Degradation of 2,4-dichlorophenol from aqueous using UV activated persulfate: kinetic and toxicity investigation†

Juxiang Chen,[ab] Naiyun Gao,*[a] Xian Lu,[a] Meng Xia,[a] Zhenchuan Gu,[a] Chuang Jiang[a] and Qiongfang Wang[a]

2,4-DCP is a high-toxicity phenol compound, which is difficult to remove, harmful to the health of people and seriously influences the aquatic ecosystems. In this study, the degradation of 2,4-DCP using UV/persulfate (UV/PS) process was investigated for the first time. The results showed pseudo-first-order rate constants of 2,4-DCP photo-degradation by UV/PS was 35.1×10^{-3} min^{-1}. The reaction rate constants increased with pH increasing from 5 to 7 and then decreased at pH 8. Different anions (Cl$^-$, HCO$_3^-$ and NO$_3^-$) in water presented different effects on the photo-degradation reaction. The photo-degradation rates of 2,4-DCP in three actual water conditions (Xidong water works, Xijiu reservoir, Henshan reservoir) were higher than in the ultrapure water. Two possible (hydroxylated and dechlorinated) pathways for the degradation of 2,4-DCP by UV/PS were proposed. The luminescent bacteria inhibition rate greatly decreased with the concentration of 2,4-DCP decreasing in the reaction process.

1 Introduction

Chlorophenols (CPs) constitute a particular group of priority toxic pollutants listed by the US EPA in the Clean Water Act and by the European Decision 2455/2001/EC.[1,2] They have acted as the raw materials of wood, paints, vegetable fibers, paper, leather and disinfectants for many years. Environmental contamination with these chemicals occurs from industrial effluents, decolouration of paper and paper mill effluents, agricultural runoff, breakdown of chlorophenoxyacetic acid herbicides and hexachlorobenzene and from spontaneous formation following chlorination of water for disinfections and deodorization.[3,4] They have been found more in the wastewater than in the rivers and lakes. 2,4-Dichlorophenol (2,4-DCP) was one of the chlorophenols widely presented in aquatic environment. It has been extensively used in pesticide, plasticizer, fuel and other many productions,[5–8] which has been listed as a priority control pollutant in China due to its high toxicity and resistant to degradation.[9] So the removal of 2,4-DCP in water has attracted considerable attention. Many researchers have focused on the development of all kinds of methods to reduce the 2,4-DCP pollution. For example: physical, chemical and biological strategies. However, the physical methods are mainly

based on activated carbon adsorption and membrane filtration, they all produced secondary pollution on the physical materials and not really removed from the environment;[10–12] the chemical methods are mainly based on some oxidizing or reducing agents, such as potassium permanganate, ferric salt, chlorine and so on, which may cause color, turbidity, and even more harmful by-products in water;[13,14] the biological methods have two drawbacks. On the one hand, it is difficult to cultivate the microorganisms. On the other hand, the 2,4-DCP is toxic to the microorganisms, so the biological methods are controlled.[15–17] It is therefore necessary to find the effective method for the degradation of 2,4-DCP.

Advanced oxidation technologies (AOTs) represent high efficiency and easy operational methods for degrading toxic and difficult degradation organic compounds. Those AOTs make full use of hydroxyl radicals (OH˙) to form a high redox potential ($E_O = 2.7$ V).[18–21] There are many examples of AOTs including UV, Fenton-like (H$_2$O$_2$/Fe^{2+}), UV/TiO$_2$/H$_2$O$_2$, photo-Fenton (H$_2$O$_2$/Fe^{2+}/UV), all of which have been shown to degrade 2,4-DCP effectively.[22–25] Recently, an innovative oxidation technology based on the generation of sulfate radical anions (SO$_4$˙$^-$) has aroused great attention and was found as an alternative technology for water decontamination application. And the reason is that persulfate (PS, $E_O \sim 3.2$ V) is more stable than other oxidants such as ozone and has a higher oxidation ability after being activated. Generally, peroxydisulfate (S$_2$O$_8^{2-}$) or peroxymonosulfate (HS$_2$O$_5^-$) can be activated forming SO$_4$˙$^-$ or OH˙ by heat, UV and transition metals.[26,27] Some literature has proved that both SO$_4$˙$^-$ and OH˙ are existing in the experimental condition and played important role in the degradation of 2,-

[a]*State Key Laboratory of Pollution Control and Resource Reuse, Tongji University, Shanghai 200092, China*

[b]*College of Architecture and Civil Engineering, Xinjiang University, Urumqi 830047, China*

MIB and geosmin when the persulfate was activated by UV.[28] It has been reported that $SO_4^{\bullet-}$ could efficiently degrade many organic pollutants and exhibit a stronger oxidative ability than $OH^{\bullet}$.[29–31] However, $SO_4^{\bullet-}$ is more selective than $OH^{\bullet}$ reacting with many organic substrates. Previous work related to $SO_4^{\bullet-}$ based on AOPs mostly aimed at the removal efficiency and kinetics studies of other organic compounds. However, there are few literatures about the degradation of 2,4-DCP by UV-activated persulfate.

In this study, the main objectives of this study were (1) to evaluate the feasibility of UV/PS to degradate the 2,4-DCP; (2) to investigate the kinetics of the removal of 2,4-DCP by UV/PS under different initial PS dosages; (3) to determine the influence of the pH and environment factors on the photo-degradation of 2,4-DCP; (4) to compare the degradation efficiencies of two reservoirs, a water plant raw water and ultra pure water background conditions; (5) to investigate the intermediate products and propose the possible degradation pathway of photo oxide of 2,4-DCP with UV/PS; (6) to evaluate the acute toxicity during photo-oxidation process.

2 Materials and methods

2.1 Chemical

All the chemicals were at least of analytical grade and used as received. The chemical compounds 2,4-DCP, potassium peroxydisulfate (PDS), benzoic acid (BA), sodium carbonate, sodium bicarbonate, sodium chloride, sodium nitrate, nitrous acid were purchased from Sinopharm Chemical Reagent CO., Ltd. Methanol (MeOH) and acetaminophen (HPLC grade) was supplied by Sigma-Aldrich Co. The demanded solutions were prepared after necessary dilutions with ultra-pure water (18.2 MΩ cm, Milli-Q) for batch studies. The bacteria of toxicity evaluation experiment were Qinghai Vibrio (*Vibrio qinghaiensis* sp.-Q67, or Q67), which was purchased Beijing Hamamatsu Hikaruko technology Limited by Share Ltd.

2.2 Experimental procedure

All the experiments were conducted with quasi parallel beam instrument, which is designed according to the International Association of ultraviolet light standard. A low pressure Hg lamp (75 W, emmition at 253.7 nm, Tianjin Xinjing Co., China) was installed in a sealed cylindrical tube. Lamp above quiescently-stirred Petri dishes was employed for the batch UV/PS studies. At predetermined time intervals, samples were taken and mixed with excess methanol (v/v = 4 : 1) to quench the reaction before analysis. The pH of the reaction solution was adjusted by phosphate buffer (2 mM) solutions to desired value; all the experiments were replicated at least two times independently. The error bars in fingers represent the standard deviation among replicates.

2.3 Analytical methods

The 2,4-DCP concentration was measured by high performance liquid chromatography (HPLC Shimadzu-2010, Japan) with a UV detector, and its detection wave length was 230 nm. The

HPLC apparatus equipped with a C18 column (150 mm × 4.6 mm × 5 μm) was calibrated and tested prior to injection of the samples. Mixtures of acetonitrile (HPLC grade, ≥99.9%) ultra-pure water (70/30, the ultrapure water contained 0.1% of formic acid before mixing) were used as the mobile phase, and the flow rate was 1.0 mL min⁻¹. Solution pH was measured using an Acumen AB15 pH meter from Fisher Scientific. The actual water including of Henshan reservoir, Xijiu reservoir, Xidong water works were all sampled from the actual source of water. pH, CO_3^{2-}/HCO_3^-, NO_3^-/NO_2^-, TOC and other water quality indexes were detected every time. A certain concentration solution of 2,4-DCP was diluted with the actual water at each time.

The intermediate products were measured by GC-MS-MS (Thermo TSQ Quantum Access MAX, USA) with a chromatographic column (30 m × 0.25 mm × 0.25 m, Thermo, USA). The temperature process was programmed as: initial temperature 80 °C, residence time: 10 min and then improved to 100 °C at a rate of 10 °C min⁻¹ residence 2 min. The temperature was raised to 250 °C at an increasing temperature rate of 5 °C min⁻¹.

The toxicity evaluation experiment was executed with long-term micro toxicity analysis method (LTM).[32] The data was measured with the Power Wave micro plate spectrophotometer (Biotech Instruments Inc.) and was analyzed with Aptos software. For the test chemicals, 12 diluted concentration series in three parallels and 24 controls were arranged in the white 96-well standard opaque plates with 12 rows and 8 columns (Corning Corp.). The volume of the 2,4-DCP was 100 mL, the total volume was 200 mL. The toxicity or effect of 2,4-DCP to Q67 was expressed as the inhibition ratio (IBR)[33] according to the following formula:

$$\text{IBR} = \frac{I_0 - I_t}{I_0} \times 100\% \qquad (1)$$

where I_t is the average RLU of Q67 exposed to the test toxicant (3 parallels) and I_0 refers to the average RLU of Q67 exposed to the controls (12 parallels). Three duplicates were at least done at the same time. The experimental data were analyzed using APTox software.

3 Results and discussion

3.1 Effect of PS on the removal efficiency of 2,4-DCP with and without UV

The degradation efficiency of 2,4-DCP in the PS, UV, and UV/PS processes at pH 6.6 are compared and shown in Fig. 1. Negligible degradation of 2,4-DCP was observed using PS alone at a concentration of 900 μM, because of less than 4% of degradation percentage. With the presence of UV, the degradation of 2,4-DCP was progressively increased. Thereafter, the degradation increased gradually. However, 46% of 2,4-DCP was degraded in 45 min by UV alone, which was in accordance with other reports and consistent with their strong UV absorption at 254 nm.[34,35] In contrast, the degradation yield reached to about 96.4% at the same reaction time for UV/PS process. The results indicated the presence of PS accelerated the photo-oxide efficiency, and the degradation efficiency of 2,4-DCP was nearly two
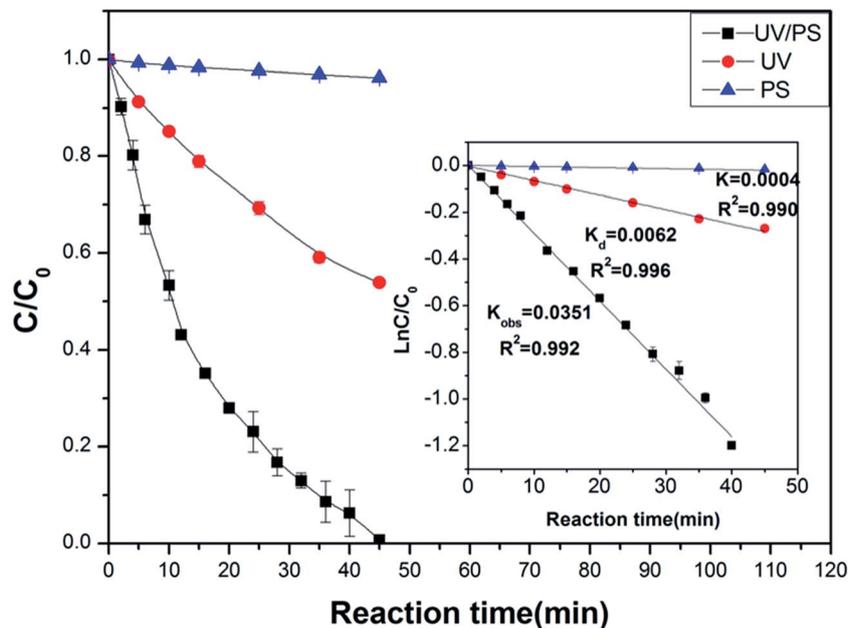
Fig. 1 Degradation of 2,4-DCP in PS, UV, UV/PS processes; processes condition: $[2,4\text{-DCP}]_0 = 6$ μM, 2 mM phosphate buffer, pH = 7.0, $[PS]_0 =$ 900 μM, 25 ± 1 °C.

times than UV without PS, it could attribute to $SO_4^{•-}$ and $OH^•$ were formed when the PS was activated by UV in this process.[36] Moreover, from the inserting figures in Fig. 1, the pseudo-first rate constants for 2,4-DCP using PS, UV and UV/PS process were 0.4×10^{-3}, 6.2×10^{-3} and 35.1×10^{-3} min^{-1}, respectively. These results also demonstrate the UV/PS is feasible for the 2,4-DCP degradation.

3.2 Effect of dosages of PS

Since $OH^•$ or $SO_4^{•-}$ were generated by UV activated sodium persulfate have been confirmed by Section 3.1 part, the amount of $OH^•$ or $SO_4^{•-}$ were decided by the dosage of sodium persulfate. The concentrations of 100, 300, 500, 700 and 900 μM PS were chosen to study the change rate constants with the increasing of initial concentration of PS. The reaction can be expressed as the following eqns:

$$-\frac{\mathrm{d}[2,4\text{-DCP}]}{\mathrm{d}t} = k_{\mathrm{obs}}[2,4\text{-DCP}]^a \qquad (2)$$

The k_{obs} (min^{-1}) is the pseudo-first-order kinetic constant, as the Fig. 2 indicated the disposed rate of 2,4-DCP during UV/PS process within 45 min increased with the dosage of PS increasing.

In whole, the trend showed that the greater the amount of oxidant dosages was, the higher removal rate of 2,4-DCP was achieved. The degradation rate constants of 2,4-DCP were fitted by pseudo-first-order kinetics under the conditions of adding amounts of oxidant. The reaction rate constants are 4.7×10^{-3}, 10.6×10^{-3}, 15.3×10^{-3}, 28.7×10^{-3} and 35.1×10^{-3} min^{-1}, when the oxidant dosage are 100, 300, 500, 700 and 900 μM, respectively. Through the fitting of the pseudo-first-order
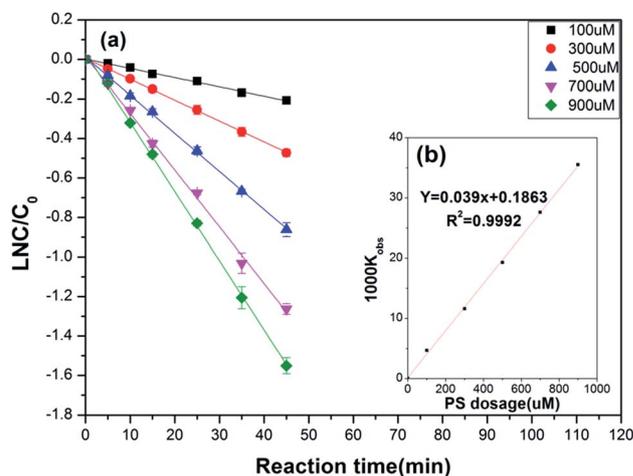
Fig. 2 Effect of initial PS concentration on the degradation of 2,4-DCP; process condition: $[2,4\text{-DCP}]_0 = 6$ μM, 2 mM phosphate buffer, pH = 7.0.

degradation rate constant k_{obs} and the oxidant dosage ($[\text{oxidant}]_0$), they were found to have a linear relationship and accord with the formula (3):

$$k_{\mathrm{obs}} = 0.039[PS]_0 + 0.1863, \ R^2 = 0.999 \qquad (3)$$

In the study of UV/H_2O_2 degradation of phenol in water of Olmez-Hanci T.[37] when the oxidant dosage is less than 30 mM, it was found the degradation rate constant increased with the increasing of oxidant dosage. However, when the oxidant dosage is too high (>30 mM), the quenching reaction of free radicals with oxidants will happen, which lead to decrease the

degradation rate of pollutants. While in this experiment, the maximum amount of oxidant dosage was far more than 30 mM and it was not observed that the reaction rate of high oxidant dosage decreased.

3.3 Effect of pH

$$S_2O_8^{2-} + UV \rightarrow 2SO_4^{\bullet-} \quad (4)$$

$$S_2O_8^{2-} + H^+ \rightarrow HS_2O_8^- \quad (5)$$

$$HS_2O_8^- \rightarrow SO_4^{\bullet-} + SO_4^{2-} + H^+ \quad (6)$$

$$SO_4^{\bullet-} + H_2O \rightarrow SO_4^{2-} + OH^{\bullet} + H^+ \quad (7)$$

$$SO_4^{\bullet-} + OH^- \rightarrow SO_4^{2-} + OH^{\bullet} \quad (8)$$

$$SO_4^{\bullet-} + SO_4^{\bullet-} \rightarrow S_2O_8^{2-} \quad (9)$$

$$SO_4^{\bullet-} + OH^{\bullet} \rightarrow HSO_5^- \quad (10)$$
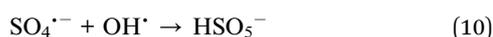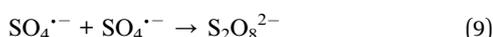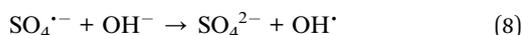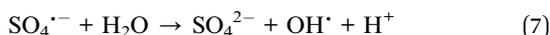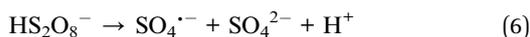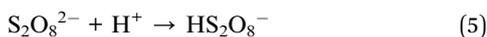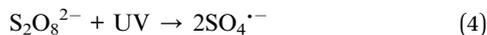
Fig. 3(a) describes the photolysis of 2,4-DCP in different pH condition; it demonstrated this reaction process can be well described by the pseudo-first-order kinetics. As the Fig. 3(b) shows, the maximum degradation rate constant of 2,4-DCP occurred at near neutral pH (*i.e.*, pH 7) over the range of pH used in this study. The k_{obs} increased with the pH improved from 5 to 7, and then decreased in pH 8, which is in accordance with the results of Chenju Liang and Goulden, P.D.[38,39] Under acidic conditions, additional $SO_4^{\bullet-}$ could be formed due to acid-canalization as show in eqn (5) and (6).[40] However, as shows in eqn (8) (ref. 41) ($k_9 = 8.1 \times 10^8 \, M^{-1} \, s^{-1}$, pH = 5.8) and eqn (9),[42] the higher $SO_4^{\bullet-}$ generation rate causes higher radical concentrations, which could favor radical with radical reactions or radical with radical scavenger reactions, over radical with organic reactions, so the concentration of $SO_4^{\bullet-}$ in pH 7 was the

highest among in the pH 5, 6, 7, then the degradation rate and the k_{obs} is the highest in pH 7. In an alkaline solution, one aspect: with a higher redox potential of sulfate radical and hydroxyl ions combined to generate a large number of lower redox potential hydroxyl radicals. Another aspect: $SO_4^{\bullet-}$ may play a role in scavenging $OH^{\bullet}$ and slowing down the 2,4-DCP degradation rate. Relatively more hydroxyl radicals are formed at pH 8 compared to pH 7 in accordance with eqn (6) and (7). Therefore, it is likely that more hydroxyl radicals would be scavenged at pH 8 by sulfate ions than at pH 7; thereby the above two reasons resulted in decreases in 2,4-DCP degradation rates at pH 8 and a relatively improved performance at pH 7.

3.4 Effect of anions

In actual water body, it contains a large number of anions, for example: SO_4^{2-}, Cl^-, CO_3^{2-}, HCO_3^- and NO_3^-, and so on. To some extent, the anions of the water body will affect the degradation rate of the target pollutants. So, three kinds of anions, Cl^-, CO_3^{2-} and NO_3^-, with high concentrations and great influence in the water were investigated. Once these anions were added to the system, it will produce many reactions, as shown in eqn (11)–(24):

$$Cl^- + OH^{\bullet} \rightarrow ClOH^{\bullet-} \quad (11)$$

$$ClOH^{-\bullet} + H^+ \rightarrow HClOH^{\bullet} \quad (12)$$

$$HClOH^{\bullet} \Leftrightarrow Cl^{\bullet} + H_2O \quad (13)$$

$$Cl^{\bullet} + Cl^- \Leftrightarrow Cl_2^{\bullet-} \quad (14)$$

$$CO_3^{2-} + H_2O \rightarrow HCO_3^- + OH^- \, (k_1 = 4.3 \times 10^{-7}) \quad (15)$$

$$HCO_3^- + OH^{\bullet} \rightarrow OH^- + CO_3^{\bullet-}, \quad (16)$$

$$CO_3^{2-} + OH^{\bullet} \rightarrow OH^- + CO_3^{\bullet-}, \quad (17)$$

$$HCO_3^- + SO_4^{\bullet-} \rightarrow SO_4^{2-} + HCO_3^{\bullet-}, \quad (18)$$

$$CO_3^{2-} + SO_4^{\bullet-} \rightarrow SO_4^{2-} + CO_3^{\bullet-} \quad (19)$$

$$NO_3^- \rightarrow NO_2^- + 1/2O_2 \quad (20)$$

$$NO_3^- \rightarrow NO_2^{\bullet} + O^{\bullet-} \quad (21)$$

$$O^{\bullet-} + H_2O \rightarrow OH^{\bullet} + OH^- \quad (22)$$

$$OH^{\bullet} + NO_2^- \rightarrow NO_2^{\bullet} + OH^- \quad (23)$$

$$SO_4^{\bullet-} + NO_3^- \rightarrow NO_3^{\bullet} + SO_4^{2-} \quad (24)$$
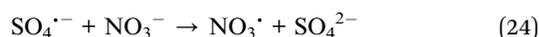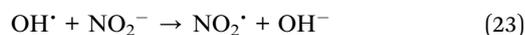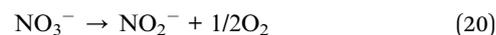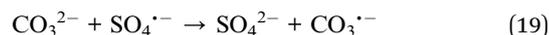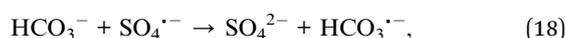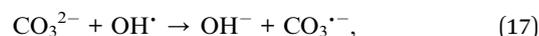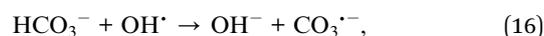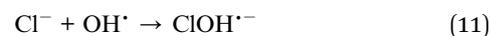
As the Table S1† shows, the photo-oxidation rate of different concentrations of Cl^-, CO_3^{2-} and NO_3^- were fitted by the pseudo-first-order model. The R^2 values were all above 0.95. As shows in the Fig. 4(a). The reaction rate of 5 mM chlorine ion was lower than that of without chlorine ions and then significantly increased with the increasing of chlorine ion concentration between 10 mM and 200 mM. It can attribute to the small concentration of chlorine ion consumed some $OH^{\bullet}$. While

Fig. 3 Degradation of 2,4-DCP under different pH by UV/PS; process condition: [2,4-DCP]₀ = 6 μM; [PS] = 900 μM.

anions of solution were HCO_3^- and OH^- (the alkalinity value was mainly determined by the value of HCO_3^-). The pH value of 2,4-DCP solution is improved from acidic, neutral to alkaline value with the increasing of initial concentration of carbonate. As the conclusions of the parts 3.3 with the pH value became from acidic, neutral to alkaline value, the reaction rate constant is increased firstly and then decreased. However, when the concentration of carbonate ion is too high, it will react with the $OH^•$ and $SO_4^{•-}$ according with the eqn (16)–(19). So low concentration of carbonate ion obviously promoted the reaction process and higher initial carbonate concentration has begun to inhibit the reaction.

As the Fig. 4(c) described, with the increasing of NO_3^- concentration, the removal rate of 2,4-DCP increased significantly. Owing to NO_3^- can generate the oxidation active factor ($NO_3^•$) under UV light irradiation eqn (20)–(24) condition. The $NO_3^•$ is also a high redox potential (2.5 V) radical, though the redox potential is lower than $SO_4^{•-}$, while the formation amounts of $NO_3^•$ are enough to oxide the 2,4-DCP completely. Therefore, the existence of NO_3^- can promote the degradation of 2,4-DCP to a certain extent. The result is in good accordance with that of Ghauch[43] in the literature of ibuprofen removal by heated persulfate.

3.5 Photolysis effect under the condition of actual water samples

The photo-degradation of 2,4-DCP in raw water of water works and reservoir water were conducted to assess the performance of UV/PS in dealing with real waters polluted with trace 2,4-DCP. As shown in Fig. 5, the degradation efficiency of 2,4-DCP in raw water was much higher than that in the deionized water. The degradation rates in ultrapure water, Henshan reservoir, Xijiu reservoir, and Xidong waterworks are about 86.3, 89.6, 94.5, and 96.7%, respectively. As the Table S2† shows there are low concentration (<5 mM) of NO_3^-, Cl^-, HCO_3^- in three kinds actual water sources. The sections of 3.4 parts demonstrate the low concentration of NO_3^-, HCO_3^- can promote the photo-degradation obviously while the low concentration of Cl^- can

Fig. 4 Degradation of 2,4-DCP by UV/PS under different initial concentrations of anion. (a) Cl^-, (b) CO_3^{2-}, (c) NO_3^-; the initiation concentration of 2,4-DCP is 1 mg L^{-1} = 6 µM; [PS] = 900 µM; the concentration of anions are 0, 5, 10, 100, 200 mM, respectively.

the high concentration of chlorine ion can accelerate the formation of $Cl^•$ which according with the eqn (11)–(14). Many $Cl^•$ are generated and the oxidation reduction potential of $Cl^•$ is higher than that of $OH^•$, which improved the reaction rate obviously.

As the Fig. 4(b) shown, the degradation rates increased with increasing carbonate ion concentration from 0 to 100 mM and then began to decrease when the carbonate concentration was 200 mM. As the reaction (15) and the k_1 constant indicated the main

Fig. 5 Effects of actual water samples on the degradation of 2,4-DCP, process condition: [2,4-DCP]$_0$ = 6 µM, [PS]$_0$ = 900 µM.
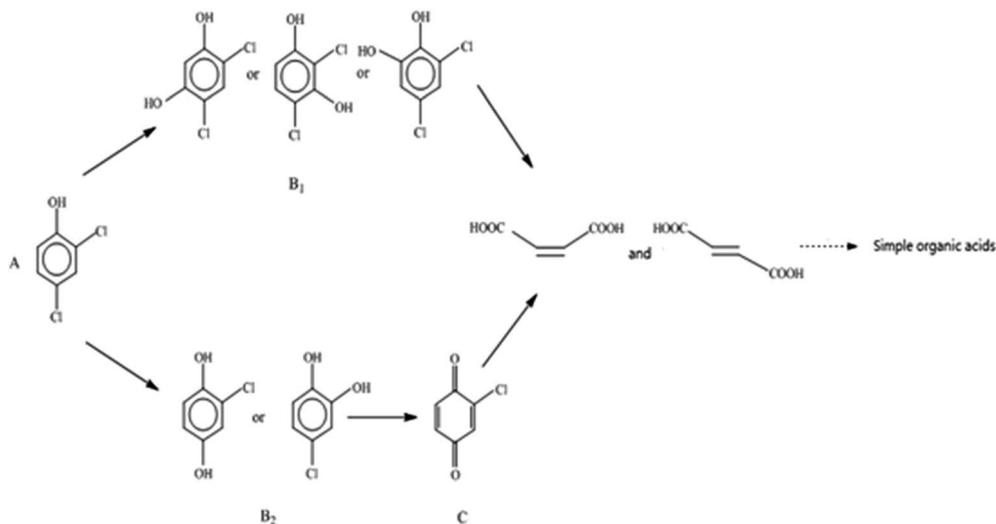
Fig. 6 Proposed reaction pathway of the photodegradation of 2,4-DCP in UV/PS oxidation process. Process condition: $[2,4\text{-DCP}]_0 = 6$ μM, $[\text{PS}]_0 = 900$ μM.

inhibit the reaction slightly. The NO_3^- concentrations are so little in three actual water bodies that the difference of effect can be neglected. The HCO_3^- concentrations are larger than Cl^- in three actual water bodies. Overall, the promotion effect of anion on photolysis is larger than that of inhibition. So the degradation rates of actual water bodies are higher than the free-anion ultra pure water. Owing to the concentration of HCO_3^- of Xidong waterworks is the largest and the Cl^- concentration is the least among three actual water bodies. While the anion condition of Henshan reservoir water is the opposite. So the degradation rate of Xidong waterworks is the highest and Henshan is the least.

3.6 Intermediate products and possible degradation pathways

To investigate the intermediates of the 2,4-DCP transformation by UV/PS process, a reaction mechanism based on the GC/MS/MS was proposed in Fig. 6. Two possible pathways for the degradation of 2,4-DCP by UV/PS were proposed: (a) 2,4-DCP is hydroxylated and formatted the isomers 3,5-dichlorocatechol, 4,6-dichlororesorcin, 2,4-dichlororesorcinol. These intermediates may be further oxidized by $OH^•$ and $SO_4^{•-}$ to form the products such as maleic acids or fumaric acids. (b) 2,4-DCP is dechlorinated: the process is initiated by the breaking of the C–Cl-bond at *para* position on the benzene ring of 2,4-DCP by $OH^•$ and $SO_4^{•-}$, simultaneously generate the intermediate products of chlorohydroquinone and 4-chlorocatechol and further oxidized by $OH^•$ and $SO_4^{•-}$ to maleic acids or fumaric acids. Parts of these organic acids were mineralized to CO_2 and H_2O finally. This was in good agreement with the research results of degradation pathway of W. Z. Tang and W. Chu.[44,45]

3.7 Toxicity assessment

In this study we used the *Vibrio qinghaiensis* sp.-Q67 to measure the transformation products toxicity. The bioluminescence was

detected after the samples were exposed to the luminescent bacteria for 0.25, 0.5, 1, 2, and 3 h, respectively. As shown in the Fig. 7. The inhibition rate degradate from 98% to 10% in 45 min when the solution was contacted to the photo bacteria for 3 h, the inhibition rate degradate from 97% to 8% in 45 min when the solution was contacted to the photo bacteria for 2 h, the inhibition rate degradate from 96.3% to 7.8% in 45 min when the solution was contacted to the photo bacteria for 1 h, the inhibition rate degradate from 95% to 6% in 45 min when the solution was contacted to the photo bacteria for 0.5 h, the inhibition rate degradate from 94% to 9% in 45 min when the solution was contacted to the photo bacteria for 0.25 h. From the value we can see the inhibition rate significantly decrease with the degradation of 2,4-DCP by UV/PS and the relative inhibition rate were almost the same 89% within 3 h.
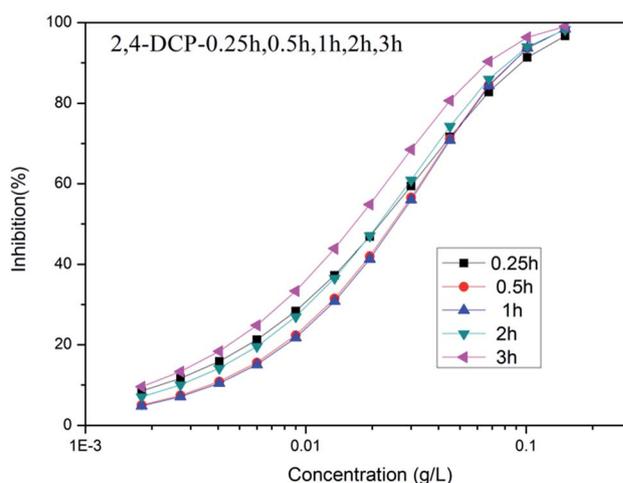
Fig. 7 The concentration–response curves of 2,4-DCP to Q67 at five different exposure times. The data in the figures were represented as mean and standard deviation calculated from the three replicates.

4 Conclusions

This study has demonstrated the process of UV/PS was a high effectively process to remove 2,4-DCP in actual water body. The reaction followed the first-order kinetics. The value of k_{obs} increased significantly from 4.7×10^{-3} to 35.1×10^{-3} min^{-1}, as the dosage of PS increased from 100 μM to 900 μM. The optimal reaction pH value was 7. In general, low concentration of anions in water presented promoting effect on the reaction. The degressive bioluminescence inhibition rate value indicated that the toxicity significantly decreased with the degradation of 2,4-DCP. While the high content PS were very toxic on the bioluminescence, so low concentration PS in UV/PS process is feasible to degradate the organic matter. All of this provides a theoretical and practical significance for degradation of other chlorophenols and persistent refractory organic compounds.

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