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Free radical-enhanced formation of toxic byproduct benzoyl benzoquinone during the combined UV-chlorine treatment on BP-1

Xuefeng Sun [a,b], Dongbin Wei [a,b,*], Jun Liu [a,b], Yuguo Du [a,b]

[a] State Key Laboratory of Environmental Chemistry and Ecotoxicology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China

[b] University of Chinese Academy of Sciences, Beijing 100049, China

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ABSTRACT

2,4-Dihydroxybenzophenone (BP-1), an important benzophenone-type (BPs) UV filter, is widely used in personal care products and other industrial products, it has been frequently detected in environmental media and even in organism samples. The transformation behaviors of BPs during environmental processes and their potential risk should be concerned. In this study, the variation of acute toxicity and transformation characteristics of BP-1 during the combined UV-chlorine disinfection process were explored. The acute toxicity of reaction mixtures was significantly higher than that of BP-1, a key toxic product (2-chloro-3-hydroxyl-6-benzoyl benzoquinone) was successfully identified, whose toxicity was about 40 times higher than BP-1. It was firstly found that $^1O_2$ played crucial role in the toxic products formation during UV alone and combined UV-chlorine systems. Besides, Cl_2^{-}• and HO• had great impact on the transformation of both BP-1 and toxic products. Overall, this work comprehensively revealed the formation mechanisms of toxic benzoyl benzoquinone from benzophenone-type UV filter during combined UV-chlorine process, it is expected that these results can provide scientific evidence for optimizing water disinfection process and evaluating potential risk of benzophenone-type UV filter.

1. Introduction

Disinfection is an essential unit in water treatment process to inactivate water-borne microbial pathogens. Chlorination is the most common used disinfection technology due to its low cost, high efficiency and convenient operation. But it cannot kill the chlorine-resistant microorganisms effectively, such as Cryptosporidium and Giardia [1]. The combination of UV and chlorination (UV-Cl) has been considered as an effective disinfection method for killing various microorganisms [2]. Besides, combined UV-Cl has also been regarded as an advanced oxidation process (AOP) to degrade contaminants due to the formation of hydroxyl radicals (HO•) and reactive chlorine species (RCSs) including chlorine radical (Cl•), dichloride radical anion (Cl_2^{-}•), and chlorine oxide radical (ClO•) [3–5]. However, toxicity elevation of reaction solutions after combined UV-Cl treatment has been observed frequently, and some toxic disinfection by-products (DBPs) were identified as well [6,7]. For examples, previous study found that, CHO cytotoxicity increased by 70% in combined UV-Cl system of natural organic matter (NOM) compared to chlorination system alone due to the presence of HO• and RCSs [6]. And another study reported that polybrominated diphenyl ethers could be transformed to carcinogenic dibenzofuran (DF) and 2-hydroxydibenzofuran (2-OH-DF) in the presence of Cl• or HO•, and the total yield of DF and 2-OH-DF in combined UV-Cl system was 1.46 times to that in UV treatment alone due to the presence of RCSs [8]. Therefore, the formation of toxic DBPs is an issue should be concerned in UV-Cl process.

UV filters are active ingredients widely used in personal care products especially in sunscreens to protect the skin from UV damage such as suntan, sunburn, and even cancer [9,10]. Benzophenones (BPs), one group of UV filters, are widely used in cosmetics (such as sunscreen lotions, skin care, facial makeup and lip care products), plastics, adhesives, paint and rubber [11,12], and BPs have been frequently detected in the environment [13]. Especially, many studies have shown that BPs exhibited many biological risks, such as potential endocrine disrupting activity and genotoxicity [14,15]. 2,4-Dihydroxy-BP (BP-1), is one of the most popular UV-filters used in cosmetics and also directly used in some sunscreen lotions [16]. Besides, BP-1 is also used as UV stabilizers in food packaging to prevent quality loss of food and polymer degradation [17,18]. BP-1 has been detected in human body fluids, such as urine, breast milk and semen [19–22]. The median concentration of BP-1 was

* Corresponding author.
E-mail address: weidb@rcees.ac.cn (D. Wei).

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0.21 ng/mL in Chinese adults' urine samples [23] and 0–0.7 ng/mL in human serum samples [24]. BP-1 was ca. 4 ng/L in outdoor swimming pool water in Changsha, China [25].

The effluents of wastewater treatment plants are important source of BPs and some other pollutants in the environment. Some studies have shown that the traditional secondary treatment processes, such as biological treatments, adsorption, and coagulation/filtration, could not completely remove BPs. The average concentrations of 2-hydroxyl-4-methoxyl benzophenone (BP-3) in the influent and effluent of WWTP in Australia were up to 2086 ± 1027 ng/L and 153 ± 121 ng/L, respectively [26]. However, BPs exhibited high chemical reaction activity towards sodium hypochlorite and converted into high toxicity products in chlorination system [27–29]. Our previous study found that 4-hydroxyl benzophenone could form chlorophenol during chlorination treatment, and the acute toxicity of reaction mixtures had significant increase [30]. More importantly, benzophenone is a sensitizer of singlet oxygen ($^1O_2$), UV irradiation would readily induce BP-1 and generate $^1O_2$ besides HO• and RCSs. Previous studies mainly focused on the roles of HO• and RCSs in UV-Cl system, while few studies explored the role of $^1O_2$ in UV-Cl system so far. Whether these active species can promote oxidation reaction and form toxic products, or promote degradation of toxic products and eliminate toxicity of the system is worth further study. The results would be useful to optimize treatment technologies and control the formation of toxic DBPs.

Therefore, BP-1 was selected as representative substrate, the purposes of this work were to investigate the toxicity variation during combined UV-Cl treatment; to identify transformation products and disclose possible formation pathways of toxic products during combined UV-Cl treatment; and to illustrate the roles of reactive radicals and environmental factors in the formation of toxic products.

2. Materials and methods

2.1. Chemicals and solution preparation

2,4-Dihydroxybenzophenone (BP-1, 99% purity) was purchased from Sigma-Aldrich (Missouri, USA), NaClO was purchased from Wako Pure Chemical Industries Ltd. (Tokyo, Japan). Acetonitrile used to prepare BP-1 stock solution and methanol used as mobile phase in the UHPLC-QTOF-MS analysis were obtained from Fisher Scientific (Belgium, USA). Formic acid used in the UHPLC-QTOF-MS analysis to enhance ionization efficiency was obtained from Acros Organics (New Jersey, USA). The other chemicals used in this study were of analysis grade. The water used in this study was generated by a Milli-Q ultrapure water system (Merck-millipore, Germany). BP-1 stock solution (0.2 M) was prepared by dissolving BP-1 in acetonitrile, wrapped with aluminum foil and stored in refrigerator at 4℃. The freeze-dried powder of *P. phosphoreum* T3 was purchased from the Institute of Soil Science, Chinese Academy of Sciences (Nanjing, China). The concentration of free available chlorine (FAC) in NaClO solution was standardized using the iodometric titration method according to the recommended procedure [31], and the working solution of FAC was prepared by diluting the stock solution of NaClO with ultrapure water.

2.2. Combined UV-Cl treatment experiments

The combined UV-Cl treatment of BP-1 was performed in a 300 mL quartz photochemical reactor with magnetic stirring system and water bath system to maintain the temperature at 23 ± 0.5℃. The UV light source was a 300 W xenon lamp, the wavelength of 200 to 400 nm was applied in UV-Cl experiments through an optical filter, and the UV intensities were set as 1.2, 2.5 and 3.5 mW/cm^2 (about 52.8, 110 and 154 mW, respectively) to explore its effects on BP-1 transformation. Wavelength filters (254 nm and 365 nm) were used to explore the effects of UV wavelengths on BP-1 transformation. In order to accurately measure the intensity of UV irradiation, a UV radiometer (made by Beijing Normal University) was placed at the center of photochemical reactor, ca. 35 cm perpendicularly below the xenon lamp. The initial concentration of BP-1 in this study was 0.2 mM, which was prepared by 1000-times of dilution from the BP-1 stock solution. In BP-1 working solution, the content of acetonitrile was 0.1%. Different initial FAC doses were set ($[FAC]_0$:$[BP\text{-}1]_0$ = 0.4:1, 1:1, 3:1 and 6:1, respectively) to explore the effects on BP-1 transformation. The reaction was initiated by spiking FAC into BP-1 solution and immediately putting the quartz photochemical reactor under the preheated xenon lamp. In order to test the acute toxicity of the treatment systems and screen possible toxic products, the reaction mixtures were directly measured at a given reaction time. For exploring the effects of various operational parameters on BP-1 transformation and considering the quench agent such as Na_2SO_3 may react with some transformation products, 5 mL samples were withdrawn at a given reaction time and immediately flow through the C18 solid phase extraction (SPE) cartridges (6 cc, 500 mg, Waters) to quench FAC as the inorganic components in the sample including FAC will not be adsorbed on C18 cartridge. And then the enriched BP-1 and its transformation products were eluted with acetonitrile for UHPLC-MS analysis. For better quality assurance, an extra solvent control was set, 0.1% of acetonitrile aqueous was similarly treated with UV-Cl process. All experiments were performed in triplicates.

2.3. UHPLC-QTOF-MS analysis

A UHPLC (Ultimate 3000, Thermo Fisher Scientific, USA), equipped with an Agilent ZORBAX SB C18 column (4.6*150 mm, 5 μm), was applied to separate the major products in the reaction mixtures. Subsequently, a high-resolution quadrupole time-of-flight mass spectrometer (Bruker, Germany) (micrOTOF QII, resolution > 16,500 FWHM and $\triangle$M/M < 2 ppm) was used to analyze the accurate molecular mass and possible molecular structure. The gradient elution conditions of the UHPLC and the operating parameters of the QTOF-MS are available in SI Text S1.

2.4. Acute toxicity tests

Photobacterium phosphoreum growth inhibition acute toxicity test is a convenient and rapid toxicity screening method, which has been widely and successfully used for determining the adverse biological effects of various compounds and environmental samples [32]. The test procedure was described in our previous study [33], which was a modified ISO method [34]. The solutions of Zn^{2+} and 3% NaCl were respectively set as positive and negative controls. The luminescence intensities of samples and controls were measured by Synergy™ 2 Multi-Mode Microplate Reader (Biotek, USA). The acute toxicity effect of samples was expressed as the inhibition ratio (IR, %) to photobacterium:

$$IR = \frac{L_{NC} - L_{sample}}{L_{NC}} * 100\%$$

L_{sample} and L_{NC} represented the luminescence intensity of the samples and negative control, respectively.

Additionally, a special control experiment was performed, FAC solution was exposed under UV irradiation for 5 min. The control did not exhibit any acute toxicity, indicated that FAC could be degraded by UV irradiation within 5 min.

3. Results and discussion

3.1. Acute toxicity variation

Toxicity assay is an efficient method to primarily screen the formation of harmful by-products during disinfection treatment [35]. In this study, the acute toxicity of BP-1 solutions treated with combined UV-Cl under different pH (5, 7.5, 10) conditions and chlorine doses ($[FAC]_0$: $[BP\text{-}1]_0$ = 0.4, 1, 3, 6) were measured. As shown in Fig. 1, comparing to

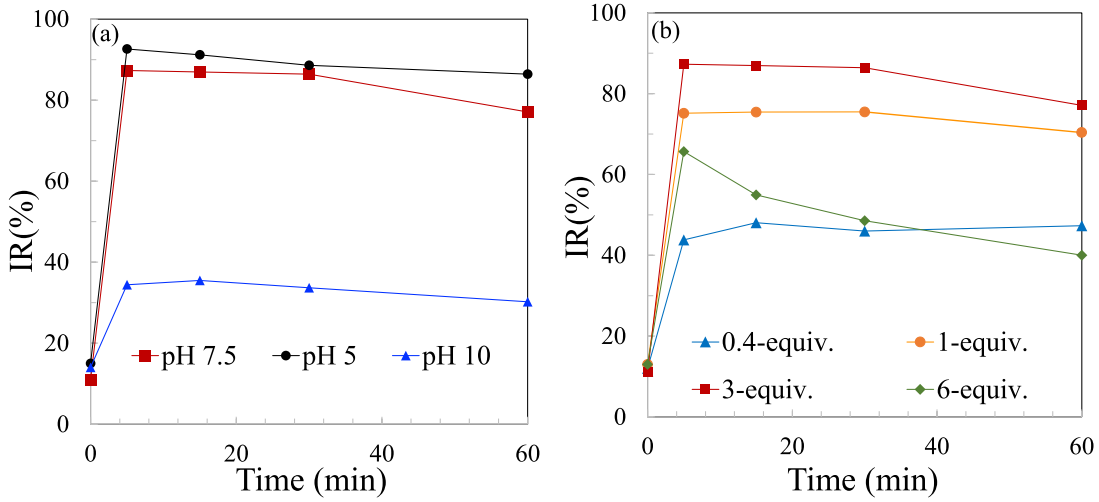

Fig. 1. Acute toxicity variation of BP-1 solution after combined UV-Cl treatment under (a) pH 5, 7.5, and 10 with 3-equiv. of FAC, and (b) pH 7.5 with 0.4-, 1-, 3- and 6-equiv. of FAC, I_{254nm} = 3.5 mW/cm^2.

control, the bioluminescence inhibition ratio (IR%) had significant increase after combined UV-Cl treatment. And the level of acute toxicity was dependent on the experimental conditions. When FAC dose was 3-equiv. (Fig. 1(a)), IR% of the system was lower than 36% within 60 min of treatment at pH = 10, whereas IR% increased to 87% and 93% at pH = 7.5 and 5, respectively. The acute toxicity of controls, including cosolvent control (0.1% acetonitrile in water) and pH buffer controls, treated with combined UV-Cl under different conditions was tested, and no obvious acute toxicity was observed (SI Fig. S1). So, the different IR% values for various reaction solutions in Fig. 1(a) could be attributed to the formation of toxic products. That was, more toxic products formed in acid and neutral systems than in alkaline system. As shown in Fig. 1(b), IR% values of the samples treated with different initial FAC doses exhibited similar pattern, that was, a rapid increase and slight decrease during the 60 min of treatment under neutral pH condition. When the initial FAC doses were 0.4-, 1-, 3-, 6-equiv., IR% values rapidly increased to 43.8%, 75.2%, 87.3% and 65.7% within the initial 5 min, respectively. With the prolonging reaction period, IR% values at 0.4-, 1-, and 3-equiv. of FAC kept stable, whereas at 6-equiv. of FAC, the maximum IR% at 5 min was lower than that at 1-equiv. of FAC, and it had obvious decrease during the prolonging reaction period. This may be attributed to the further transformation of toxic products with the excessive FAC.

UHPLC-QTOF was used to isolate and identify the structure of toxic products during combined UV-Cl treatment. By comparing the acute toxicity variation and the amount of each product, it was found that the relative content of one product TP6 (m/z = 260.9968) had good correlation with the acute toxicity of samples. Fortunately, TP6 was successfully isolated from the reaction solution, it was dissolved in water and its acute toxicity was tested. The dose–response curve of pure TP6 to *Photobacterium Phosphoreum* was shown in SI Fig. S2, its EC50 was 0.8 mg/L. The EC50 value of BP-1 was measured as 30 mg/L in our previous study, the toxicity of TP6 was ca. 40 times higher than that of BP-1. In addition, the detection calibration curve of TP6 was obtained in UHPLC-QTOF-MS, with which the absolute concentration of TP6 in the combined UV-Cl system was determined. As shown in SI Table S1, it was found that the yield of TP6 was about 13% (ca. 6.8 mg/L) at 3-equiv. of initial FAC in neutral pH system. Under this experimental condition, the IR% (87.3%) of the reaction mixture was well consistent with the IR% (ca. 85%) of isolated standard product TP6 calculated from its dose–response curve (SI Fig. S2(a)). And the results obtained at all FAC doses except that at 6-equiv. were similar. According to the above results, TP6 is one of the dominant toxic products in the combined treatment systems, whereas some unknown low-molecular-weight toxic products may be formed under 6-equiv. of FAC.

3.2. Transformation pathways of BP-1 during combined UV-Cl treatment

Totally 8 major transformation products were tentatively identified in UV-Cl system of BP-1. Among them, TP6 is the dominant toxic product with high yield. As shown in SI Fig. S3, BP-1 and its transformation products were well separated after optimizing the UHPLC gradient elution conditions (SI Text S1). A successful separation of the transformation products is beneficial for obtaining a better mass spectrum. The structure analysis for unknown transformation products is a difficult and complicated process, take TP6 as an example to describe the analysis process. High-resolution MS^1 gives an accurate molecular mass for inferring possible molecular formula of TP6 (m/z 260.9950). And there is another peak (m/z 262.9959) in mass spectrum whose intensity is about 1/3 to the peak m/z 260.9950, this information infers that there is a chlorine atom in TP6 molecule. According to the accurate mass-to-charge ratio (m/z), the molecular formula of TP6 is recommended as $C_{13}H_7O_4Cl$ by smart formula software (*Bruker Compass DataAnalysis*), whose theoretical m/z is 260.9955. Besides, the MS^2 of TP6 provides the information of fragment ions, which will be helpful to determine functional group. For example, the fragment ion m/z 232.9965 was formed after removing -C = O from the parent ion. In order to identify the absolute molecular structure of TP6, the fraction of TP6 in the reaction mixtures was isolated and was measured with NMR spectrum. As shown in SI Fig. S4, the results of ^{1}H NMR, ^{13}C NMR and ^{1}H-^{1}HCOSY spectra indicate that TP6 is 2-chloro-3-hydroxyl-6-benzoyl benzoquinone. Additionally, in order to further validate the structure of TP6, ascorbic acid was added to the roughly isolated fraction of TP6, as shown in SI Fig. S5, the peak intensity of TP6 decreased and correspondingly the peak intensity of TP5 increased. The measured m/z of TP5 was 263.0106, 2 larger than that of TP6, implied that TP6 could be reduced to TP5. Therefore, the structure of TP5 can be recommended as phenolic-type product (Fig. 2), whose theoretical m/z is 263.0111. With the similar procedure, the structures of other products were identified based on the MS^1, MS^2 spectra and isotope abundance information, which were shown in SI Figs. S6 and S7.

Based on the identified products and chemical reaction principles, the formation pathway of toxic product TP6 in combined UV-Cl system was proposed and shown in Fig. 2. There are two types of reactions. Electrophilic chlorine substitution was first observed in the initial stage of BP-1 degradation and gradually formed mono-, di-, and trichlorinated BP-1. Subsequently, the chlorinated BP-1 (TP2) were oxidized into TP4, which would be transformed into TP5 in aqueous system. The corresponding reactions were theoretically supported by computation chemistry [36]. Finally, the unstable structure of 1,4-

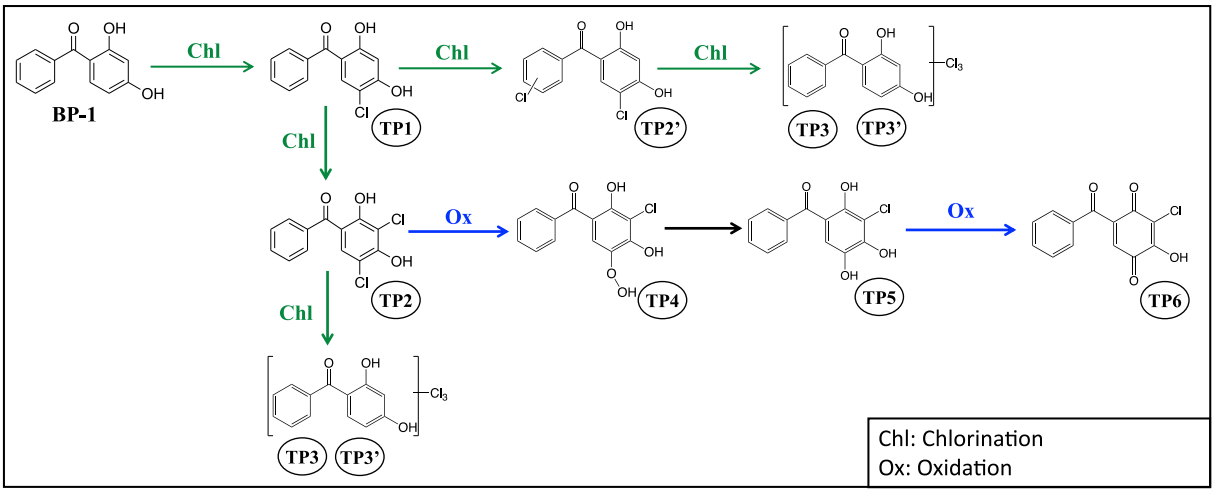

Fig. 2. Proposed formation pathway of TP6 in combined UV-chlorine system.

dihydroxybenzene-type would be readily oxidized into benzoquinone-type TP6. Moreover, a supplementary experiment was designed to confirm that TP2 was an upstream intermediate of TP5. After adding 6-equiv. of FAC into BP-1 working solution, UHPLC-MS spectrum showed that BP-1 was exhausted and TP2 was formed within one hour. Then, the reaction solution was placed under UV irradiation (I_{254nm} = 3.5 mW/cm^2) for 5 min. As shown in SI Fig. S8, the production of TP5 and TP6 increased significantly after UV irradiation. Besides, the energy of C-Cl bond on the aromatic ring is lower than that of C–H bond, the break of C-Cl bond is easier than C–H bond. Especially, the two electron withdrawing groups on the benzene ring, chlorine atom and carbonyl group, make the chlorine atom on the active benzene ring easier to leave [37,38].

3.3. Roles of the reactive species in BP-1 transformation

Many studies have reported that hydroxyl radicals (HO•) and RCSs (Cl•, ClO•, Cl_2^-•) played important roles in the micropollutants degradation during combined UV-chlorine treatment [3,4,8]. Singlet oxygen ($^1O_2$) is another important reactive species, which was also detected in the UV-chlorination system of BP-1 by using ESR. In this study, TP1, TP2 and TP6 were the main transformation products, especially, TP6 was one of the toxic products. Therefore, if HO•, $^1O_2$, and RCSs played important roles in the degradation of BP-1 and the formation of main products should be further explored.

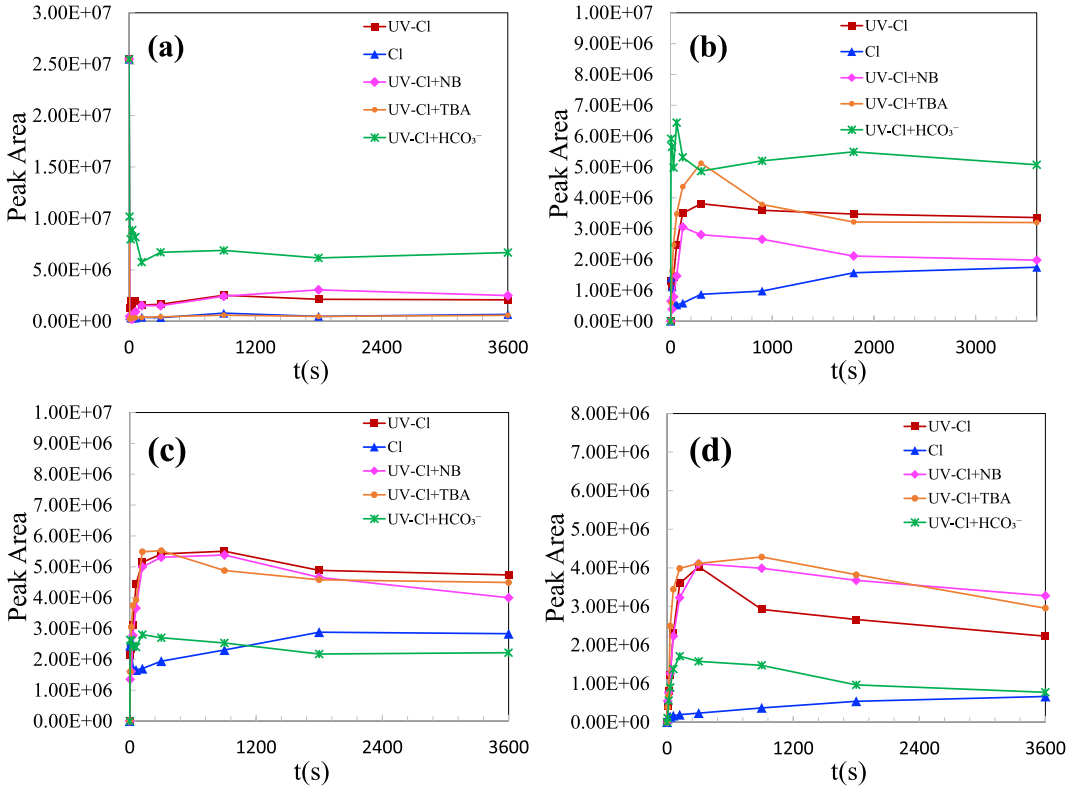

Fig. 3. Effects of radical scavengers on the removal of BP-1 (a), and further transformation of TP1 (b), TP2 (c) and TP6 (d). Conditions: pH = 7.5, $[BP\text{-}1]_0$ = 0.2 mM, $[FAC]_0$ = 3-equiv., I_{254nm} = 3.5 mW/cm^2, $[NB]_0$ = 30 mM, $[TBA]_0$ = 30 mM, $[HCO_3^-]_0$ = 30 mM.

3.3.1. Role of radicals HO·

In order to confirm the formation of HO• in the combined UV-chlorine system of BP-1, DMPO was applied as spin-trapping agent for HO• and ESR spectrum was recorded. As shown in SI Fig. S9(a), the trapped adduct DMPO-•OH had typical four lines (1:2:2:1) which was consistent with other studies [39]. To further confirm the specific contribution of hydroxyl radical to the transformation of BP-1, nitrobenzene (NB) was added to scavenge HO• in the reaction system. As shown in Fig. 3, after adding NB, the relative contents of BP-1, TP1, TP2 did not show obvious changes within the initial 1 h compared with those without adding NB. However, the relative content of TP6 reached a maximal peak but did not decrease significantly in the combined UV-chlorine system spiked with NB. This result implied that HO• merely promoted the further transformation of TP6.

3.3.2. Role of RCSs

So far, the direct ESR detection methods for RCSs were not well developed, the roles of RCSs were indirectly measured in this study. It has been reported that HCO_3^- can scavenge HO•, Cl•, and Cl_2^-•, but not ClO•; *tert*-butyl alcohol (TBA) can scavenge HO•, Cl• and ClO•, but not Cl_2^-• [40]. The rate constants between the two scavengers and radicals were presented in SI Table S3. In addition, as shown in Fig. 3 (a), almost all BP-1 was degraded in both chlorination system (98%) and UV-Cl system (95%) in the initial 5 s. Spiking of TBA had no significant effect on BP-1 degradation, while spiking HCO_3^- inhibited BP-1 degradation (36.7%). These results implied that FAC played more important role in BP-1 degradation than free radicals Cl_2^-•. Correspondingly, for the formation characteristics of main products, the addition of HCO_3^- not only inhibited the transformation of TP1, but also inhibited the formation of TP2 and TP6. Spiking TBA did not vary the trend of TP2, slightly promoted the formation of TP1, whereas inhibited the further transformation of TP6. Based on these results, it could be concluded that Cl_2^-• promoted the formation of TP2 and TP6 in the combined UV-chlorine system. A recent study reported that Cl_2^-• played important role in the degradation of aromatic compounds [5], which was in good agreement with our experiments.

3.3.3. Role of $^1O_2$

ESR experiments were performed to identify $^1O_2$ presence in the combined UV-chlorine treatment of BP-1, in which 2,2,6,6-tetramethyl-4-piperidinol (TEMP) was applied as spin-trapping agent for $^1O_2$. As shown in SI Fig. S9(b), the formed adduct TEMP-$^1O_2$ had typical three lines, which was consistent with previous studies [41]. A small amount of $^1O_2$ was also detected in the chlorination system of BP-1 (SI Fig. S9 (e)). A previous study also found that FAC could directly produce $^1O_2$, and light irradiation promoted the formation of $^1O_2$ [42], which was consistent with our study (SI Fig. S9 (b)(d)). To further confirm the specific contribution of $^1O_2$ to the transformation of BP-1, NaN_3 was added into the combined UV-chlorine system. Interestingly, neither TP5 nor TP6 produced in the presence of NaN_3. A control test showed that spiking of NaN_3 could decrease FAC from 0.62 to 0.47 mM. As discussed in section 3.4.2, TP5 and TP6 could also be produced even at 0.08 mM or 0.2 mM of FAC. Therefore, TP5 and TP6 were not found in the system with NaN_3, the possible reason would be the quench of $^1O_2$ by NaN_3. This result indicated that $^1O_2$ was crucial to the formation of toxic product TP6. The introduction of UV into chlorination system promoted the formation of $^1O_2$, and then promoted the formation of toxic product TP6 (Fig. 4). It was reported that phenanthrene (PEH) would be attacked by $^1O_2$ in UV treatment and two hydroxyl groups were introduced into PEH molecule [43]. Besides, $^1O_2$ was the main reactive species for bisphenol A degradation in peroxy monosulfate / humic acid / visible light system [44].

On the other hand, benzophenone moiety in BP-1 is an important chromophore that can be excited to form triplet state, which can react with dissolved oxygen to generate $^1O_2$ in sunlit environment (Eqs. (1) and (2)) [45]. If this reaction can work, BP-1 would be transformed into benzoyl-benzoquinone in UV irradiation system (Eq. (3)). As shown in SI Fig. S9 (g) and Fig. 5, a weak $^1O_2$ signal was detected and a product benzoyl-benzoquinone analog was observed in UV irradiation system of BP-1. Therefore, in the UV-Cl system of BP-1, $^1O_2$ may be generated via two pathways, one is via the decomposition of FAC, the other is via the reaction between ^{3}BP-1* and O_2 under UV irradiation. As shown in SI Fig. S9 (b)(c)(g), decomposition of FAC is the major pathway of $^1O_2$ generation. To further disclose the intrinsic reaction mechanisms, 3,4,5-trimethylphenol (TMP) and NaN_3 were respectively spiked into UV irradiation system for selectively scavenging ^{3}BP-1* and $^1O_2$, however, neither 2,4,5-Trihydroxybenzophenone (T1) nor 3-hydroxyl-6-benzoyl benzoquinone (T2) were found in the UV systems. Since TP6 and T2 have similar molecular structures, their ionization efficiency and mass peak areas can be compared to roughly estimate the relative production of TP6 and T2 under the same analysis conditions. As shown in SI Fig. S10, the matrix effect on T2 and TP6 determination in UV treatment and UV-Cl treatment could be ignored. Therefore, the production of T2 in UV system (SI Fig. S11 (d)) was quite less than that of TP6 in UV-Cl system (SI Fig. S12 (d)), which could be attributed to the less production of $^1O_2$ in UV system (SI Fig. S9) and lower activity of BP-1

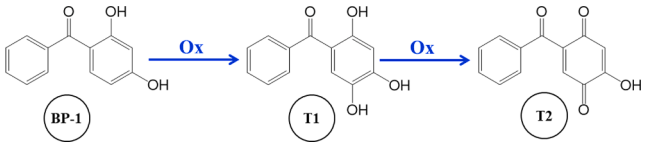

Fig. 5. Proposed pathway for BP-1 transformation under UV irradiation.

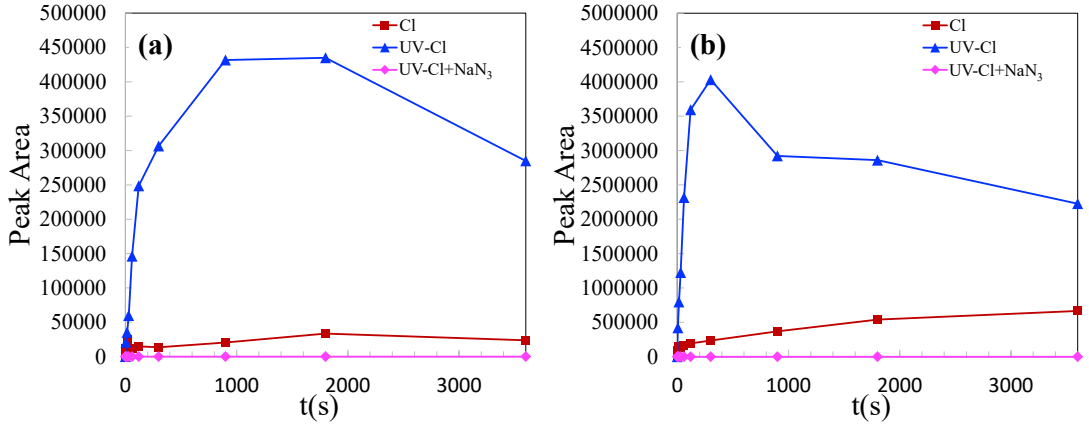

Fig. 4. Effects of $^1O_2$ on the formation of TP5 (a) and TP6 (b). Conditions: pH = 7.5, $[BP\text{-}1]_0$ = 0.2 mM, $[FAC]_0$ = 3-equiv., I_{254nm} = 3.5 mW/cm^2.

comparing with TP2. However, as shown in SI Fig. S11 (a) (b), the reaction mixture of UV system exhibited high toxicity, which were positively correlated with the peak areas of T2. Since T2 and TP6 have similar skeleton, it implies that T2 has similar toxicity with TP6 [46]. Based on the facts mentioned above, it can be concluded that BP-1 could be converted into toxic product benzoyl-benzoquinone analogs in UV, chlorine and combined UV-chlorine systems due to the presence of $^1O_2$; And the different amount of $^1O_2$ in different system resulted in the formation amount of the toxicity product was different distinctly.

$$BP-1 \xrightarrow{h\nu} {}^3BP-1^* \quad (1)$$

$${}^3BP-1^* + O_2 \rightarrow BP-1 + {}^1O_2 \quad (2)$$

$${}^1O_2 + BP-1 \rightarrow T1 \rightarrow T2 \quad (3)$$

3.4. Effects of the operational conditions

3.4.1. Effects of pH conditions

From the results shown in SI Fig. S12, pH conditions had significant effects on BP-1 degradation, the highest degradation percentage was observed in alkaline system, while the lowest in acid system. Considering free radicals played a relatively minor role in BP-1 degradation as discussed in section 3.3, the significant degradation of BP-1 should be attributed to the high reactivity between FAC and BP-1. On one hand, the pKa values of BP-1 are 8.26 and 11.42 [47], so the deprotonation of hydroxyl-groups of BP-1 in alkaline system would increase electron density of benzene ring and promote the electrophilic substitution of BP-1 and FAC. On the other hand, although UV irradiation would decay FAC partially, more FAC remained in alkaline system since the decay of FAC was much faster in acid system ($k_{obs} = 2.46 \times 10^{-4}$ min^{-1}, pH 5) than in alkaline system ($k_{obs} = 1.65 \times 10^{-4}$ min^{-1}, pH 10) under 254 nm irradiation [3]. Correspondingly, it was observed that the species and relative content of each transformation product were dependent on pH conditions. In acid system, less of TP1 was converted into TP2 and TP6, and most of TP1 still remained in solution. However, in neutral and alkaline systems, more TP1 would be further transformed into TP2 and TP6. From this point, we can conclude that pH conditions would not only directly affect the amount of FAC, but also affect the activity of BP-1 and its chlorinated products, which indirectly affect the relative content of toxic product TP6. Especially, TP6 was hardly dissolved and could not be directly detected in the aqueous solution under alkaline condition, but it could be detected after solid phase extraction and acetonitrile elution in the same concentration, which led to lower acute toxicity under alkaline conditions.

3.4.2. Effects of chlorine dose

Since all chlorinated products can be well detected under neutral pH conditions, the impacts of chlorine dose on the BP-1 degradation were explored at pH 7.5. As shown in SI Fig. S13, BP-1 degraded rapidly in the initial 5 s and the degradation percentages reached certain steady levels at different chlorine doses. When chlorine dose increased from 0.4-, to 1-, to 3- and to 6-equiv., the removal percentages of BP-1 within the initial 5 s increased from 42%, to 49%, to 90% and to 93%, respectively. On the other hand, with the increase of chlorine dose, the production of most transformation products, especially TP1, TP2 and TP6, appeared similar trend of first increase and then decrease. The possible reason is that sufficient chlorine would promote the further transformation of intermediate products to down-stream and final products. For example, our previous reported that BP-1 could take place Baeyer-Villiger oxidation and form chloroform in chlorination system [48].

3.4.3. Effects of UV intensity and wavelength

SI Fig. S14 shows the effect of UV intensity on the degradation of BP-1 in the combined UV-chlorine system. When the UV intensity (measured at 254 nm) increased from 1.2, to 2.5 and to 3.5 mW/cm^2, the removal percentages of BP-1 first decreased and then increased. There were two possible reasons, on the one hand, the higher UV intensity promoted degradation of FAC, inhibiting the degradation of BP-1 due to the insufficient FAC. Huang et al. found that high irradiation intensity promoted the production rate of bromate, but decreased its total generation amount due to acceleration of chlorine decomposition in ultraviolet/chlorination processes for bromide-containing water [49]. On the other hand, higher UV intensity increased the production rate of $Cl_2^{-}\bullet$, promoting the degradation of BP-1. As for transformation products, the content of TP1 was the highest under low UV intensity (1.2 mW/cm^2). However, the peaks of TP2 and TP3 reached the maximum at the UV intensity of 2.5 mW/cm^2, and then decreased to the minimum at 3.5 mW/cm^2. The possible reason might be that the higher UV intensity promoted the decomposition of FAC and then inhibited the production of TP1. On the other hand, higher UV intensity promoted the production of reactive species ($Cl_2^{-}\bullet$ and $^1O_2$), and then promoted the transformation of TP1, TP2 and TP3. As shown in SI Fig. S14(d), TP6 degrades slightly with the extension of reaction time when the light intensity is 3.5 mW/cm^2, and there was little difference in the content of TP6 under different irradiation intensities. Particularly, as shown in SI Fig. S15, less TP2 and TP6 were formed under UV_{365} irradiation than under UV_{254} and $UV_{200\text{-}400}$ even at intensity of 1 mW/cm^2. These results suggested that UV_{254} was more effective than UV_{365} on the transformation of Cl-BP-1, probably because the BP-analogues mixture likely absorbed more light energy at smaller wavelengths. The UV spectra of BP-1, TP1 and TP2 shown in SI Fig. S16 provided consistent evidence. Li et al. found that shorter wavelengths of UV-LED were demonstrated to be more effective in acetaminophen degradation [50].

3.5. Environmental significance

Due to the wide use of BP-1 in industrial products, it is easy to be released into the environment and water treatment plants. BP-1 had average concentrations of 31–148 ng/L in influent of a sewage treatment plant in Spain [51]. The transformation of BP-1 in disinfection process may affect water quality safety due to their potential formation of toxic products benzoquinone analogues, especially in combined UV-Cl process. In order to study the transformation mechanism of BP-1 and the formation of toxic products in the real water environment, a combined solar light-chlorine treatment of BP-1 was conducted in 500 mL tap water. Considering the real environmental parameters, the initial concentration of BP-1 was set as 100 ng/L, the initial chlorine dose was set as 0.5 mg/L. The reactor was placed on the top of our building, during the experimental period, the sunlight intensity was measured as 0.2–0.5 mW/cm^2. After one hour of treatment, the 500 mL mixture was evaporated and concentrated to 50 μL for UHPLC-MS analyze. As shown in SI Fig. S17, TP1, TP2 and TP6 were detected out although the yield of TP6 was not as high as that in section 3.1, the possible reason could be attributed to the low concentration of FAC and the low intensity of sunlight. In this study, BP-1 was just taken as an example, although the concentration of BP-1 and its toxic transformation products in samples were very low, the potential risk of benzoquinone-analogues transformed from BPs cannot be ignored [29].

4. Conclusions and practical implications

BP-1 could be efficiently degraded in combined UV-chlorine system, FAC played an important role in the degradation of BP-1, and $Cl_2^{-}\bullet$ promoted the degradation of BP-1. The reaction mixture exhibited much higher acute toxicity than BP-1, the key toxic product TP6 (benzoyl benzoquinone analogue) was successfully isolated, whose acute toxicity was 40 times higher than BP-1. Active species $^1O_2$ played a crucial role in the formation of TP6, while HO• had a slight effect on the further degradation of TP6. The operational conditions such as chlorine dosage, pH, UV intensity and wavelength could affect the formation and distribution of the transformation products including toxic product TP6.

Combined UV-chlorine system is currently used as AOP technique for pollutants degradation, in which newly identified reactive species $^1O_2$ plays an important role in pollutants degradation. The contribution of $^1O_2$ to the formation of toxic product TP6 was firstly reported in this study, there is no reason to doubt that $^1O_2$ can play important role in other disinfection or AOP systems, it is worthy of further exploring in the future. Especially, with the help of a toxicity-directed identification method [35], a highly toxic product TP6 benzoyl benzoquinone was rapidly identified. Halobenzoquinones have been proved as the most toxic DBPs so far [52], which could be further converted into smaller molecular DBPs, such as THMs and HAAs during disinfection process [53]. Therefore, the potential environmental impacts of benzoyl benzoquinone analogues should be concerned seriously, and the toxicity-directed identification method should be popularized.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.cej.2021.134344.

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