

## Comparison of the degradation of molecular and ionic ibuprofen in a UV/H<sub>2</sub>O<sub>2</sub> system

Rongkui Su, Liyuan Chai, Chongjian Tang, Bo Li and Zhihui Yang

### ABSTRACT

The advanced oxidation technologies based on  $\cdot\text{OH}$  can effectively degrade the pharmaceutical and personal care products under operating conditions of normal temperature and pressure. In this study, direct photolysis of ibuprofen (IBU) is slow due to the relatively low molar extinction coefficient and quantum yield. Compared to direct photolysis, the degradation kinetics of IBU was significantly enhanced in the UV/H<sub>2</sub>O<sub>2</sub> system, mainly by  $\cdot\text{OH}$  radical mediated oxidation. In the UV/H<sub>2</sub>O<sub>2</sub> system, the degradation rate of ionic IBU was slightly faster than that of the molecular form. Kinetic analysis showed that the second-order reaction rate constant of ionic IBU ( $5.51 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ) was higher than that of the molecular form ( $3.43 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ). The pseudo first-order rate constant for IBU degradation ( $k_{\text{obs}}$ ) increased with increasing H<sub>2</sub>O<sub>2</sub> dosage.  $k_{\text{obs}}$  can be significantly decreased in the presence of natural organic matter (NOM), which is due to (i) NOM radical scavenging effects (dominant role) and (ii) UV absorption. The degradation of IBU was inhibited by HCO<sub>3</sub><sup>-</sup>, which was attributed to its scavenging effect. Interestingly, when NO<sub>3</sub><sup>-</sup> was present in aqueous solution, a slight increase in the degradation rate was observed, which was due to NO<sub>3</sub><sup>-</sup> absorbing photons to generate  $\cdot\text{OH}$  at a low quantum yield. No obvious effects were observed when SO<sub>4</sub><sup>2-</sup> and Cl<sup>-</sup> were present.

**Key words** | hydroxyl radical, ibuprofen, ionic, kinetics, molecule

Rongkui Su  
Liyuan Chai  
Chongjian Tang  
Bo Li  
Zhihui Yang (corresponding author)  
School of Metallurgy and Environment,  
Central South University,  
Changsha 410083,  
China  
and  
Chinese National Engineering Research Center for  
Control and Treatment of Heavy Metal Pollution,  
Changsha 410083,  
China  
E-mail: yangzh@csu.edu.cn

### INTRODUCTION

Pharmaceutical and personal care products (PPCPs) are commonly used chemicals, which can be easily found in various water matrices, such as wastewater effluent, seawater and surface water (Kim *et al.* 2007; Yu *et al.* 2009; Yuan *et al.* 2009). PPCPs are usually present in the environment at the order of ng L<sup>-1</sup> and µg L<sup>-1</sup> (Kim *et al.* 2007; Yu *et al.* 2009). The impact on both the human body and ecological environments is unclear under the low residual PPCP concentrations in surface water. Many toxicological studies have shown that fish and other aquatic organisms show reproductive disorders and behavioral changes when exposed to PPCPs (Christensen *et al.* 2006; Flippin *et al.* 2007). Ibuprofen (IBU), a common anti-inflammatory analgesic, is chosen as the target recalcitrant PPCP due to its frequent occurrence in surface water and potential long-term adverse effects. The detection of IBU in the surface water has been reported in the concentration range of 0.087 to 5 µg L<sup>-1</sup> (Dębska *et al.* 2004; Kim *et al.* 2007). Flippin *et al.* (2007) found that there was a delay in the spawning time and breeding period of medaka (*Oryzias*

*latipes*) that were exposed to aqueous solutions containing 0–100 µg L<sup>-1</sup> IBU for 6 weeks.

However, current wastewater treatment plants are not specially designed to remove PPCPs (Kim *et al.* 2007; Vieno *et al.* 2007). Kim *et al.* (2007) investigated the removal of IBU and other drugs at a pilot scale. The results showed that the traditional water treatment technologies, such as coagulation, precipitation and filtration, cannot effectively remove these compounds. Vieno *et al.* (2007) reported that rapid sand filtration following coagulation and sedimentation only eliminated an additional 10% of the studied PPCPs, including ibuprofen. More than 95% of ibuprofen was found to be removed in the aeration tank, with aerobic biodegradation being the dominant mechanism (Smook *et al.* 2008). But the biological removal of PPCPs by secondary treatment process is unreliable, ranging from no removal to complete removal (Yu *et al.* 2009). Therefore, it is necessary to develop more efficient and stable water treatment methods to remove such compounds.

The  $\bullet\text{OH}$  ( $E_0 = 1.89\text{--}2.72\text{ V vs. NHE}$ ) is a strong oxidizing agent, which has a high oxidation-reduction potential (Vogna *et al.* 2004).  $\bullet\text{OH}$  based advanced oxidation technologies (AOTs), including UV/H<sub>2</sub>O<sub>2</sub>, Fenton, ozonation, and sonication, can oxidize target contaminants by attacking electron-rich sites on molecules (Crittenden *et al.* 2005). They can effectively degrade PPCPs under operating conditions of normal temperature and pressure (Vogna *et al.* 2004). Laboratory studies have demonstrated that  $\bullet\text{OH}$  based AOTs have a high ability to degrade PPCPs in deionized water, surface water, saltwater and wastewater (Grebel *et al.* 2010; Guo *et al.* 2013; Kwon *et al.* 2015; Yang *et al.* 2016). However, there are still some problems that need to be studied before large-scale application, such as the effect of target compound species and matrix components (i.e. natural organic matter (NOM), inorganic anions).

In recent years, studies have reported the degradation of IBU in UV and UV/H<sub>2</sub>O<sub>2</sub> systems (Szabó 2010; Chianese *et al.* 2016; Peng *et al.* 2017). The IBU degradation rate is related to initial IBU concentration, initial H<sub>2</sub>O<sub>2</sub> concentration, light intensity, effective optical path, solution pH, IBU properties (i.e. IBU species, absorption characteristics, secondary reaction rate constant with  $\bullet\text{OH}$ ), and matrix components (i.e. NOM, inorganic anions) in the UV/H<sub>2</sub>O<sub>2</sub> system (Crittenden *et al.* 2005). Due to the different structures and properties of IBU species (molecular and ionic forms), Chianese *et al.* (2016) found that ionic IBU was degraded more rapidly than the molecular form under light conditions. However, the absorption characteristics of IBU species were not determined. Kwon *et al.* (2015) found that the degradation of IBU was accelerated in UV/H<sub>2</sub>O<sub>2</sub> system in neutral conditions, but the comparison of IBU degradation between the ionic form and the molecular form was not studied. Moreover, previous studies have also identified that the H<sub>2</sub>O<sub>2</sub> dosage and matrix components (i.e. NOM, inorganic anions) have impacts on PPCPs degradation (Guo *et al.* 2013; Xiao *et al.* 2015). However, studies of the correlation impacts between IBU and H<sub>2</sub>O<sub>2</sub> dosage and matrix components are studied.

Hence, the degradation kinetics of ionic and molecular IBU were thoroughly investigated under two different treatment methods (i.e. UV and UV/H<sub>2</sub>O<sub>2</sub>). The molar absorptivity and quantum yield of IBU species at the wavelength of 254 nm were measured. The second-order reaction rate constants ( $k_{\text{IBU}, \bullet\text{OH}}$ ) of IBU species with  $\bullet\text{OH}$  were determined by using competitive kinetics. The mechanism of IBU degradation in the UV/H<sub>2</sub>O<sub>2</sub> system was studied

by establishing a pseudo first-order reaction kinetics model based on a steady-state approach. Then the effects of H<sub>2</sub>O<sub>2</sub> dosage and matrix components (such as NOM, inorganic anions) on the photodegradation kinetics of IBU were further evaluated.

## EXPERIMENTAL METHOD

### Materials

Ibuprofen (IBU, 99%), 4-chlorobenzoic acid (*p*CBA, 99%), disodium phosphate (99%), sodium dihydrogen phosphate (99%), and humic acid (technical) were purchased from Sigma Aldrich. Sodium chloride (guaranteed reagent), sodium sulfate (guaranteed reagent), sodium nitrate (guaranteed reagent), hydrogen peroxide (30% by weight), sulfuric acid (guaranteed reagent), potassium permanganate (analytical grade), sodium sulfate (analytical grade) and sodium oxalate (analytical grade) were purchased from Sinopharm Chemical Reagent, China.

### Irradiation experiments

In aqueous solution, anionic (A<sup>-</sup>) and molecular (HA) species of IBU coexist, mainly determined by the solution pH at a constant temperature. The Henderson-Hasselbalch equation can be used to calculate the ratio of anions and molecules in dilute solutions (Hasselbalch 1916).

$$\text{pH} = \text{pK}_a + \log \frac{[\text{A}^-]}{[\text{HA}]} \quad (1)$$

The dissociation constant (pK<sub>a</sub>) of IBU is 4.9 at the solution temperature of 20°C. As shown in Equation (1), when pH is lower than pK<sub>a</sub>, IBU is present in the molecular form. And the anionic form is more likely to be present when pH is higher than pK<sub>a</sub>. In particular, at pH = 3.00, the molecular form of IBU accounts for 98.76%, while at pH = 7.55, the anionic form of IBU accounts for 99.78%.

IBU and *p*CBA stock solutions were prepared in deionized water and stored at 4°C in the dark. For the kinetic studies, the initial concentrations of IBU and *p*CBA in the working solutions were 10 μM (2.06 mg L<sup>-1</sup> and 1.57 mg L<sup>-1</sup>, respectively). The solution pH was adjusted to pH = 7.55 or pH = 3.00 with 10 mM phosphate buffer solution. The selection of pH = 7.55 is based on two factors: (1) pH = 7.55 is environmentally relevant and (2) IBU is a weak acid with pK<sub>a</sub> = 4.9, thus the majority (i.e. 99.8%) of IBU is in its ion form at pH = 7.55.

The photochemical reactor is a cylindrical glass tube with an effective volume of 450 mL, with two casings. The schematic diagram of the photochemical reactor was shown in our previous study (Yang *et al.* 2017). The outer casing is connected to the water bath circulator (SC150-A25B, Thermo Fisher Scientific) and maintains a constant system temperature ( $20 \pm 1$  °C). A low-pressure UV lamp (GPH212T5 L/4, 10 W, Heraeus) is placed in the quartz cold trap in the center of the inner casing, and a small stirring bar was placed at the bottom of the reactor to ensure homogeneous UV exposure. The water bath circulator and the ultraviolet lamp were pre-opened to stabilize the system temperature and light intensity. One millilitre of solution was taken from the reactor at scheduled times using a 2.5 mL glass syringe (Gastight 1001, Hamilton) and chemical analysis in the solution was immediately carried out by ultra-performance liquid chromatography (Waters ACQUITY H-Class). All kinetic experiments were replicated independently at least three times.

The average light intensity per volume ( $I_0$ ) in the UV reactor was estimated to be  $6.16 \times 10^{-6}$  Einstein L<sup>-1</sup> s<sup>-1</sup> (which corresponds to a power output of  $3.83$  mW cm<sup>-2</sup>) with potassium ferrioxalate chemical actinometry (Parker 1953) and the effective optical path length ( $b$ ) was 1.32 cm measured by H<sub>2</sub>O<sub>2</sub> chemical actinometry (Beltrán *et al.* 1995) in this study.

## Analytical methods

The emission wavelength and intensity of the UV lamp were determined using fiber optic spectrometers (USB 2000+, Ocean Optics) and the absorption spectra of IBU and *p*CBA in solution were measured by a UV-1800 spectrometer (Shimadzu, Japan). The pH of the solutions was measured by a S220 pH meter (Mettler Toledo). The concentration of H<sub>2</sub>O<sub>2</sub> was measured by the KMnO<sub>4</sub> titration method (Klassen *et al.* 1994).

Analysis of IBU and *p*CBA was performed using ultra-performance liquid chromatography (Waters ACQUITY H-Class) with a BEH C18 column (1.7 μm, 2.1 mm × 50 mm, Waters). The column temperature was set at 35 °C. An isocratic mobile phase of 50% acetonitrile and 50% phosphate buffer (20 mM, pH = 3.00) was used for the quantification of IBU and 30% acetonitrile and 70% phosphate buffer (20 mM, pH = 3.00) was used for the quantification of *p*CBA. The sample injection volume was 5 μL and a flow rate was 0.3 mL min<sup>-1</sup>. The UV detection wavelengths of IBU and *p*CBA were set at 220 nm and 238 nm, respectively.

## RESULTS AND DISCUSSION

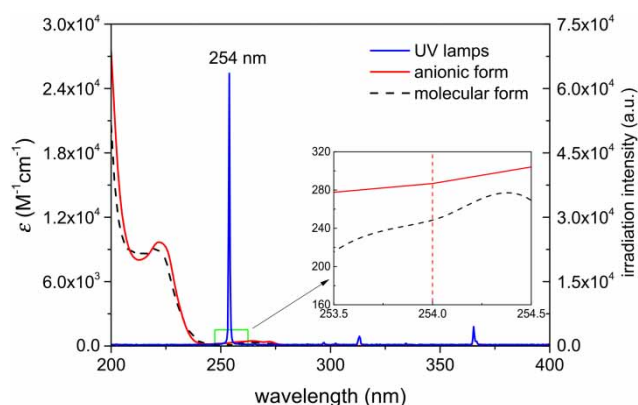
### Degradation of IBU in UV and UV/H<sub>2</sub>O<sub>2</sub> systems

The degradation of IBU in the UV/H<sub>2</sub>O<sub>2</sub> system at pH = 7.55 fitted the first-order kinetic models with a higher  $R^2$  (0.994) than zero-order ( $R^2 = 0.826$ ) and second-order kinetics ( $R^2 = 0.708$ ), indicating that IBU degradation follows first-order kinetics. The same result was obtained under direct UVs and at pH = 3.00 in the UV/H<sub>2</sub>O<sub>2</sub> system. Under UV intensity of  $3.83$  mW cm<sup>-2</sup> and initial IBU concentration of 10 μM (2.06 mg L<sup>-1</sup>), the initial direct photolysis degradation rates of IBU were  $4.25 \times 10^{-3}$  μM min<sup>-1</sup> (pH = 3.00) and  $28.80 \times 10^{-3}$  μM min<sup>-1</sup> (pH = 7.55), respectively. As shown in Figure 1, IBU absorbed light with a relatively low molar absorption coefficient at the wavelengths of 200–230 nm, thus it is expected that direct photolysis of IBU by UV light at 254 nm is low.

Molar extinction coefficient and the quantum yield have a significant effect on the direct photolysis of a compound (Pereira *et al.* 2007; Szabó 2010). The capacity of a target compound to absorb incident light determines the kinetics of its photolysis. The decadic molar extinction coefficient ( $\epsilon$ ) represents the ability of the compound to absorb light at a certain wavelength ( $\lambda$ ).  $\epsilon$  can be calculated by measuring the absorbance ( $A$ ) of 10 μM (2.06 mg L<sup>-1</sup>) IBU solutions at pH = 3.00 and pH = 7.55 with a 1 cm path length ( $l$ ) quartz cuvette in this study:

$$A = \epsilon \times [\text{IBU}] \times l \quad (2)$$

Figure 1 illustrates the decadic molar extinction coefficient for IBU with reference to Hg lamp emission spectra.



**Figure 1** | Decadic molar absorption coefficient ( $\epsilon$ ) of IBU with reference to the UV lamp emission spectra from 200 to 400 nm.

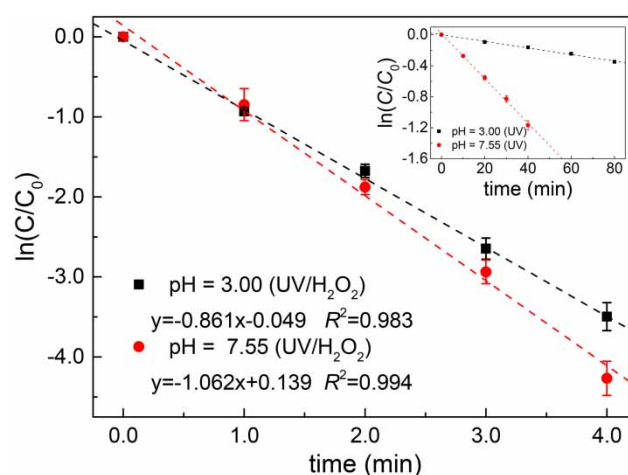
At the wavelength of 254 nm, the  $\epsilon$  values of IBU were 248.41 M<sup>-1</sup> cm<sup>-1</sup> (pH = 3.00) and 283.64 M<sup>-1</sup> cm<sup>-1</sup> (pH = 7.55), which were relatively low compared to the values of other PPCPs (Yang *et al.* 2016). The value of  $\epsilon_{\text{IBU}}$  at 254 nm determined by Kwon *et al.* (2015) was 256 M<sup>-1</sup> cm<sup>-1</sup> (pH = 7.00), which is between the two values we measured. The molar extinction coefficient of IBU was positively correlated with the pH value, indicating that the  $\epsilon_{\text{IBU}}$  was dependent on the species of IBU.

The quantum yield describes the ratio of the total numbers of molecules of the compound destroyed to the total numbers of photons absorbed by the system. The quantum yield of IBU can be calculated as follows (Pereira *et al.* 2007):

$$\phi_{\text{IBU}} = \frac{r_{\text{UV}}}{I_0 \times (1 - 10^{-\epsilon_{\text{IBU}} b [\text{IBU}]})} \quad (3)$$

where  $\phi_{\text{IBU}}$  is the quantum yield of IBU at 254 nm (mol Einstein<sup>-1</sup>),  $r_{\text{UV}}$  (M s<sup>-1</sup>) is the direct photolytic degradation rate at an initial concentration of 10  $\mu\text{M}$  (2.06 mg L<sup>-1</sup>).  $I_0$  is the incident UV intensity,  $\epsilon_{\text{IBU}}$  is the molar extinction coefficient of IBU at wavelength 254 nm, and  $b$  is the reactor light path. The  $\phi_{\text{IBU}}$  was calculated to be 0.015 mol Einstein<sup>-1</sup> (pH = 3.00) and 0.091 mol Einstein<sup>-1</sup> (pH = 7.55), respectively. Different PPCPs have different molecular structures, which can result in different quantum yield values. (Yuan *et al.* 2009). The  $\phi_{\text{IBU}}$  is higher than the reported value of carbamazepine (0.0006 mol Einstein<sup>-1</sup>) and naproxen (0.0093 mol Einstein<sup>-1</sup>), while it is lower than that of phenytoin (0.279 mol Einstein<sup>-1</sup>) and clofibric acid (0.5390 mol Einstein<sup>-1</sup>) (Pereira *et al.* 2007; Yuan *et al.* 2009).

Due to both  $\epsilon_{\text{IBU}}$  and  $\phi_{\text{IBU}}$  at pH = 3.00 being lower than at pH = 7.55, the direct photolysis degradation rates of molecular IBU is slower than ionic IBU. As shown in Figure 2, the degradation kinetics of IBU was significantly enhanced by adding 625  $\mu\text{M}$  (21.25 mg L<sup>-1</sup>) H<sub>2</sub>O<sub>2</sub> compared to direct photolysis. In the UV/H<sub>2</sub>O<sub>2</sub> system, the initial degradation rate of ionic IBU at pH = 3.00 (10.62  $\mu\text{M min}^{-1}$ ) was also slightly faster than that of the molecular form at pH = 7.55 (8.61  $\mu\text{M min}^{-1}$ ). The dark reaction experiments showed that IBU did not degrade without UV irradiation, and the same results were obtained by adding 625  $\mu\text{M}$  (21.25 mg L<sup>-1</sup>) H<sub>2</sub>O<sub>2</sub> to the dark reaction experiments. These results indicate that degradation of IBU in UV/H<sub>2</sub>O<sub>2</sub> systems includes direct photolysis and radical degradation, but radical degradation plays a major role (more than 95%). The enhanced degradation of IBU with the



**Figure 2** | Time-dependent degradation kinetics of IBU in the UV and UV/H<sub>2</sub>O<sub>2</sub> systems ([IBU] = 10  $\mu\text{M}$ , [H<sub>2</sub>O<sub>2</sub>] = 625  $\mu\text{M}$ , and  $I_0 = 3.83 \text{ mW cm}^{-2}$ ,  $b = 1.32 \text{ cm}$ ). The degradation was fitted to a first-order kinetic model (shown by the lines).

addition of H<sub>2</sub>O<sub>2</sub> is due mainly to  $\bullet\text{OH}$  radical mediated oxidation. The results are consistent with the results reported by Xiao *et al.* (2015), and they also demonstrated that  $\bullet\text{OH}$  plays a major role in the degradation of iodinated trihalomethanes by UV/H<sub>2</sub>O<sub>2</sub>. Therefore, the degradation rate constants of IBU largely depend on the formation of  $\bullet\text{OH}$  in the UV system.

### Competitive kinetics

The second-order rate constant of IBU with  $\bullet\text{OH}$  ( $k_{\text{IBU}, \bullet\text{OH}}$ ) can be determined by competitive kinetics (Packer *et al.* 2003; Kwon *et al.* 2015). *p*CBA was chosen as a reference compound in this study for two significant reasons. First,  $k$  values for *p*CBA reacting with  $\bullet\text{OH}$  are known ( $5.0 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  at neutral and  $4.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  at acidic) (Buxton *et al.* 1988). Second, the reaction of *p*CBA with  $\bullet\text{OH}$  is less affected by other substances (Katsoyiannis *et al.* 2011). The  $k$  values of IBU reacting with  $\bullet\text{OH}$  was calculated as follows (Yuan *et al.* 2009):

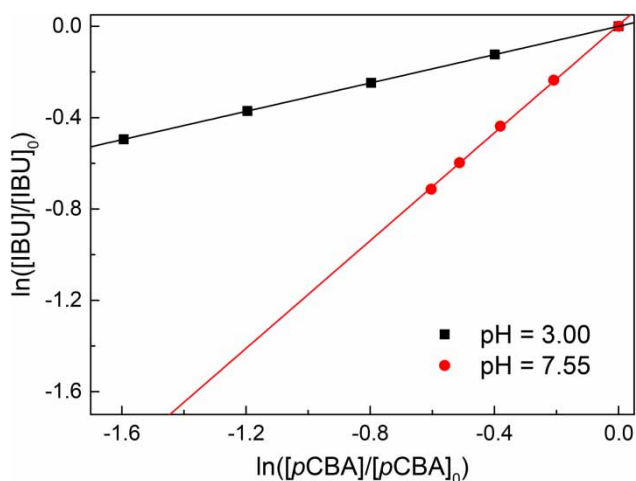
$$\frac{k_{\text{IBU}, \bullet\text{OH}}}{k_{\text{pCBA}, \bullet\text{OH}}} = \frac{\left( \ln \frac{[\text{IBU}]_t}{[\text{IBU}]_0} \right)_{\text{tot}} - \left( \ln \frac{[\text{IBU}]_t}{[\text{IBU}]_0} \right)_{\text{UV}}}{\left( \ln \frac{[\text{pCBA}]_t}{[\text{pCBA}]_0} \right)_{\text{tot}} - \left( \ln \frac{[\text{pCBA}]_t}{[\text{pCBA}]_0} \right)_{\text{UV}}} = \frac{k_{\text{tot}, \text{IBU}} - k_{\text{UV}, \text{IBU}}}{k_{\text{tot}, \text{pCBA}} - k_{\text{UV}, \text{pCBA}}} \quad (4)$$

where  $k_{\text{tot}, \text{IBU}}$  and  $k_{\text{tot}, \text{pCBA}}$  are the first-order rate constants for the total degradation of IBU and *p*CBA,  $k_{\text{UV}, \text{IBU}}$  and  $k_{\text{UV}, \text{pCBA}}$  are the first-order rate constant for the direct UV

photolysis of IBU and *p*CBA, respectively. The value of  $k_{tot} - k_{UV}$  will then be the degradation rate of IBU by the radical reaction. A straight line with the slope  $k_{IBU, \bullet OH} / k_{pCBA, \bullet OH}$  and the intercept of zero was plotted with  $k_{tot, IBU} - k_{UV, IBU}$  against  $k_{tot, pCBA} - k_{UV, pCBA}$ . As shown in Figure 3, an average reaction rate constant ratio of IBU and *p*CBA with  $\bullet OH$  was 0.686 (unitless) and 1.047 (unitless) at pH = 3.00 and pH = 7.55, respectively. The  $k_{IBU, \bullet OH}$  values of molecular and ionic IBU with  $\bullet OH$  were determined to be  $3.43 (\pm 0.09) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  (pH = 3.00) and  $5.93 (\pm 0.15) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  (pH = 7.55), respectively. Packer *et al.* (2003) have determined the value of  $k_{IBU, \bullet OH}$  to be  $6.50 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  (pH = 3.00) in the Fenton system, which is different from our measurement ( $3.43 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ). Some of the difference stem from two factors: (i) Packer *et al.* (2003) determined the value of  $k_{IBU, \bullet OH}$  in the Fenton system, whereas we measured it in the UV/H<sub>2</sub>O<sub>2</sub> system, (ii) acetophenone was used as a reference substance in the study of Packer *et al.* (2003), whereas *p*CBA was used in this study. However, under the same conditions of the UV/H<sub>2</sub>O<sub>2</sub> system and reference substance (*p*CBA), the  $k_{IBU, \bullet OH}$  ( $5.93 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  at pH = 7.55) is consistent with the result ( $5.57 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  at pH = 7.00) reported by Kwon *et al.* (2015).

### Pseudo first-order reaction kinetics

The degradation of target compounds in UV-based processes can be predicted and explained by the method of the steady-state approximation for the kinetic description



**Figure 3** | Competitive kinetics of IBU and *p*CBA in the UV/H<sub>2</sub>O<sub>2</sub> system ([IBU] = 10 μM, [pCBA] = 10 μM, [H<sub>2</sub>O<sub>2</sub>] = 100 μM, and  $I_0 = 3.83 \text{ mW cm}^{-2}$ ,  $b = 1.32 \text{ cm}$ , pH = 7.55).

of radicals (Yuan *et al.* 2009). The method is established based on the assumption that the radicals (i.e.  $\bullet OH$ ) produced by UV photolysis of H<sub>2</sub>O<sub>2</sub> play a major role on the degradation of target compounds (Yuan *et al.* 2009). The reactions in the UV/H<sub>2</sub>O<sub>2</sub> system and their rate constants are presented in Table 1.

Under steady-state conditions, the reaction rate ( $r_{tot}$ ,  $\text{M s}^{-1}$ ) of IBU degradation in the UV/H<sub>2</sub>O<sub>2</sub> process can be expressed with the following equation (Crittenden *et al.* 1999):

$$r_{tot} = r_{UV} + r_{OH} \quad (5)$$

where  $r_{UV}$  is the initial IBU direct photolytic degradation rate in the UV/H<sub>2</sub>O<sub>2</sub> process and  $r_{OH}$  is the IBU reaction rate with  $\bullet OH$ .

$$r_{UV} = \varphi_{IBU} \times I_0 \times \frac{b \varepsilon_{IBU} [IBU]}{A} \times (1 - 10^{-A}) \quad (6)$$

$$r_{OH} = k_{IBU, \bullet OH} \times [\bullet OH]_{SS} \times [IBU] \quad (7)$$

$$A = b(\varepsilon_{IBU} [IBU] + \varepsilon_{H_2O_2} [H_2O_2]) \quad (8)$$

where  $I_0$  is the incident UV intensity ( $3.83 \text{ mW cm}^{-2}$ ), and  $b$  is the reactor light path (1.32 cm).  $A$  is the absorbance of the reaction solution.  $\varepsilon_{H_2O_2}$  is the molar extinction coefficient of H<sub>2</sub>O<sub>2</sub> ( $19.6 \text{ M}^{-1} \text{ cm}^{-1}$ ), and  $\varphi_{OH}$  (in Equation (11) below) is the quantum yield of H<sub>2</sub>O<sub>2</sub> ( $0.5 \text{ mol Einstein}^{-1}$ ) at wavelength 254 nm (Crittenden *et al.* 1999).

The degradation of IBU in UV/H<sub>2</sub>O<sub>2</sub> systems follows pseudo first-order kinetics (the unit for pseudo first-order is  $\text{s}^{-1}$ ), and can be described by an equation as follows:

$$k_{tot} \times [IBU] = k_{UV} \times [IBU] + k_{IBU, \bullet OH} [\bullet OH]_{SS} [IBU] \quad (9)$$

Under steady-state conditions, the formation rate of  $\bullet OH$  ( $r_{0, \bullet OH}$ ) is equal to the rate of consumption. Thus, the steady-state concentrations for  $\bullet OH$  (i.e.  $[\bullet OH]_{SS}$ ) can be calculated as follows:

$$0 = \frac{d[\bullet OH]}{dt} = r_{0, \bullet OH} - (k_{IBU, \bullet OH} + [IBU]) [\bullet OH]_{SS} + k_1 [H_2O_2] [\bullet OH]_{SS} + k_2 [HO_2^-] [\bullet OH]_{SS} + k_{H1} [\bullet OH]_{SS} [H_2PO_4^-] + k_{H2} [\bullet OH]_{SS} [HPO_4^{2-}] + k_{Hi} [\bullet OH]_{SS} [Si] \quad (10)$$

**Table 1** | Summary of the reactions in the UV/H<sub>2</sub>O<sub>2</sub> system (10 mM phosphate buffer)

#	Reaction	$k$ (M <sup>-1</sup> s <sup>-1</sup> )	Reference or note
1	H <sub>2</sub> O <sub>2</sub> + $h\nu$ → 2•OH	$r_{0, \bullet\text{OH}} = 2\varphi_{\text{H}}E_{\text{H}}, \text{ s}^{-1}$	Crittenden <i>et al.</i> (1999)
2	H <sub>2</sub> O <sub>2</sub> + •OH → HO <sub>2</sub> <sup>•</sup> + H <sub>2</sub> O	$k_1 = 2.7 \times 10^7$	Buxton <i>et al.</i> (1988)
3	•OH + HO <sub>2</sub> <sup>-</sup> → HO <sub>2</sub> <sup>•</sup> + OH <sup>-</sup>	$k_2 = 7.5 \times 10^9$	Crittenden <i>et al.</i> (1999)
4	H <sub>2</sub> O <sub>2</sub> ↔ H <sup>+</sup> + HO <sub>2</sub> <sup>-</sup>	$k_3 = 2.51 \times 10^{-12}$	Crittenden <i>et al.</i> (1999)
5	H <sub>3</sub> PO <sub>4</sub> ⇌ H <sup>+</sup> + H <sub>2</sub> PO <sub>4</sub> <sup>-</sup>	$\text{p}K_{\text{a}1} = 2.17$ unitless	Stumm & Morgan (1996)
6	H <sub>2</sub> PO <sub>4</sub> <sup>-</sup> ⇌ H <sup>+</sup> + HPO <sub>4</sub> <sup>2-</sup>	$\text{p}K_{\text{a}2} = 7.21$ unitless	Stumm & Morgan (1996)
7	HPO <sub>4</sub> <sup>2-</sup> ⇌ H <sup>+</sup> + PO <sub>4</sub> <sup>3-</sup>	$\text{p}K_{\text{a}3} = 12.35$ unitless	Stumm & Morgan (1996)
8	•OH + H <sub>2</sub> PO <sub>4</sub> <sup>-</sup> → HPO <sub>4</sub> <sup>•-</sup> + H <sub>2</sub> O	$k_{\text{H}1} = 2.0 \times 10^4$	Buxton <i>et al.</i> (1988)
9	•OH + HPO <sub>4</sub> <sup>2-</sup> → HPO <sub>4</sub> <sup>•-</sup> + OH <sup>-</sup>	$k_{\text{H}2} = 1.5 \times 10^5$	Buxton <i>et al.</i> (1988)
10	•OH + PO <sub>4</sub> <sup>3-</sup> → PO <sub>4</sub> <sup>•-</sup> + OH <sup>-</sup>	$k_{\text{H}3} < 1.5 \times 10^7$	Buxton <i>et al.</i> (1988)
11	•OH + H <sub>3</sub> PO <sub>4</sub> → H <sub>2</sub> PO <sub>4</sub> <sup>•</sup> + H <sub>2</sub> O	$k_{\text{H}4} = 2.7 \times 10^6$	Buxton <i>et al.</i> (1988)
<b>In the presence of NOM</b>			
12	•OH + NOM → products	$k_4 = 1.40 \times 10^4 \text{ L mgC}^{-1} \text{ s}^{-1}$	Lutze <i>et al.</i> (2015)
<b>Degradation of IBU</b>			
13	IBU + $h\nu$ → products	$r_{\text{UV}}, \text{ M s}^{-1}$	Measured in this study
14	•OH + IBU → products	$k_{\text{IBU}, \bullet\text{OH}}$	Measured in this study

In the UV/H<sub>2</sub>O<sub>2</sub> system,  $r_{0, \bullet\text{OH}}$  can be calculated as follows (Crittenden *et al.* 1999):

$$r_{0, \bullet\text{OH}} = 2\varphi_{\bullet\text{OH}}I_0 f_{\text{H}_2\text{O}_2} (1 - 10^{-A}) \quad (11)$$

$$f_{\text{H}_2\text{O}_2} = \frac{b \varepsilon_{\text{H}_2\text{O}_2} [\text{H}_2\text{O}_2]}{A} \quad (12)$$

The averages of  $r_{0, \bullet\text{OH}}$  and  $k_{\text{tot}}$  were  $2.24 \times 10^{-7} \text{ M s}^{-1}$  and  $1.42 \times 10^{-2} \text{ s}^{-1}$  at pH = 3.00, then  $2.24 \times 10^{-7} \text{ M s}^{-1}$  and  $1.77 \times 10^{-2} \text{ s}^{-1}$  at pH = 7.55, respectively.

From the above formula, we calculated the secondary reaction rate constant of IBU with •OH and the steady-state concentration of •OH with Equations (13) and (14):

$$k_{\text{IBU}, \bullet\text{OH}} = \frac{(k_{\text{tot}} - k_{\text{UV}}) \times (k_1 \times [\text{H}_2\text{O}_2] + k_2 \times [\text{HO}_2^-] + k_{\text{H}1} [\text{H}_2\text{PO}_4^-] + k_{\text{H}2} [\text{HPO}_4^{2-}] + k_{\text{H}i} [\text{S}_i])}{2\varphi_{\text{H}}E_0f_{\text{H}} (1 - 10^{-b \sum \varepsilon_i C_i}) - (k_{\text{tot}} - k_{\text{UV}}) \times [\text{AC}]} \quad (13)$$

$$[\bullet\text{OH}]_{\text{SS}} = \frac{2\varphi_{\text{H}}I_0f_{\text{H}} (1 - 10^{-b \sum \varepsilon_i C_i})}{k_1 \times [\text{H}_2\text{O}_2] + k_2 \times [\text{HO}_2^-] + k_{\text{IBU}, \bullet\text{OH}} \times [\text{AC}] + k_{\text{H}1} [\text{H}_2\text{PO}_4^-] + k_{\text{H}2} [\text{HPO}_4^{2-}] + k_{\text{H}i} [\text{S}_i]} \quad (14)$$

The  $k_{\text{IBU}, \bullet\text{OH}}$  of molecular and ionic IBU with •OH were calculated to be  $3.47(\pm 0.11) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  (pH = 3.00) and  $5.89(\pm 0.19) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  (pH = 7.55), which were consistent with the values determined by

competitive kinetics. The average of  $[\bullet\text{OH}]_{\text{SS}}$  were calculated to be  $4.06 \times 10^{-12} \text{ M}$  and  $2.93 \times 10^{-12} \text{ M}$  at pH = 3.00 and pH = 7.55, respectively. Kwon *et al.* (2015) has determined the  $[\bullet\text{OH}]_{\text{SS}}$  to be  $0.27 \times 10^{-12} \text{ M}$  in the UV/H<sub>2</sub>O<sub>2</sub> system ( $[\text{H}_2\text{O}_2]_0 = 0.5 \text{ mM}$ ,  $I_0 = 0.5 \text{ mW cm}^{-2}$ ,  $b = 0.79 \text{ cm}$ ,  $[\text{IBU}]_0 = 10 \mu\text{M}$ , pH = 7.00), which was lower than the value we have measured ( $4.06 \times 10^{-12} \text{ M}$  at pH = 3.00 and  $2.93 \times 10^{-12} \text{ M}$  at pH = 7.55). This is mainly due to both  $I_0$  and  $b$  in the research of Kwon *et al.* (2015) are lower than that in this study ( $I_0 = 3.83 \text{ mW cm}^{-2}$ ,  $b = 1.32 \text{ cm}$ ).

Here we used the mean value of  $k_{\text{HO}, \text{IBU}}$ ,  $[\bullet\text{OH}]_{\text{SS}}$ , and Equations (5)–(7) to calculate the contribution of direct

photolysis and •OH in the UV/H<sub>2</sub>O<sub>2</sub> system.

$$\frac{r_{\text{tot}}}{r_{\text{tot}}} (r_{\text{tot}}) = \frac{r_{\text{UV}}}{r_{\text{tot}}} (r_{\text{UV}}) + \frac{r_{\bullet\text{OH}}}{r_{\text{tot}}} (r_{\bullet\text{OH}}) \quad (15)$$

In the UV/H<sub>2</sub>O<sub>2</sub> system, the  $r_{UV}$  and  $r_{OH}$  were determined to be  $6.95 \times 10^{-10} \text{ M s}^{-1}$  and  $1.41 \times 10^{-7} \text{ M s}^{-1}$  at pH = 3.00, respectively. Therefore,

$$100\%(r_{tot}) = 0.49\% (r_{UV}) + 99.51\% (r_{OH}) \quad (16)$$

Meanwhile, the  $r_{UV}$  and  $r_{OH}$  were determined to be  $4.72 \times 10^{-9} \text{ M s}^{-1}$  and  $1.72 \times 10^{-7} \text{ M s}^{-1}$  at pH = 7.55, respectively. Therefore,

$$100\%(r_{tot}) = 2.67\% (r_{UV}) + 97.33\% (r_{HO\cdot}) \quad (17)$$

The calculated contributions of direct photolysis and  $\cdot\text{OH}$  to IBU degradation are shown in Equations (16) and (17).  $\cdot\text{OH}$  is the main reactive species in the UV/H<sub>2</sub>O<sub>2</sub> system, which is responsible for more than 97% of IBU degradation at both pH = 3 and pH = 7.55 (i.e. the contribution of direct photolysis ( $r_{UV}$ ) was less than 3%). The results support the previous conclusion that  $\cdot\text{OH}$  play a major role in IBU degradation in the UV/H<sub>2</sub>O<sub>2</sub> system.

Thus, under the same initial conditions, the secondary reaction rate constants of molecular and ionic IBU with  $\cdot\text{OH}$  and the steady-state concentration of  $\cdot\text{OH}$  determine the IBU degradation rate in the UV/H<sub>2</sub>O<sub>2</sub> system. These also explain why the IBU degradation rate at pH = 7.55 is faster than at pH = 3.00 in UV/H<sub>2</sub>O<sub>2</sub> system.

The pseudo first-order reaction kinetics model can also be used to study and simulate the effects of other factors on IBU degradation (Xiao *et al.* 2015). In this study, we used the pseudo first-order reaction kinetics model to predict and explain the effects of H<sub>2</sub>O<sub>2</sub> dosage and NOM on IBU degradation in the UV/H<sub>2</sub>O<sub>2</sub> system. Then the contributions of direct photolysis and  $\cdot\text{OH}$  to IBU degradation (i.e.  $k_{cal,UV}$  and  $k_{cal,\cdot OH}$ ) under various experimental conditions were calculated according to Equations (18) and (19), respectively.

$$k_{cal,UV} = \varphi_{IBU} \times I_0 \times \frac{b \varepsilon_{IBU}}{A} \times (1 - 10^{-A}) \quad (18)$$

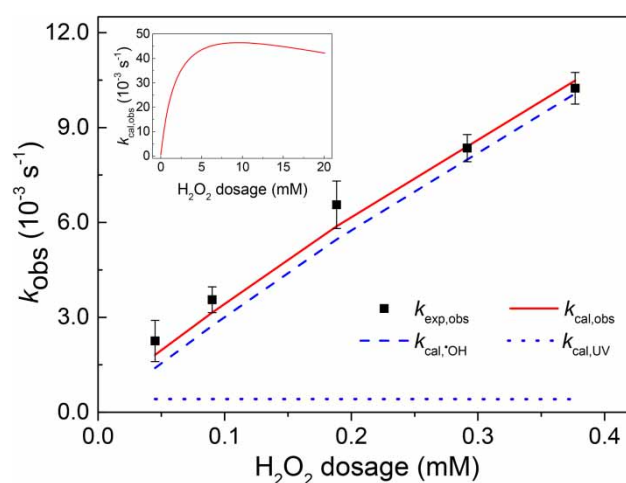
$$k_{cal,\cdot OH} = k_{IBU,\cdot OH} \times [\cdot\text{OH}]_{SS} \quad (19)$$

The total contribution of direct photolysis and  $\cdot\text{OH}$  to IBU degradation ( $k_{cal,obs}$ ) can be expressed by Equation (20).

$$k_{cal,obs} = k_{cal,UV} + k_{cal,\cdot OH} \quad (20)$$

### Effect of the initial H<sub>2</sub>O<sub>2</sub> dosage

The concentration of H<sub>2</sub>O<sub>2</sub> in the UV/H<sub>2</sub>O<sub>2</sub> system affected the degradation rates of IBU. As shown in Figure 4, the



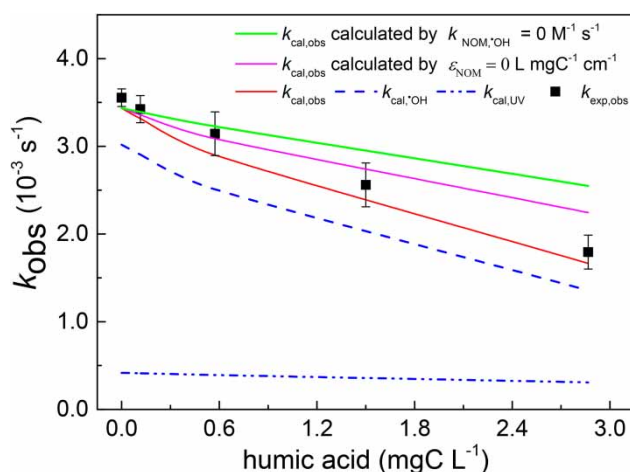
**Figure 4** | Impacts of H<sub>2</sub>O<sub>2</sub> dosages on the pseudo first-order constants of IBU ( $k_{obs}$ ) ( $[IBU]_0 = 10 \mu\text{M}$ , pH = 7.55, and  $I_0 = 3.33 \text{ mW cm}^{-2}$ ,  $b = 0.93 \text{ cm}$ ).

experimental results of the pseudo first-order rate constants for IBU degradation ( $k_{exp,obs}$ ) increased from  $2.25 \times 10^{-3} \text{ s}^{-1}$  to  $10.24 \times 10^{-3} \text{ s}^{-1}$  when the H<sub>2</sub>O<sub>2</sub> concentration increased from 45 to 375  $\mu\text{M}$  ( $1.53 \text{ mg L}^{-1}$ – $12.75 \text{ mg L}^{-1}$ ) at pH = 7.55. This result could be well predicted by the kinetic model. In Figure 4, the  $k_{exp,obs}$  was consistent with the modeling results ( $k_{cal,obs}$ ). The calculated contributions of direct photolysis and  $\cdot\text{OH}$  to IBU degradation are also shown in Figure 4. The  $\cdot\text{OH}$  was the main reactive species in the UV/H<sub>2</sub>O<sub>2</sub> system, whose contribution to IBU degradation ( $k_{cal,\cdot OH}$ ) was always greater than 97% with the increase of H<sub>2</sub>O<sub>2</sub> concentration from 45  $\mu\text{M}$  to 375  $\mu\text{M}$  (from  $1.53 \text{ mg L}^{-1}$  to  $12.75 \text{ mg L}^{-1}$ ) (i.e. the contribution of direct photolysis ( $k_{cal,UV}$ ) was less than 3%). The calculated contributions of direct photolysis and  $\cdot\text{OH}$  were 2.67% and 97.33% at the initial concentration of H<sub>2</sub>O<sub>2</sub> (625  $\mu\text{M}$ ) at pH = 7.55, which were consistent with experimental data (Equation (17)). Guo *et al.* (2013) found that the apparent rate constant ( $k_{app}$ ) of ciprofloxacin (CIP) increased from  $0.39 \times 10^{-3} \text{ s}^{-1}$  to  $3.72 \times 10^{-3} \text{ s}^{-1}$  when H<sub>2</sub>O<sub>2</sub> concentrations were in the range of 0–5 mM. The modeling result also showed that a negative effect would be found as the concentration of H<sub>2</sub>O<sub>2</sub> further increased, but only when the concentration of H<sub>2</sub>O<sub>2</sub> was above 10 mM, when the decreasing trend of  $k_{cal,obs}$  occurred (the inset in Figure 4). The possible explanation is that  $\cdot\text{OH}$  could be scavenged by the excess H<sub>2</sub>O<sub>2</sub> with the second-order rate constant of  $1.4 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  (Buxton *et al.* 1988).

### Effect of organic matter

Since humic acid is the main component of organic matter, the effect of organic matter on the degradation of IBU in

the UV/H<sub>2</sub>O<sub>2</sub> system at pH = 7.55 was studied by adding different concentrations of humic acid (0–2.87 mgC L<sup>-1</sup>). Figure 5 shows that  $k_{\text{exp,obs}}$  decreased from  $3.55 \times 10^{-3} \text{ s}^{-1}$  to  $1.79 \times 10^{-3} \text{ s}^{-1}$  with humic acid concentration increasing from 0 mgC L<sup>-1</sup> to 2.87 mgC L<sup>-1</sup>. Moreover,  $k_{\text{cal,obs}}$  of the model calculation slowed down slightly faster than that of the experimental data ( $k_{\text{exp,obs}}$ ) with the increasing humic acid concentration. These indicated that humic acid not only acted as a radical scavenger and the inner filter in the UV/H<sub>2</sub>O<sub>2</sub> system, but also reacted with hydroxyl radicals to form secondary radicals that can continue to react with IBU. Then, the kinetic model was used to estimate the relative contributions of the inner filter effect (Equation (8) can be modified to  $A = b(\varepsilon_{\text{IBU}}[\text{IBU}] + \varepsilon_{\text{H}_2\text{O}_2}[\text{H}_2\text{O}_2] + \varepsilon_{\text{NOM}} [\text{humic acid}])$ , the  $\varepsilon_{\text{NOM}}$  of humic acid being 0.10 L mgC<sup>-1</sup> cm<sup>-1</sup> as measured in this work) and radical scavenger to the decrease of  $k_{\text{obs}}$ . As shown in Figure 5,  $k_{\text{cal,obs}}$  changed slightly as compared to the experimental result (magenta line), if the inner filter effect of humic acid was ignored (i.e. assuming that  $\varepsilon$  of humic acid was zero). While the calculated values of  $k_{\text{cal,obs}}$  greatly deviated from the experimental result (green line), if the radical scavenging effect of humic acid was left out (i.e. assuming that the second-order rate constant of reactions between humic acid and  $\bullet\text{OH}$  ( $k_4$  in Table 1) in Equation (12) were zero). These contrasting results indicate that the radical scavenger effect of humic acids has a greater significant role than its inner filter effect in decreasing IBU degradation rate in the UV/H<sub>2</sub>O<sub>2</sub> process. Even in the presence of humic acid, the calculated contributions of  $\bullet\text{OH}$  was still clearly higher than the direct

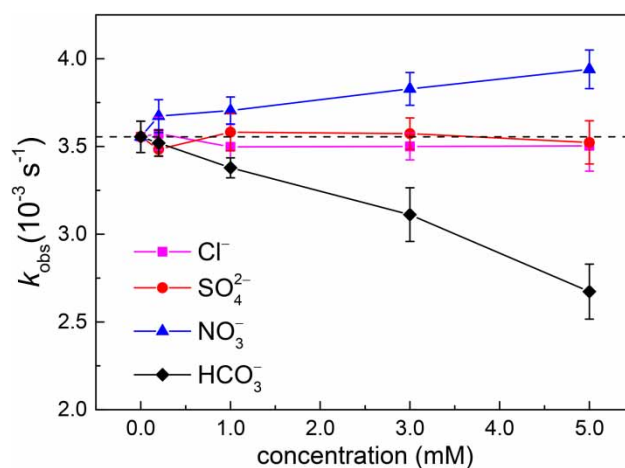
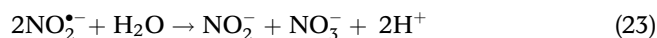


**Figure 5** | Impacts of humic acid dosages on the pseudo first-order constants of IBU ( $k_{\text{obs}}$ ) ( $[\text{IBU}]_0 = 10 \mu\text{M}$ ,  $[\text{H}_2\text{O}_2]_0 = 100 \mu\text{M}$ , pH = 7.55, and  $I_0 = 3.33 \text{ mW cm}^{-2}$ ,  $b = 0.93 \text{ cm}$ ). Please refer to the online version of this paper to see this figure in color: <http://dx.doi.org/10.2166/wst.2018.129>.

photolysis (Figure 5). This phenomenon suggests that  $\bullet\text{OH}$  is still the most important candidate regarding IBU degradation.

### Effect of inorganic anions

In aquatic environments,  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$  and  $\text{HCO}_3^-$  are common inorganic anions. Therefore, the effects of  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$  and  $\text{HCO}_3^-$  on IBU degradation in the UV/H<sub>2</sub>O<sub>2</sub> system at pH = 7.55 were studied at the concentration range of 0–5 mM. As shown in Figure 6, the degradation rate of IBU was slightly increased in the presence of  $\text{NO}_3^-$ . Xiao *et al.* (2015) found that  $\text{NO}_3^-$  can promote the degradation of  $\text{CHCl}_2\text{I}$  in UV/H<sub>2</sub>O<sub>2</sub> system. The redox potentials of  $\text{NO}_3^-/\text{NO}_2^-$  (2.3–2.6 V) is almost similar to that of  $\bullet\text{OH}/\text{H}_2\text{O}$  (2.39 V) (Xiao *et al.* 2015) in neutral conditions. Thus,  $\text{NO}_3^-$  reacts slowly with  $\bullet\text{OH}$  and its scavenging effect is limited. Nitrate also absorbs UV photons, and then  $\bullet\text{OH}$  can be generated at a low quantum yield during the photolysis of nitrate as shown in Equations (21)–(25) (Keen *et al.* 2012).



**Figure 6** | Impacts of inorganic anions on the pseudo first-order constants of IBU ( $k_{\text{obs}}$ ) ( $[\text{IBU}]_0 = 10 \mu\text{M}$ ,  $[\text{H}_2\text{O}_2]_0 = 100 \mu\text{M}$ , pH = 7.55, and  $I_0 = 3.33 \text{ mW cm}^{-2}$ ,  $b = 0.93 \text{ cm}$ ).



The degradation of IBU was not affected by adding SO<sub>4</sub><sup>2-</sup> and Cl<sup>-</sup> in the UV/H<sub>2</sub>O<sub>2</sub> system. The results are consistent with the previous studies of Xiao et al. (2015) and Guo et al. (2013). In the presence of SO<sub>4</sub><sup>2-</sup> and Cl<sup>-</sup> with concentration ranging from 1 to 5 mM, Xiao et al. (2015) found that the degradation rates of CHCl<sub>2</sub>I remained constant. Guo et al. (2013) reported that SO<sub>4</sub><sup>2-</sup> had no significant influence on CIP degradation. The redox potentials of SO<sub>4</sub><sup>•-</sup>/SO<sub>4</sub><sup>2-</sup> (2.43 V) and Cl<sup>•</sup>/Cl<sup>-</sup> (2.41 V) (Huie et al. 1991) are almost similar to that of •OH/H<sub>2</sub>O (2.39 V) (Xiao et al. 2015) in neutral conditions. These indicate that the scavenging effect of SO<sub>4</sub><sup>2-</sup> can be ignored and the scavenging effect of Cl<sup>-</sup> is limited. However, previous studies reported that the fast reaction of •OH with Cl<sup>-</sup> yielded secondary reactive chlorine radical species such as Cl<sup>•</sup>, ClOH<sup>•-</sup>, and Cl<sub>2</sub><sup>•-</sup> through complex chain reactions and ClOH<sup>•-</sup> can convert to •OH and Cl<sup>-</sup> at pH higher than 7.2 (Yang et al. 2014). This suggests that the effect of those secondary radicals with compounds could not be ignored in the degradation of IBU in the UV/H<sub>2</sub>O<sub>2</sub> process in the presence of Cl<sup>-</sup>. For instance, Cl<sup>•</sup> is a highly selective oxidant (Grebel et al. 2010). Cl<sub>2</sub><sup>•-</sup> and Cl<sup>•</sup> have high oxidation capacities, with oxidation potentials of 2.0 V and 2.47 V, respectively (Beitz et al. 1998). Thus, the scavenging effect of Cl<sup>-</sup> is offset by the release of •OH from the transient intermediate (ClOH<sup>•-</sup>) under basic conditions and the reaction of secondary radicals with compounds (Deng et al. 2013). These explain the observation that the photodegradation rates of IBU in the UV/H<sub>2</sub>O<sub>2</sub> system at pH = 7.55 were not affected by the presence of Cl<sup>-</sup>.

As reported in a previous study, HCO<sub>3</sub><sup>-</sup> is the predominant carbonate species in neutral conditions (Kwon et al. 2015). As shown in Figure 6, the presence of HCO<sub>3</sub><sup>-</sup> has an inhibitory effect on IBU degradation. The *k*<sub>obs</sub> of IBU decreased significantly when HCO<sub>3</sub><sup>-</sup> was present. When the initial concentration of HCO<sub>3</sub><sup>-</sup> was increased to 5 mM, the *k*<sub>obs</sub> of IBU was further decreased by 25%. The inhibitory effect of HCO<sub>3</sub><sup>-</sup> on other PPCPs degradation in the UV/H<sub>2</sub>O<sub>2</sub> system has also been reported in other literature (Grebel et al. 2010; Yang et al. 2014; Kwon et al. 2015). This could be mainly attributed to the scavenging effects of HCO<sub>3</sub><sup>-</sup> (*k*<sub>•OH,HCO<sub>3</sub><sup>-</sup></sub> = 8.5 × 10<sup>6</sup> M<sup>-1</sup> s<sup>-1</sup>) (Buxton et al. 1988; Grebel et al. 2010).

In the UV/H<sub>2</sub>O<sub>2</sub> process, although the PPCPs can easily be degraded in most cases, the complete mineralization of PPCPs may be an uneconomical goal for treatment (Yuan et al. 2009). The cost limits the wide application of the process in practical engineering at full scale (Yu et al. 2009). Hence, two aspects should be further addressed in future studies, including the full-scale operation cost and the toxicity of byproducts.

## CONCLUSIONS

The degradation rate of IBU was significantly increased after the addition of H<sub>2</sub>O<sub>2</sub> in the UV reactor, indicating the major primary role of •OH. Due to the higher molar absorption coefficient and quantum yield, direct UV photolysis of ionic IBU is faster than of the molecular form. In the UV/H<sub>2</sub>O<sub>2</sub> system, the degradation rate of ionic IBU is also slightly faster than that of molecular IBU, and the main determinants are *k*<sub>IBU,•OH</sub> and [•OH]<sub>SS</sub>. The effect of matrix components on IBU degradation in the UV/H<sub>2</sub>O<sub>2</sub> system was predicted and simulated by developing a steady-state approximation and kinetic parameters method. The *k* values and effect of matrix components are helpful for predicting and explaining IBU degradation mechanisms and selecting better performing treatment processes for the removal of PPCPs in wastewater.

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## REFERENCES

- Beitz, T., Bechmann, W. & Mitzner, R. 1998 Investigations of reactions of selected azaarenes with radicals in water. 2. chlorine and bromine radicals. *J. Phys. Chem. A* **102** (34), 6766–6771.
- Beltrán, F. J., Ovejero, G., García-Araya, J. F. & Rivas, J. 1995 Oxidation of polynuclear aromatic hydrocarbons in water. 2. UV radiation and ozonation in the presence of UV radiation. *Ind. Eng. Chem. Res* **34** (5), 1607–1615.
- Buxton, G. V., Greenstock, C. L., Helman, W. P. & Ross, A. B. 1988 Critical review of rate constants for reactions of hydrated electrons, hydrogen atoms and hydroxyl radicals (•OH/•O<sup>-</sup>) in aqueous solution. *J. Phys. Chem. Ref. Data* **17** (2), 513–886.
- Chianese, S., Iovino, P., Canzano, S., Prisciandaro, M. & Musmarra, D. 2016 Ibuprofen degradation in aqueous solution by using UV light. *Desalination and Water Treatment* **57** (48–49), 22878–22886.
- Christensen, A. M., Ingerslev, F. & Baun, A. 2006 Ecotoxicity of mixtures of antibiotics used in aquacultures. *Environ. Toxicol. Chem.* **25** (8), 2208–2215.

- Crittenden, J. C., Hu, S., Hand, D. W. & Green, S. A. 1999 A kinetic model for H<sub>2</sub>O<sub>2</sub>/UV process in a completely mixed batch reactor. *Water Res.* **33** (10), 2315–2328.
- Crittenden, J. C., Trussell, R. R., Hand, D. W., Howe, K. J. & Tchobanoglous, G. 2005 *Water Treatment Principles and Design*, 2nd edn. John Wiley & Sons, Hoboken, New Jersey.
- Dębska, J., Kot-Wasik, A. & Namieśnik, J. 2004 Fate and analysis of pharmaceutical residues in the aquatic environment. *Crit. Rev. Anal. Chem.* **34** (1), 51–67.
- Deng, J., Shao, Y., Gao, N., Xia, S., Tan, C., Zhou, S. & Hu, X. 2013 Degradation of the antiepileptic drug carbamazepine upon different UV-based advanced oxidation processes in water. *Chem. Eng. J.* **222**, 150–158.
- Flippin, J. L., Huggett, D. & Foran, C. M. 2007 Changes in the timing of reproduction following chronic exposure to ibuprofen in Japanese medaka, *Oryzias latipes*. *Aquat. Toxicol.* **81** (1), 73–78.
- Grebel, J. E., Pignatello, J. J. & Mitch, W. A. 2010 Effect of halide ions and carbonates on organic contaminant degradation by hydroxyl radical-based advanced oxidation processes in saline waters. *Environ. Sci. Technol.* **44** (17), 6822–6828.
- Guo, H. G., Gao, N. Y., Chu, W. H., Li, L., Zhang, Y. J., Gu, J. S. & Gu, Y. L. 2013 Photochemical degradation of ciprofloxacin in UV and UV/H<sub>2</sub>O<sub>2</sub> process: kinetics, parameters, and products. *Environ. Sci. Pollut. Res. Int.* **20** (5), 3202–3213.
- Hasselbalch, K. A. 1916 Die berechnung der wasserstoffzahl des blutes aus der freien und gebundenen kohlenäure desselben, und die sauerstoffbindung des blutes als funktion der wasserstoffzahl. *Biochemische Zeitschrift* **78**, 112–144.
- Huie, R. E., Clifton, C. L. & Kafafi, S. A. 1991 Rate constants for hydrogen abstraction reactions of the sulfate radical, SO<sub>4</sub><sup>•-</sup>: experimental and theoretical results for cyclic ethers. *J. Phys. Chem.* **95** (23), 9336–9340.
- Katsoyiannis, I. A., Canonica, S. & von Gunten, U. 2011 Efficiency and energy requirements for the transformation of organic micropollutants by ozone, O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> and UV/H<sub>2</sub>O<sub>2</sub>. *Water Res.* **45** (13), 3811–3822.
- Keen, O. S., Love, N. G. & Linden, K. G. 2012 The role of effluent nitrate in trace organic chemical oxidation during UV disinfection. *Water Res.* **46** (16), 5224–5234.
- Kim, S. D., Cho, J., Kim, I. S., Vanderford, B. J. & Snyder, S. A. 2007 Occurrence and removal of pharmaceuticals and endocrine disruptors in South Korean surface, drinking, and waste waters. *Water Res.* **41** (5), 1013–1021.
- Klassen, N. V., Marchington, D. & McGowan, H. C. 1994 H<sub>2</sub>O<sub>2</sub> determination by the I<sub>5</sub> method and by KMnO<sub>4</sub> titration. *Anal. Chem.* **66** (18), 2921–2925.
- Kwon, M., Kim, S., Yoon, Y., Jung, Y., Hwang, T., Lee, J. & Kang, J. 2015 Comparative evaluation of ibuprofen removal by UV/H<sub>2</sub>O<sub>2</sub> and UV/S<sub>2</sub>O<sub>8</sub><sup>2-</sup> processes for wastewater treatment. *Chem. Eng. J.* **269**, 379–390.
- Lutze, H. V., Bircher, S., Rapp, I., Kerlin, N., Bakkour, R., Geisler, M., von Sonntag, C. & Schmidt, T. C. 2015 Degradation of chlorotriazine pesticides by sulfate radicals and the influence of organic matter. *Environ. Sci. Technol.* **49** (3), 1673–1680.
- Packer, J. L., Werner, J. J., Latch, D. E., McNeill, K. & Arnold, W. A. 2003 Photochemical fate of pharmaceuticals in the environment: Naproxen, diclofenac, clofibrac acid, and ibuprofen. *Aquat. Sci.* **65** (4), 342–351.
- Parker, C. 1953 A new sensitive chemical actinometer. I. Some trials with potassium ferrioxalate, Proceedings of the Royal Society of London A: mathematical, physical and engineering sciences. *The Royal Society* **200** (1140), 104–116.
- Peng, M., Li, H., Kang, X., Du, E. & Li, D. 2017 Photo-degradation of ibuprofen by UV/H<sub>2</sub>O<sub>2</sub> process: response surface analysis and degradation mechanism. *Water Sci. Technol.* **75** (12), 2935–2951.
- Pereira, V. J., Weinberg, H. S., Linden, K. G. & Singer, P. C. 2007 UV degradation kinetics and modeling of pharmaceutical compounds in laboratory grade and surface water via direct and indirect photolysis at 254 nm. *Environ. Sci. Technol.* **41** (5), 1682–1688.
- Smook, T., Zho, H. & Zytner, R. 2008 Removal of ibuprofen from wastewater: comparing biodegradation in conventional, membrane bioreactor, and biological nutrient removal treatment systems. *Water Sci. Technol.* **57** (1), 1–8.
- Stumm, W. & Morgan, J. 1996 *Aquatic Chemistry: Chemical Equilibria and Rates in Natural Waters*. Wiley, New York.
- Szabó, R. K. 2010 *Decomposition of Some Pharmaceuticals by Advanced Oxidation Processes*. University of Szeged Doctoral School of Environmental Sciences, Hungary.
- Vieno, N. M., Härkki, H., Tuhkanen, T. & Kronberg, L. 2007 Occurrence of pharmaceuticals in river water and their elimination in a pilot-scale drinking water treatment plant. *Environ. Sci. Technol.* **41** (14), 5077–5084.
- Vogna, D., Marotta, R., Napolitano, A., Andreozzi, R. & d'Ischia, M. 2004 Advanced oxidation of the pharmaceutical drug diclofenac with UV/H<sub>2</sub>O<sub>2</sub> and ozone. *Water Res.* **38** (2), 414–422.
- Xiao, Y., Zhang, L., Yue, J., Webster, R. D. & Lim, T. T. 2015 Kinetic modeling and energy efficiency of UV/H<sub>2</sub>O<sub>2</sub> treatment of iodinated trihalomethanes. *Water Res.* **75**, 259–269.
- Yang, Y., Pignatello, J. J., Ma, J. & Mitch, W. A. 2014 Comparison of halide impacts on the efficiency of contaminant degradation by sulfate and hydroxyl radical-based advanced oxidation processes (AOPs). *Environ. Sci. Technol.* **48** (4), 2344–2351.
- Yang, Y., Pignatello, J. J., Ma, J. & Mitch, W. A. 2016 Effect of matrix components on UV/H<sub>2</sub>O<sub>2</sub> and UV/S<sub>2</sub>O<sub>8</sub><sup>2-</sup> advanced oxidation processes for trace organic degradation in reverse osmosis brines from municipal wastewater reuse facilities. *Water Res.* **89**, 192–200.
- Yang, Z., Su, R., Luo, S., Spinney, R., Cai, M., Xiao, R. & Wei, Z. 2017 Comparison of the reactivity of ibuprofen with sulfate and hydroxyl radicals: an experimental and theoretical study. *Sci. Total Environ.* **590–591**, 751–760.
- Yu, T.-H., Lin, A. Y.-C., Lateef, S. K., Lin, C.-F. & Yang, P.-Y. 2009 Removal of antibiotics and non-steroidal anti-inflammatory drugs by extended sludge age biological process. *Chemosphere* **77** (2), 175–181.
- Yuan, F., Hu, C., Hu, X., Qu, J. & Yang, M. 2009 Degradation of selected pharmaceuticals in aqueous solution with UV and UV/H<sub>2</sub>O<sub>2</sub>. *Water Res.* **43** (6), 1766–1774.