

## Research Article

# Photodegradation of Trace Trichloronitromethane in Water under UV Irradiation

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This study's objective was to study the photodegradation of TCNM (trichloronitromethane) in water under UV light. The effects of light intensity, nitrate ions, chloride ions, humic acid, and pH on the photochemical degradation of TCNM were investigated under the irradiation of low pressure mercury lamp ( $\lambda = 254$  nm, 12 W). The photodegradation rate of TCNM was found to increase with increasing the concentration of nitrate ions, chloride ions, humic acid, pH, and light intensity. The photodegradation of TCNM was examined at pH 6.0 with initial concentrations ( $C_0$ ) of TCNM at 10.0–200.0  $\mu\text{g/L}$ . The overall rate of degradation of TCNM was modeled using a pseudofirst-order rate law. Finally, the proposed mechanism involved in the photodegradation of TCNM was also discussed by analysis. Results of this study can contribute to the development of new source control strategies for minimization of TCNM risk at drinking water and wastewater utilities.

## 1. Introduction

Disinfectants used in water treatment, such as chlorine, chloramines, and ozone, react with dissolved natural organic matter to form a range of disinfection byproducts (DBPs). Since the discovery of chloroform as a DBP in drinking water in the early 1970s [1], significant research efforts have been made to improve our understanding of DBP formation and control. To date, more than 600 DBPs have been identified in drinking waters [2, 3]. Despite this daunting number, only 11 DBPs (4 trihalomethanes (THMs), 5 haloacetic acids (HAAs), bromate, and chlorite) are currently regulated under the US Environmental Protection Agency's (USEPA's) Disinfectants/DBP Rule [4]. Additional DBP regulations may be proposed and implemented after potential health risks of many unregulated DBPs were determined [5]. In a nationwide occurrence study funded by the USEPA, approximately 70 unregulated DBPs that were identified to cause the highest potential human health risks were selected and monitored in 12 water utilities across USA in 2000–2002 [6, 7]. Among those DBPs, one class of DBPs that has been the focus of recent reports is the halonitromethanes (HNMs)

[2, 3, 6, 8]. Of the HNMs, trichloronitromethane ( $\text{Cl}_3\text{CNO}_2$ , chloropicrin, TCNM) is the most common, being formed in disinfected waters containing nitrite [9–11]. Both ozonation and chlorination affect TCNM concentrations [12, 13], and it has been found as high as 6.5 nM when preozonation was followed by chloramination [14, 15]. TCNM has also been introduced to water systems through various commercial applications, for example, pesticide; resin [16].

In recent years, limited studies have been reported on the treatment of TCNM. It was reported that experiments with corrosion products collected from water distribution systems were conducted to determine the ability of corrosion solids to degrade TCNM, such as iron water main corrosion products [17]. UV disinfection may be particularly attractive because its lack of chemical application suggests that its use could avoid DBPs formation. Photolysis of aqueous TCNM produced phosgene, and under cryogenic conditions nitrosyl chloride was obtained [18]. Xenon light (solar simulator) degraded 1 mM TCNM at 25°C and pH 7 to  $\text{CO}_2$ ,  $\text{Cl}^-$ ,  $\text{NO}_3^-$ , and  $\text{NO}_2^-$  with a half-life of 31.1 h, whereas dark controls were stable in solution for 240 h [19]. Ultrasound degraded 99% of a 10  $\mu\text{M}$  TCNM solution with recovery ratios for Cl and

inorganic nitrogen ( $\text{NO}_3^-$ ,  $\text{NO}_2^-$ ) at  $72 \pm 1$  and  $91 \pm 2\%$ , respectively [20]. Absolute rate constants for the free-radical-induced degradation of trichloronitromethane were determined using electron pulse radiolysis and transient absorption spectroscopy. Rate constants for hydroxyl radical,  $\cdot\text{OH}$ , and hydrated electron,  $e_{\text{aq}}^-$ , reactions were  $(4.97 \pm 0.28) \times 10^7 \text{ M}^{-1}\text{s}^{-1}$  and  $(2.13 \pm 0.03) \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$ , respectively. The mechanisms of these free radical reactions with TCNM were investigated, using  $^{60}\text{Co}$  gamma irradiation at various absorbed doses, measuring the disappearance of TCNM and the appearance of the product nitrate and chloride ions [21]. However, the previous paper reports focused mainly on the degradation of TCNM by iron water main corrosion products or Xenon light, and so on, while studies on the direct photodegradation of TCNM have hardly been reported on drinking waters under UV light.

The objective of this study was to explore the utility of UV light processes for treatment of TCNM in drinking water. Of particular interest were the kinetics and possible mechanisms on direct photodegradation of TCNM. It will be helpful to know the characteristics of TCNM in the drinking waters under UV light. Results of this study can contribute to the development of new source control strategies for minimization of TCNM risk at drinking water and wastewater utilities.

## 2. Materials and Methods

**2.1. Chemicals and Reagents.** TCNM, tert-butanol (TBA), humic acid, and sodium nitrate ( $\text{NaNO}_3$ ) were obtained from Sigma-Aldrich, with purity higher than 99%. Methyl tertiary-butyl ether (MTBE) was obtained from Fisher and sodium chloride (100%) were purchased from Mallinckrodt. All chemicals used for making the solutions (buffer, eluents, etc.) were of reagent grade and used without further purification. All aqueous solutions were prepared with ultrapure water (conductivity  $>18 \text{ m}\Omega\cdot\text{cm}$ ) generated by a Millipore Milli-Q water purification system (Billerica, MA). Fifty millimolar aqueous stock solutions of TCNM, humic acid, and  $\text{NaNO}_3$  were prepared and stored at room temperature, in the dark by covering with aluminum foil. The concentration of the TCNM stock solution was spectrophotometrically checked for variance prior to use.

**2.2. Experimental Methods and Analyses.** All experiments were performed in a magnetically stirred 60 mL cylindrical quartz reactor (Figure 1). UV irradiation was supplied from one side of the quartz reactor by up to three 4 W LP lamps (G4T5 Hg lamps, Philips TUV4W) peaking at 254 nm at ambient temperature ( $22^\circ\text{C}$ ). The photochamber was equipped with a fan for cooling during the experiments. The incident light irradiance in the active wavelength region was  $2.0\text{--}5.4 \text{ mW}/\text{cm}^2$  to the reactor center measured by a UVX (UVP, USA) radiometer. The solution pH was controlled to be constant ( $\pm 0.2$ ) during the reaction time by 2 mM phosphate buffer for pH 5–9. The solution was vigorously mixed using a magnetic stirrer. The lamps were stabilized for about 30 min prior to their use for illumination. As the photochemical

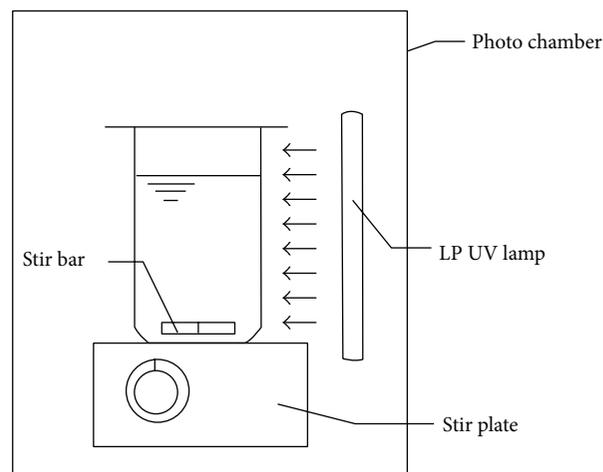


FIGURE 1: Illustration of experimental set-up (The 60 mL cylindrical quartz reactor has a diameter of 2.75 cm and a height of around 10.1 cm. Up to three LPUV lamps in parallel was used.).

reaction proceeded, sample aliquots of 5 mL were withdrawn from the reactor using a syringe.

Samples were withdrawn from the cylindrical Pyrex reactor at proper intervals (e.g., 10, 20, 30, 40, 50, and 60 min) by a 5 mL plastic straw. The samples were extracted with 2.0 mL of methyl tertiary-butyl ether (MTBE) for 2 min. One mL of the MTBE layer was transferred to a GC vial and analyzed for TCNM by an Agilent 6890 gas chromatography system equipped with a HP-5MS capillary column ( $30 \text{ m} \times 250 \mu\text{m} \times 0.25 \mu\text{m}$ ) and an electron capture detector (Palo Alto, CA). Detailed temperature programs have been reported previously [22]. In order to investigate that the effects of nitrate ions, chloride ions, and humic acid,  $2.2 \times 10^{-4} \text{ mol/L}$  nitrate ion,  $2.2 \times 10^{-4} \text{ mol/L}$  chloride ion, and  $0.2 \text{ mg/L}$  humic acid were added into the reactive solution, respectively.

The calibration curve equation for TCNM was  $Y_{\text{Area}} = 2.29\text{E}6 + 179729.50C_{\text{TCNM}}$ ,  $R^2 = 0.9995$  ( $n = 6$ ), where  $C_{\text{TCNM}}$  was the concentration of TCNM in the range of  $0.0\text{--}500 \mu\text{g/L}$ . The standard error of analyses methods was  $2.37 \mu\text{g/L}$ . All vitreous apparatus were dipped in  $\text{HNO}_3/\text{water}$  (the volume ratio was 1:1) overnight, and then put them into the incubator at  $80^\circ\text{C}$ . All the experiments were triplicate. The results presented were the mean values with a total error less than 5%.

## 3. Results and Discussion

**3.1. Photodegradation of TCNM in the Presence of UV.** Conditions favoring TCNM photodegradation were evaluated by varying approaches. In order to investigate the effects of low pressure mercury lamp on the photodegradation of TCNM, a bench-scale experiment was designed to study interactions between UV light and TCNM. A dark control on reaction solution containing TCNM  $10.0 \mu\text{g/L}$  concentration without UV was carried out under magnetic stirring condition. As shown in Figure 2, the results showed that the degradation rate of TCNM was 25.51% after 60 min without UV. The other

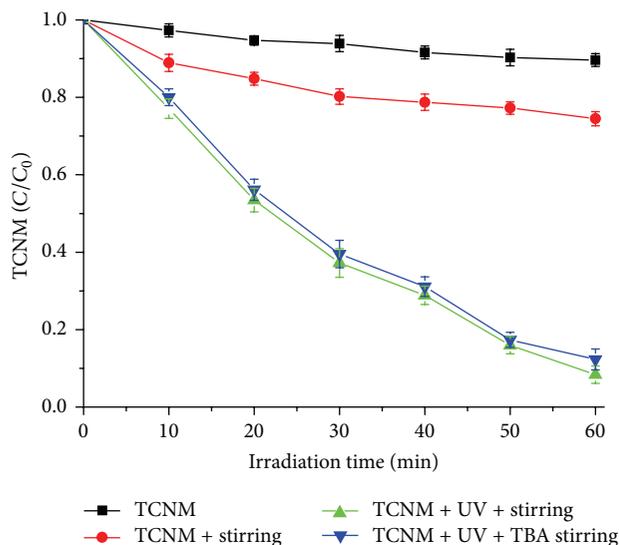


FIGURE 2: TCNM concentration change in the control experiments.

test on reaction solution containing TCNM  $10.0 \mu\text{g/L}$  concentration without UV was carried out. The results showed that the degradation rate of TCNM was 10.36% after 60 min without UV. When the reaction solution containing TCNM  $10.0 \mu\text{g/L}$  concentration with UV was carried out under 12 W low pressure mercury lamps, the results showed that the photodegradation rate of TCNM was 91.65% after 60 min with UV. From the experimental results, the degradation rate of TCNM increased with increasing exposure time. In order to further evaluate the photodegradation of TCNM, 1.0 g/L TBA was added into reactive solution to evaluate the effect of reactive radical on formation of TCNM. The results suggest that TBA had little effect on photodegradation of TCNM. Without TBA under LP UV irradiation, the photodegradation rate of TCNM increased from 22.9% to 91.65% in 60 min, while with TBA under LP UV irradiation, the photodegradation rate of TCNM increased from 19.98% to 87.69% in 60 min. It means that TCNM featuring nitro ( $-\text{NO}_2$ ) and nitrile ( $-\text{CN}$ ) functional groups are of particular concern because of their toxicity and optical absorption properties. From the experimental results, the direct photolysis of TCNM was the main reason that TCNM featuring nitro ( $-\text{NO}_2$ ) and nitrile ( $-\text{CN}$ ) functional groups is of optical absorption properties.

**3.2. Effect of Light Intensity on the Photodegradation of TCNM.** The experiments were carried out to study effect of light intensity on the photodegradation of TCNM in aqueous solution under low pressure mercury lamp. These solutions were irradiated under varying irradiation intensity. The results showed in Figure 3 that the photodegradation of TCNM increased with increasing light intensity. When the light intensity was 4 w, 68.42% of TCNM disappeared from the aqueous solution after 60 min irradiation. When the light intensity was 8 w, 90.62% of TCNM disappeared from the aqueous solution after 60 min irradiation. When the light intensity was 12 w, 91.82% of TCNM disappeared

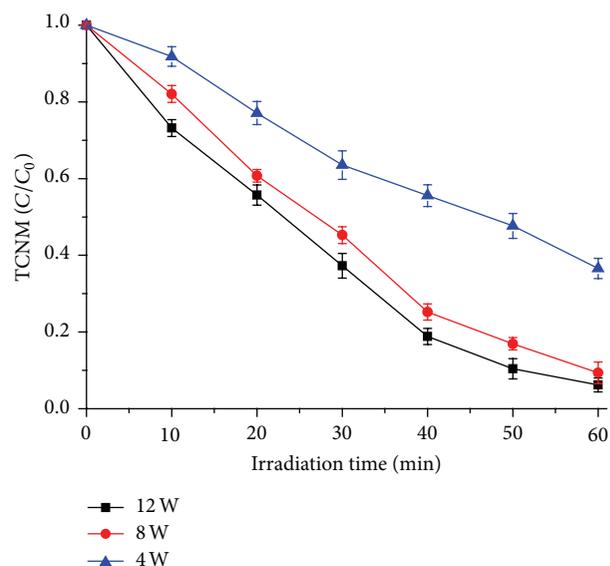


FIGURE 3: Effect of light intensity on the photodegradation of TCNM.

from the aqueous solution after 60 min irradiation. From the experimental results, the degradation rate of TCNM increased with increasing light intensity. According to the experimental results, 12 W was selected as the light intensity of following experiments.

**3.3. Effect of Reaction Conditions on the Photodegradation of TCNM.** The photodegradation of TCNM was further evaluated for the impact of reaction conditions including solution pH, the presence of chloride ion, nitrate ion, and humic acid. Those factors were selected because they formed intermediate levels of TCNM in drinking water and were abundantly available in our lab.

**3.3.1. Effect of pH.** The effect of pH was studied at pH 5.0, 6.0, 7.0, 8.0, and 9.0 (buffered by 10 mM phosphate buffer and NaOH) using  $10 \mu\text{g/L}$  TCNM. The photodegradation experiment was performed in TCNM aqueous solutions at several pH values ranging from 5 to 9. As shown in Figure 4, it is not very obvious that the photodegradation efficiency of TCNM increased with increasing pH. At pH = 9, up to 97.55% of TCNM was removed from the suspension after 60 min light irradiation. At pH = 5.0, 6.0, 7.0, and 8.0, the photodegradation efficiency of TCNM was 90.04%, 89.15%, 92.61%, and 96.00%, respectively, after 60 min light irradiation. From the experimental results, the photodegradation rate of TCNM changed a little between different from pH = 5 to pH = 9. These phenomena were similar to the results reported earlier by Fang et al. [23]. The authors proposed that the UV spectrum of TCNM displayed only a characteristic peak centered at 208 nm and it changed little between different pH values.

PH 7.0 was selected in the all experiments, because both natural water and not only has the TCNM suspension a similar pH value, but also the different pH values have little effect on the degradation rate of TCNM.

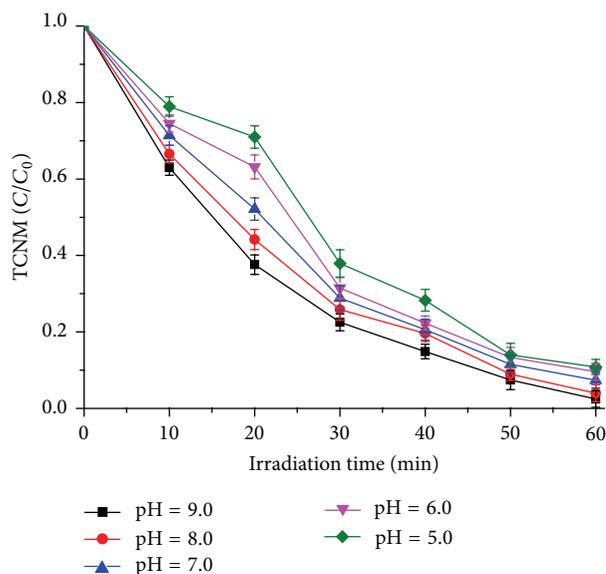


FIGURE 4: Effect of pH on the photodegradation of TCNM.

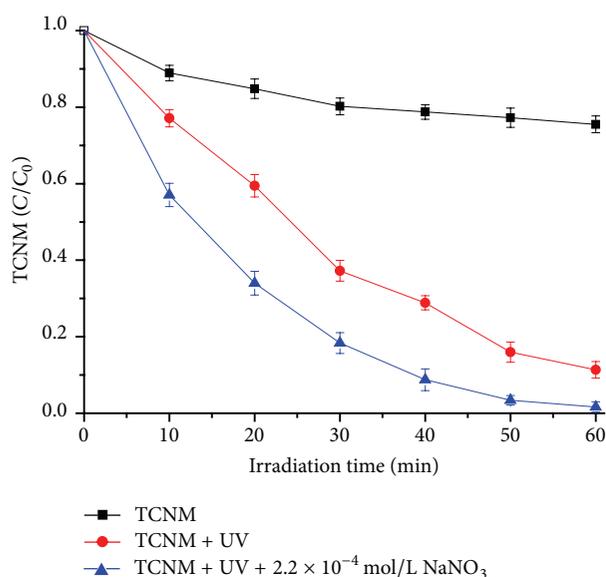


FIGURE 5: Effect of nitrate ion on the photodegradation of trichloronitromethane.

### 3.3.2. Effect of Nitrate Ion on the Photodegradation of TCNM.

Nitrate ion is a component of natural water because of their important role in the fate and transport of many pollutants. In our experiments, nitrate ion could also affect the photodegradation of TCNM as shown in Figure 5. The results showed that the degradation rate of TCNM was 25.5% after 60 min without UV. When the reaction solution containing TCNM 10.0  $\mu\text{g/L}$  concentration was carried out under UV irradiation, the results showed that the photodegradation rate of TCNM was 91.6% after 60 min. In the presence of  $2.2 \times 10^{-4}$  mol/L nitrate ion, the results showed that the photodegradation rate of TCNM was 98.5% after 60 min with UV. From the experimental results, nitrate ion can promote

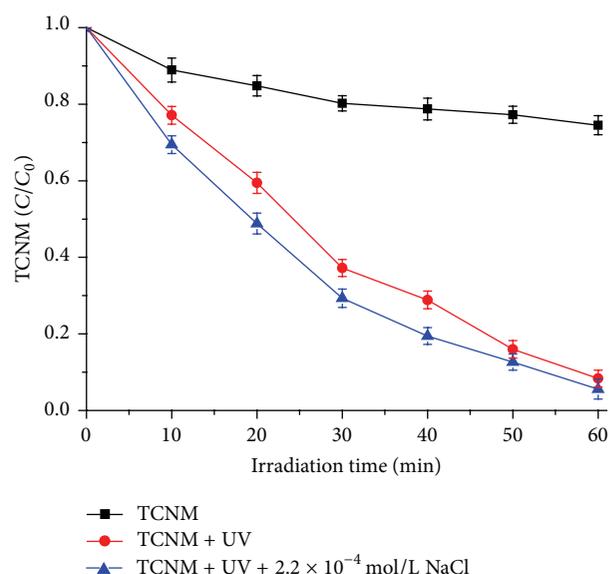
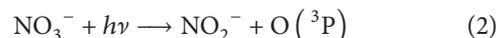
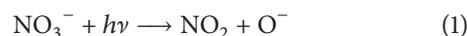


FIGURE 6: Effect of chloride ion on the photodegradation of TCNM.

the degradation rate of TCNM under LP UV irradiation. Moreover, nitrate and nitrite ions can undergo photolysis to produce OH radicals according to reactions (1)–(3) [24], which, in turn, facilitated the oxidation of TCNM in water



### 3.3.3. Effect of Chloride Ion on the Photodegradation of TCNM.

In nature, chlorine is found primarily as the chloride ion, a component of the salt that is deposited in the earth or dissolved in the oceans. Most chloride salts are soluble in water; thus, chloride ion is also a ubiquitous group of natural water. So chloride ion needs also be studied if there is an effect on the photodegradation of TCNM. As shown in Figure 6, the results showed that the degradation rate of TCNM 10.0  $\mu\text{g/L}$  concentration was 25.5% after 60 min without UV. When the reaction solution containing TCNM 10.0  $\mu\text{g/L}$  concentration was carried out under UV irradiation, the results showed that the photodegradation rate of TCNM was 91.6% after 60 min. In the presence of  $2.2 \times 10^{-4}$  mol/L chloride ion, the results showed that the photodegradation rate of TCNM 10.0  $\mu\text{g/L}$  concentration was 94.4% after 60 min under UV irradiation. From the experimental results, chloride ion can promote the degradation rate of TCNM under LP UV irradiation.

### 3.3.4. Effect of Humic Acid on the Photodegradation of TCNM.

Humic acid is a ubiquitous and heterogenous group of natural organic compounds because of their important role in the fate and transport of many pollutants. In our case, humic acid could also affect the photodegradation of TCNM as shown in Figure 7. The results showed that the degradation rate of TCNM 10.0  $\mu\text{g/L}$  was 28.5% after 60 min without UV. In

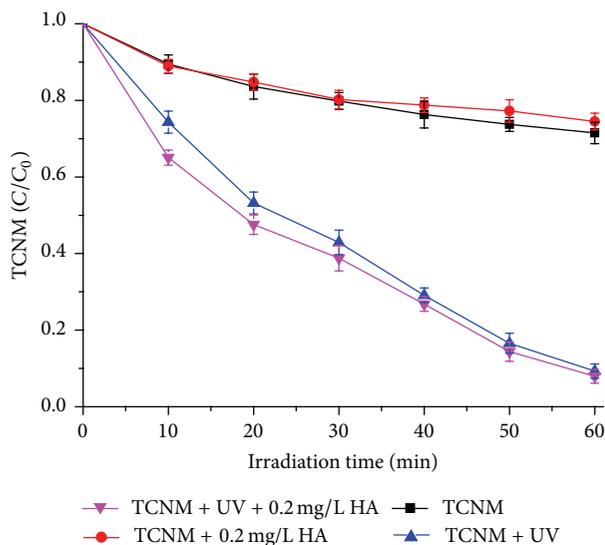


FIGURE 7: Effect of humic acid on the photodegradation of TCNM.

the presence of 0.2 mg/L humic acid, the results showed that the photodegradation rate of TCNM 10.0  $\mu\text{g/L}$  was 25.5% after 60 min without UV. When the reaction solution containing TCNM 10.0  $\mu\text{g/L}$  was carried out under UV irradiation, the results showed that the photodegradation rate of TCNM was 90.7% after 60 min. In the presence of 0.2 mg/L humic acid, the results showed that the photodegradation rate of TCNM was 89.1% after 60 min with UV. These results indicated that humic acid could promote the photodegradation of TCNM.

**3.4. Kinetic Model for TCNM Photodegradation.** The influence of initial TCNM concentration on the photodegradation of TCNM was examined by irradiating the suspensions at pH 7.0 with initial concentrations ( $C_0$ ) of TCNM at 10, 50, 100, and 200  $\mu\text{g/L}$ , respectively. As shown in Table 1, LP UV could evidently induce photodegradation of TCNM in aqueous solution. The photodegradation rate of low concentration TCNM decreased faster than that of high concentration of TCNM in aqueous solution. Under these conditions, with initial concentration ( $C_0$ ) of TCNM increasing, the degradation rate of TCNM decreased. The disappearance of TCNM in terms of percentage of the initial TCNM concentration was higher at lower initial TCNM concentration. In this experiment,  $r_A = d[C]/dt$  (the change in  $C$  versus  $t$ ) can be measured from the slope of the exponential curve at early times in the reaction. It is notable that such measurement must be done at the instantaneous initial velocity because the concentration of TCNM was always changing. It is well known that instantaneous initial velocity  $\approx$  slope at initial point. Thus a plot of  $r_A$  versus  $[C]$  could be obtained by plotting the instantaneous initial velocity of the reaction, as determined by the slope of the tangent to the curve at the initial time against the  $[C]$ . This plot was a straight line whose slope was equal to  $k$ , the rate constants for the reaction. After the experiment datum was fitted with a range

TABLE 1: Kinetic model for TCNM photodegradation.

Concentration	Fitting equation	$R^2$	$k$
200 $\mu\text{g/L}$	$-\ln(C_t/C_0) = 0.0434t - 0.04876$	0.9781	0.0434
100 $\mu\text{g/L}$	$-\ln(C_t/C_0) = 0.0412t - 0.06118$	0.9831	0.0412
50 $\mu\text{g/L}$	$-\ln(C_t/C_0) = 0.0415t - 0.1445$	0.9831	0.0415
10 $\mu\text{g/L}$	$-\ln(C_t/C_0) = 0.0404t - 0.1659$	0.9796	0.0404

of initial concentrations from 10  $\mu\text{g/L}$  to 200  $\mu\text{g/L}$  at pH 7.0, the initial photodegradation rate  $\ln(C_t/C_0)$  as listed in Table 1 was plotted as a function of initial concentration of TCNM. The overall rate of degradation of TCNM was modeled using a pseudofirst-order rate law. Values of  $k$  were determined by regression of  $\ln(C_t/C_0)$  versus time. From Table 1, the kinetic model of TCNM photodegradation fits a pseudofirst-order rate law.

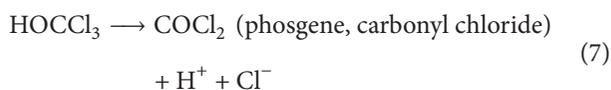
**3.5. Proposed Mechanism for TCNM Photolysis.** Frequent sampling of TCNM in a dark control revealed only the slight decrease in concentration due to sampling during the 60 min of each experiment (e.g., Figure 2). Photolysis rate in water indicated that TCNM can be degraded at UV light (254 nm). Fang et al. [23] reported that degradation pathways initiated by heterolytic cleavage and homolytic cleavage of C–X bond or C–N bond in HNMs by UV photolysis were proposed.

Based on the observed photoproducts and reaction kinetics and information available in the relative literatures [21, 25, 26], the photodegradation of TCNM might undergo an  $n-\pi^*$  transition to the diradical **A**, followed by Nesmeyanov rearrangement to **B**, ring-closure to the oxazirane N-oxide **C**, and decomposition to  $\text{COCl}_2$  and  $\text{NOCl}$  (Figure 8). Relatively stable oxaziranes have been synthesized, and their proposed N-oxides indeed decompose spontaneously to the expected carbonyl and nitroso compounds.

While others researchers thought that TCNM was photodegraded by  $\cdot\text{OH}$  under UV,  $\cdot\text{OH}$  can oxidatively degrade TCNM rapidly, which may react through the following two paths [27–29]:



Hydroxyl radical degrades TCNM through reactions (4) and (5) because it is electrophilic reagent that is more likely to react with the nitrogen atom of the nitro in TCNM.  $\cdot\text{CCl}_3$ , the product of reaction (5), then react with  $\cdot\text{OH}$ . The reaction formulas are as follows:



Phosgene and water then react to form  $\text{CO}_2$  and  $\text{HCl}$ . The reaction formula is as follows:



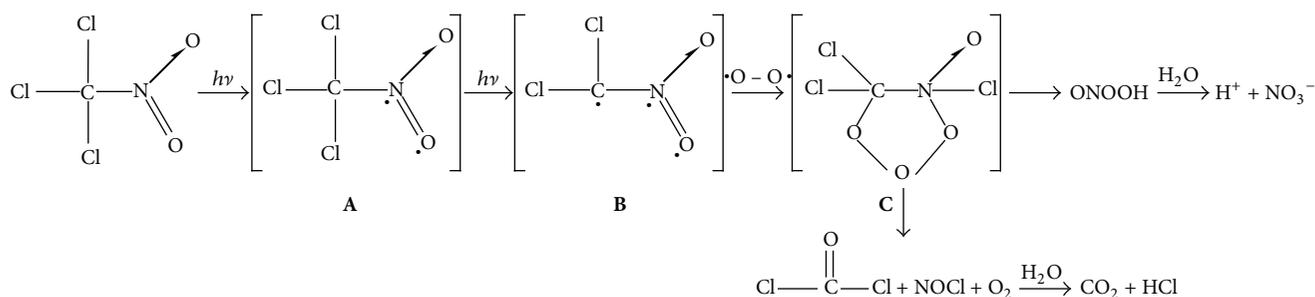
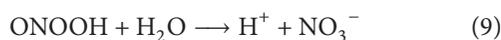
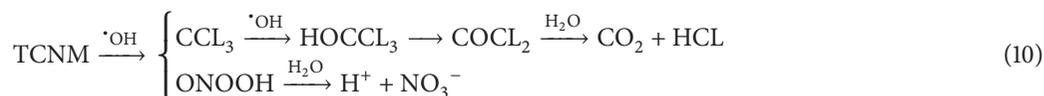


FIGURE 8: Proposed mechanisms for TCNM photolysis.

ONOOH, another product in the reaction formula (5), reacts with water to form  $H^+$  and  $NO_3^-$ . The reaction formula is as follows:



In summary, the paths that  $\cdot OH$  degrades TCNM are as follows:



#### 4. Conclusions

The findings in this study are highly relevant for both TCNM analysis and water treatment operations. The UV/chlorine oxidation process followed by post treatment has been assessed at technical scale. Under these conditions the direct photodegradation of TCNM was achieved for 68.42–97.55%. The direct photolysis of TCNM was the main reason that TCNM featuring nitro ( $-NO_2$ ) and nitrile ( $-CN$ ) functional groups are of optical absorption properties. The effects of light intensity, nitrate ions, chloride ions, humic acid, and pH on the photochemical degradation of TCNM were investigated under the irradiation of low pressure mercury lamp ( $\lambda = 254\text{ nm}$ , 12 W). The photodegradation rate of TCNM was found to increase with increasing the concentrations of light intensity, nitrate ions, chloride ions, humic acid, and pH. The influence of TCNM initial concentration on the photodegradation of TCNM was examined at pH 6.0 with initial concentrations ( $C_0$ ) of TCNM at 10.0–200.0  $\mu\text{g/L}$ . The overall rate of degradation of TCNM was modeled using a pseudofirst-order rate law. Values of  $k_{\text{obs}}$  were determined by regression of  $\ln(C_t/C_0)$  versus time, with a correlation coefficient for the kinetic data  $R^2 > 0.9781$ . The proposed mechanism involved in the photodegradation of TCNM was also discussed by analysis. Insights obtained in this study are useful for reducing TCNM formation during water treatment.

#### Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper. Any opinions, findings, and conclusions or recommendations expressed in this

material are those of the authors and do not necessarily reflect the views of the National Science Foundation.

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