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UV/H_2O_2 oxidation of tri(2-chloroethyl) phosphate: Intermediate products, degradation pathway and toxicity evaluation

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ABSTRACT

Tri(2-chloroethyl) phosphate (TCEP) with the initial concentration of 5 mg/L was degraded by UV/H_2O_2 oxidation process. The removal rate of TCEP in the UV/H_2O_2 system was 89.1% with the production of Cl^- and PO_4^{3-} of 0.23 and 0.64 mg/L. The removal rate of total organic carbon of the reaction was 48.8% and the pH reached 3.3 after the reaction. The oxidative degradation process of TCEP in the UV/H_2O_2 system obeyed the first order kinetic reaction with the apparent rate constant of 0.0025 min^{-1} (R^2=0.9788). The intermediate products were isolated and identified by gas chromatography-mass spectrometer. The addition reaction of HO• and H_2O and the oxidation reaction with H_2O_2 were found during the degradation pathway of 5 mg/L TCEP in the UV/H_2O_2 system. For the first time, environment risk was estimated via the "ecological structure activity relationships" program and acute and chronic toxicity changes of intermediate products were pointed out. The luminescence inhibition rate of photobacterium was used to evaluate the acute toxicity of intermediate products. The results showed that the toxicity of the intermediate products increased with the increase of reaction time, which may be due to the production of chlorine compounds. Some measures should be introduced to the UV/H_2O_2 system to remove the highly toxic Cl-containing compounds, such as a nanofiltration or reverse osmosis unit.

Introduction

Since 2004, the use of polybrominated diphenyl ethers (PBDEs) has been gradually banned in many industrial countries, due to the adverse health effects of PBDEs on humans (Wang et al., 2013). Therefore, as the main substitute for PBDEs, organophosphorus flame retardants (OPFRs) have been increasing in production and use year by year (Yan et al., 2012; Jurgens et al., 2014). Chlorinated OPFRs are commonly used as flame retardants in products such as textiles, electronics and furniture (Butt et al., 2014; Petropoulou et al., 2016). Chlorinated OPFRs are added to the product through physical addition rather than covalent bonding, so it is easy to enter the environmental medium through abrasion and penetration during the use of the product (Stapleton et al., 2009), which causes

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the detection of chlorinated OPFRs to varying degrees in soil, water and atmosphere, and the potential harm to the environment is gradually exposed. Tri(2-chloroethyl) phosphate (TCEP) is a typical chlorinated organophosphate esters (Cl-OPEs), mainly used as a plasticizer and coating additive in the rubber manufacturing industry (Grieco and Ramarao, 2013). It has found that TCEP can induce cell senescence and cause growth arrest (Zhang et al., 2017). The World Health Organization (WHO) pointed out as early as 1998 that TCEP has potential cancer treatment properties. The study of environmental behavior of TCEP, including its migration, transformation, and degradation processes in the environment, helps to deepen the understanding of organic phosphorus flame retardants, and provides a scientific basis for the comprehensive prevention and control of such substances and the formulation of environmental regulations.

Organophosphate esters (OPEs) have been detected in rivers, soil and atmosphere worldwide. According to research reports, concentrations of OPEs in rivers reached several hundred ng/L (Zeng et al., 2015). Besides, some OPEs were detected even in drinking water (Stackelberg et al., 2004), and some studies have been reported that OPEs could not be directly degraded by the conventional activated sludge treatment (Cristale et al., 2016), indicating that traditional water treatment processes were ineffective for removal of OPEs. It is difficult to degrade Cl-OPEs such as TCEP under natural conditions due to its special physical and chemical properties. Some microorganisms have been reported to be effective in degrading TCEP (Jenkins et al., 2019; Wang et al., 2019). Besides, advanced oxidation processes (AOPs) have proven effective in removing TCEP from water, such as TiO_2 photocatalytic degradation (Abdullah and O'Shea, 2019), MIL-101(Fe)/persulfate system (Hu et al., 2019a, 2019b), pyrite-activated persulfate (Lian et al., 2019a, 2019b), ozone/granular activated carbon (Vatankhah et al., 2019), UV/persulfate (Ou et al., 2017) and UV/H_2O_2 (Da Rocha et al., 2018) etc. Researches show that AOPs are environmental-friendly and low-cost technologies for organic pollutants removal. However, most researches have focused on the efficiency of Cl-OPEs degradation by AOPs, including optimization of conditions to increase the reaction rate. Few studies are dedicated to studying the intermediate products, degradation pathways and toxicity evaluation of TCEP during the process of degradation AOPs. Additionally, there has been no report on calculation of the bond dissociation enthalpies (BDEs) and frontier electron densities (FEDs) of TCEP.

A toxicity evaluation of the degradation products of OPEs is essential. To date, the existing toxicological assessments of OPEs has been reported using certain tests, such as zebrafish test (Kim et al., 2015), water flea test (Li et al., 2017) and cell line test (Ta et al., 2014). Luminescent bacteria method is a new type of biological toxicity monitoring technology used to assess the comprehensive toxicity of water quality (Zhang et al., 2019). Toxicity tests using luminescent bacteria can detect the acute toxicity of environmental pollutants (Yan and Sun, 2001; Pivato and Gaspari, 2006). Light from luminescent bacteria is easily suppressed by chemicals. The related exploration of the luminescence inhibition rate of luminous bacteria will reveal the unknown negative effects of OPEs on organisms. ECOSAR is an easy-to-use computer program developed by the US Environmental Protection Agency (EPA) for predicting aquatic toxicity to fish, daphnids and green algae. The classification of defined toxicity can be divided into four classes, including very toxic, toxic, harmful and not harmful (**Appendix A Table S1**) according to the values of predicted concentration for 50% of maximal effect (EC_{50}) and lethal concentration 50% (LC_{50}) (Reuschenbach et al., 2008). Some studies have applied ECOSAR program to toxicity assessment and risk assessment, especially the toxicity assessment of intermediate products (Peng et al., 2019; Zhuang et al., 2019).

The present work aims to study the kinetics, pathways and toxicity of TCEP during the process of UV/H_2O_2. In this paper, degradation kinetics of TCEP in the UV/H_2O_2 system, and the conversion rates of Cl^- and PO_4^{3-} were investigated. Qualitative analysis of intermediate products was performed by GC–MS. The reaction pathways were inferred based on the intermediate products and quantum calculations. For the first time, environment risk was estimated via the ECOSAR program and acute and chronic toxicity changes of intermediate products of TCEP were pointed out. The toxicity of the intermediate products was verified by the photoluminescence inhibition experiment using luminescent bacteria *Photobacterium phosphoreum* T3 (*P. phosphoreum*) as a model organism.

1. Experimental section

1.1. Chemicals

The Tris(2-chloroethyl) phosphate (TCEP) was set as the target pollutant (Aldrich, Milwaukee, USA). The oxidanthydrogen peroxide solution was purchased from the Fisher Company. The HPLC-grade methanol, acetonitrile, dimethysulphoxide (DMSO) and ethyl acetate were obtained from Tedian Company. The luminescent bacteria *P. phosphoreum* was purchased from Institute of Soil Science, Nanjing, China.

1.2. Experimental procedures

The schematic diagram of photochemical reactor with an ultraviolet lamp (250 W, Shanghai Yaming Lighting Co., Ltd., China) as the irradiation source was shown in **Appendix A Fig. S1**. The UV-light optical power density was measured by an illuminometer (Beijing Normal University, Beijing, China). The concentration of TCEP was set as 5 mg/L, the concentration of hydrogen peroxide solution was 50 mg/L and the volume of solution was 50 mL for each reaction.

1.3. Analytical methods

1.3.1. Analysis of degradation products

The residual TCEP was obtained from a fast liquid-liquid extraction method after reaction. At each sampling time, 1 mL of solution was taken from UV/H_2O_2 system and extracted with 1 mL ethyl acetate. The extracted samples were measured by a 7890 N gas chromatograph (Agilent Technologies, USA). The initial temperature of oven maintained at 353.15 K for 1 min. The temperature ramped to 413.15 K at a speed of 293.15 K/min (2 min), and then ramped to 553.15 K at a speed of 277.15 K/min (6 min). The temperature of injector and detector was set to 523.15 K. The helium was the carrier gas at a flow rate of 1.5 mL/min and nitrogen was the make-up gas at a flow rate of 20 mL/min. Hydrogen and synthetic air were detector gasses at flow rates of 65 and 100 mL/min, respectively.

The intermediates were characterized by GC–MS (Thermo Fisher, USA). Samples were extracted by solid phase extraction (SPE) column before GC–MS detection. All SPE columns were firstly adjusted with 5 mL of methanol and water (1 mL/min) and then eluted with 5 mL ethyl acetate/acetonitrile (1:1, V/V). The extracted solution was then dehydrated by Na_2SO_4, concentrated to 1 mL by rotary evaporator and purged with nitrogen. Then, trimethylsilylation was conducted with 0.2 mL of bis(trimethylsilyl)trifluoroacetamide (BSTFA) at 333.15 K for 15 hr. The temperature of the column oven was at 313.15 K for 1 min and then heated to 573.15 K at 279.15 K/min. Helium was the carrier gas and mass spectrometry and the electron impact (EI) mode was performed as 70 eV. Some of the intermediates were identified by the U.S. National Library of Medicine identification process.

1.3.2. Analysis of Cl^-, PO_4^{3-}, pH and total organic carbon (TOC)

The formation of Cl^- and PO_4^{3-} in the system was analyzed by ion chromatograph (ICS 1000, Dionex, USA). The mineralization efficiency of target compounds was evaluated using a TOC analyzer (5000A, Shimadzu, Japan). The pH of the system was measured by

inhibiting the eluent using a Dionex anion ASRS 300 electrolytic suppressor (4 mm) in an auto-suppressed external water mode.

1.3.3. *Calculation of molecular orbital*

The molecular orbital calculation was conducted by Gaussian 03 program (Gaussian, Inc.). Besides, a density functional theory (DFT) based on B3LYP/6–311+G* basis set was used to fully optimize the structure. The FEDs of the highest occupied molecular orbital (FED_{HOMO}) and the lowest unoccupied molecular orbital (FED_{LUMO}) were calculated. The values of (FED_{HOMO}^2 + FED_{LUMO}^2) responded to the possible reaction sites for radical attack. The C-H and O-H bond dissociation enthalpies (BDEs) were employed to predict the possible reaction sites for hydrogen reaction.

1.3.4. *Risk assessment and toxicity evaluation*

The risk assessment of TCEP and its intermediates were carried out by ECOSAR program, and the chronic and acute toxicities of TCEP and its intermediates on fish, daphnid and green algae were predicted. The acute toxicity was expressed by EC_{50} for green algae and LC_{50} for fish and daphnid. EC_{50} represents the concentration at which 50% of green algae is adversely damaged after 96 hr of exposure, and LC_{50} is the concentration at which 50% of fish and daphnid are dead after 96 hr and 48 hr of exposure, respectively. The unit of predicted concentration was mg/L. The data of predicted concentration of LC_{50} and EC_{50} could be directly obtained through a calculation process with the input of corresponding chemical formulas.

The rate of photoluminescence inhibition of photobacterium was used to assess toxicity. Prior to the toxicity evaluation test, the solution before or after the degradation process was collected. The sample was filtered through a membrane filter (d=0.45 μm) and eluted through a column with a non-polar neutral resin (XAD-2). The eluate was concentrated to 1 mL by rotary evaporator and then dissolved in 1 mL DMSO after dried by the gentle nitrogen. The pH values of all samples were adjusted to 7.0 with NaOH solution before toxicity experiments. The photobacterium *P. phosphoreum* was activated in 1 mL of 2.5% NaCl solution. Afterwards, each sample (0.2 mL) and photobacterium (10 μL) were added to of 3% NaCl (2 mL) solution. Then, samples were tested by DeltaTox analyzer (SDI, USA) and DMSO was employed as a control solvent. The toxicity of samples can be expressed in terms of luminescence inhibition rate (r, %) (Eq. (1)).

$$r=\frac{LI_c-LI_s}{LI_c}\times 100\% \quad (1)$$

where, LI_c (mV) is the control luminescence intensity, LI_s (mV) is the sample luminescence intensity.

2. Results and discussion

2.1. *Degradation of TCEP in UV/H_2O_2 system*

In the UV/H_2O_2 system, hydroxyl radical (HO•) is the main active species, which has a relatively high oxidation potential (2.8 eV) and has the ability to oxidize and degrade organic pollutants. Hydroxyl radicals have extremely strong oxidation ability, which can undergo rapid chain reactions, oxidize harmful substances into CO_2, H_2O or mineral salts without selection. No obvious absorbance of TCEP was observed from **Appendix A Fig. S2**, because of the poor UV absorbance properties of TCEP in the UV-C range (λ=200~280 nm). Therefore, H_2O_2 was the only significant photon absorber (λ=254 nm) in irradiated solutions. The removal rate of TCEP was obtained according to sampling at different time periods, and the reaction kinetics was fitted. It can be seen in Fig. 1a, the degradation kinetics of TCEP in UV/H_2O_2 accords with pseudo first order kinetics. The k value indicates oxidation rate of TCEP in the UV/H_2O_2 system, which is 0.0025 min^{-1} (R^2=0.9788). When the reaction time was at 900 min, the removal rate of TCEP can reach about 89.9% in the UV/H_2O_2 system, indicating that UV/H_2O_2 system is an effective method for the degradation of TCEP. The simplified oxidation pathway for TCEP in the UV/H_2O_2 system is shown as Eq. (2):

$$C_6H_{12}Cl_3O_4P \xrightarrow{\text{Oxidation}} CO_2+H^++Cl^-+PO_4^{3-}+\text{Intermediates} \quad (2)$$

In the UV/H_2O_2 oxidation system, TCEP could be oxidized to CO_2, H^+, Cl^-, PO_4^{3-} and other intermediates. Thus, the determination of residual concentration of Cl^-, PO_4^{3-}, TOC and pH can indirectly reflect the degradation of TCEP. The concentrations of Cl^- and PO_4^{3-} in the TCEP solution, TOC and pH value were measured after reaction. The theoretical values of Cl^- and PO_4^{3-} and the removal rate of TOC under the conditions of complete mineralization were calculated.

From Fig. 1b and c, the concentration of Cl^- and PO_4^{3-} of the test samples increased during the experiment process. At 900 min, Cl^- concentration reached 0.23 mg/L and PO_4^{3-} concentration reached 0.64 mg/L. According to calculation (Table 1), the theoretical concentrations of Cl^- and PO_4^{3-} should be 1.86 and 1.66 mg/L, respectively. Thus, the conversion rates of Cl^- and PO_4^{3-} were 12.4% and 38.6%. Combined with the remaining concentration of TCEP, the conversion rate of Cl-containing and P-containing intermediate products can be calculated, which was 22.6% and 51.2%, respectively. From 0 to 60 min, the Cl^- concentration was 0 but the concentration of PO_4^{3-} increased from 0 to 0.06 mg/L, suggesting that the bond with PO_4^{3-} was broken before the bond with Cl^-.

The TOC values of the reaction were measured to evaluate the mineralization degree of TCEP. The removal rate of TOC (r_{TOC}, %) can be described as Eq. (3):

$$r_{TOC}=\frac{TOC_0-TOC_t}{TOC_0}\times 100\% \quad (3)$$

where, the TOC_0 (mg/L) and TOC_t (mg/L) are the initial concentration of TOC and post-reaction concentration of TOC, respectively. From Fig. 1d, it is obvious that the removal rate of TOC increased with increasing reaction time. The removal rate of TOC reached about 48.8% at 900 min, indicating that nearly half of the TCEP was mineralized to CO_2 in the UV/H_2O_2 system, and a part of TCEP was converted into intermediate products. From 0 to 180 min, the pH of the reaction solution dropped rapidly from 8.0 to 3.9 because of the generation of H^+ during the process of degradation in the UV/H_2O_2 system. From 180 to 900 min, the pH was stable between 3.0 and 4.0.

2.2. *Identification of intermediates during TCEP degradation*

The intermediates of TCEP degraded by UV/H_2O_2 system was analyzed by GC–MS with EI full-scan patterns and identified based on the values of mass-to-charge ratio (m/z). The retention time (t_R), EI-MS spectrum ions and possible molecular structure of the intermediate products were listed in **Appendix A Table S2**. The toxicity data of the intermediates were obtained from U.S. National Library of Medicine. It can be seen that eleven compounds were detected by GC–MS, including carboxylic acids, alcohols, phosphate and chlorine compounds, etc. It is obvious that chlorine compounds such as chloroethene, tris(2-chloroethyl) phosphite, 2-chloroethanol are highly toxic with the LD_{50} of rat (oral) of 500, 100 and 71 mg/kg. The LD_{50} of ethane-1,2-diol (4700 mg/kg), oxalic acid (7500 mg/kg), phosphoric acid (1530 mg/kg) and ethyl dihydrogen phosphate (1600 mg/kg) is more than that of TCEP (1230 mg/kg), indicating that TCEP can also be converted into less toxic substances in UV/H_2O_2 systems.

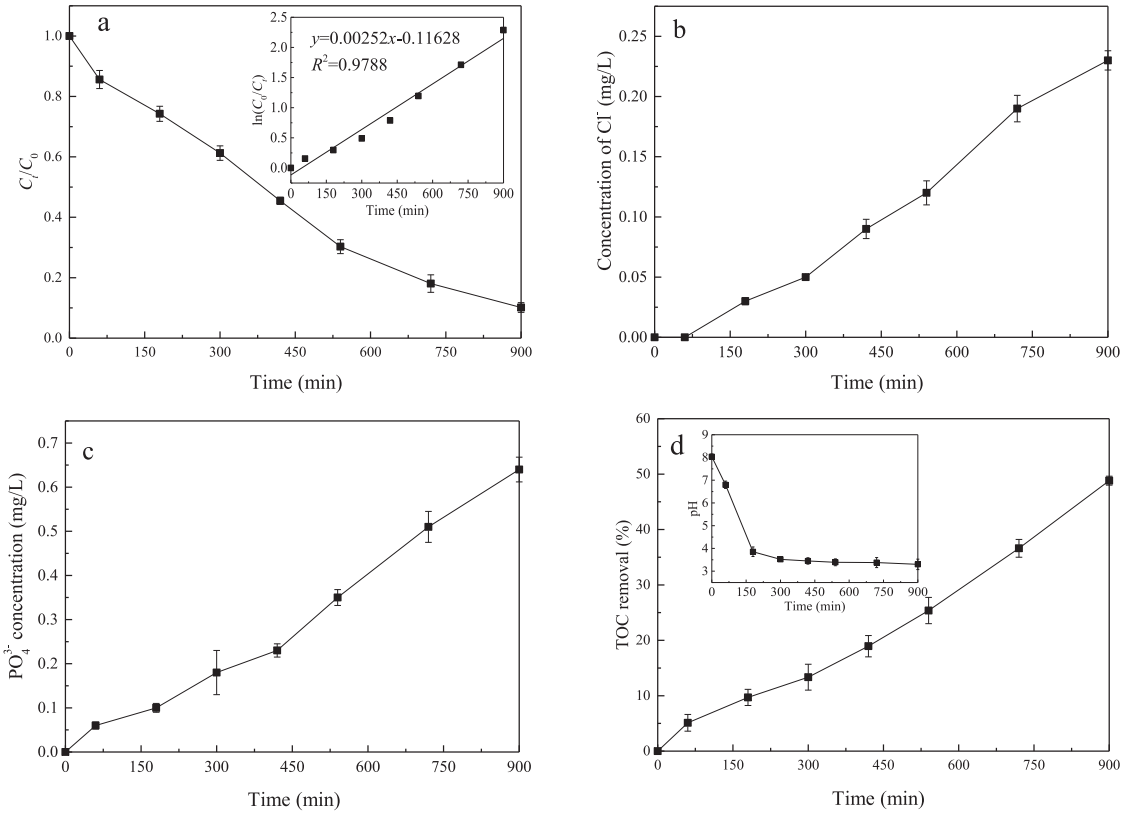

Fig. 1 – (a) The degradation rate of the TCEP and (b) the concentration of Cl^-, (c) PO_4^{3-}, (d) TOC removal and pH value of TCEP from 0 to 900 min in the UV/H_2O_2 system.

Table 1 – Theoretical and actual values of Cl^- and PO_4^{3-} conversion during TCEP degradation.

Name	Total concentration (theoretical value, mg/L)	Concentration in solution (actual value, mg/L)	Concentration in remaining TCEP (actual value, mg/L)	Concentration in intermediates (theoretical value, mg/L)
Cl^-	1.86	0.23	0.19	1.44
PO_4^{3-}	1.66	0.64	0.17	0.85

2.3. *Reaction pathways of TCEP in the UV/H_2O_2 system*

Sites susceptible to free radical attack were obtained using frontier electron densities (FEDs) calculation. According to frontier orbital theory, a higher position of $2FED_{HOMO}^2$ indicates easier electron excitation. The higher value of $FED_{HOMO}^2+FED_{LUMO}^2$ presents the greater possibility of being attacked by free radicals. From Table 2, the values of $2FED_{HOMO}^2$ for Cl11 and O2 are 0.642 and 0.335, suggesting that the electron excitation is more likely to happen at the position of Cl11 and O2. The values of $FED_{HOMO}^2+FED_{LUMO}^2$ for Cl11, C5, C13 and P1 are 0.469, 0.442, 0.432 and 0.399, implying that these sites are more vulnerable to attack by reactive free radicals. In Table 3, the bond energy in TCEP further verified the results of possible bond breaking. The bond energy of P1-O2 was 1.5576 kJ/mol and was larger than other bonds. However, the π bond in the double bond of P1-O2 is small and therefore easy to break (Barrows and Eberlein, 2005), indicating that the P1-O2 bond is unstable and vulnerable to attack. Besides, bonds with smaller bond energy can be easily broken, such as P1-O3, P1-O7 and P1-O8 in TCEP.

Based on the results of intermediate identification, FEDs calculation and bond energy information, the degradation pathways of TCEP in the UV/H_2O_2 system can be speculated. The degradation of TCEP mainly included two pathways (Fig. 2a and b). The first pathway contained three routes. An addition reaction of HO• occurred in Route I, and the generated •O-C-C-Cl further reacted with TCEP and replaced Cl6 of TCEP to form Compound 10. The Compound 9 was formed by another part of •O-C-C-Cl with hydrogen abstraction. Compound 9 was dehydrated to generate Compound 2 and combined with HO• to form Compound 1. Compound 1 was further oxidized to form Compound 4. Route II was an addition reaction with H_2O to form Compound 9 and bis(2-chloroethyl) hydrogen phosphate. Route III was an oxidation reaction with H_2O_2 to form O_2 and Compound 8. An addition reaction performed between Compound 8 and HO• to further generate Compound 3. The second pathway was as follows. The •O-C-C-Cl and bis(2-chloroethyl) hydrogen phosphate were formed by bis(2-chloroethyl) hydrogen phosphate with the addition reaction of HO•, and Compound 9 and bis(2-chloroethyl) hydrogen phosphate were produced with the addition reaction of H_2O. Compound 6, Compound 5 and 2-hydroxyethyl dihydrogen phosphate

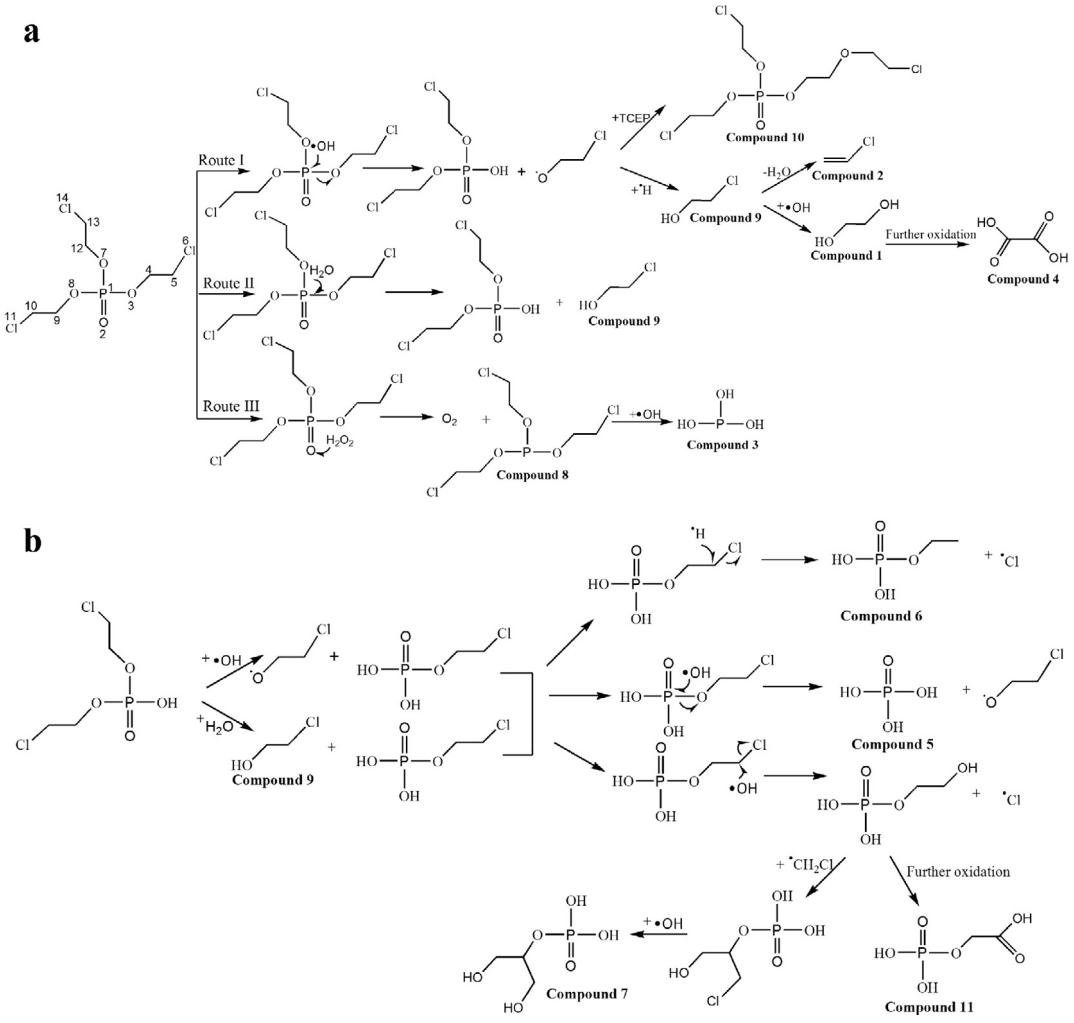

Fig. 2 – Degradation pathways of TCEP in the UV/H_2O_2 system (a and b).

were formed by bis(2-chloroethyl) hydrogen phosphate with a hydrogen extraction reaction and an addition reaction. Compound 11 was formed by the further oxidation of 2-hydroxyethyl dihydrogen phosphate and Compound 7 was formed by further reaction with 2-hydroxyethyl dihydrogen phosphate, •C-Cl and HO•. According to the literature, a series of hydroxylated and dechlorinated products such as $C_4H_9Cl_2O_4P$, $C_6H_{13}Cl_2O_5P$ and $C_2H_6ClO_4P$ were produced by TCEP in the UV/H_2O_2 system (TCEP was 3.5 μmol/L and H_2O_2 was 44.0 μmol/L) (Liu et al., 2018). Thus, different initial concentration of TCEP and H_2O_2 could produce different products.

2.4. *Risk assessment and toxic evaluation*

Many intermediate products can be produced during the degradation of TCEP. The acute and chronic toxicities of TCEP were firstly calculated in this study by ECOSAR program to determine the potential environmental risk of TCEP and its degradation products. First, we obtained the predicted values of acute and chronic toxicity of all intermediate products in the ECOSAR program (**Appendix A Table S3**). The numbers correspond to the serial numbers in **Appendix A Table S2**. The number 0 represents TCEP. Fig. 3 shows the evolution of acute and chronic toxicity. The trend of the acute toxicity of the intermediates of TCEP for fish, daphnid and green algae was generally the same. However, compound 2 were more harmful to fish, daphnid and green algae than TCEP, which were two of the final products of TCEP. The chronic toxicity was much more complex than acute toxicity and distributed across three spans. The chronic toxicity of intermediates for fish was lower than that of TCEP. However, the chronic toxicity of degradation products for daphnid and green algae was higher than that of TCEP. Compound 2 has very strong chronic toxicity to daphnid and green algae. From the results of ECOSAR, acute and chronic toxicity of intermediates such as chloroethene to fish, daphnid and green algae may be higher than TCEP, indicating the generation of intermediates with higher biological toxicity than TCEP itself.

Luminescent bacteria method is a new type of biological toxicity monitoring technology used to assess the comprehensive toxicity of water quality. The acute toxicity of environmental pollutants can be detected by the luminescent bacteria toxicity test. The light emitted by luminescent bacteria is easily suppressed by chemical substances. A lyophilization agent of luminescent bacteria is used as the source of luminescent bacteria and the pH of all samples was adjusted to 7.0 with NaOH to exclude the influence of pH on luminescence inhibition. The acute toxicity of pollutants can be reflected by the luminescence inhibition rate of luminescent bacteria. Luminescence inhibition rate will increase as the toxicity of environmental pollutants increases. As shown in Fig. 4, when the sample is diluted 100 times, the luminescence inhibition rate gradually increases with time. Under the condition of dilution of 20 times, the luminescence inhibition rate increased rapidly in the first 60 min. After 400 min, the luminescence inhibition rate of TCEP was about 90% and the increasing trend became gentle. The bacterial luminescence inhibition rate of TCEP reached 100% at 900 min. As shown in the **Appendix A Table S2**, the LD_{50}

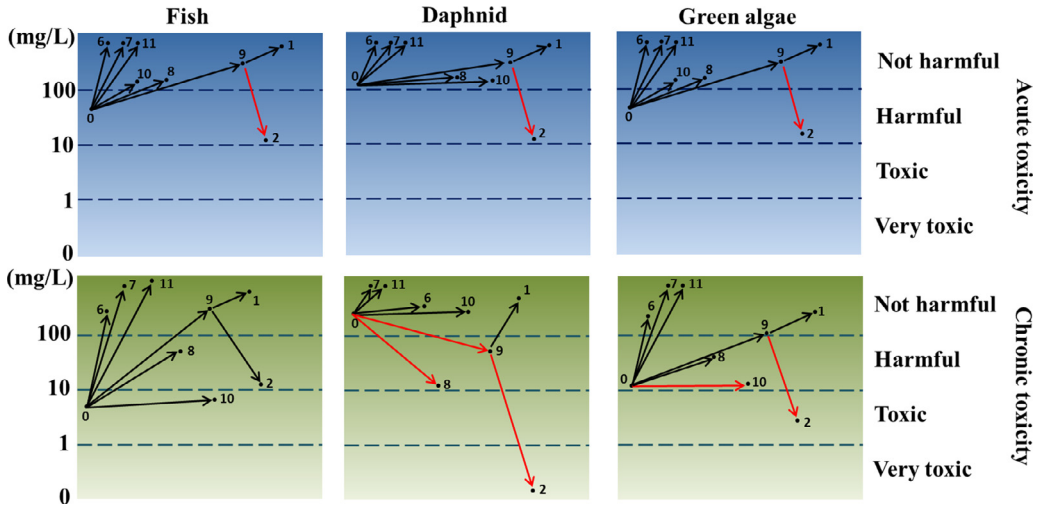

Fig. 3 – Risk assessment of TCEP and its intermediates via ECOSAR in the UV/H_2O_2 system. The numbers from 1 to 11 correspond to the numbers in Appendix A Table S2 and 0 represents TCEP.

Table 2 – Frontier electron densities (FEDs) of TCEP.

Atom	$2FED_{HOMO}^2$	$FED_{HOMO}^2 + FED_{LUMO}^2$
P1	0.021	**0.399**
O2	**0.335**	0.229
O3	0.010	0.209
C4	0.003	0.105
C5	0.001	**0.442**
Cl6	0.007	0.388
O7	0.056	0.199
O8	0.195	0.244
C9	0.049	0.086
C10	0.070	0.194
Cl11	**0.642**	**0.469**
C12	0.015	0.067
C13	0.011	**0.432**
Cl14	0.078	0.399

*FED_{HOMO} means frontier electron densities of the highest occupied molecular orbital and FED_{HOMO} means frontier electron densities of the lowest unoccupied molecular orbital. Bold means the possible reaction sites for radical attack.

Table 3 – Bond energy in TCEP.

Bonds	Bond energy (kJ/mol)
P1-O2	1.5576
P1-O3	0.8571
P1-O7	**0.6987**
P1-O8	**0.6981**
O3-C4	0.9200
C4-C5	0.9972
C5-Cl6	0.9437
O7-C12	0.9986
C12-C13	0.9932
C13-C14	0.9442
O8-C9	0.9988
C9-C10	0.9932
C10-Cl1	0.9442

* Bold means that the possible bond breaking position.

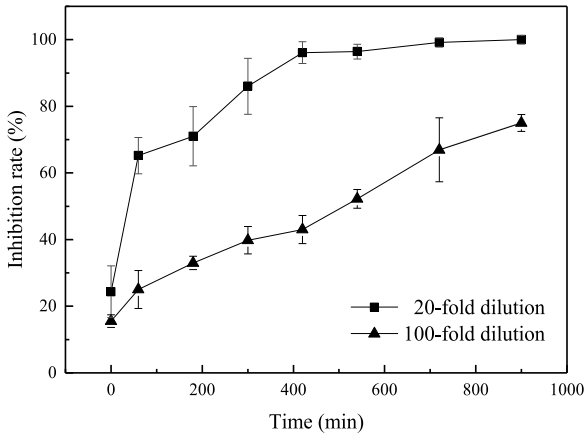

Fig. 4 – Luminescence inhibition rate of 20-fold and 100-fold dilution of degraded TCEP.

of the intermediate products Compound 9, Compound 8 and Compound 2 of TCEP were 71, 100 and 500 mg/kg respectively, which were highly toxic. Their high toxicity was due to the presence of Cl-containing compounds. To relieve the acute toxicity of aqueous solution, the removal of Cl-containing compounds from aqueous solution should be taken into account. It has been reported that the toxicity of the intermediates of TCEP (initial concentration = 3.5 μmol/L) produced by UV/H_2O_2 was obviously weakened according to the test of *E. coli* (Liu et al., 2018). The results from literature were contrary to the conclusions of this paper, probably because the initial concentration of TCEP was much smaller than the concentration in this paper (5 mg/L). Besides, it may also be because the reaction time too short to reach the point of decreasing toxicity.

Nanofiltration (NF) membranes have been used in wastewater treatment, such as the removal of bivalent and trivalent ions, organic matter, as well as microorganisms, colloids, heat sources, viruses, etc. (Lee et al., 2004). Reverse osmosis (RO) is a membrane separation process driven by pressure, which has been applied in urban sewage, heavy metal wastewater, oily wastewater and so on (Kang and Cao, 2012). NF or RO unit can be used in combination with advanced oxidation methods to remove chlorine-containing compounds that are difficult to degrade.

3. Conclusions

This study clearly revealed the degradation pathway and intermediate products of TCEP in designed UV/H_2O_2 system and compared the toxicity of TCEP degradation products. The 2-chloroethanol, tris(2-chloroethyl) phosphite and chloroethene were the main toxic intermediate products of TCEP. The addition reaction of HO• and H_2O and the oxidation reaction with H_2O_2 were found during the degradation pathway of 5 mg/L TCEP in the UV/H_2O_2 system. The ECOSAR program also showed that some of intermediates possessed higher biological toxicity than TCEP itself. The increase in the luminescence inhibition rate of luminescent bacteria indicated that during the degradation of TCEP, there might be the production of chlorine-containing compounds that are more toxic than TCEP. To relieve the acute toxicity of TCEP degradation solution, the removal of Cl-containing compounds from aqueous solution should be taken into account, such as introducing a RO or NF unit to the UV/H_2O_2 system.

Declaration of Competing Interests

None.

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Appendix A Supplementary data

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.jes.2020.05.015.

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