Journal of Photochemistry and Photobiology A: Chemistry 230 (2012) 1–9

Contents lists available at SciVerse ScienceDirect

Journal of Photochemistry and Photobiology A: Chemistry

journal homepage: www.elsevier.com/locate/jphotochem

Degradation of polycyclic musk HHCB in water by O_3, UV, and UV/O_3

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ARTICLE INFO

Article history:
Received 10 October 2011
Received in revised form
12 December 2011
Accepted 30 December 2011
Available online 8 January 2012

Keywords:
Polycyclic musk HHCB
Ozonation
UV radiation
Kinetics
Quantum yield

ABSTRACT

An investigation on the degradation of polycyclic musk HHCB by three processes (ozone alone (O_3), UV radiation alone (UV), and UV plus ozone (UV/O_3)) was conducted and the kinetic parameters (second-order reaction rate constants and quantum yield) were determined as well. HHCB underwent rapid degradation during ozonation process, but unsatisfied performance was shown for UV and UV/O_3 processes. Degradation efficiencies of HHCB follow the trend of O_3 > UV/O_3 > UV. Removal of HHCB by O_3 was appreciably affected by pH, ozone dosage, and bicarbonate alkalinity, while only the bicarbonate alkalinity and UV intensity exerted influence on HHCB degradation for UV process. Scavenger experiments indicated that the synergistic effect between direct ozonation and indirect free radical oxidation contributed to the HHCB destruction for ozonation process, while direct photolysis was responsible for UV degradation of HHCB. According to the yeast estrogen screen (YES) bioassay results, intermediates with similar estrogenic activity to the parent compound HHCB were assumed to be generated during the three degradation processes. The second-order reaction rate constants of HHCB with O_3 and hydroxyl radical (OH•) and quantum yield of HHCB under 254 nm UV light were determined to be $k_{O_3\text{-HHCB}} = 153.8 \pm 6\ M^{-1}\ S^{-1}$, $k_{OH\bullet\text{-HHCB}} = 6.3 \pm 0.7 \times 10^9\ M^{-1}\ S^{-1}$, and $\phi_{HHCB} = 0.012 \pm 0.002$ mol Einstein^{-1}, respectively, which suggested HHCB had moderate reactivity towards ozone and was resistant to UV radiation.

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1. Introduction

The occurrence of polycyclic musks (PCMs) in different environmental compartments was first reported in 1994 [1]. The two typical PCMs are 7-acetyl-1,1,3,4,4,6-hexamethyltetrahydronaphthalene (AHTN, tonalide) and 7-acetyl-1,1,3,4,4,6-hexahydro-4,6,6,7,8,8-hexamethylcyclopenta (g)-2-benzopyrane (HHCB, galaxolide), representing about 95% of the total market volume for the class of fragrance ingredients [2]. These two PCMs are widely used as fragrances in soaps, air fresheners, perfumes, detergents, and other household cleaning products [3]. The frequent use of these two chemicals, combined with their hydrophobic properties ($\log K_{ow} \approx 5.7$) and lack of ready biodegradability [4,5], has resulted in their widespread occurrence in the environment [6–8]. PCMs are to be found not only in various environmental compartments, but also in the aquatic food chain, as well as in fatty tissue and mothers' milk [9].

Due to the widespread use of AHTN and HHCB and their potential for bioconcentration, there is increasing concern about the toxicity of AHTN and HHCB to human and other receptors, such as wildlife species and fish. AHTN and HHCB have been regarded as environmental contaminants classified as pharmaceuticals and personal care products (PPCPs), and their potential risk is being increasingly assessed.

Since surface water is most affected and there is no device specifically designed to remove PCMs, AHTN and HHCB may first pose a problem to utilities that use surface water as a source for drinking water production. Therefore, there is an urgent need for additional advanced technologies that can reduce the amount of AHTN and HHCB in the environment. In the last few years, a number of advanced technologies for the removal of AHTN and HHCB in the aqueous environment have been developed, including ozonation and ozone based advanced oxidation processes (AOPs) [10], flotation [11], biodegradation [12,13], direct photolysis or photocatalytic degradation [14,15], and activated carbon absorption [16]. Frequent detection of AHTN and HHCB with a relative high concentration in the sewage sludge indicated that AHTN and HHCB tend to be sorbed onto the sludge but not ready to biodegrade [17]. Although absorption and air stripping can effectively remove AHTN and HHCB because of their high octanol/water partition coefficient ($\log K_{ow}$) and Henry's constants (Table 1), further treatment before final disposal may be needed due to the fact that the pollutants are just transferred from water to another medium. Ozonation, UV radiation, and advanced oxidation processes have proven to be effective for the degradation of AHTN and HHCB [10,12–14,18].

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1010-6030/$ – see front matter. Published by Elsevier B.V.
doi:10.1016/j.jphotochem.2011.12.017

Table 1
Molecular structure and characteristic of HHCB.

Property	Value	Ref.	Structure formula for HHCB
Empirical formula	$C_{18}H_{26}O$	[1]	
Molecular weight ($g\,mol^{-1}$)	258.4	[1]	
Water solubility ($mg\,L^{-1}$, 25 °C)	1.75	[4]	
Log K_{ow} (25 °C)	5.9	[4]	
Henry's law constant (25 °C)	36.9	[4]	

Currently, limited data are available in the literature on the removal of typical polycyclic musk HHCB from contaminated water and the objective of these literatures was primarily focused on establishing the degree of degradation of HHCB. Little or no emphasis has been given to the effects of operational parameters, such as water quality, pH, initial concentration of HHCB, oxidant dosage and UV intensity, on the degradation efficiency, as well as the kinetic parameters.

Byproducts of organic contaminants formed during treatment must always be considered because of their potential risk. Several studies have found that oxidation of some endocrine disrupting chemicals (EDCs) with chlorine resulted in an increase in estrogenic activity [19–21]. Ozonation products of antibiotics roxithromycin and trimethoprim were reported to preserve intact moiety responsible for antimicrobial activity [22]. A discrepancy between removal of estrogenic activity and parent compound reduction was discovered when BPA was treated via UV/H_2O_2 AOP, suggesting the presence of some oxidation byproducts that may retain estrogenic activity [23]. Trovo et al. [24] found that photoproducts of sulfamethoxazole showed an increase from 60% to 100% immobilization of *Daphnia magna* after 30 h of solar radiation. That is to say, the loss of chemical detection of organic pollutants by HPLC or other instruments does not mean the loss of biological activity under certain circumstances. In addition, HHCB was found to show a weak estrogenic activity [25–27]. Therefore, the estrogenic activity associated with HHCB degradation by UV, O_3, and UV/O_3 processes is also to be examined, thus allowing evaluating the detoxification efficiency of the three processes.

The goal of the present work is (i) to compare the degradation efficiencies of HHCB during O_3, UV, and O_3/UV processes, (ii) to obtain information on the toxicity evaluation of intermediates formed during the three investigated processes, the YES bioassay was employed, (iii) to provide information on the influence of different parameters, including ozone dosage, UV intensity, bicarbonate ion concentration, and pH of the aqueous solution, and (iv) to study the reaction kinetics of HHCB with O_3 and UV. The quantum yield of direct photolysis for HHCB at 254 nm and second-order reaction rate constants of HHCB with O_3 and $OH^{\bullet}$ will be determined.

2. Materials and methods

2.1. Materials

HHCB (Galaxolide) was provided by the John D. Walsh Company. All other chemical reagents were purchased from Sigma–Aldrich Chemical Company or Merck and used in experiments without further purification. Ultra high purity water used to prepare solutions was produced by Milli Q gradient A10 system (Millipore Corporation, Chicago, IL). Ozone was generated in an Ozone Engineering LG-7 ozone generator (Ozone Engineering Inc., El Sobrante, CA) fed with pure oxygen (99.5%). Low-pressure mercury lamps (Tokyo Optical Co., Ltd., Tokyo, Japan) were used as UV-radiation source. The recombinant yeast strain used in the YES bioassay was kindly provided by Research Center for Eco-Environmental Science, Chinese Academy Sciences, authorized by Professor Sumpter, Brunel University (Middlesex, UK).

2.2. Experimental approach and conditions

The schematic diagram of experimental set-up used in present study is shown in Fig. 1. The set-up consists of a photochemical chamber and a reaction vessel. The photochemical chamber contained 16 installed positions for UV lamps and different UV intensities were obtained by using different numbers of lamps. The UV transparent quartz reaction vessel has an internal diameter of 13 cm and a height of 30 cm, and was filled with 3 L of solution during each experiment. The reaction vessel was equipped with openings for adding concentrated ozone solution, aqueous ozone and pH probe, and sampling collection.

The reactor was operated in a batch mode and the agitation was provided using a magnetic stirrer. HHCB stock solution (about $5\,g\,L^{-1}$) was prepared using acetonitrile as solvent due to its low water solubility (Table 1). Standard solution was prepared in 250 mL volumetric flask by transferring an appropriate volume (2.5 mL) of HHCB stock solution followed by dilution in Milli-Q water and evaporation of acetonitrile (placed in a 60 °C water bath for 4.5 h), and then the accurate concentration of HHCB was calibrated. Working solution was made by diluting the standard solution with Milli-Q water. For ozonation experiment, ozone stock solution instead of ozone gas bubbling was used to dose ozone to achieve designed dose [28]. For UV experiment, appropriate numbers of UV lamps were inserted into the photochemical chamber and solution of HHCB prepared at desired concentration was placed inside the reactor. The experiments were conducted at room

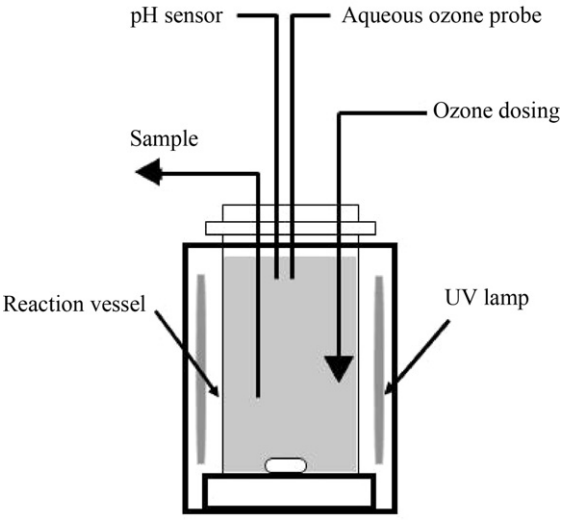

Fig. 1. Experimental setup.

temperature and the increase in temperature due to UV light exposure was less than 2 °C.

Solution pH was adjusted by means of H_3PO_4, KH_2PO_4 and Na_2HPO_4 addition. The concentration of bicarbonate ion (HCO_3^-) was adjusted using 1.0 M sodium bicarbonate ($NaHCO_3$) solution. The ionic strength was kept at a constant value of 0.1 M by using a proper amount of NaCl. Finally, 2.0 mL of aliquot samples were withdrawn periodically and analyzed for residual concentration of HHCB. The residual ozone in samples was quenched with 20 μL pre-added acidified sodium thiosulfate ($Na_2S_2O_3$) at 0.5 mM to stop further reaction after sample withdrawal.

In addition, a control experiment was conducted to check whether there was loss of HHCB resulted from volatilization or adsorption. In the control experiment, model solution containing HHCB was continuously stirred and the concentration of HHCB was monitored. The results indicated that few HHCB was lost in 30 min.

To determine the second-order rate constant of HHCB with hydroxyl radical ($k_{OH^\bullet\text{-HHCB}}$) and the quantum yield of HHCB under UV light at 254 nm (ϕ_{HHCB}), the competitive kinetic methods were applied [29,30]. The $k_{OH^\bullet\text{-HHCB}}$ was determined from ozonation of mixtures of HHCB (1 mg L^{-1}) and *p*-chlorobenzoic acid (*p*CBA, 0.5 μM) and the ϕ_{HHCB} was finally obtained from direct photolysis of mixtures containing 1 mg L^{-1} HHCB and 10 mg L^{-1} atrazine whose photolytic parameters are known [31].

2.3. Analytical methods

The aqueous ozone concentration was determined using Q45H Dissolved Ozone Analyzer (Analytical Technology, Inc., Collegeville, PA) calibrated by the Indigo method [32]. Hydrogen peroxide (H_2O_2) was determined using the peroxidase-DPD method [33]. The total organic carbon (TOC) was analyzed by TOC analyzer (TOC-V_{CPH}, Shimadzu, Japan). The average UV fluence rate (W L^{-1}) was measured by the method of potassium ferrioxalate actinometry [34].

UV–vis spectra of HHCB with varying concentration in distilled water at pH = 7 were determined with a UV-2550 UV–vis spectrophotometer (Shimadzu, Japan) in the wavelength range of 200–800 nm. Molar extinction coefficient (ε) at 254 nm can be obtained according to the Beer's law.

The concentrations of HHCB, *p*CBA, and atrazine are determined using a Dionex Ultimate 3000 high performance liquid chromatography equipped with a Dionex 120 C18 column (3 μm). An eluent consisting of 60%:40% methanol:H_2O (adjusted to pH 2 with H_3PO_4) was used for *p*CBA and 50:50 methanol:H_2O was used for atrazine. A 60% acetonitrile (ACN) and 40% water (v/v) mobile phase was applied to measure HHCB. The flow rate was fixed at 0.5 mL min^{-1} and the column temperature was maintained at 25 °C. UV absorbance at 234 and 221 nm was used for *p*CBA and atrazine measurement, respectively. HHCB is quantified using fluorescence spectroscopy detection at λ_{ex} = 275 nm, λ_{em} = 295 nm. Sample vials for HHCB were filled with no headspace in an effort to avoid loss to volatilization. Determinations were performed in triplicate, and each experiment was repeated three times, and the data were averaged. The standard deviations were usually within 3% unless otherwise noted.

2.4. Toxicity evaluation

The YES assay was performed according to the method described by Rosenfeldt et al. [35] and Chen et al. [23]. All optical density (OD) values from YES assays were presented as $OD_{405\,nm} - OD_{630\,nm}$ and converted to HHCB equivalent concentration units via transformation of a linear dose response regression curve of HHCB standards. HHCB equivalent concentration (C) was normalized to initial HHCB equivalent concentrations (C_0) as C/C_0 and plotted with HPLC results. When OD values of samples below the detection limit, samples were concentrated 100 fold by freeze-drying. The recovery for freeze-dried samples was 103–114%.

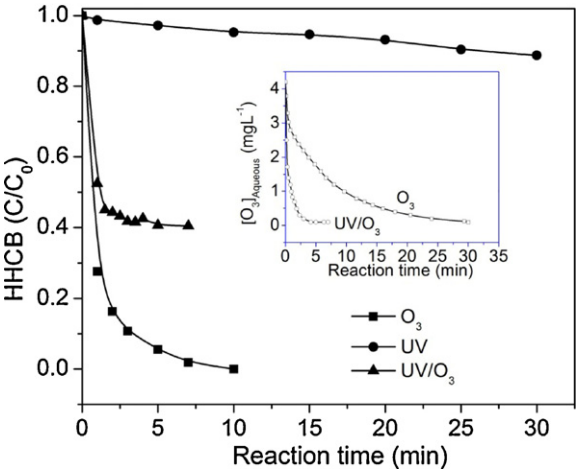

Fig. 2. Degradation curves of HHCB by different processes. Experimental conditions: pH = 7.0, ionic strength 0.1 M, $[HHCB]_0$ = 1 mg L^{-1}, $[O_3]_0$ = 4.0 mg L^{-1}, UV incident intensity I_0 = 0.42 W L^{-1}, oxygen gas flow rate 0.31 L min^{-1}.

3. Results and discussion

3.1. Degradation of HHCB by different processes

Fig. 2 shows the degradation curves of HHCB as a function of reaction time in O_3, UV, UV/O_3, and O_2 stripping processes. The UV process led to only 11.3% HHCB degradation after a reaction time of 30 min, which indicated that HHCB was resistant to UV irradiation. The low extinction coefficient and quantum yield, which was discussed in the following section, could illustrate this phenomenon. Better HHCB degradation rate (94.5% after 5 min of reaction time) was observed for ozonation process. However, the combined use of UV and O_3 (UV/O_3), one of AOPs, produced only 59.4% HHCB degradation after 5 min.

The results described previously indicated that HHCB was easy to degrade by O_3, and thus stabilizing the ozone residual was of great benefit to the degradation of HHCB. It can be seen from the insert in Fig. 2, UV/O_3 process showed a rapid ozone depletion compared to the ozonation process. As is known to us, ozone exhibits a strong absorbance at 258 nm (ε_{258} = 3000 M^{-1} cm^{-1}) [36], so most of ozone in the solution was destroyed rapidly under the irradiation of the 254 nm UV light (no ozone residual after 5 min), thus decreasing the ozone involved in the degradation of HHCB. This may explain why the use of UV together with ozonation shows an unsatisfying performance in HHCB degradation. On the other hand, the UV/O_3 process, representing a kind of AOPs, did not show the advantage of strong oxidative $OH^\bullet$. This may attribute to the nonselectivity of $OH^\bullet$ which is capable of reacting with both HHCB and reaction intermediates.

However, the UV/O_3 process displayed the best performance for TOC removal among the UV, O_3 and UV/O_3 processes in the presence of ozone residual (as shown in Fig. 3). The TOC removal rates after reaction time of 5 min by O_3 and UV/O_3 process are 5.9% and 12.1%, respectively. For UV process, although 11.3% of HHCB was removed within 30 min, no obvious TOC removal was observed. It was estimated that there might be accumulation of intermediate products and the HHCB intermediates was more resistant to photodegradation than HHCB itself.

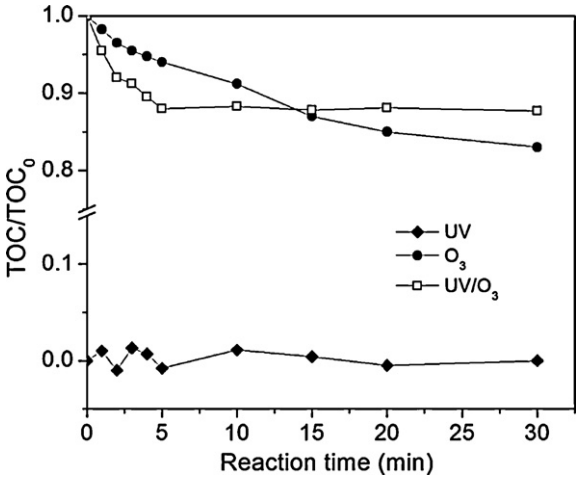

Fig. 3. Degradation curves of TOC by O_3, UV, and UV/O_3. Experimental conditions: pH = 7, ionic strength 0.1 M, $[HHCB]_0 = 4.79\,mg\,L^{-1}$, $[O_3]_0 = 4.0\,mg\,L^{-1}$, UV incident intensity $I_0 = 0.42\,W\,L^{-1}$.

3.2. Scavenger experiment

Based upon the results in Section 3.1, it could be deduced that direct ozonation and UV photolysis mainly contributed to the removal of HHCB. To clarify the possible degradation pathway, ozonation and photolysis experiments were conducted in the presence of *t*-butanol (20 mM), known as scavenge OH• ($k_{•OH} = 6.0 \times 10^8\,M^{-1}\,S^{-1}$) [37]. With the addition *t*-butanol, the removal rate of HHCB during O_3 and UV processes respectively decreased by about 8.9% and 2.7% after 30 min of reaction time compared to the case without scavenger (Fig. 4). Therefore, it can be concluded that the synergistic effect between direct ozonation and radical-type oxidation contributed to the HHCB degradation for ozonation process. As to the UV process, minor change was observed in the presence and absence of scavengers, reflecting that direct photolysis is the main pathway responsible for HHCB degradation, although indirect photolysis characterized by the formation of reactive species such as OH• also made its contribution.

3.3. Toxicity assessment

If one or more transformation intermediates of HHCB possessed a similar or even a higher level of estrogenic activity compared to the parent compound HHCB, the rate of estrogenic activity reduce

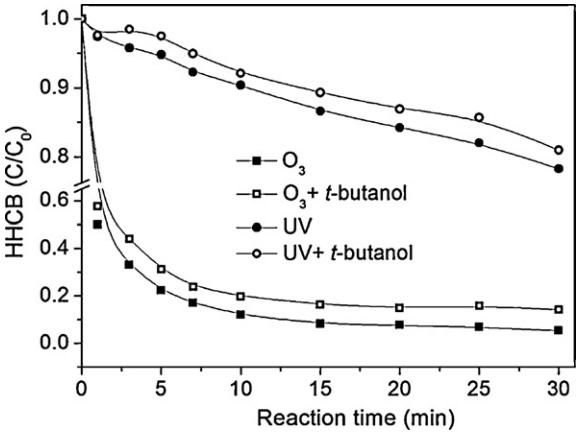

Fig. 4. Effect of *t*-butanol on the degradation of HHCB by O_3 and UV. Experimental conditions: pH = 7, ionic strength 0.1 M, *t*-butanol 20 mM, $[HHCB]_0 = 1\,mg\,L^{-1}$, $[O_3]_0 = 1.2\,mg\,L^{-1}$, UV incident intensity $I_0 = 0.88\,W\,L^{-1}$.

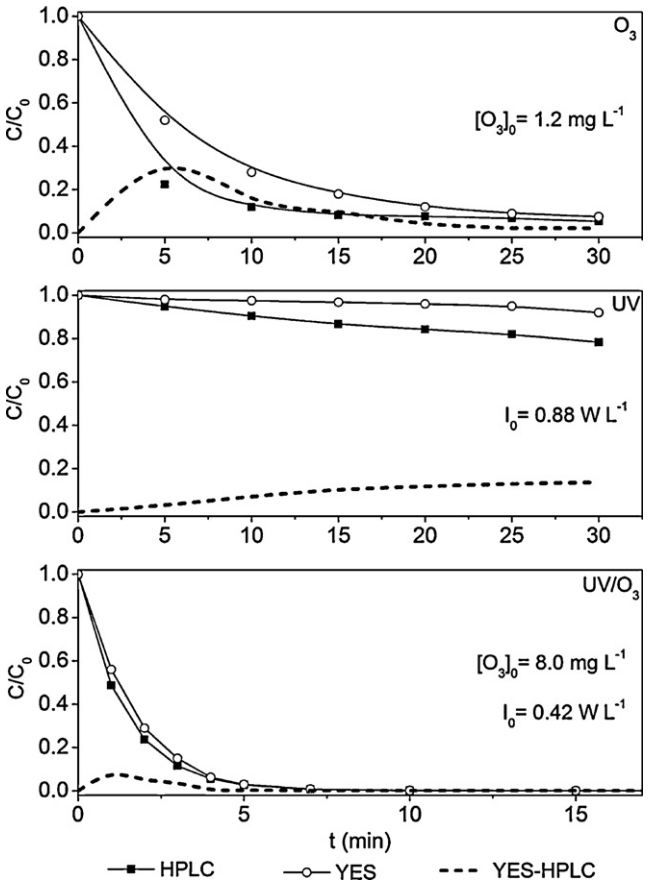

Fig. 5. Evolution of toxicity associated with HHCB degradation by O_3, UV, and UV/O_3 processes. Experimental conditions: pH = 7, ionic strength 0.1 M, $[HHCB]_0 = 1\,mg\,L^{-1}$. Empty circles (○) represent the normalized values of estrogenic activity. Full squares (■) represent the normalized concentrations of parent HHCB. Dashed lines show differences between two averages.

would be retarded compared to the degradation rate of HHCB. Interestingly, discrepancy was observed between C/C_0 value of estrogenic activity and that of HHCB for all the three processes at certain stages (UV/O_3 process) or during the whole reaction course (O_3 and UV processes), as shown in Fig. 5. The difference between the two values was assumed to represent the estrogenic activity of degradation products (shown as short dashed lines in Fig. 5). The results suggested that while HHCB was transformed and the total estrogenic activity was decreasing, certain degradation byproducts were produced which retain estrogenic activity. However, one point should be noted: these data may reflect activity of a single or possibly a mixture of estrogenic degradation product(s) that lead to additive or synergistic effects together with the remaining HHCB. Further study is needed. Another point was important to mention that different aqueous ozone concentrations and UV incident intensity were applied for the three treatment processes in order to favor conducting the relative bioassay experiments, although different oxidant or UV dose may result in different influence on the toxicity evolution during the degradation process [23]. We here just attempted to establish proof for the question: whether the decrease of HHCB concentration corresponded to the loss of its biological activity.

Ozone reactivity limited to particular sites (mainly double bonds, activated aromatic systems and non-protonated amines) is commonly observed during ozonation processes [38] and small modifications in the parent compound's structure are expected for the primary attack. Direct UV photolysis achieves contaminant removal mainly through dimerization, hydroxylation,

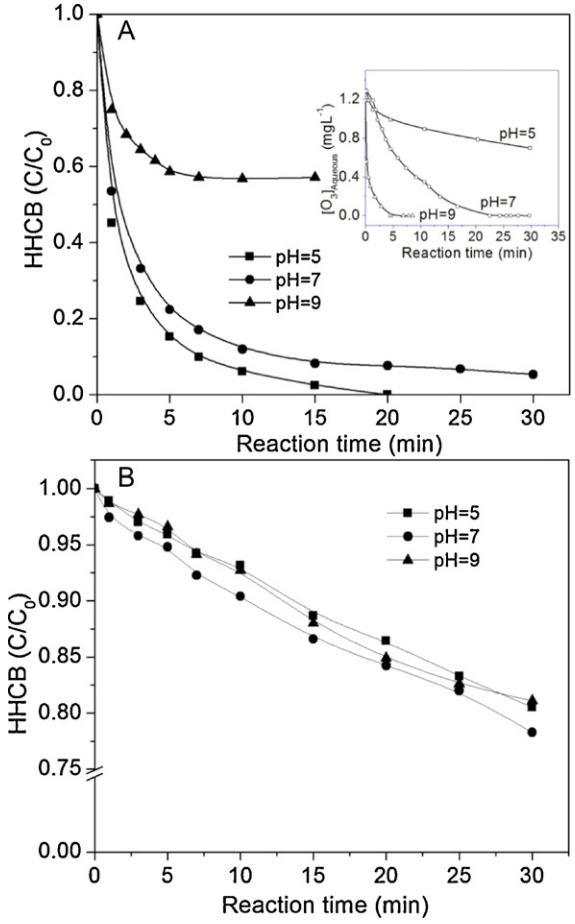

Fig. 6. Effect of pH on the degradation of HHCB by O_3 and UV. Experimental conditions: ionic strength 0.1 M, $[HHCB]_0 = 1\,mg\,L^{-1}$, $[O_3]_0 = 1.2\,mg\,L^{-1}$, UV incident intensity $I_0 = 0.88\,W\,L^{-1}$.

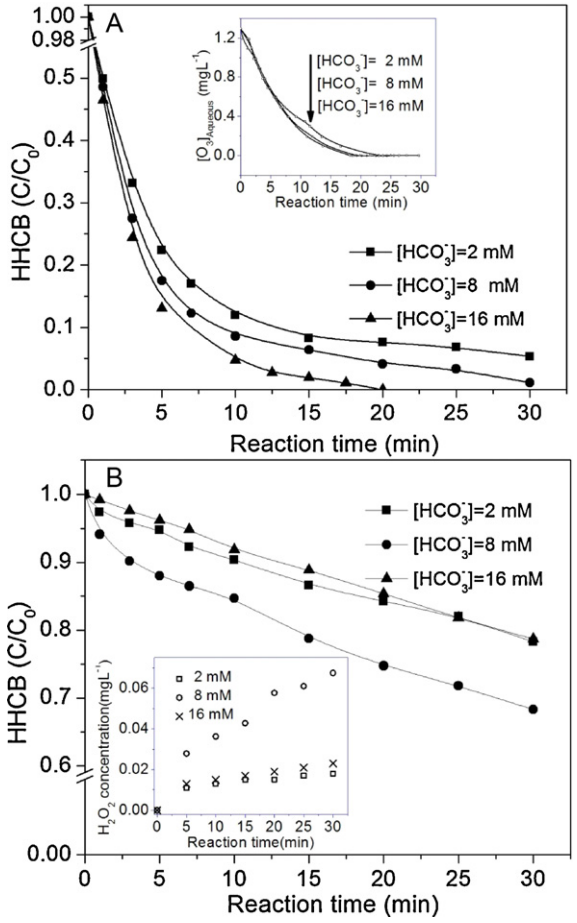

Fig. 7. Effect of bicarbonate on the degradation of HHCB by (A) O_3 and (B) UV. Experimental conditions: pH = 7.0, ionic strength 0.1 M, $[HHCB]_0 = 1\,mg\,L^{-1}$, $[O_3]_0 = 1.2\,mg\,L^{-1}$, UV incident intensity $I_0 = 0.88\,W\,L^{-1}$.

H-abstraction, heterolytic cleavage, and scission of bonds [39]. The characteristics of ozonation and direct UV photolysis processes make them poorly mineralize organic pollutants [40–42], causing accumulation of degradation products. It was reasonable to suppose that the more accumulated intermediates there were, the higher potential for toxicity reserving or increasing the treated water would show. For UV/O_3 AOP, the main oxidative specie is OH•, which reacts with most water constituents with nearly diffusion controlled rates [38]. This high reactivity leads to a high mineralization capacity and thus can reduce accumulation of degradation products. However, OH• attack initiates oxidation of compounds by hydrogen abstraction to form carbon center radicals or addition to double bonds to form hydroxylation products [36], which keep the intact structure as the parent compounds. Similar products were reported in Calza's work, where two transformation products formed through HHCB hydroxylation were identified [15]. This may illustrate the discrepancy between HHCB disappearance and estrogenic activity removal during the first 5 min for UV/O_3 process.

3.4. Effects of operational parameters

3.4.1. Effect of pH

Fig. 6 presents the effect of pH on the removal of HHCB during O_3 and UV processes. At pH 5.0, the maximum HHCB removal of about 97.5% was observed at 15 min of O_3 process. HHCB removal efficiency decreased as the pH increased from 5.0 to 9.0, with removal of 91.7 and 42.9% at pH 7.0 and 9.0, respectively. It is well known that at lower pH levels the decomposition of aqueous ozone occurs very slowly and the removal of organic chemicals is primarily due to its reaction with aqueous ozone, while increasing the pH will accelerate decomposition of aqueous ozone (insert in Fig. 5). Thus an increase in pH, going against the stability of ozone residual, will result in a decrease in HHCB removal, despite of increase of OH• formation on this moment. The variation of pH exerted little influence on HHCB elimination during UV process, indicating the reactivity of HHCB with UV light was almost not affected by the solution pH.

3.4.2. Effect of bicarbonate

The effect of bicarbonate (HCO_3^-) on the degradation rate of HHCB during O_3 and UV was investigated by varying HCO_3^- concentration from 2.0 mM to 16 mM (Fig. 7). For O_3 process, the removal of HHCB increased with an increase in HCO_3^- concentration up to 16 mM (Fig. 7A). Bicarbonate is known as inhibitor of ozone decomposition and scavenger of OH• [43], which means the presence of HCO_3^- benefits the stability of aqueous zone and thus favors the degradation of HHCB. However, promotion on HHCB degradation during the UV process was observed with the HCO_3^- concentration increasing from 2 mM to 8 mM, and the further increasing of HCO_3^- concentration (16 mM) result in slight increase of HHCB degradation compared to the case of 2 mM HCO_3^- (Fig. 7B). Under UV irradiation alone, HHCB was mostly degraded through direct photolysis and indirect photolysis was believed to occur to a certain extent, as mentioned above. In addition, HCO_3^- does not absorb UV light. So the HCO_3^- ion was supposed to affect the indirect photolysis of HHCB in some other ways.

Hydrated electrons and hydrogen atoms may be generated by the UV irradiation of water, these species together with oxygen could produce the peroxide precursor ($HO_2^{\bullet}$ and $O_2^{-\bullet}$), which then may form hydrogen peroxide (H_2O_2) [44–47]. In addition, H_2O_2 could be generated due to the photo-chemical breakdown of organic substrates [48].

$$O_2^{-\bullet} + H^+ \rightarrow HO_2^{\bullet} \quad (1)$$

$$O_2^{-\bullet} + HO_2^{\bullet} \rightarrow HO_2^- + O_2 \quad (2)$$

$$HO_2^- + H^+ \rightarrow H_2O_2 \quad (3)$$

$$HO_2^{\bullet} + HO_2^{\bullet} \rightarrow H_2O_2 + O_2 \quad (4)$$

$$OH^{\bullet} + OH^{\bullet} \rightarrow H_2O_2 \quad (5)$$

$$\text{Substrates} + h\upsilon \rightarrow H_2O_2 + \text{Products} \quad (6)$$

On the other hand, H_2O_2 also can be consumed by direct photolysis or reacting with other intermediate species produced in the reactions mentioned above through the termination steps [46,48,49].

$$H_2O_2 + HO_2^{\bullet} \rightarrow OH^{\bullet} + H_2O + O_2 \quad (7)$$

$$H_2O_2 + O_2^{-\bullet} \rightarrow OH^{\bullet} + OH^- + O_2 \quad (8)$$

$$H_2O_2 \rightarrow HO_2^- + H^+ \quad (9)$$

$$H_2O_2 + h\upsilon \rightarrow 2OH^{\bullet} \quad (10)$$

Hydrogen peroxide combined with UV light can promote the production of $OH^{\bullet}$, thus enhancing the degradation of organic pollutants. So the equilibrium concentrations of H_2O_2 during UV process may explain the effect of HCO_3^- on HHCB removal. In order to testify this point, the concentration of H_2O_2 is monitored during the UV photolysis of HHCB in presence of HCO_3^- (insert in Fig. 7B). UV irradiation of water containing 2 mM and 16 mM HCO_3^- resulted in small and almost constant amount of H_2O_2, presumably resulted from the low formation of H_2O_2 or the generation rate being equal to the depletion rate. Explicit accumulation of H_2O_2 was observed when 8 mM HCO_3^- was present in the solution, suggesting that the formation fate was higher than the consumed rate. Zhao et al. [50] also found that the presence of HCO_3^- at low concentration can promote the formation of H_2O_2 but decrease the H_2O_2 formation at high concentration for catalytic ozonation of nitrobenzene. Besides, HCO_3^- can capture $OH^{\bullet}$ to form bicarbonate radical, and bicarbonate radical was able to further react with H_2O_2 to the produce $OH_2^{\bullet}$. That is to say, the presence of HCO_3^- could influence the formation of H_2O_2 by involving in the chain reactions mentioned above and thus exert effect on HHCB degradation during UV process.

3.4.3. Effect of ozone dosage and UV intensity

The effect of ozone dosage and UV intensity on the removal of the target HHCB was investigated using ozone dosage of 1.2, 2.4, and 4.0 mg L^{-1} and UV intensity of 0.42, 0.88, and 1.71 W L^{-1}. The results are presented in Fig. 8 on a semi-log scale. Results revealed that as the ozone dosage or UV intensity increased, the removal of HHCB also increased. Within 15 min of ozonation, ozone dosage of 1.2, 2.4, and 4.0 mg L^{-1} resulted in HHCB removal of about 92.8, 97.5, and 100%, respectively. This could be expected because an increase in ozone dosage results in an increase in aqueous ozone which either directly reacts with HHCB or directly decomposes to produce $OH^{\bullet}$, and the $OH^{\bullet}$ in turn reacts with HHCB. Only 11.3, 21.7, and 34.0% of HHCB were removed within 30 min at the UV intensity of 0.42, 0.88, and 1.71 W L^{-1}, respectively. The results could be attributed to the increasing available incident photon with the increasing UV intensity.

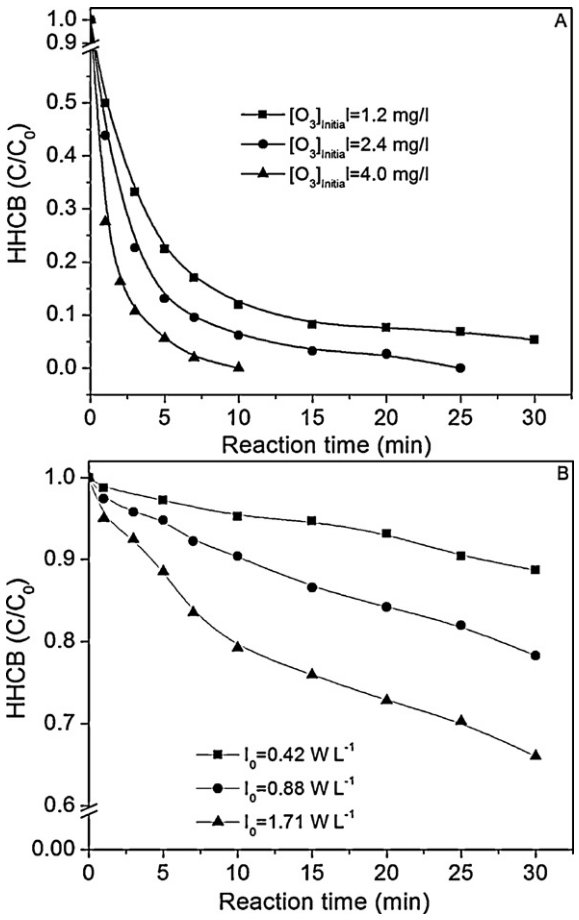

Fig. 8. Effect of ozone dosage (A) and UV intensity (B) on HHCB degradation. Experimental conditions: pH = 7.0, ionic strength 0.1 M, $[HHCB]_0$ = 1 mg L^{-1}.

3.5. Kinetics of HHCB degradation by O_3 and UV

3.5.1. Ozonation process of HHCB

The reaction of HHCB with aqueous ozone and $OH^{\bullet}$ during ozonation can be expressed by the second-order kinetics as follows:

$$\frac{d[\text{HHCB}]}{dt} = -k_{OH^{\bullet}\text{-HHCB}}[\text{HHCB}][OH^{\bullet}] - k_{O_3\text{-HHCB}}[\text{HHCB}][O_3] \quad (11)$$

where [HHCB] refers to the concentration of HHCB at time t, $k_{OH^{\bullet}\text{-HHCB}}$ is the reaction rate constant of HHCB with $OH^{\bullet}$ and $k_{O_3\text{-HHCB}}$ is the reaction rate constant with aqueous ozone.

At lower pH levels, direct reaction with aqueous ozone is the primary pathway for HHCB degradation and the indirect free radical oxidation can be negligible. In present work, t-butanol was added at a concentration of 1 mM with the pH set at 2.0 for the determination of rate constant of HHCB with ozone ($k_{O_3\text{-HHCB}}$). Thus, a contribution to the degradation of HHCB made by $OH^{\bullet}$ can be neglected. On the contrary, direct reactions with ozone will play a minor role in HHCB degradation at higher pH levels, for example pH 10.0 in present study. So Eq. (11) can be simplified into Eqs. (12) and (13), respectively, corresponding to the low and high pH levels:

$$\ln\left(\frac{[\text{HHCB}]}{[\text{HHCB}]_0}\right) = -k_{O_3}\int [O_3]\,dt \quad (12)$$

$$\ln\left(\frac{[\text{HHCB}]}{[\text{HHCB}]_0}\right) = -k_{OH^{\bullet}\text{-HHCB}}\int [OH^{\bullet}]\,dt \quad (13)$$

As shown in Fig. 9, the plot of $\ln([\text{HHCB}]/\ln[\text{HHCB}]_0)$ vs. $\int [O_3]\,dt$ at pH 2 in the presence of 2.0 mM t-butanol yielded a straight line with a slope of $k_{O_3\text{-HHCB}} = 153.8 \pm 6\ M^{-1}\ S^{-1}$, which was similar to

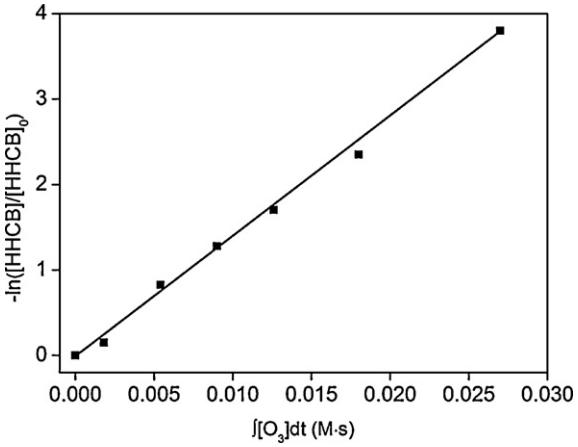

Fig. 9. Ozonation of HHCB. Experimental conditions: pH = 2, ionic strength 0.1 M, $[HHCB]_0 = 1\ mg\ L^{-1}$, $[O_3]_0 = 1.2\ mg\ L^{-1}$, *t*-butanol 2.0 mM.

the reported value of $140\ M^{-1}\ S^{-1}$ by Nothe et al. [51]. This value indicated that HHCB had a moderate reactivity towards ozone.

Similarly, $k_{OH\bullet}$ was calculated form the plot of ln $([HHCB]/[HHCB]_0)$ vs. $\int [OH^\bullet]\,dt$ at pH 10. However, it is difficult to measure the concentration of OH• directly. So the ozone-resistant probe compound, *p*CBA, which reacts quickly with OH•, was applied. The change in concentration of *p*CBA was monitored as the function of time. The oxidation rate of *p*CBA, which reacts only with OH• ($k_{OH\bullet\text{-}pCBA} = 5.2 \times 10^9\ M^{-1}\ S^{-1}$) [52], is given by:

$$\ln\left(\frac{[pCBA]}{[pCBA]}\right) = -k_{OH\bullet\text{-}pCBA}\int [OH^\bullet]\,dt \tag{14}$$

Substituting OH• exposure ($\int [OH^\bullet]\,dt$) from Eq. (14) in Eq. (13) gives:

$$\ln\left(\frac{[HHCB]}{[HHCB]_0}\right) = \left(\frac{k_{\bullet OH\text{-}HHCB}}{k_{OH\bullet\text{-}pCBA}}\right)\ln\left(\frac{[pCBA]}{[pCBA]_0}\right) \tag{15}$$

Based on the Eq. (15), the $k_{OH\bullet\text{-}HHCB}/k_{OH\bullet\text{-}pCBA}$ was calculated according to the plot of ln $([HHCB]/[HHCB]_0)$ vs. $([pCBA]/\ln[pCBA]_0)$ (Fig. 10). And the calculated value was $(6.3 \pm 0.7) \times 10^9\ M^{-1}\ S^{-1}$ for $k_{OH\bullet\text{-}HHCB}$. HHCB can therefore be considered to be fast-reacting compounds in this process.

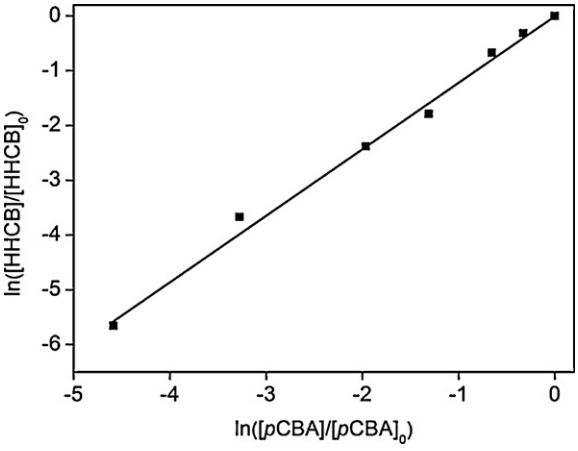

Fig. 10. Ozonation of a mixture of HHCB and *p*CBA. Experimental conditions: pH = 10, ionic strength 0.1 M, $[HHCB]_0 = 1\ mg\ L^{-1}$, $[pCBA]_0 = 0.5\ \mu M$, $[O_3]_0 = 1.2\ mg\ L^{-1}$.

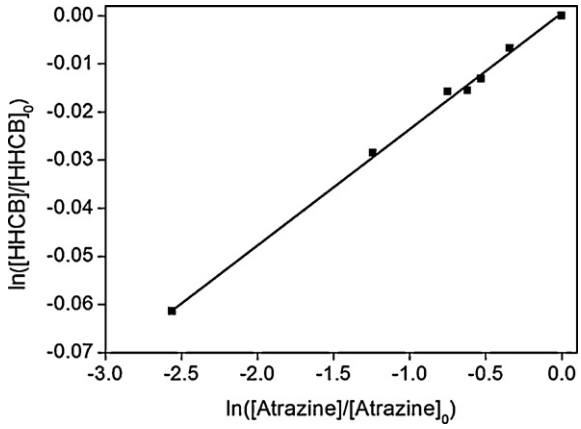

Fig. 11. Direct photolysis of a mixture of HHCB and atrazine. Experimental conditions: pH = 7.0, ionic strength 0.1 M, $[HHCB]_0 = 1\ mg\ L^{-1}$, $[Atrazine]_0 = 10\ mg\ L^{-1}$, UV incident intensity $I_0 = 0.42\ W\ L^{-1}$.

3.5.2. UV degradation of HHCB

Generally, when target compound and other organic compounds or intermediates absorbing UV are present in water simultaneously, the direct photolysis of an organic chemical by UV irradiation at a specific wavelength can be expressed as the following equation [53,54]:

$$\frac{dC_i}{dt} = -I_0\phi_i f_i\left[1 - \exp\left(-2.3L\sum_{j=1}^{N}\varepsilon_j C_j\right)\right] \tag{16}$$

where I_0 represents the UV intensity (Einstein s^{-1}), ε is the molar extinction coefficient ($M^{-1}\ cm^{-1}$), L is the effective optical light path (cm), ϕ_i is the quantum yield of photolysis (mol Einstein^{-1}), C_i is the concentration of organic compound (M), and f_i is the fraction of total absorbed light which is absorbed by compound *i*:

$$f_i = \frac{\varepsilon_i C_i}{\sum_{j=1}^{N}\varepsilon_j C_j} \tag{17}$$

Similar to the case of OH•, the effective optical light path (L) is unable to measure directly, and thus quantum yield of photolysis cannot be calculated from Eq. (16) directly. In order to avoid the necessity of determining effective optical light path and the composition of the mixture, the quantum yield of HHCB was determined from the direct photolysis of mixtures of HHCB and actinometer (atrazine) whose photolytic parameters are known. Applying Eq. (16) to both HHCB and atrazine, after dividing the resulting equations, the following is obtained:

$$\frac{d[HHCB]}{d[Atrazine]} = \left(\frac{\phi_{HHCB}\varepsilon_{HHCB}[HHCB]}{\phi_{Atrazine}\varepsilon_{Atrazine}[Atrazine]}\right) \tag{18}$$

where [HHCB] and [Atrazine] refer to the concentration of HHCB and atrazine. Rearranging Eq. (18) and integrating we obtain:

$$\ln\left(\frac{[HHCB]}{[HHCB]_0}\right) = \alpha\ln\left(\frac{[Atrazine]}{[Atrazine]_0}\right) \tag{19}$$

$$\alpha = \frac{\phi_{HHCB}\varepsilon_{HHCB}}{\phi_{Atrazine}\varepsilon_{Atrazine}} \tag{20}$$

The plot of $\ln([HHCB]/\ln[HHCB]_0)$ vs. $\ln([Atrazine]/\ln[Atrazine]_0)$ yielded a straight line with a slope of α, as shown in Eq. (20). Eq. (19) was applied to the direct photolysis of mixtures of HHCB ($1\ mg\ L^{-1}$) and atrazine ($10\ mg\ L^{-1}$) and the results are plotted in Fig. 11. Extinction coefficient of HHCB at 254 nm was determined to be $\varepsilon_{HHCB} = 248.8\ M^{-1}\ cm^{-1}$, while the extinction coefficient and quantum yield of atrazine at

254 nm have been reported to be $\varepsilon_{Atrazine} = 2486\,M^{-1}\,cm^{-1}$ and $\phi_{Atrazine} = 0.05$ mol Einstein^{-1}, respectively [30]. According to these values and applying Eq. (12), the quantum yield of HHCB at 254 nm was found to be $\phi_{HHCB} = 0.012 \pm 0.002$ mol Einstein^{-1}.

4. Conclusions

Ozonation process can degrade polycyclic musk HHCB more efficiently than UV and UV/O_3 processes. Accumulation of degradation products with similar estrogenic activity to the parent compound HHCB occurred during the three degradation processes. The conditions including pH, O_3 dosage, and bicarbonate alkalinity affected the aqueous equilibrium concentration and decomposition rate of ozone and thus influenced the ozonation of HHCB. However, besides UV intensity, UV degradation of HHCB was only affected by bicarbonate alkalinity, which may influence the formation of H_2O_2 during UV process. Scavenger experiments indicated that at neutral condition direct oxidation and radical-type oxidation were involved in the HHCB degradation by O_3, while direct photolysis was responsible for HHCB degradation by UV irradiation. The kinetic results suggested that HHCB exhibited moderate reactivity towards aqueous O_3 ($k_{O_3\text{-HHCB}} = 153.8 \pm 6\,M^{-1}\,S^{-1}$) but underwent reaction with OH• rapidly ($k_{OH\bullet\text{-HHCB}} = 6.3 \pm 0.7 \times 10^9\,M^{-1}\,S^{-1}$). The low quantum yield of HHCB under 254 nm UV light ($\phi_{HHCB} = 0.012 \pm 0.002$ mol Einstein^{-1}) suggested HHCB was resistant to UV photolysis.

Acknowledgements

This work was financially supported by the National Natural Science Foundation of China (Grant Nos. 50821002 and 51078105), the Funds for Creative Research Groups of China (Grant No. 51121062), State Key Laboratory of Urban Water Resource and Environment (Harbin Institute of Technology) (No 2010DX12), and the National Important Items of Science and Technology for the Control and Treatment of Water Pollution (Grant No. 2009ZX07424-004-06). The authors also greatly appreciate the supports from China Scholarship Council and San Diego State University Division of Research Affairs.

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