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Study on the gas-phase photolytic and photocatalytic oxidation of trichloroethylene

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Abstract

Direct sampling mass spectrometer was used to study photolytic and photocatalytic oxidation of trichloroethylene (TCE) in gas-phase. The experiments were conducted under UV lamps with 365 nm (black lamp) and 253.7 nm (germicidal lamp) dominant wavelength, respectively, in the presence or absence of TiO_2. Concentrations of TCE and CO_2 were detected quantitatively. Mass spectrograph peaks of the documented intermediates and products were detected on-line during the process of photolysis and photocatalysis of TCE. The results indicated that TCE could be directly photodegraded under the irradiation of germicidal lamp, but black lamp could hardly work on TCE by photolysis. This photolytic degradation rate of TCE was much quicker than that of photocatalysis for the same irradiation intensity of germicidal lamp. The products and intermediates detected showed that both photolysis and photocatalysis of TCE were dominated by a free-radical-offence mechanism.

Keywords: Photocatalysis; Photolysis; Trichloroethylene; Direct sampling mass spectrometer

1. Introduction

The use of photocatalytic oxidation technology to remove organic pollutants from air has increasingly been paid great attention to in recent years [1,2]. It is likely that this technology in air purification reveals strong advantage and also capacious application foreground. And that, studies on the gas-phase photocatalytic oxidation of trichloroethylene (TCE) has become an active field. Research reports on photocatalytic degradation of TCE mainly focused on the following three aspects: preparation method of catalyst [3], reaction mechanisms [5–16] and kinetic discussions [3,4,17,18]. However, there have been some ambiguous points in literature. This was probably because of the problems in study from photoreactor design, analysis method, lamp used, reaction condition, etc.

Alberici and Jardim [4] systematically investigated the photocatalytic reaction for 17 volatile organic compounds and compared their photocatalysis characteristics on the basis of kinetics parameters obtained from Langmuir–Hishewood model; it was experimentally observed that TCE could be oxidized into CO_2 and HCl directly in a photolytic way. But Li et al. [16] indicated that degradation would not have happened to TCE without the irradiation of ultraviolet light. Some literature data does not mention the photolysis phenomenon in their studies. However, our experimental results all demonstrated that photolysis effect on TCE degradation would not easily be avoided experimentally.

It was generally considered in published literature that the photocatalytic degradation of TCE went on in a mechanism of free-radical-initiation, including OH-radical-initiation and Cl-radical-initiation. Both Nimlos et al. [5] and Yamazaki-Nishida et al. [7–9] demonstrated that TCE molecule in photocatalytic system would be oxidized and degraded in a mechanism of Cl-free-radical-initiation. Fan and Yates [14] have studied the photocatalytic mechanism by introducing $H_2{}^{18}O$ into reaction system, and the experimental results obtained in tracking ^{18}O supported that the photocatalytic reaction proceeded on by an O-radical-offence mechanism instead of OH-radical-initiation. Hwang et al. [15] have also proved it by using an in situ solid-state NMR.

In order to elucidate some of the ambiguities in literature, a self-designed photoreactor was therefore applied in this study. A method based on a direct sampling mass spectrometer was come into use in the experiments, which is quite

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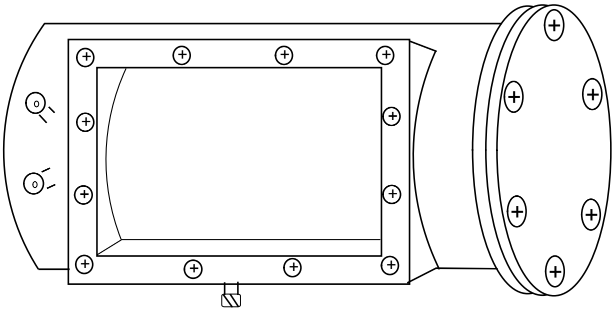


Fig. 1. Schematic drawing of photoreactor.

suitable to fulfill a quick qualitative and quantitative analysis of vapors and gases in air.

2. Experimental

The gas-phase photoreaction was conducted in a self-designed photoreactor, which was illustrated in Fig. 1. It was composed of a quartz window of approximately 100 cm^2 surface and a columnar stainless steel chamber with 10 cm diameter and 25 cm length, both of which were adhered together with thermomelting adhesive to form a space of approximately 3.3 l.

The photocatalyst used was P-25 titanium dioxide supplied by Degussa. One could blend de-ionic distilled water (about 5 ml) with 1 g TiO_2 and the mixture obtained could be uniformly coated onto the inner surface of the light window. This could avoid organic vapor to directly absorb ultraviolet light. Light source was an ultraviolet lamp of 20 W with a dominant wavelength of 253.7 nm (germicidal lamp) or 365 nm (black lamp). Ultraviolet irradiation intensity was determined with a UV radiometer UV-B-253.7 nm or UV-A-365 nm (Photoelectric Instrument Factory of Beijing Normal University). Vapor of TCE was generated with a method of static vacuum, i.e. to degas the reactor, and to inject TCE liquid into vacuum chamber with micro-syringe, then to introduce air upon complete vaporization.

Vapor and gas concentrations in reactor were qualitative and quantitatively analyzed by a Mass-spectrometer (OmniStar^{TM} of Balzers) in a manner of consecutive sampling. The products and intermediates were also monitored in a manner of multiple ion detect (MID). Whole photoreactions were carried out under the conditions of 20–25 °C and 30–50% relative humidity.

3. Results and discussion

3.1. Direct photodegradation

When TCE vapor was generated in photoreactor, it was chemically stable in darkness as demonstrated by concentration detection with MS. Once germicidal lamp of 253.7 nm started to irradiate the reactor with an intensity of 0.6 mW/cm^2, measured nearby inner surface of light window, TCE concentration would sharply decrease down. This was presented in Fig. 2. One can observe that 99.9% of TCE in air could be chemically degraded within 1 min for the vapor of 4000 ppm concentration and CO_2 concentration will quickly increase up to a maximum value. However,

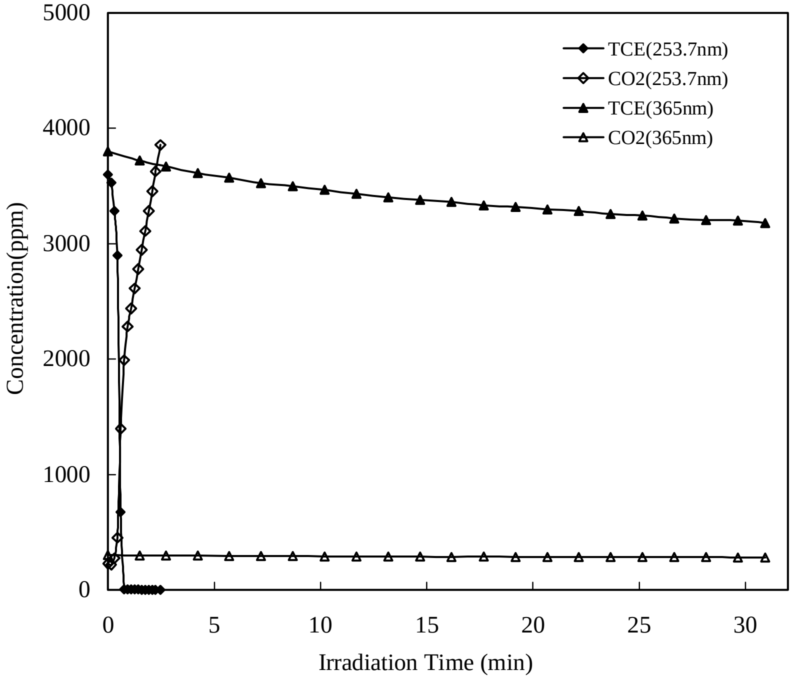


Fig. 2. Photolytic degradation of TCE, irradiation intensity was 0.6 mW/cm^2 for a germicidal lamp of 253.7 nm, 0.96 mW/cm^2 for a black lamp of 365 nm.

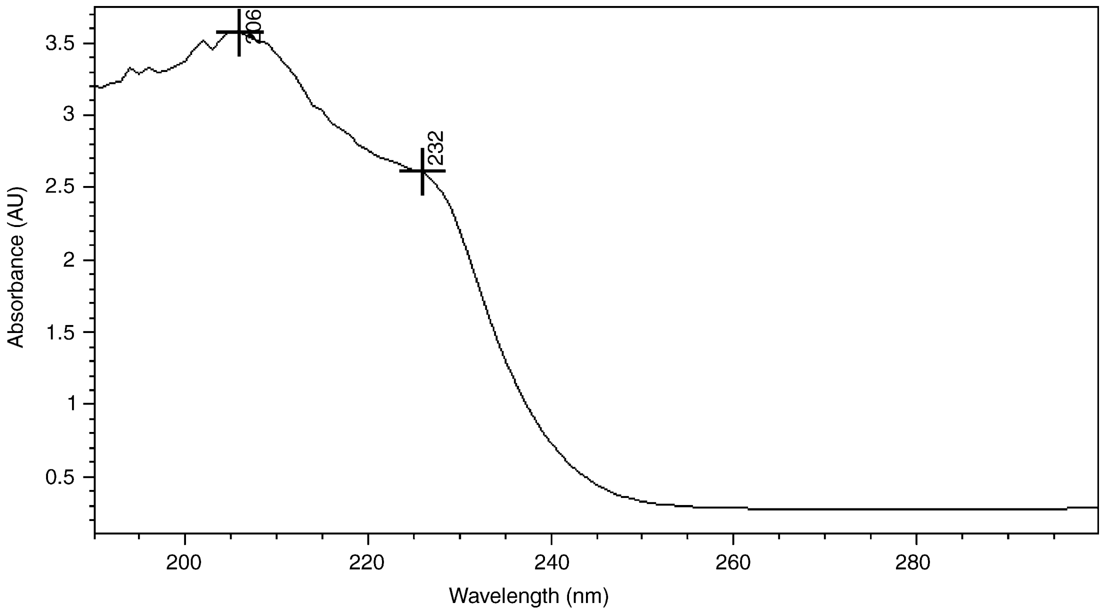


Fig. 3. UV absorption spectrum of TCE vapor.

TCE could hardly be degraded if one used a black lamp of 365 nm as light source to irradiate the reactor in an intensity of 0.96 mW/cm^2. Therefore, it is clearly that UV light of 253.7 nm is able to directly photolyze TCE vapor in air while that of 365 nm does not work. These results were quite consistent with those reported by Alberici and Jardim [4].

The UV absorption spectrum of TCE vapor was measured by a UV-Vis spectrometry (HP8453). Fig. 3 demonstrated the UV absorption spectrum of TCE vapor, which showed that TCE have a strong adsorption band at 206 nm and a weaker one at 232 nm. A same measurement was also conducted by using alcohol as solvent, the two adsorption band were also clearly observed, and that when the concentration of TCE decreased, the 232 nm peak weakened till it vanished as the concentration below 2×10^{-4} M. So the 232 nm absorption band could attribute to the n–σ* transition of the lone paired electron of Cl.

Furthermore, it was experimentally found that TCE degradation rate would slow down if the irradiation intensity decreases. The product of CO_2 will also decrease along with the lowering of irradiation intensity. These were shown in Fig. 4. One could come into the conclusion that not only wavelength but also irradiation intensity could be the most important factors to affect the rate of TCE degradation.

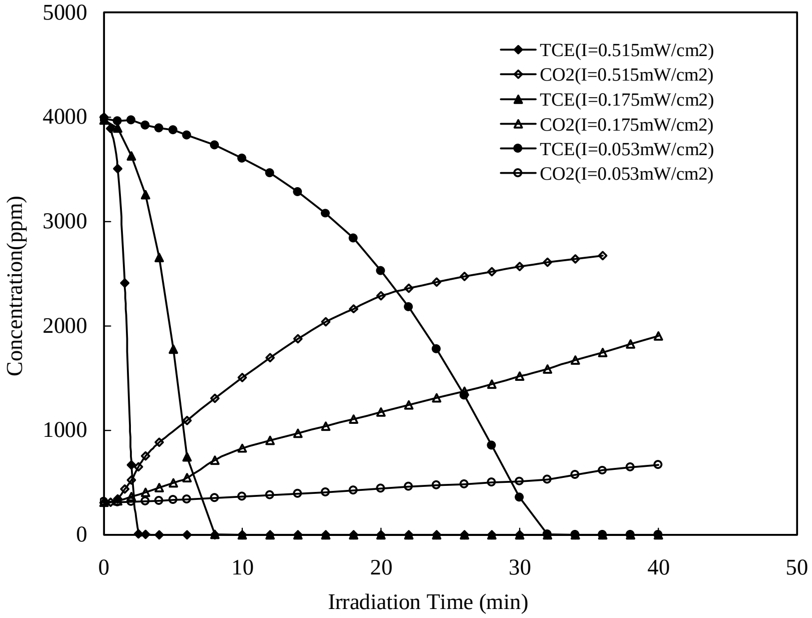


Fig. 4. Effect of irradiation intensity on photolysis of TCE, irradiation intensity was 0.6 mW/cm^2 for a germicidal lamp of 253.7 nm.

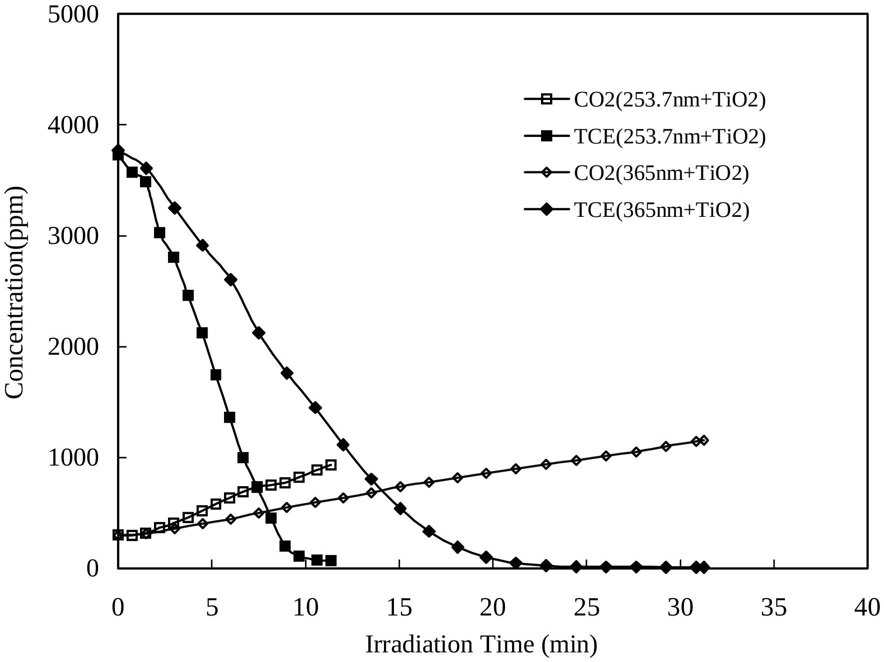


Fig. 5. Photocatalytic degradation of TCE on TiO_2, irradiation intensity was 0.6 mW/cm^2 for a germicidal lamp of 253.7 nm, 0.96 mW/cm^2 for a black lamp of 365 nm.

3.2. Photocatalytic degradation

It was experimentally demonstrated that light window in quartz only causes 10% lowering irradiation intensity of UV light. However, irradiation intensity will greatly decrease from 0.6 to 0.025 mW/cm^2 when UV light of 253.7 nm irradiated the reactor through the light window of inner surface coated with TiO_2. It implied that most of irradiated light was absorbed or reflected by TiO_2 coating. This would ensure that UV light will not directly irradiate the vapor of TCE in photoreactor and little light of very weak intensity can be absorbed by the reactants within reactor.

Fig. 5 shows that UV light of both 253.7 and 365 nm, i.e. germicidal and black lamps, is able to work for the photocatalytic degradation of TCE. When germicidal lamp irradiates TCE vapor of 4000 ppm through light window with an intensity of 0.6 mW/cm^2, it needs 8 min to degrade 99.9% of TCE. But, it needs only 1 min to achieve the same degradation

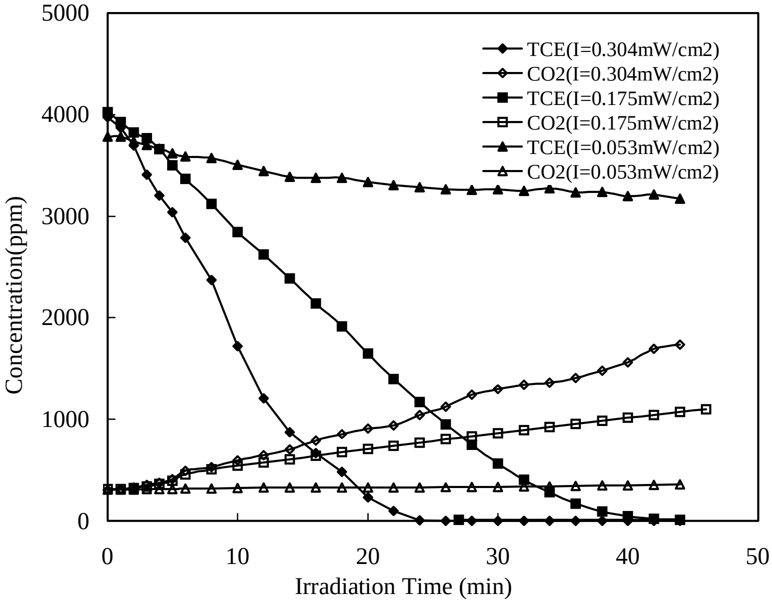


Fig. 6. Effect of irradiation intensity on photocatalysis of TCE, irradiation intensity was 0.6 mW/cm^2 for a germicidal lamp of 253.7 nm.

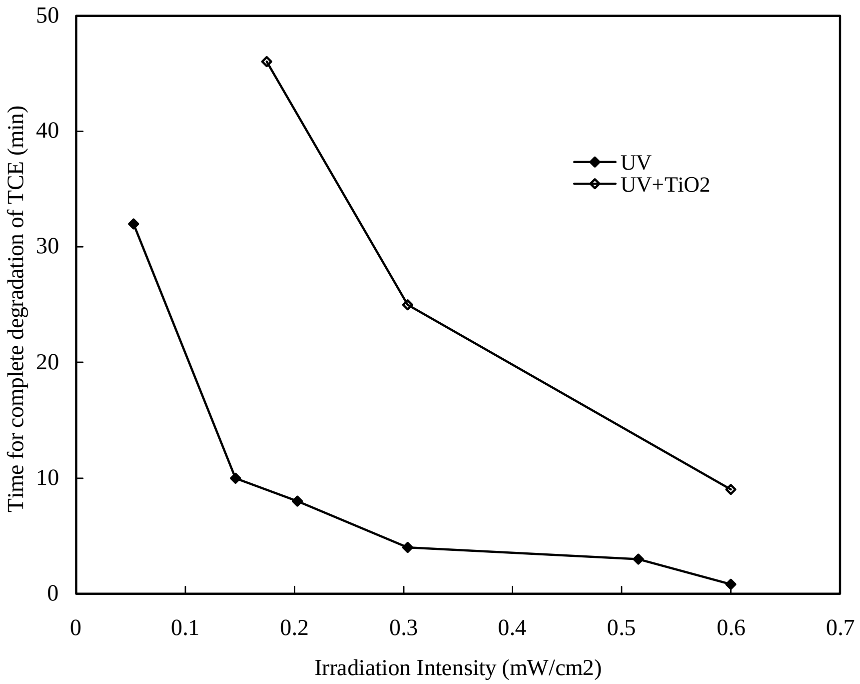


Fig. 7. Comparison on effect of UV irradiation intensity on degradation of TCE by photolysis and photocatalysis. Concentration of TCE was 4000 ppm, light source was a germicidal lamp of 253.7 nm. Where 1 ppm = 4.46×10^{-8} mg/l.

level for a direct photolysis in the same conditions as indicated in Fig. 2. So, TCE degradation rate become much slower than that of direct photolysis. In addition, when the irradiation intensity was lowered down to 0.025 mW/cm^2, i.e. the UV light intensity upon UV light of 0.6 mW/cm^2 through light window coated with TiO_2, TCE degradation time will be prolonged over 30 min. This implied that the degradation of TCE within 8 min could be mainly associated with photocatalysis.

And yet, when black lamp irradiated on the photoreactor window, TCE vapor could not be degraded by photolysis but it could be done by photocatalysis. It needs about 20 min to photocatalytically degrade 99.9% of TCE in 4000 ppm under the irradiation intensity of 0.96 mW/cm^2.

It has already been experimentally shown that photolytic degradation rate decreased down along with the lowering of 253.7 nm light irradiating intensity. For the aim to investigate the relationship between photolysis and photocatalysis, a similar study was also done, the results was shown in Fig. 6. The results for a comparison of photolysis with photocatalysis were presented in Fig. 7. One could find that photocatalysis like photolysis needed more time to completely degrade TCE vapor along with the lowering of irradiation intensity, and photolysis was still much quicker than photocatalysis with equal irradiation intensity.

3.3. Mechanism aspect

The products and intermediates for photocatalysis of TCE documented in literature [5,16] were also detected in our study. Fig. 8 illustrated the products and intermediates detected by MS during the reaction of TCE photolysis. They are the molecules of CO_2 (44), HCl (36), Cl_2 (70, 72), $COCl_2$ (98, 65, 63), ClCOCOCl (126, 65, 63), $CHCl_3$ (118, 85, 83), $CHCl_2COCl$ (146, 111, 85, 83, 65, 63), $CHCl_2CH_2Cl$ (132, 97, 85, 83, 63, 61). These species were also detected during the photocatalysis of TCE as presented in Fig. 9. The experimental results concerning product analysis and also degradation rate seem to suggest that both photolysis and photocatalysis of TCE proceeded with a similar way. Then, one would raise a question how about the difference and relationship between photolysis and photocatalysis of TCE.

Using a germicidal lamp as light source, photolytic degradation of TCE was extremely quick, and degradation rate

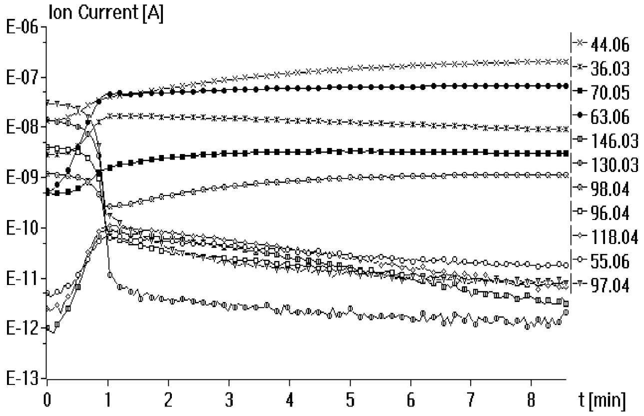


Fig. 8. Multiple ion detection of species in air during photolysis of TCE, irradiation intensity was 0.6 mW/cm^2 for a germicidal lamp of 253.7 nm.

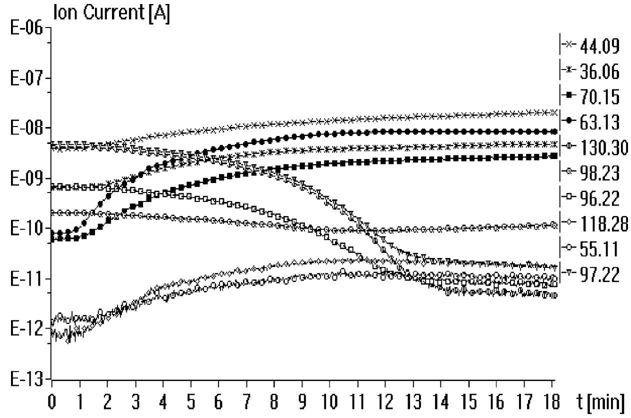
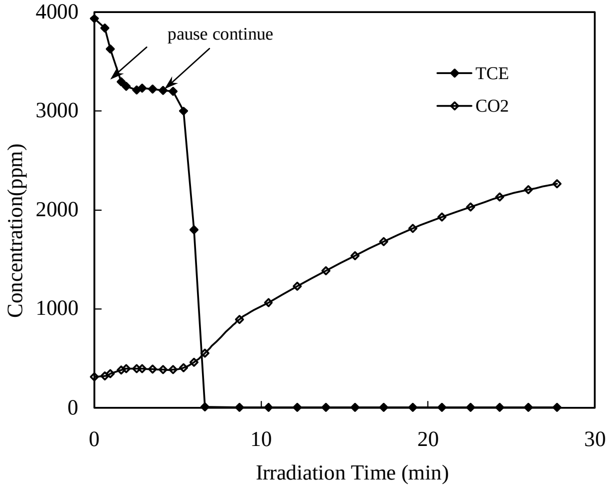
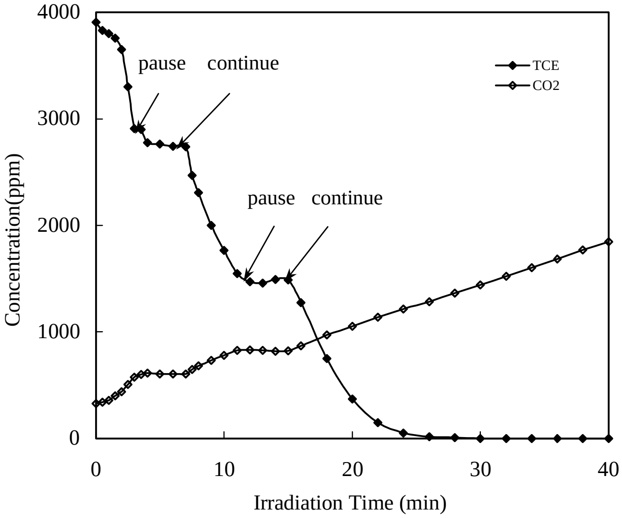


Fig. 9. Multiple ion detection of species in air during photocatalysis of TCE, irradiation intensity was 0.6 mW/cm^2 for a germicidal lamp of 253.7 nm.



(a) Photolysis



(b) Photocatalysis

Fig. 10. Shut off the lamp during the photodegradation course, irradiation intensity was 0.6 mW/cm^2 for a germicidal lamp of 253.7 nm.

seemed to pass over an accelerative process. Then, one would imagine this reaction as a free-radical-initiation one. If the photolysis of TCE goes on this way, it would come to an end without additional energy to activate reactant molecules once the reaction was initiated. But, this was not supported by the following experimental results. When UV light of germicidal lamp irradiated the TCE vapor in reactor, the photolysis of TCE will occur immediately, and yet the photolysis will cease immediately once one gave a pause to the irradiation. This result indicated that TCE photolysis greatly relied on irradiation of UV light, and irradiation of UV light was a key factor not only to initiate but also to maintain the photolysis of TCE. For the photocatalysis of TCE over TiO_2, a similar phenomenon was observed. These results were presented in Fig. 10. It was likely that both photolysis and photocatalysis of TCE did not behavior like a “free-radical-initiation reaction”.

It was early considered that UV light irradiating TiO_2 surface in the presence of O_2 would produce some radical surface species like active oxygen and OH radical. And that, it is well known that UV light is able to activate O_2 in air to produce oxidative species such as O_3, O radical, etc. These reactive species seem to be produced under the irradiation of UV light in the primary photoreaction step and could possibly act on both reactants and intermediates on surface or in gas phase. In addition, TCE molecule was able to absorb energy from UV light to possibly self-decompose and form radical species. Finally, this study would likely suggest that both photolysis and photocatalysis proceed with a free-radical-offence mechanism, rather than a free-radical-initiation mechanism.

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