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Conversion characteristics and mechanism analysis of gaseous dichloromethane degraded by a VUV light in different reaction media

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Abstract

The photodegradation of gaseous dichloromethane (DCM) by a vacuum ultraviolet (VUV) light in a spiral reactor was investigated with different reaction media and initial concentrations. Through the combination of direct photolysis, O₃ oxidation and HO· oxidation, DCM was ultimately mineralized into inorganic compounds (such as HCl, CO₂, H₂O, etc.) in the air with relative humidity (RH) of 75%–85%. During the photodegradation process, some small organic acids (including formic acid, acetic acid) were also detected and the intermediates were more soluble than DCM, providing a possibility for its combination with subsequent biodegradation. Based on the detected intermediates and the confirmed radicals, a photodegradation pathway of DCM by VUV was proposed. With RH 75%–80% air as the reaction medium, the DCM removal followed the second-order kinetic model at inlet concentration of 100–1000 mg/m³. Kinetic analysis showed that the reaction media affected the kinetic constants of DCM conversion by a large extent, and RH 80% air could cause a much lower half-life for its conversion. Such results supported the possibility that VUV photodegradation could be used not only for the mineralization of DCM but also as a pretreatment before biodegradation.

Key words: dichloromethane; VUV photodegradation; mechanism; carbon balance; kinetic analysis

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Introduction

Volatile organic compounds (VOCs) are common gaseous pollutants found in industrial and wastewater treatment air emissions, and their indiscriminate discharge usually causes many regional environmental problems, such as urban aerosol haze and photochemical smog (Gallastegui et al., 2011). In 2010, the Chinese government first listed VOCs as one of the four major pollutants that need to be priority-controlled (the others are SO₂, NO_x and particles). Dichloromethane (CH₂Cl₂, DCM), one typical chlorinated VOC which is utilized widely as a solvent in industry, has been discharged arbitrarily to the environment without any purification, with its emission amounting to 15 million tons every year (Fu et al., 2012). Since DCM has the characteristic of biological accumulation, its enduring existence in the environment might be harmful to humans and the ecosystem. DCM has also been listed as one of the priority-controlled pollutants by the USEPA (Green, 1997; Torgonskaya et al., 2011). Therefore, there is a need for the development of efficient approaches for the treatment of DCM.

As an advanced oxidation process (AOP), vacuum-ultraviolet (VUV) photodegradation, which is usually conducted under ambient temperature and pressure, has several advantages over traditional technologies such as thermal oxidation and chemical oxidation. Since oxygen photolysis by 184.9 nm light can produce ozone and other active radicals (such as hydroxyl radical), this technology is considered to be efficient for the removal of several VOCs (Yang et al., 2007; Cheng et al., 2011). Some researchers proposed that the oxidation extents would determine the operational cost, and thus the cost for complete mineralization would be much higher than that for partial oxidation (Mohseni and David, 2003). Therefore, to obtain complete mineralization without any secondary pollution and reduce the costs, a proper subsequent technology needs to be developed.

Recently, biopurification has frequently been applied for air emission control since it could offer many economical and environmental advantages over conventional physical and chemical treatment technologies (such as air stripping, adsorption and condensation) (Park et al., 2009; Popat and Deshusses, 2010). However, this technology is not suitable for the treatment of some hydrophobic and recalcitrant VOCs, since mass transfer limits and

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biodegradation inhibition would have negative effects on the removal capability. The reported critical elimination capabilities for DCM were much lower than those for the soluble and biodegradable compounds (methanol at 250 g/(m³·hr) and methyl ethyl ketone at 174 g/(m³·hr)) (Ramirez-Lopez et al., 2010; Raghuvanshi and Baku, 2009). Alternatively, some researchers proposed that biological technology could be utilized as the subsequent treatment for AOPs, and several studies also proved that the toxic effects of intermediates produced by chemical oxidation were much lower than those of the target compounds. The successful operation of AOP combined with biofiltration for the removal of special compounds (alpha-pinene, chlorobenzene, mixed VOCs) provided a possibility for its industrial application (Wang et al., 2009; Neti et al., 2010; Cheng et al., 2010, 2011). However, less biodegradable and more toxic intermediates would be produced under some inappropriate photodegradation conditions. Hence, such conditions should be optimized to minimize the negative effect of photodegradation and ensure the efficient and stable operation of a subsequent biological system. Kuo and Lin (2009) found that with the irradiation of a 15-min solar photo-Fenton treatment, the BOD/COD values of 2-chlorophenol, 4-chlorophenol and 2,4-dichlorophenol solutions increased from 0 to 0.23, 0.25 and 0.19, respectively. Chen et al. (2010) also found that the photodegradation intermediates produced under proper conditions were utilized more than the target α -pinene by the microorganisms from the biofilter. These results supported the hypothesis that proper photodegradation conditions could positively change the characteristics of parent compounds, thus providing a possibility for their complete mineralization by subsequent biological treatments.

In the present study, gaseous DCM was photodegraded in a custom-made spiral reactor with an ozone-producing UV lamp. Different reaction media were tested for the investigation of the effect of process parameters on the conversion efficiency of DCM. Based on the detected intermediates and carbon-balance analysis, a photodegradation pathway for DCM was proposed. Furthermore, a kinetic model was developed to describe the removal behaviors of

DCM with different initial concentrations under different reaction conditions.

1 Materials and methods

1.1 Chemicals

Analytical grade DCM obtained from J&K Chemical (China) was used without any further purification. The purified air/nitrogen (99.99%) was supplied by Jingong Gas Company (Hangzhou, China). The standard gas of DCM (500 mg/m³, N₂ balance) supplied by Weichuang Standard Gas Company (Shanghai, China) was used for the calibration of standard concentrations. All the other chemicals were of the highest purity commercially available.

1.2 Experimental set-up

Figure 1 is a schematic diagram of the photodegradation system. A self-made spiral quartz column with an effective volume of 150 cm³ was used as the main photoreactor, in the center of which was a special low-pressure mercury vapor lamp (18 W, Electrical Light Sources Research Institute, Beijing, China), producing ozone online through the photolysis of oxygen. The main wavelength was 184.9 nm and the light intensity was 0.206 mW/cm² at 1 m, measured by the National Electric Light Source Quality Supervision and Inspection Center (Shanghai, China). Before a series of experiments, the lamp was switched on for 20 min to reach its stable intensity and the whole system was purged by purified air. A DCM-contaminated stream was generated by passing air through a sparger containing DCM liquid and then mixed with the other flows of purified air in the mixer chamber. Different ratios of these streams, which were controlled by mass flow meters and a humidifier, determined the inlet concentration of DCM and the relative humidity (RH) (a hygrometer equipped with a temperature sensor, Testo 625, Germany, was used) of the simulation gas.

1.3 Experimental procedures

Several pre-designed experimental conditions were tested, with the initial concentration of DCM and RHs being fixed

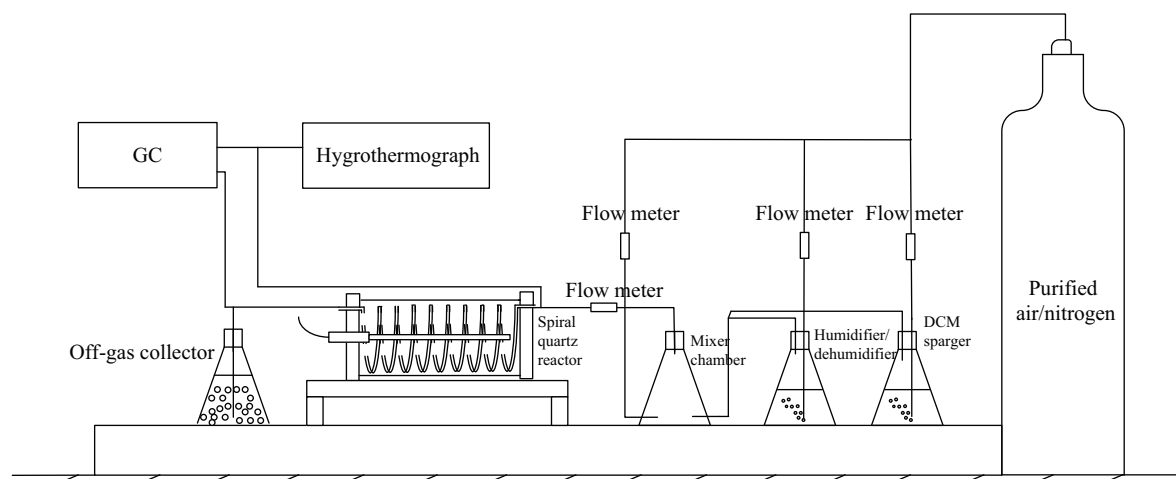


Fig. 1 Schematic diagram of VUV photodegradation system.

at 200 mg/m³ and 2%–80%, respectively. Gaseous samples (800 μL) were collected from the inlet and outlet of the reactor for concentration measurement. Three gas-washing impingers connected in series were respectively filled with 50 mL absorption solution at the outlet of the reactor and used to capture any photodegradation intermediates. Four types of absorption solutions were used as: (1) nanopure water for the measurement of TOC, Cl⁻ and small organic acids; (2) 0.1 mol/L NaOH solution for the measurement of CO₂; (3) 0.05 mol/L indigo disulphonate-phosphate solution for measurement of ozone and (4) 0.5 g/L 2,4-dinitrophenylhydrazine (DNPH) solution for measurement of aldehydes. The volume of the outlet gas captured was 19.98 L (0°C and 101.32 kPa) by an automatic gas sampler (LaoYing 3072, Qingdao, China). Each photodegradation experiment was repeated three times.

1.4 Analytical methods

Inlet and outlet concentrations of DCM were determined by a gas chromatograph (GC) (Agilent 6890, America) equipped with an electron capture detector (ECD). Gas of 800 μL was sampled by a syringe and transferred into a HP-5 capillary column (30 mm × 0.32 mm × 0.25 μm, J&W Scientific, USA). The operating conditions were as follows: oven, 70°C for 5 min; injector, 250°C and detector, 300°C. The sampling method of CO₂ was similar to that of DCM and its analysis was conducted on a GC (Agilent 6890, USA) equipped with a thermal conductivity detector (TCD) and a silica HP-Plot-Q capillary column (30 mm × 0.32 mm × 20 μm, J&W Scientific, USA). The operating conditions were as follows: oven, 40°C for 4 min; injector, 90°C and detector, 100°C.

The measurement of DAPH solution containing aldehydes was conducted on a high efficiency liquid chromatography system (Agilent 1200, USA) according to the method of Jiang et al. (2010). Small organic acids and the TOC value were determined by an ion chromatograph (ICS 2000, Dionex, USA) and a Shimadzu TOC-VCPH (Japan), respectively. The ozone concentration was measured by the indigo disulphonate spectrophotometry method (GB/T 15437-1995). All the detailed descriptions of these methods can be found in our previous studies (Chen et al., 2010; Cheng et al., 2011).

2 Results and discussion

2.1 Effect of reaction media on the conversion of DCM

Different reaction media strongly influence the conversion and reaction mechanism of specific compounds since the types and amounts of reactive radicals are different. Generally, three decomposition modes were proposed for the photodegradation of chlorinated organic compounds: direct photolysis, indirect photo-oxidation by active radicals such as ozone and hydroxyl radical, and the chain reaction by chlorine atoms (Chen et al., 2002).

2.1.1 Direct photolysis of DCM in purified nitrogen

DCM was degraded by VUV light under different relative humidities with purified nitrogen as the reaction media,

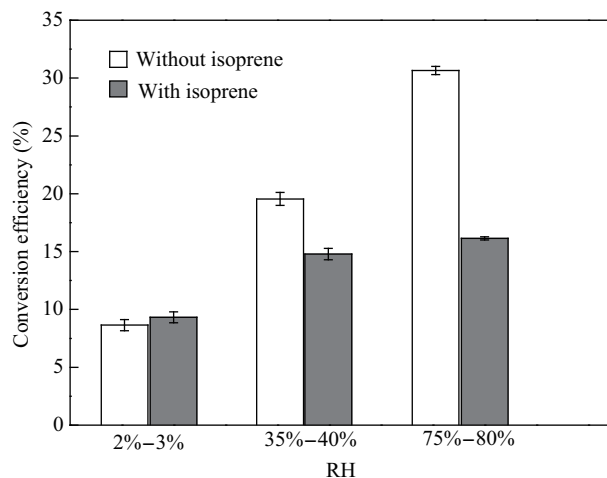
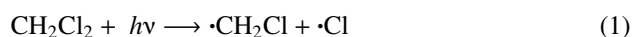


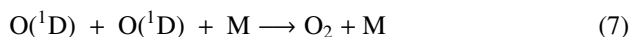
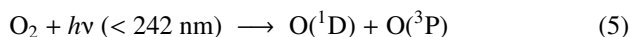
Fig. 2 Conversion efficiency of DCM in the nitrogen with and without isoprene as the scavenger under different RH. Conditions: DCM concentration 200 mg/m³; residence time 45 sec.

and the results are shown in Fig. 2. The initial DCM concentration was 200 mg/m³, and residence time was controlled at 45 sec. When RH of purified nitrogen was increased from 2%–3% to 75%–80%, the corresponding conversion efficiency was increased by 2.5 times (12.31% to 30.66%). Since nitrogen could only absorb the UV light below 125 nm (Koh et al., 2004), no radicals were generated at the wavelength of 184.9 nm and the conversion of DCM would be only induced by direct photolysis. As is known, the energy of 185 nm wavelength light (647.23 kJ/mol) is much higher than that of C–H (411.6 kJ/mol) and C–Cl (339.0 kJ/mol) bonds, and thus the DCM molecule could directly absorb UV light and form excited states or Cl radical (Reactions (1) and (2)). When water molecules were introduced into the reaction medium, the conversion efficiency increased dramatically owing to the presence of hydroxyl radical from the photolysis of water (Reaction (3)), which could strongly oxidize most organic compounds. As hydroxyl radical was difficult to analyze qualitatively or quantitatively, a scavenger could be applied for the indirect measurement of hydroxyl radical. Isoprene was chosen as the scavenger because its rate constant for combining with hydroxyl radical was higher than that of DCM (1.0 × 10⁻¹⁰ cm³/(mol·sec) vs. 1.10 × 10⁻¹³ cm³/(mol·sec)) (Jang and Kamens, 1999; Villenave et al., 1997). The differences between the appearance and disappearance of isoprene indicated that hydroxyl radical was indeed present in this photodegradation system and its amount increased greatly with a higher RH. By calculation, when RH was 75%–85%, the conversion efficiency of DCM induced by hydroxyl radical was nearly 15% (Reaction (4)), suggesting that the photolysis and photooxidation respectively accounted for 50% in the total conversion.



2.1.2 Photooxidation of DCM by ozone generated by air-photolysis

Oxygen, the other main component of air, could absorb 185 nm light to form ozone through photolysis (Reactions (5)–(7)), and the conversion efficiency of organic compounds would be much higher since the electron affinity of ozone is higher than that of oxygen (2.1 eV vs. 0.44 eV) (Pichat et al., 2000). Figure 3 shows the ozone variation and the conversion efficiency of DCM in air media under different RH. The initial DCM concentration was 200 mg/m³, and the residence time was controlled at 45 sec. It was found that ozone generation was inhibited by higher RH, which was similar with the reports by Jeong et al. (2005) and Cheng et al. (2011). Since the precursor of ozone (O(¹D)) could react with a water molecule and its photolysis product ·H (Reactions (8)–(9)), less ozone was detected under much higher RH. The difference in ozone amount between the inlet and outlet suggested that most ozone reacted with DCM when gaseous DCM was introduced into the photoreactor.



where, M stands for N₂ or O₂.

Although ozone generation was less when RH was higher, the conversion efficiency of DCM increased, which was different from the result in the conversion of α -pinene reported by Cheng et al. (2011). In the present study, the conversion efficiency of DCM reached 67.4% for RH of 75%–80%, which was more than 2 times its value under almost dry conditions. The different effects of RH on DCM and α -pinene might be attributed to the presence of chlorine atoms. Since Tsuneda et al. (2002) reported that chlorine atoms could be utilized as hydroxyl radical scavengers, it could be speculated that chlorine atoms originating from DCM photolysis would react with hydroxyl radical, and thus reduce the reaction probability

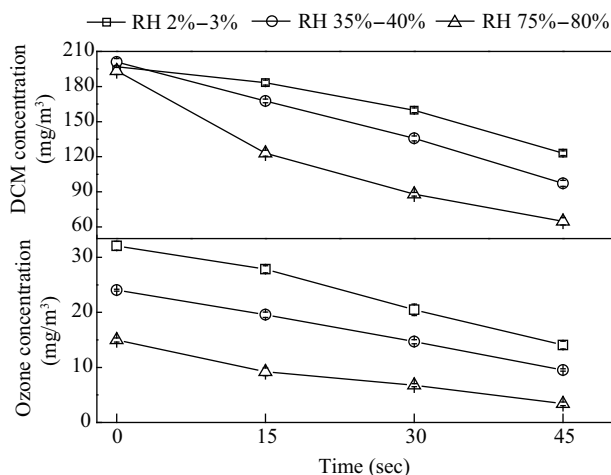


Fig. 3 Effect of ozone production on DCM conversion efficiency. Conditions: DCM concentration 200 mg/m³; residence time 45 sec.

between ozone and hydroxyl radical. As a result, the remaining ozone was much more than that in the system containing no chlorine atoms, which led to a much higher conversion efficiency of DCM. With a small amount of chlorine introduced into the moist reaction system, the ozone amount became higher (nearly 24.45 mg/m³), indirectly proving that the appearance of chlorine atoms could reduce the inhibition of hydroxyl radical toward ozone.

2.1.3 Photooxidation of DCM by hydroxyl radical generated by water-vapor analysis

As previously reported in the literature, RH of a reaction medium could significantly affect the UV photodegradation process (Zhang et al., 2003). Figure 4 shows the effects of RH (2%–80%) on the conversion efficiencies of DCM in air or nitrogen. It could be found that RH was critical to the photodegradation of DCM, and more radicals generated under higher RH would help the oxidation of DCM in purified nitrogen or air. When more water molecules were introduced into the reaction media, DCM removal efficiencies were enhanced by 3.5 and 1.7 times respectively for nitrogen and air. The differences between the increase levels are attributed to the presence of ozone and other radicals in the air medium, which could competitively react with hydroxyl radical (Reactions (10) and (11)). Although there were complex radical reactions that affected the ozone generation and the removal of DCM, the conversion efficiency still increased with the RH. This finding is different from the effect of water vapor on the photodegradation of α -pinene, which is attributed to the roles of Cl atoms in the photodegradation of chlorinated organic compounds. When isoprene as the scavenger was introduced into the reaction system, the conversion efficiency of DCM was lower than that obtained under the same conditions without any isoprene fed in. These results suggest that hydroxyl radical indeed played an important role during the conversion process of DCM, higher RH would be helpful, and the appearance of Cl atoms counteracts the inhibition produced by radical reactions.

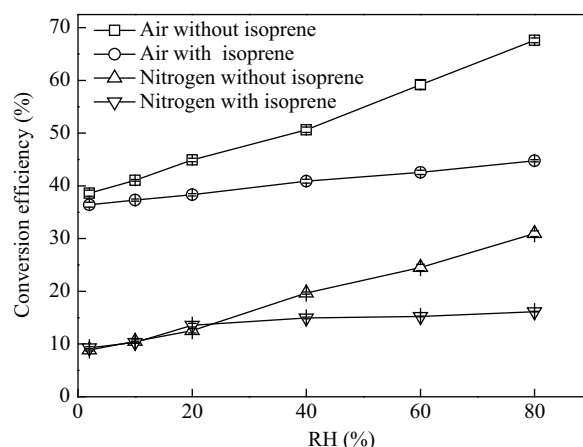
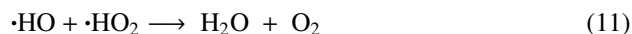


Fig. 4 Effect of RH on DCM conversion efficiency in air and nitrogen media. Conditions: DCM concentration 200 mg/m³; residence time 45 sec.

2.1.4 Analysis of conversion mechanisms for DCM photodegradation

The qualitative and quantitative analysis of radicals indicated that the conversion of DCM was mainly caused by direct photolysis, oxidation by ozone and oxidation by hydroxyl radical. Table 1 shows the significance of each conversion mechanism during the DCM photodegradation process. Among these main conversion mechanisms, O₃ oxidation played the dominant role, followed by hydroxyl radical oxidation and direct photolysis. In theory, 1 mg O₃ could only completely mineralize 1.18 mg DCM. But in the present study, 1 mg O₃ oxidized 3.60, 3.91 and 5.19 mg DCM under different RHs (20%, 40%, 80%) of air as the reaction media. These results indicate that DCM was not completely mineralized by ozone and only converted to some intermediates. The differences between the actual conversion and theoretical conversion amounts (the sum of values by photolysis, hydroxyl radical oxidation and ozone oxidation) became larger when higher RH was introduced into the reaction system. This might result from the positive interaction between active components. Cheng et al. (2011) found that the actual conversion amount was lower than the theoretical one due to the fact that both the amounts of hydroxyl radical and ozone decreased as a result of the effect of hydroxyl radical on ozone generation.

However, in the photodegradation of DCM, the appearance of chlorine atom which might act as a scavenger (Table 1), would reduce the reaction possibility of hydroxyl radical and ozone, and thus more and more ozone from the photolysis of oxygen could react with DCM. From the calculated results, it was found that DCM was converted by

the combination of ozone, hydroxyl radical, photolysis and the chlorine-induced chain reaction, among which ozone played the dominant role.

2.2 Kinetic analysis of DCM conversion

2.2.1 Effect of initial concentrations on kinetics

The effects of variations in concentration on the DCM conversion under different residence time are shown in Fig. 5. Initial DCM concentrations varied from 50–1000 mg/m³ under the same RH of 75%–80%, and it was found that the conversion of DCM followed the second-order kinetic model at the designed initial concentrations (the kinetic constants are shown in Table 2).

Since the amount of radicals remained at the same level and the light intensity was still maintained at the normal level under different reaction media, the absolute conversion amount might be equal at unit volume per unit time. When the initial DCM concentrations were lower, most DCM molecules could be converted to other intermediates. But when higher amounts of DCM were introduced into the reaction system, the generated radicals and light intensity might be not enough for the reaction with DCM. Therefore, the conversion efficiency decreased with increasing initial concentration. It was also found that the deviation to the fitting curves was greater for much higher initial concentrations, suggesting that the second-order kinetic model might not be a good fit for higher target concentrations. This finding was attributed to the fact that the dominant type of radicals reacting with DCM was different at various concentrations. Cheng et al. (2011) reported that hydroxyl radical played the

Table 1 Comparison of conversion amount caused by radicals in different reaction media

Reaction medium	Conversion amount (mg/m ³)				
	Photolysis	·HO oxidation	O ₃ oxidation	Total (actual)	Total (theoretical)
Air, RH 2%	16.56 ± 1.23	3.27 ± 0.45	57.54 ± 1.87	77.61 ± 2.98	77.37 ± 2.24
Air, RH 40%	18.03 ± 1.98	14.36 ± 1.21	60.12 ± 2.31	93.76 ± 2.17	92.51 ± 2.58
Air, RH 80%	18.87 ± 1.47	33.87 ± 2.07	64.92 ± 2.14	137.25 ± 3.01	117.66 ± 2.17
Air, RH 40% with isoprene	17.26 ± 1.57	–	61.34 ± 1.98	78.24 ± 2.41	78.60 ± 2.36
Air, RH 80% with isoprene	18.45 ± 1.87	–	60.68 ± 2.45	78.45 ± 1.97	79.13 ± 2.04

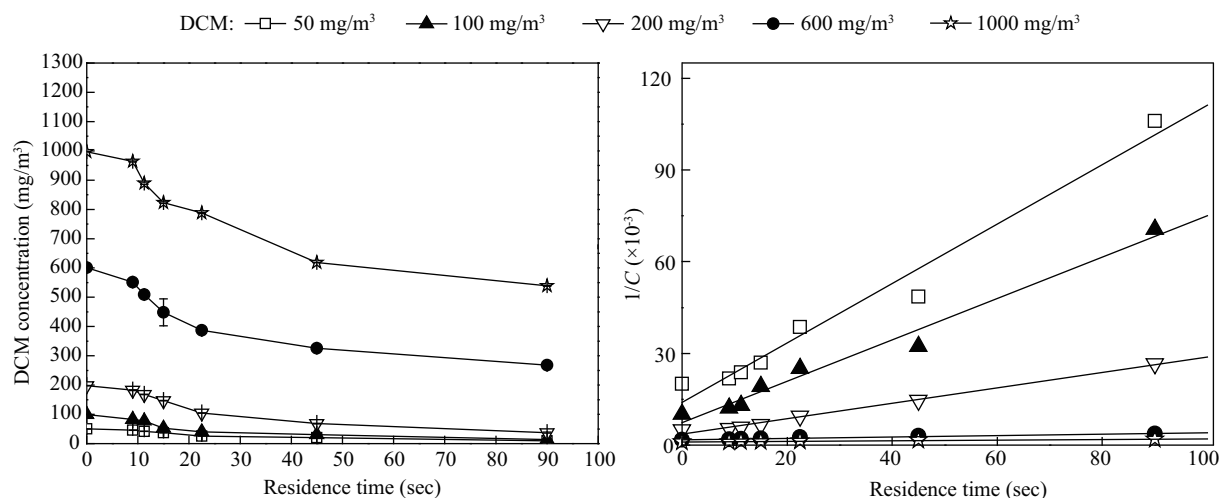


Fig. 5 Kinetic fitting for various concentrations of DCM photodegradation at RH 75%–80%.

dominant role for lower initial α -pinene concentration and ozone for high initial concentration, resulting in the kinetic model converting from first-order to second-order. Such results indicated that initial concentrations could affect the kinetics so that the mechanism and rate constants might be different with various dominant radicals.

2.2.2 Effect of reaction media on kinetics

As illustrated before, the types and amounts of reactive radicals affect the conversion efficiency and conversion mechanism, and thus the kinetic constants would be different from each other. Table 3 shows the rate constants and half-life for different reaction media. The initial DCM concentration was controlled at 200 mg/m³, and the second-order kinetic model was applied to fit the experimental results. Compared with the reaction medium of nitrogen, the rate constant was much higher in the air system. Simultaneously, the rate constant also increased with RH when the same reaction medium (nitrogen or air) was introduced. When dry nitrogen was used as the reaction medium, the rate constant was much lower owing to the appearance of direct photolysis only. The introduction of water molecules would create hydroxyl radical, and the rate constant was nearly 5 times that in the dry reaction medium. Besides the strong oxidizer hydroxyl radical, ozone would appear when air was used as the reaction medium. By comparing the extent of increase in different reaction media, it is suggested that ozone contributed more to the conversion of DCM. This speculation is based on the fact that the positive effect of ozone on the rate constants was more noticeable than that of hydroxyl radical.

2.3 Carbon balance analysis

Under proper photodegradation conditions, DCM would be converted to different intermediates, such as soluble organic compounds and inorganic compounds (CO₂, HCl). In the present study, four main carbon-species were detected to perform the carbon balance analysis: carbon in the inlet stream (mainly DCM), carbon in the outlet

stream (mainly the remaining DCM and CO₂) and water soluble carbon in the captured liquid (mainly the organic intermediates characterized by TOC). Different reaction media were chosen for evaluating reaction conditions based on the formed carbon-species amount, while the initial DCM concentration and the photodegradation time were respectively fixed at 200 mg/m³ and 45 or 90 sec. From Table 4, it is worth noting that moister air contributed to the conversion of DCM to a large amount of water soluble intermediates, and longer residence time led to more generation of mineralization products (inorganic carbon such as CO₂).

Since the combination of direct photolysis, ozone photooxidation and hydroxyl radical photooxidation contributed more to DCM conversion, more water soluble intermediates were produced under higher relative humidity. This would provide a possibility for their complete removal by biofiltration owing to the much lower mass transfer limit of water soluble compounds in the biofilter (Raghuvanshi and Baku, 2009; Ramirez-Lopez et al., 2010). Residence time was another factor that affected the formation of intermediates (Sanchez et al., 1999). Linear correlations between the removal loads and CO₂ productions were fitted and the calculated mineralization rates were 26.9% and 43.9% under the residence time of 45 and 90 sec, respectively. Such results indicated that higher mineralization rates could be attributed to longer residence time, which was similar to several photodegradation processes of VOCs. Therefore, the RH of the reaction medium and the residence time must be strictly controlled for different purposes. Longer residence time and higher RH are required for the sole UV technology while short residence time and lower RH are suitable for its utilization as a pretreatment technology.

2.4 Intermediates and proper photodegradation pathway of DCM

Since DCM is a simple compound structurally, its photodegradation intermediates would be expected to be small organic and inorganic compounds. When varying RH air/nitrogen was used as the reaction medium, several intermediates were identified by IC and HPLC through the comparison of retention time with commercially available standards.

Some researchers indicated that free reactive species generated by different gaseous reaction media could strongly affect the types and amounts of photodegradation intermediates, with different conversion mechanisms produced. In this reaction system, ozone and hydroxyl radicals with oxidation potential of 2.80 and 2.07 eV were considered to be the most important oxidants (Chen et al., 2002; Den et al., 2006). Therefore, based on the detected intermediates, a detailed degradation pathway for DCM is proposed, with the main conversion pathways being direct photolysis, oxidation by ozone and oxidation by hydroxyl radical (Fig. 6).

Gaseous DCM, first stimulated by 185 nm light, generated $\cdot\text{Cl}$ and $\cdot\text{CH}_2\text{Cl}$, and the latter $\cdot\text{CH}_2\text{Cl}$ could be continuously stimulated by 185 nm light, forming $\cdot\text{Cl}$ and

Table 2 Kinetic analysis of DCM photodegradation at variable initial concentrations

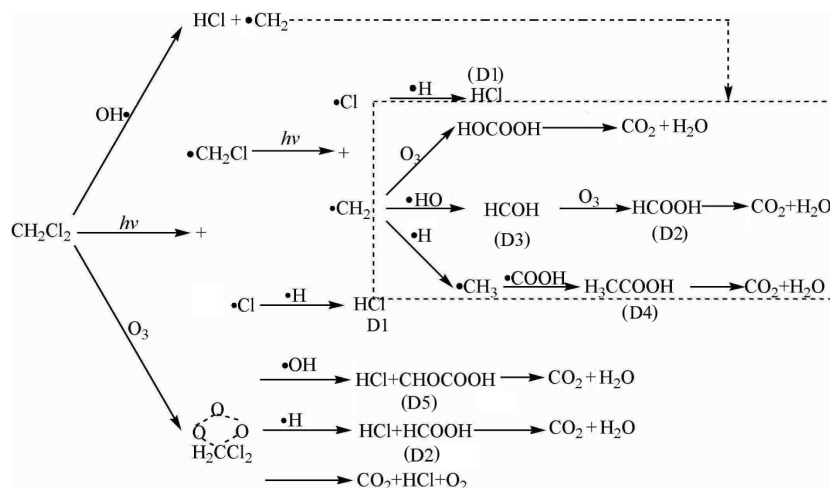
Inlet concentration (mg/m ³)	Kinetic equation	R ²
50	$y = 0.972x + 14.03$	0.972
100	$y = 0.676x + 7.410$	0.978
200	$y = 0.251x + 3.660$	0.991
600	$y = 0.023x + 1.794$	0.934
1000	$y = 0.010x + 1.028$	0.944

Table 3 Kinetic parameters of DCM photodegradation under different reaction media

Reaction medium	Kinetic constant		R ²
	Second order rate constant ($\times 10^3 \text{ m}^3/\text{mg}$)	Half-life (sec)	
Nitrogen RH 2%	0.010	500	0.982
Nitrogen RH 40%	0.027	185	0.984
Nitrogen RH 80%	0.049	102	0.989
Air RH 2%	0.069	72	0.987
Air RH 40%	0.110	45	0.994
Air RH 80%	0.251	20	0.991

Table 4 Carbon balance under various photodegradation reaction media

Reaction medium	Residence time (sec)	Carbon species (mg)				Δ Carbon
		GC _{inlet}	GC _{outlet}	TOC	IC	
Air RH 2%	45	3.955	2.420	0.952	0.186	0.397
Air RH 40%		3.902	1.923	1.329	0.230	0.420
Air RH 80%		4.024	1.223	1.813	0.756	0.232
Air RH 2%	90	3.891	1.854	1.198	0.624	0.215
Air RH 40%		3.980	1.223	1.698	0.934	0.125
Air RH 80%		3.978	0.586	1.595	1.489	0.308

**Fig. 6** Probable degradation pathway of DCM.

$\cdot\text{CH}_2$. The formed $\cdot\text{Cl}$ combined with $\cdot\text{H}$ to form HCl (D1, "D" means that the intermediate was detected in this study), which was confirmed by the appearance of Cl^- detected by IC and the lower pH value of the absorption liquid. Since $\cdot\text{CH}_2$ was a more active radical, it could be converted through ozone and $\cdot\text{OH}$, the corresponding products of which were respectively acetic acid (HCOOH, D2) and hydroxy acid (actually CO_2 and H_2O). With oxidation by some strong oxidants (such as hydroxyl radical, ozone and oxygen), the aldehyde (D3, HCOH) could be continuously oxidized to form acetic acid (D2). The detection of formic acid (D4, H_3CCOOH) by IC also suggested that $\cdot\text{CH}_3$ originating from $\cdot\text{CH}_2$ could combine with $\cdot\text{COOH}$. All these organic compounds would be finally mineralized to CO_2 and H_2O with a much longer residence time.

$\cdot\text{OH}$, which was produced by photolysis of water molecules, directly attacked DCM to form gaseous HCl and radical $\cdot\text{CH}_2$. As illustrated before, $\cdot\text{CH}_2$ underwent three similar conversions to form the intermediates acetic acid (D2), HOCOOH and formic acid (D4). Ozone, another main strong oxidant, first attacked the C–Cl bond and formed an energy-rich ozonide, which rapidly converted to some final compounds (CO_2 , H_2O and HCl). Simultaneously, the ozonide could also be converted by $\cdot\text{OH}$ and $\cdot\text{H}$, producing glyoxylic acid (D5, CHOCOOH), acetic acid (D2) and HCl (D1). All of these small organic acids were mineralized in similar ways, suggesting that DCM could be completely oxidized without any secondary pollution being generated.

3 Conclusions

Gaseous DCM was photodegraded by a VUV light in a custom-made spiral quartz reactor. Several reaction media were tested and the main photodegradation intermediates were detected. DCM was removed by the combination of direct photolysis, ozone oxidation and hydroxyl radical oxidation. Air with RH 75%–85% was much better for the conversion of DCM, since the removal efficiency was higher. Carbon balance analysis showed that under proper photodegradation condition, DCM could be converted to much more soluble intermediates, which provided a possibility for their subsequent removal by biodegradation. The conversion of DCM followed the second-order kinetic model at initial concentrations between $100\text{--}1000\text{ mg/m}^3$, and the reaction media affected the kinetic constants of DCM conversion by a large extent. Preliminary results indicated that VUV photodegradation is an appropriate technology for the removal of DCM not only as a single treatment but also as a treatment coupled with biodegradation.

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