri dish (60 mm in diameter) was filled with the NCl_3 standard solution (pH 6.66–7.15) prepared according to the described method in preparation of NCl_3 solution in MATERIALS AND METHODS, or sodium hypochlorite solution with a stir bar, and the glass Petri dish was sealed with a square quartz plate (100 × 100 mm) to achieve a head-space free condition. The volume of the sample measured with a graduated cylinder was approximately 50 mL. The Petri dish was placed on a magnetic stirrer and irradiated with UV light while the magnetic stir bar was rotated at 250 rpm. The same procedure was performed without UV irradiation as a control experiment (hereafter “no irradiation”).

The UV-SHiPLA irradiance was fixed at 1.0 mW/cm^2, and NCl_3 decomposition experiments were conducted for 0, 1, 10, 30, and 60 min. In addition, NCl_3 decomposition experiments were conducted at 2.0 mW/cm^2 irradiation for 0, 10, 30, 60, and 120 min. **Table 1** shows the conditions of the UV irradiation experiments.

All glassware and magnetic stir bars were rinsed with the NCl_3 standard solution and prepared chlorine solution (pH 7 or 9) before conduct experiments to avoid contamination because they are highly reactive with impurities.

The pH of the HOCl solution was adjusted to 6.64–6.79 by adding phosphate buffer. The pH of OCl^- solution was 8.02 to 9.60, the experiments were conducted without further pH adjustment, and each was subjected to UV irradiation experiments to confirm changes in concentration and decomposition rate. UV degradation experiment was conducted in a same manner as NCl_3 degradation.

pH of the sample solution was analyzed by pH meter (LAQUAact D-73, HORIBA, Kyoto, Japan). Apparent rate constant (k in $cm^2/(mW·s)$) was obtained from equation (1) for each irradiation condition and compared to evaluate the removal efficiencies of NCl_3.

$$\ln (C_t/C_0) = -kF \tag{1}$$

where C_t (mg/L) is a concentration at the irradiation time t (s), C_0 (mg/L) is a initial concentration of NCl_3 and F (mJ/cm^2) is the total fluence.

These obtained k values were used for the comparison of NCl_3 decomposition efficiencies between UV-LEDs (265, 280, and 300 nm) and UV-SHiPLA (350 nm) in this study.

Determination of the concentrations of NCl_3 and free chlorine (HOCl and OCl^-)

The concentrations of NCl_3 and free chlorine was determined by the *N*,*N*-diethyl-*p*-phenylenediamine (DPD) photometric method [7]. In brief, 0.5 mL of phosphate buffer and 0.5 mL of DPD solution were placed in a test tube. In another test tube, about 0.1 mg of Potassium iodide was taken and 10 mL of sample was added. After adding the solution in the second test tube to the first tube to develop the color, the absorbance at 515 nm was immediately measured with a quartz cell (1 cm) using a UV-visible spectrophotometer (UV-1800, Shimadzu, Kyoto, Japan). The value obtained was designated as N. For the free residual chlorine of the same sample, after placing 0.5 mL of phosphate buffer and 0.5 mL of DPD solution in a test tube, 10 mL of the sample was added and the absorbance at 515 nm was measured. The value obtained was designated as A. The NCl_3 concentration ($mg\text{-}Cl_2/L$) and free chorine concentration were calculated from $2(N-A)$ and A, respectively, using a calibration curve. The range of the calibration curve was from 0.1 to 1.0 $mg\text{-}Cl_2/L$. Also, UV spectrum analysis of the experimental solution was conducted to confirm whether the other chloramine (mono or dichloramine) were produced or not after NCl_3 decomposition by UV-visible spectrophotometer (UV-1800).

RESULTS AND DISCUSSION

Figure 4 shows the time-concentration profiles of NCl_3 with UV irradiation. **Figure 5** shows molar absorption coefficient of NCl_3, HOCl, and OCl^-. **Figure 6** shows UV absorption spectrum of experimental solution before and after decomposition by UV irradiation. **Figure 7** is the time-concentration profiles of free chlorine in the same experiments. **Figure 8 and 9** show the time-concentration profiles of free chlorine under different pH conditions without NCl_3. Apparent reaction rate constants for the all the decomposi-

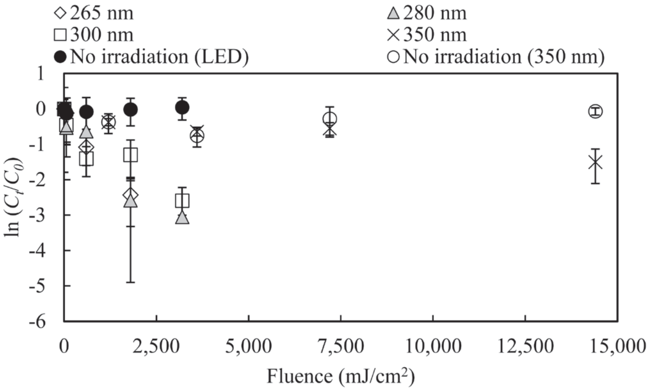

Fig. 4 Concentration change profiles of NCl_3 in the decomposition experiments. Numbers of experiment: No irradiation (LED) ($n = 9$), No irradiation (350 nm) ($n = 3$), 265 nm ($n = 3$), 280 nm ($n = 3$), 300 nm ($n = 3$) and 350 nm ($n = 3$).

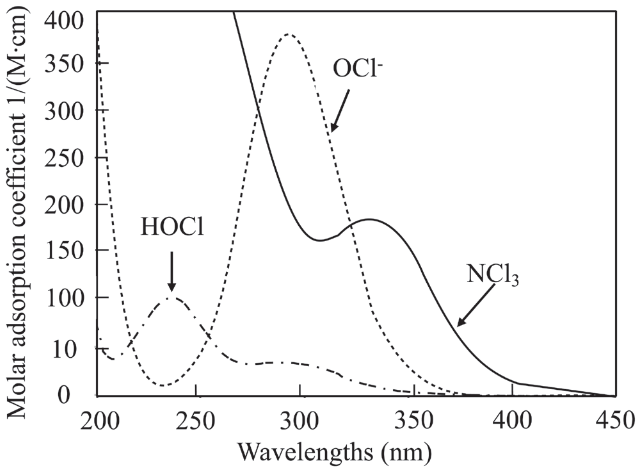

Fig. 5 Molar absorption coefficients of NCl_3, HOCl, and OCl^- composed by Kishimoto [16] and Roumiguières *et al.* [17].

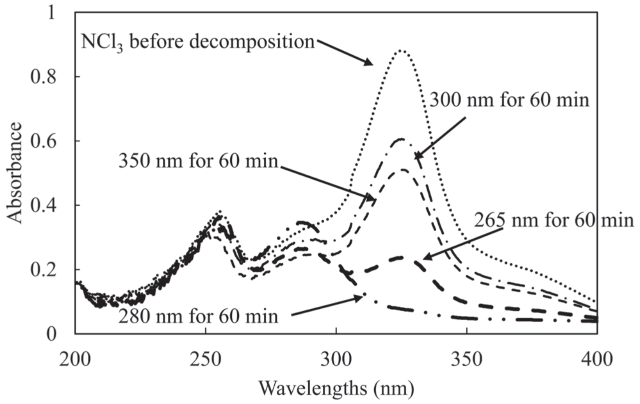

Fig. 6 UV absorption spectrum of experimental solution before and after decomposition by UV irradiation.

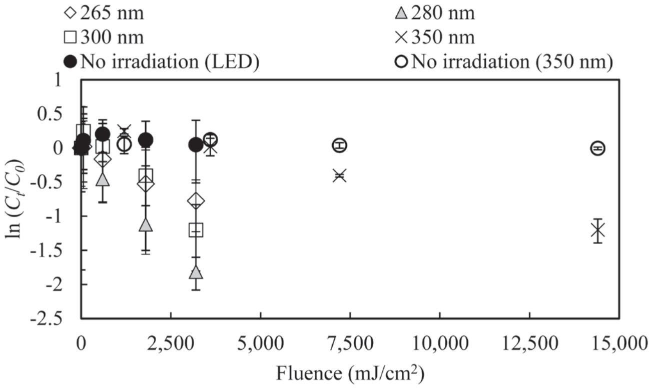

Fig. 7 Concentration change of free chlorine during NCl_3 decomposition experiments. Numbers of experiment: No irradiation (LED) ($n = 9$), No irradiation (350 nm) ($n = 3$), 265 nm ($n = 3$), 280 nm ($n = 3$), 300 nm ($n = 3$) and 350 nm ($n = 3$).

tion experiments are summarized in **Table 2**. In **Table 2**, the ratios of the rate constants of NCl_3 decomposition (k_{NCl3}) to the ones of free chlorine decomposition in the presence of NCl_3 decomposition (k_{Cl2}) were calculated as an indicator of the selective decomposition of NCl_3 (if k_{NCl3}/k_{Cl2} is small, this is preferable for the selective decomposition of NCl_3). Also, electrical energy per order (E_{EO}) was calculated to evaluate the required input energy for 1-log NCl_3 decomposition in water and summarized in **Table 3**.

Decomposition of NCl_3

As shown in **Fig. 4**, the concentration of NCl_3 in the decomposition experiment at a wavelength of 265 nm was decreased from 0.68 to 0.06 mg/L and 90.6% was decomposed after 60 min of UV irradiation. At a wavelength of 280 nm,

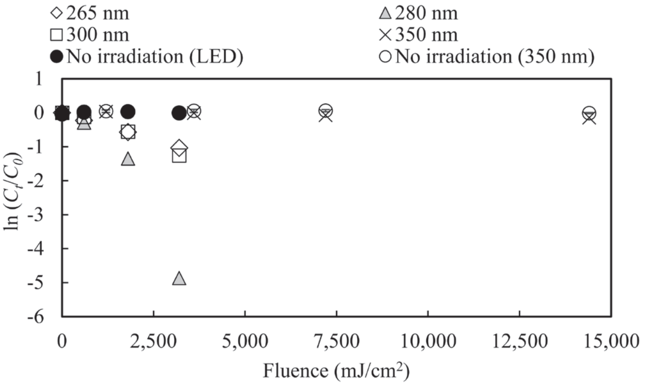

Fig. 8 Concentration change of free chlorine (HOCl dominant) in the decomposition experiments without NCl_3 at pH 7 ($n = 1$).

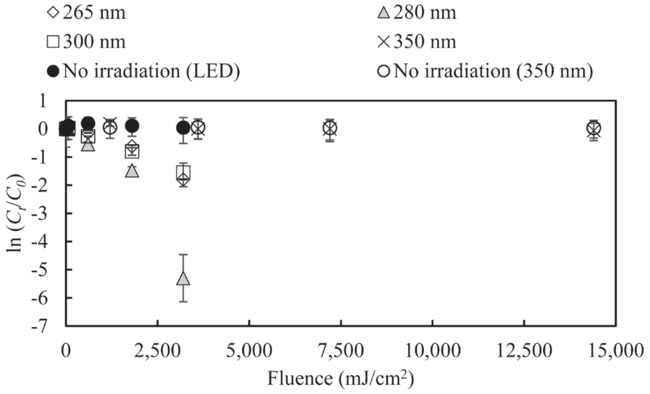

Fig. 9 Concentration change of free chlorine (OCl^- dominant) in the decomposition experiments without NCl_3 at pH 9. Numbers of experiment: No irradiation (LED) ($n = 9$), No irradiation (350 nm) ($n = 3$), 265 nm ($n = 3$), 280 nm ($n = 3$), 300 nm ($n = 3$) and 350 nm ($n = 3$).

concentration of NCl_3 was decreased from 0.96 to 0.03 mg/L and 96.6% was decomposed after 60 min irradiation. At both the 265 and 280 nm wavelengths, most of NCl_3 was decomposed within 30 min. The concentration of NCl_3 at 300 nm was decreased from 0.95 to 0.07 mg/L and 92.5% of NCl_3 was decomposed after 60 min of irradiation. At 350 nm, the concentration of NCl_3 decreased from 0.84 to 0.59 mg/L, with 30.2% removed in 60 min. In the irradiation of 350 nm, an irradiation experiment was conducted at 1.0 mW/cm^2 for 60 min, but since a sufficient removal rate was not obtained, an irradiation experiment was conducted at 2.0 mW/cm^2 for 120 min (total irradiation energy (mJ/cm^2) was four times higher than those of other wavelengths) for decomposition. As a result, the concentration of NCl_3 decreased from 1.06

Table 2 Apparent decomposition rate constant (*k*) for each chlorine species.

Wavelengths	NCl_3 ($cm^2/(mW\cdot s)$)	Free chlorine at neutral pH during NCl_3 decomposition (HOCl dominant) ($cm^2/(mW\cdot s)$)	Free chlorine at neutral pH (HOCl dominant) ($cm^2/(mW\cdot s)$)	Free chlorine at alkaline pH (OCl^- dominant) ($cm^2/(mW\cdot s)$)	NCl_3/free chlorine (during NCl_3 decomposition) ratio of decomposition rate constant (*k*)
265 nm	0.0013	0.0003	0.0003	0.0006	0.23
280 nm	0.0010	0.0006	0.0015	0.0016	0.60
300 nm	0.0007	0.0004	0.0004	0.0005	0.57
350 nm	0.0001	0.0001	0.0000	0.0000	1.11

Table 3 Comparison of E_{EO} for various contaminants removal in water by UV treatment tourniquets.

UV source	Target compound	Total E_{EO} ($kWh/(m^3\cdot order)$)	Reference
265 nm UV-LED	NCl_3	18.9	Current study
280 nm UV-LED		16.7	
300 nm UV-LED		62.6	
350 nm UV-SHiPLA		141.8	
265 nm UV-LED	Naproxen	567.2	Hashiguchi *et al.* [11]
280 nm UV-LED		102.3	
300 nm UV-LED		1,515.5	
265 nm UV-LED	Triclosan	112.0	
280 nm UV-LED		19.1	
300 nm UV-LED		34.6	
254 nm UV	Iopamidol	2.3	Tian *et al.* [12]
254 nm UV H_2O_2		0.2	
254 UV	COD	2.0	Asaithambi *et al.* [10]
254 nm UV H_2O_2 Fe	Atrazin	16.5	Luca [13]
254 nm UV*	Trimethoprim	97.1	Ngumba *et al.* [15]
254 nm UV/H_2O_2*		17.8	
254 nm UV/Cl*		35.8	
254 nm UV*	Sulfamethoxazole	5.4	
254 nm UV/H_2O_2*		4.1	
254 nm UV/Cl*		3.3	
254 nm UV*	Ciprofloxacin	6.2	
254 nm UV/H_2O_2*		4.2	
254 nm UV/Cl*		3.5	

* shows decomposition experiments conducted in wastewater.

to 0.24 mg/L, and 77.8% was removed in 120 min. The pH change during the UV irradiation experiment was from 6.66 to 6.77.

Overall, the concentration of NCl_3 remarkably decreased after UV irradiation. The rate constants were 0.0013 $cm^2/(mW\cdot s)$ at 265 nm, 0.0010 $cm^2/(mW\cdot s)$ at 280 nm, 0.0007 $cm^2/(mW\cdot s)$ at 300 nm, and 0.0001 $cm^2/(mW\cdot s)$ at 350 nm, in the order of 265 nm > 280 nm > 300 nm > 350 nm (also see in **Table 2**). This order did not correspond to the order of UV absorption (**Fig. 5**). The reason why the magnitude of the UV absorption coefficient does not correspond to the degradation rate constant is not clear, but the following degradation mechanisms can be inferred from the UV decomposition reaction mechanism of monochloramine and dichloramine. According to Yin *et al.* [8], the molar absorption coefficients of monochloramine and dichloramine, which are also combined chlorines, are 345 and 96 $1/(M\cdot cm)$ at 255 nm, respectively, and both substances are excited by

UV energy to produce chlorine radicals. This suggests that NCl_3 also generates chlorine radicals when irradiated at a wavelength of 265 nm and chlorine radicals are involved in the decomposition.

Regarding the decomposition pathway of NCl_3, UV spectrum analysis was conducted to the experimental solution before and after NCl_3 decomposition (**Fig. 6**). In the synthesis process in NCl_3 solution, mono and/or dichloramine were also synthesized as impurities (maximum absorbance peak 259 nm: monochloramine, 301 nm: dichloramine [9]). Their peaks are not significantly becoming large after NCl_3 decomposition, and it seems like they are not main decomposition by-products of NCl_3.

By compared the calculated decomposition rate constant (*k*) of the free chlorine under NCl_3 decomposition ($k = 3.00 \times 10^{-4}$ $cm^2/(mW{\cdot}s)$) and free chlorine solely decomposed at neutral pH ($k = 3.00 \times 10^{-4}$ $cm^2/(mW{\cdot}s)$), there is no difference between them. Only slight decrease was observed in the free chlorine solely decomposed at neutral pH, a little amount of free chlorine was produced as decomposition by-product of NCl_3, but it may not be a major decomposition by-product. However, more direct evaluation such as structural determination of decomposition by-products by mass spectrometry will be required to clarify the decomposition mechanisms in the future. Also, it was difficult to discuss the quantum yield (actual energy used for NCl_3 decomposition) because the thickness of the experimental solution was only 1.7 cm, and we only discuss decomposition efficiencies such as *k* value calculated based on input energy (*i.e.*, fluence) in this study. Thus, the experimental setup and the concentration increase on NCl_3 to observe the amount of UV adsorption will also be required in the future.

Figure 7 shows the change in the concentration of free chlorine remaining in the NCl_3 standard solution. At a wavelength of 265 nm, free chlorine concentration decreased from 1.10 to 0.36 mg/L, resulting in 66.9% decomposition. At 280 nm, the HOCl concentration decreased from 1.31 to 0.15 mg/L, resulting in 88.7% decomposition. At a wavelength of 300 nm, free chlorine concentration decreased from 1.27 to 0.35 mg/L, resulting in 72.8% decomposition. At a wavelength of 350 nm (irradiance of 2.0 mW/cm^2), the free chlorine decreased from 1.33 to 0.81 mg/L, a 39.6% decomposition. Similarly to NCl_3, free chlorine was decomposed more slowly at 350 nm than at other wavelengths. The pH change in the UV irradiation experiment was in the range of 6.66 and 6.77, suggesting that most of the free chlorine was present in the form of HOCl. The decomposition rate constants (*k*) of free chlorine decomposition (HOCl dominant) were 0.0003 $cm^2/(mW{\cdot}s)$ at 265 nm, 0.0006 $cm^2/(mW{\cdot}s)$ at 280 nm, 0.0004 $cm^2/(mW{\cdot}s)$) at 300 nm, and 0.0001 $cm^2/(mW{\cdot}s)$ at 350 nm. The rate constants were larger at the wavelengths 280 nm > 300 nm > 265 nm > 350 nm (**Table 2**).

From the results above, it can be said that 265 and 350 nm are appropriate options among tested because NCl_3 was selectively decomposed while maintaining free chlorine. That is, the free chlorine/NCl_3 ratios after treatment at 265 nm (0.23 $cm^2/(mW{\cdot}s)$) and 350 nm (1.11 $cm^2/(mW{\cdot}s)$ were smaller than those at other wavelengths as shown in **Table 2**.

Free chlorine decomposition at neutral pH (HOCl dominant condition)

To understand the decomposition characteristics of HOCl itself, UV irradiation experiments were also performed without the presence of NCl_3. At pH 7, as shown in **Fig. 8**, the concentration of free chlorine decreased from 1.75 to 0.62 mg/L at 265 nm, and the removal rate was 64.5% after 60 min of irradiation. At a wavelength of 280 nm, the free chlorine concentration decreased from 1.65 to 0.01 mg/L after 60 min of irradiation, and the removal rate was 99.2%. At a wavelength of 300 nm, the removal rate was 71.6% and decreased from 1.64 to 0.46 mg/L after 60 min of irradiation. At 350 nm, the removal rate was 13.6%, decreasing from 1.76 to 1.52 mg/L after 120 min of exposure. Decomposition was the highest at the 280 nm wavelength compared to the other wavelengths. On the other hand, almost no decomposition occurred at the wavelength of 350 nm.

The pH in the UV irradiation experiments slightly varied, ranging from 6.69 to 6.78. The decomposition rate constants (*k*) were 0.0003 $cm^2/(mW{\cdot}s)$ at 265 nm, 0.0015 $cm^2/(mW{\cdot}s)$ at 280 nm, 0.0004 $cm^2/(mW{\cdot}s)$ at 300 nm, and 0.00001 $cm^2/(mW{\cdot}s)$ at 350 nm. The rate constants were larger at the wavelengths 280 nm > 300 nm > 265 nm > 350 nm (**Table 2**).

Free chlorine dominated by HOCl was decomposed by UV light at 265, 280, and 300 nm, but not at 350 nm. NCl_3 was decomposed faster than HOCl at wavelengths of 265, 300 and 350 nm. Notably, decomposition rate constants (*k*) were lower in NCl_3 solution (0.0006 $cm^2/(mW{\cdot}s)$) than in HOCl solution without NCl_3 (0.0015 $cm^2/(mW{\cdot}s)$) at 280 nm, and was higher in NCl_3 solution (0.0001 $cm^2/(mW{\cdot}s)$) than in HOCl solution without NCl_3 (0.00001 $cm^2/(mW{\cdot}s)$) at 350 nm.

This suggests that the reaction rate constants at 280 nm and 300 nm were changed by interactions among intermediates during the decomposition. 280 nm shows almost no UV absorption for HOCl, while there is significant absorption for NCl_3 and OCl^-. Since the reaction rate is lower in the presence of NCl_3, it is considered that free chlorine was provided as a result of the decomposition of NCl_3.

The difference at 300 nm is difficult to explain, but the difference of intermediates or byproducts may be the reason. For example, the decomposition products of NCl_3 at 300 nm may not be HOCl, but other active species which contribute to the decomposition of free chlorine.

Free chlorine decomposition under alkaline pH (OCl^- dominant condition)

In this section, the decomposition of free chlorine at alkaline pH 9 is discussed. As shown in **Fig. 9**, at 265 nm, free chlorine decreased from 2.20 to 0.27 mg/L, resulting in 87.5% removal. At 280 nm wavelength, free chlorine decreased from 1.95 to 0.01 mg/L and 99.5% was removed in 60 min. At 300 nm, free chlorine decreased from 1.50 to 0.28 mg/L and 81.7% was removed. At 350 nm, the concentration decreased from 1.60 to 1.51 mg/L and 6.0% was removed. The pH in the UV irradiation experiment ranged from 8.02 to 9.40.

The decomposition rate constants (k) were 0.0006 $cm^2/(mW{\cdot}s)$ at 265 nm, 0.0015 $cm^2/(mW{\cdot}s)$ at 280 nm, 0.0005 $cm^2/(mW{\cdot}s)$ at 300 nm, and 0.00001 $cm^2/(mW{\cdot}s)$ at 350 nm, respectively. The decomposition rates were in the order of 280 nm > 265 nm > 300 nm > 350 nm. OCl^- was degraded by wavelengths of 265, 280, and 300 nm, but not much at 350 nm. The result indicated that the proportion of OCl^-, and thus pH, should be adjusted to maintain free chlorine during UV treatment.

Although described as 350 nm for convenience, UV-SHiPLA actually has a FWHM of 322–378 nm (maximum peak at 347 nm) and does not strictly emit emission lines at 350 nm. It will therefore be necessary in the future to confirm which wavelengths within this range actually contribute to the degradation of NCl_3 by experiments using UV-cut filters.

Comparison of E_{EO} for various contaminants removal in water by UV treatment techniques

The energy required to remove 1-log of NCl_3 (electrical energy per order, E_{EO} in $kWh/(m^3{\cdot}order)$) when treating 1 m^3 of NCl_3-containing water was determined using the equation (2) [10].

$$E_{EO} = \frac{38.4 \times P_{el}}{V \times k} \tag{2}$$

P_{el}: Input energy (kW)
V: Sample volume (L)

In this study, since there is no literature that calculates the E_{EO} of NCl_3, the E_{EO} for the UV decomposition of NCl_3 was compared to those for pharmaceuticals and COD decomposition, which are considered persistent in the environment and for which there are many examples of E_{EO} calculations related to UV treatment. **Table 3** summarizes the comparison of E_{EO} for the removal of various contaminants in water by UV treatment techniques.

The E_{EO} for UV decomposition of NCl_3 is 18.9 $kWh/(m^3{\cdot}order)$ at 265 nm, and 16.7 $kWh/(m^3{\cdot}order)$ at 280 nm, 62.6 $kWh/(m^3{\cdot}order)$ at 300 nm, and 141.8 $kWh/(m^3{\cdot}order)$ at 350 nm (**Table 3**). This indicates that the decomposition of NCl_3. The order of E_{EO} were not much different when UV-LEDs were used for NCl_3 and triclosan. However, E_{EO} for the more UV resistant pharmaceuticals like naproxen was higher than those NCl_3 decomposition. By compared to UV 254 nm and its advanced oxidation process, their E_{EO} were smaller than those in UV-LED decompositions even in wastewater. To consider that mercury-free UV sources such as LED will become core UV technologies that can be installed in the water treatment process, more studies are required to optimize recalcitrant organic in organic compounds in water [10–13]. In addition, they are somewhat comparable, and similar efficiency may be achieved as discussed below.

The absorption coefficient at 350 nm for water is negligible at 0.89×10^{-5} 1/cm [14], and when the thickness of the water is as small as 1.7 cm in our experimental system, most of the UV passes through the reactor without being effectively utilized, resulting in poor NCl_3 decomposition efficiency. Therefore, in the actual decomposition process for NCl_3 using a 350 nm UV, it is necessary to optimize the intensity and the depth of the reaction tank, and irradiation time, as well as to design the apparatus by using reflectors to amplify the light.

CONCLUSIONS

In this study, we used UV at wavelengths of 265, 280, 300, and 350 nm to decompose NCl_3, which is the causative agent of chlorine odor, and searched for wavelengths at which free chlorine, which has high disinfection ability, is difficult to decompose. As a result, the following findings were obtained.

(1) NCl_3 was decomposed at all wavelengths by UV irradiation at 265, 280, 300, and 350 nm, and free chlorine (HOCl and OCl^-) was also decomposed at 265, 280, and 300 nm. Though 350 nm decomposed NCl_3 slowly compared with other wavelengths, but the smallest free chloramine removal was observed.

(2) The amount of total E_{EO} for NCl_3 decomposition at

350 nm was larger than 265, 280, and 300 nm, and therefore, some reactor design innovations required such as adjusting the reactor depth (water thickness), irradiance and using reflectors to enhance the irradiance, are required for practical application.

(3) From the view point of the ratio of NCl_3/Free chlorine (during NCl_3 decomposition) and the total E_{EO}, the method of decomposing NCl_3 using a wavelength of 265 nm and maintaining residual chlorine by reinjecting chlorine was also selected as an option.

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