Comparison of the degradation of molecular and ionic ibuprofen in a UV/H₂O₂ system
Rongkui Su, Liyuan Chai, Chongjian Tang, Bo Li and Zhihui Yang

ABSTRACT
The advanced oxidation technologies based on *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/H₂O₂ system, mainly by *OH radical mediated oxidation. In the UV/H₂O₂ 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 × 10⁹ M⁻¹ s⁻¹) was higher than that of the molecular form (3.43 × 10⁹ M⁻¹ s⁻¹). The pseudo first-order rate constant for IBU degradation (k(obs)) increased with increasing H₂O₂ dosage. k(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 HCO₃⁻, which was attributed to its scavenging effect. Interestingly, when NO₃⁻ was present in aqueous solution, a slight increase in the degradation rate was observed, which was due to NO₃⁻ absorbing photons to generate *OH at a low quantum yield. No obvious effects were observed when SO₄²⁻ and Cl⁻ were present.

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

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⁻¹ and μg L⁻¹ (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⁻¹ (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⁻¹ 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.

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The *OH (E₀ = 1.89–2.72 V vs. NHE) is a strong oxidizing agent, which has a high oxidation-reduction potential (Vogna et al. 2004). *OH based advanced oxidation technologies (AOTs), including UV/H₂O₂, 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 *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/H₂O₂ systems (Szabó 2010; Chianese et al. 2016; Peng et al. 2017). The IBU degradation rate is related to initial IBU concentration, initial H₂O₂ concentration, light intensity, effective optical path, solution pH, IBU properties (i.e. IBU species, absorption characteristics, secondary reaction rate constant with *OH), and matrix components (i.e. NOM, inorganic anions) in the UV/H₂O₂ 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/H₂O₂ 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 H₂O₂ 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 H₂O₂ 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/H₂O₂). The molar absorptivity and quantum yield of IBU species at the wavelength of 254 nm were measured. The second-order reaction rate constants (kₐIBU,OH) of IBU species with *OH were determined by using competitive kinetics. The mechanism of IBU degradation in the UV/H₂O₂ system was studied by establishing a pseudo first-order reaction kinetics model based on a steady-state approach. Then the effects of H₂O₂ 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 (pCBA, 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), 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⁻) 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).

\[ \text{pH} = \text{pK}_a + \log \frac{[\text{A}^-]}{[\text{HA}]} \]  

(1)

The dissociation constant (pKₐ) of IBU is 4.9 at the solution temperature of 20°C. As shown in Equation (1), when pH is lower than pKₐ, IBU is present in the molecular form. And the anionic form is more likely to be present when pH is higher than pKₐ. 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 pCBA 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 pCBA in the working solutions were 10 μM (2.06 mg L⁻¹ and 1.57 mg L⁻¹, 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 pKₐ = 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 ± 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 milliliter 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\(^{-1}\) s\(^{-1}\) (which corresponds to a power output of 3.83 mW cm\(^{-2}\)) with potassium ferrioxalate chemical actinometry (Parker 1953) and the effective optical path length \( (b) \) was 1.32 cm measured by \( \mathrm{H}_2\mathrm{O}_2 \) 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 \( \mathrm{H}_2\mathrm{O}_2 \) was measured by the KMnO\(_4\) 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 (1.7μm, 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 50% acetonitrile and 50% 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\(^{-1}\). 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/\( \mathrm{H}_2\mathrm{O}_2 \) systems

The degradation of IBU in the UV/\( \mathrm{H}_2\mathrm{O}_2 \) 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/\( \mathrm{H}_2\mathrm{O}_2 \) system. Under UV intensity of 3.83 mW cm\(^{-2}\) and initial IBU concentration of 10 μM (2.06 mg L\(^{-1}\)), the initial direct photolysis degradation rates of IBU were 4.25 \( \times \) 10\(^{-3}\) μM min\(^{-1}\) (pH = 3.00) and 28.80 \( \times \) 10\(^{-3}\) μM min\(^{-1}\) (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\(^{-1}\)) IBU solutions at pH = 3.00 and pH = 7.55 with a 1 cm path length \( (l) \) quartz cuvette in this study:

\[
A = \epsilon \times [\text{IBU}] \times l
\]

Figure 1 illustrates the decadic molar extinction coefficient for IBU with reference to Hg lamp emission spectra.
At the wavelength of 254 nm, the \( \varepsilon \) values of IBU were 248.41 M\(^{-1}\) cm\(^{-1} \) (pH = 3.00) and 283.64 M\(^{-1}\) cm\(^{-1} \) (pH = 7.55), which were relatively low compared to the values of other PPCPs (Yang et al. 2016). The value of \( \varepsilon_{\text{IBU}} \) at 254 nm determined by Kwon et al. (2015) was 256 M\(^{-1}\) cm\(^{-1} \) (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 \( \varepsilon_{\text{IBU}} \) 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):

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

where \( \phi_{\text{IBU}} \) is the quantum yield of IBU at 254 nm (mol Einstein\(^{-1} \)), \( I_{\text{UV}} \) (M s\(^{-1} \)) is the direct photolytic degradation rate at an initial concentration of 10 \( \mu \)M (2.06 mg L\(^{-1} \)). \( I_0 \) 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\(^{-1} \) (pH = 3.00) and 0.091 mol Einstein\(^{-1} \) (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\(^{-1} \)) and naproxen (0.0093 mol Einstein\(^{-1} \)), while it is lower than that of phenytoin (0.279 mol Einstein\(^{-1} \)) and clofibric acid (0.5390 mol Einstein\(^{-1} \)) (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 \( \mu \)M (21.25 mg L\(^{-1} \)) \( \text{H}_2\text{O}_2 \) compared to direct photolysis. In the \( \text{UV}/\text{H}_2\text{O}_2 \) system, the initial degradation rate of ionic IBU at pH = 3.00 (10.62 \( \mu \)min\(^{-1} \)) was also slightly faster than that of the molecular form at pH = 7.55 (8.61 \( \mu \)min\(^{-1} \)). The dark reaction experiments showed that IBU did not degrade without UV irradiation, and the same results were obtained by adding 625 \( \mu \)M (21.25 mg L\(^{-1} \)) \( \text{H}_2\text{O}_2 \) to the dark reaction experiments. These results indicate that degradation of IBU in UV/\( \text{H}_2\text{O}_2 \) systems includes direct photolysis and radical degradation, but radical degradation plays a major role (more than 95%). The enhanced degradation of IBU with the addition of \( \text{H}_2\text{O}_2 \) is due mainly to \( \text{**OH} \) radical mediated oxidation. The results are consistent with the results reported by Xiao et al. (2015), and they also demonstrated that \( \text{**OH} \) plays a major role in the degradation of iodinated trihalomethanes by UV/\( \text{H}_2\text{O}_2 \). Therefore, the degradation rate constants of IBU largely depend on the formation of \( \text{**OH} \) in the UV system.

**Competitive kinetics**

The second-order rate constant of IBU with \( \text{**OH} \) (\( k_{\text{IBU, **OH}} \)) can be determined by competitive kinetics (Packer et al. 2003; Kwon et al. 2015). \( \text{pCBA} \) was chosen as a reference compound in this study for two significant reasons. First, \( k \) values for \( \text{pCBA} \) reacting with \( \text{**OH} \) are known (5.0 \( \times \) 10\(^8\) M\(^{-1}\) s\(^{-1} \) at neutral and 4.5 \( \times \) 10\(^9\) M\(^{-1}\) s\(^{-1} \) at acidic) (Buxton et al. 1988). Second, the reaction of \( \text{pCBA} \) with \( \text{**OH} \) is less affected by other substances (Katsyiannis et al. 2011). The \( k \) values of IBU reacting with \( \text{**OH} \) was calculated as follows (Yuan et al. 2009):

\[
\frac{k_{\text{IBU, **OH}}}{k_{\text{pCBA, **OH}}} = \frac{\ln [\text{IBU}]_t}{[\text{IBU}]_0} - \frac{\ln [\text{IBU}]_t}{[\text{IBU}]_0} / \frac{\ln [\text{pCBA}]_t}{[\text{pCBA}]_0} - \frac{\ln [\text{pCBA}]_t}{[\text{pCBA}]_0} / \frac{\ln [\text{IBU}]_0}{[\text{IBU}]_0} / \frac{\ln [\text{pCBA}]_0}{[\text{pCBA}]_0} / \frac{\ln [\text{IBU}]_0}{[\text{IBU}]_0}
\]

where \( k_{\text{tot, IBU}} \) and \( k_{\text{tot, pCBA}} \) are the first-order rate constants for the total degradation of IBU and \( \text{pCBA} \), \( k_{\text{UV, IBU}} \) and \( k_{\text{UV, pCBA}} \) are the first-order rate constant for the direct UV
photolysis of IBU and pCBA, respectively. The value of $k_{\text{tot}}$-$k_{\text{UV}}$ will then be the degradation rate of IBU by the radical reaction. A straight line with the slope $k_{\text{IBU,OH}}/k_{\text{pCBA,OH}}$ and the intercept of zero was plotted with $k_{\text{tot, IBU}}$-$k_{\text{UV}}$, IBU against $k_{\text{tot, IBU}}$-$k_{\text{pCBA}}$, IBU-$p$CBA. As shown in Figure 3, an average reaction rate constant ratio of IBU and $p$CBA with *OH was 0.686 (unitless) and 1.047 (unitless) at pH = 3.00 and pH = 7.55, respectively. The $k_{\text{IBU,OH}}$ values of molecular and ionic IBU with *OH were determined to be 3.43 (±0.09) × 10^9 M^-1 s^-1 (pH = 3.00) and 5.93 (±0.15) × 10^9 M^-1 s^-1 (pH = 7.55), respectively. Packer et al. (2003) have determined the value of $k_{\text{IBU,OH}}$ to be 6.50 × 10^9 M^-1 s^-1 (pH = 3.00) in the Fenton system, which is different from our measurement (3.43 × 10^9 M^-1 s^-1). Some of the difference stem from two factors: (i) Packer et al. (2003) determined the value of $k_{\text{IBU,OH}}$ in the Fenton system, whereas we measured it in the UV/H_2O_2 system, (ii) acetophenone was used as a reference substance in the study of Packer et al. (2003), whereas pCBA was used in this study. However, under the same conditions of the UV/H_2O_2 system and reference substance (pCBA), the $k_{\text{IBU,OH}}$ (5.93 × 10^9 M^-1 s^-1 at pH = 7.55) is consistent with the result (5.75 × 10^9 M^-1 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 of radicals (Yuan et al. 2009). The method is established based on the assumption that the radicals (i.e. *OH) produced by UV photolysis of H_2O_2 play a major role on the degradation of target compounds (Yuan et al. 2009). The reactions in the UV/H_2O_2 system and their rate constants are presented in Table 1.

Under steady-state conditions, the reaction rate ($r_{\text{tot}}$) of IBU degradation in the UV/H_2O_2 process can be expressed with the following equation (Crittenden et al. 1999):

$$r_{\text{tot}} = r_{\text{UV}} + r_{\text{OH}}$$

(5)

where $r_{\text{UV}}$ is the initial IBU direct photolytic degradation rate in the UV/H_2O_2 process and $r_{\text{OH}}$ is the IBU reaction rate with *OH.

$$r_{\text{UV}} = \varphi_{\text{IBU}} \times I_0 \times \frac{b}{A} \times \left(1 - 10^{-A}\right)$$

(6)

$$r_{\text{OH}} = k_{\text{IBU,OH}} \times [\text{OH}]_{\text{SS}} \times [\text{IBU}]$$

(7)

$$A = b(\varphi_{\text{IBU}}[\text{IBU}] + \varepsilon_{\text{H}_2\text{O}_2}[\text{H}_2\text{O}_2])$$

(8)

where $I_0$ is the incident UV intensity (3.83 mW cm^-2), and $b$ is the reactor light path (1.32 cm). A is the absorbance of the reaction solution. $\varepsilon_{\text{H}_2\text{O}_2}$ is the molar extinction coefficient of H_2O_2 (19.6 M^-1 cm^-1), and $\varphi_{\text{OH}}$ (in Equation (11) below) is the quantum yield of H_2O_2 (0.5 mol Einstein^-1) at wavelength 254 nm (Crittenden et al. 1999).

The degradation of IBU in UV/H_2O_2 systems follows pseudo first-order kinetics (the unit for pseudo first-order is s^-1), and can be described by an equation as follows:

$$k_{\text{tot}} \times [\text{IBU}] = k_{\text{UV}} \times [\text{IBU}] + k_{\text{IBU,OH}}[\text{OH}]_{\text{SS}}[\text{IBU}]$$

(9)

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

$$0 = \frac{d[\text{OH}]}{dt} = r_{\text{OH}} - \left(k_{\text{IBU,OH}} - [\text{IBU}] \times \varepsilon_{\text{H}_2\text{O}_2} \times [\text{IBU}] + k_{1\text{[H}_2\text{O}_2]}[\text{OH}]_{\text{SS}} + k_{2\text{[HO}_2]}[\text{OH}]_{\text{SS}} + k_{1\text{[H}_2\text{O}_2,\text{H}_2\text{O}_2]}[\text{OH}]_{\text{SS}} + k_{2\text{[H}_2\text{O}_2,\text{H}_2\text{O}_2]}[\text{HPO}_4^-] + k_{3\text{[OH]}_{\text{SS}}[\text{H}_2\text{PO}_4^-]} + k_{4\text{[OH]}_{\text{SS}}[\text{H}]_{\text{PO}_4^-}}\right)$$

(10)
# Reaction |
<table>
<thead>
<tr>
<th>#</th>
<th>Reaction</th>
<th>$k$ (M$^{-1}$ s$^{-1}$)</th>
<th>Reference or note</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$\text{H}_2\text{O}_2 + h\nu \rightarrow 2^\cdot\text{OH}$</td>
<td>$r_{\text{OH}} = 2\varphi_H E_H$, s$^{-1}$</td>
<td>Crittenden et al. (1999)</td>
</tr>
<tr>
<td>2</td>
<td>$\text{H}_2\text{O}_2 + ^\cdot\text{OH} \rightarrow \text{HO}_2^- + \text{H}_2\text{O}$</td>
<td>$k_1 = 2.7 \times 10^7$</td>
<td>Buxton et al. (1988)</td>
</tr>
<tr>
<td>3</td>
<td>$^\cdot\text{OH} + \text{HO}_2^- \rightarrow \text{HO}_2^- + ^\cdot\text{OH}$</td>
<td>$k_2 = 7.5 \times 10^9$</td>
<td>Crittenden et al. (1999)</td>
</tr>
<tr>
<td>4</td>
<td>$\text{H}_2\text{O}_2 \leftrightarrow ^\cdot\text{H} + \text{HO}_2^-$</td>
<td>$k_3 = 2.51 \times 10^{-12}$</td>
<td>Crittenden et al. (1999)</td>
</tr>
<tr>
<td>5</td>
<td>$\text{H}_3\text{PO}_4 \leftrightarrow ^\cdot\text{H} + \text{H}_2\text{PO}_4^-$</td>
<td>$pK_{a1} = 2.17$ unitless</td>
<td>Stumm &amp; Morgan (1996)</td>
</tr>
<tr>
<td>6</td>
<td>$\text{H}_2\text{PO}_4^- \leftrightarrow ^\cdot\text{H} + \text{HPO}_2^- \leftrightarrow ^\cdot\text{OH}$</td>
<td>$pK_{a2} = 7.21$ unitless</td>
<td>Stumm &amp; Morgan (1996)</td>
</tr>
<tr>
<td>7</td>
<td>$\text{HPO}_2^- \leftrightarrow ^\cdot\text{H} + \text{PO}_4^{2-}$</td>
<td>$pK_{a3} = 12.35$ unitless</td>
<td>Stumm &amp; Morgan (1996)</td>
</tr>
<tr>
<td>8</td>
<td>$^\cdot\text{OH} + \text{H}_2\text{PO}_4^- \rightarrow \text{HPO}_4^{2-} + \text{H}_2\text{O}$</td>
<td>$k_{h1} = 2.0 \times 10^4$</td>
<td>Buxton et al. (1988)</td>
</tr>
<tr>
<td>9</td>
<td>$^\cdot\text{OH} + \text{HPO}_2^- \rightarrow \text{HPO}_4^{2-} + ^\cdot\text{OH}$</td>
<td>$k_{h2} = 1.5 \times 10^5$</td>
<td>Buxton et al. (1988)</td>
</tr>
<tr>
<td>10</td>
<td>$^\cdot\text{OH} + \text{PO}_4^{2-} \rightarrow ^\cdot\text{OH} + \text{PO}_4^{2-} + ^\cdot\text{OH}$</td>
<td>$k_{h3} = 1.5 \times 10^7$</td>
<td>Buxton et al. (1988)</td>
</tr>
<tr>
<td>11</td>
<td>$^\cdot\text{OH} + \text{H}_2\text{PO}_4^- \rightarrow \text{H}_2\text{PO}_4^- + ^\cdot\text{OH}$</td>
<td>$k_{h4} = 2.7 \times 10^6$</td>
<td>Buxton et al. (1988)</td>
</tr>
</tbody>
</table>

In the presence of NOM:

**Degradation of IBU**

- $^\cdot\text{OH} + \text{NOM} \rightarrow \text{products}$
  - $k_4 = 1.40 \times 10^4$ L mg C$^{-1}$ s$^{-1}$
  - Measured in this study

**IBU + hv → products**

- $r_{\text{UV}, \text{M}}$ s$^{-1}$
  - Measured in this study

In the UV/H$_2$O$_2$ system, $r_{0, \cdot\text{OH}}$ can be calculated as follows (Crittenden et al. 1999):

$$r_{0, \cdot\text{OH}} = 2\varphi_H E_H I_0 \frac{I_{\text{H}_2\text{O}_2}}{A}$$

$$f_{\text{H}_2\text{O}_2} = \frac{b \varphi_H E_H [\text{H}_2\text{O}_2]}{A}$$

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

$$k_{\text{IBU, OH}} = \frac{(k_{\text{tot}} - k_{\text{UV}}) \times (k_1 [\text{H}_2\text{O}_2] + k_2 [\text{HO}_2^-] + k_{h1} [\text{H}_2\text{PO}_4^-] + k_{h2} [\text{HPO}_2^-] + k_{h3} [\text{S}_1])}{2\varphi_H E_H I_0 H (1 - 10^{-b} \sum e_{C_i}) - (k_{\text{tot}} - k_{\text{UV}}) \times [\text{AC}]}$$

$$[\cdot\text{OH}]_{\text{SS}} = \frac{2\varphi_H E_H I_0 H (1 - 10^{-b} \sum e_{C_i})}{k_1 [\text{H}_2\text{O}_2] + k_2 [\text{HO}_2^-] + k_{\text{IBU, OH}} [\text{AC}] + k_{h1} [\text{H}_2\text{PO}_4^-] + k_{h2} [\text{HPO}_2^-] + k_{h3} [\text{S}_1]}$$

The $k_{\text{IBU, OH}}$ of molecular and ionic IBU with *OH were calculated to be $3.47 (\pm 0.11) \times 10^9$ M$^{-1}$ s$^{-1}$ (pH = 3.00) and $5.89 (\pm 0.19) \times 10^9$ M$^{-1}$ s$^{-1}$ (pH = 7.55), which were consistent with the values determined by photoysis and *OH in the UV/H$_2$O$_2$ system.

$$\frac{r_{\text{tot}}}{r_{\text{tot}}} (r_{\text{tot}}) = \frac{r_{\text{UV}}}{r_{\text{tot}}} (r_{\text{UV}}) + \frac{r_{\cdot\text{OH}}}{r_{\text{tot}}} (r_{\cdot\text{OH}})$$
In the UV/H₂O₂ system, the \( r_{\text{UV}} \) and \( r_{\text{OH}} \) 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,

\[
100\% (r_{\text{tot}}) = 0.49\% (r_{\text{UV}}) + 99.51\% (r_{\text{OH}}) \tag{16}
\]

Meanwhile, the \( r_{\text{UV}} \) and \( r_{\text{OH}} \) were determined to be \( 4.72 \times 10^{-5} \, \text{M s}^{-1} \) and \( 1.72 \times 10^{-7} \, \text{M s}^{-1} \) at pH = 7.55, respectively. Therefore,

\[
100\% (r_{\text{tot}}) = 2.67\% (r_{\text{UV}}) + 97.33\% (r_{\text{HO}}) \tag{17}
\]

The calculated contributions of direct photolysis and *OH to IBU degradation are shown in Equations (16) and (17). *OH is the main reactive species in the UV/H₂O₂ 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 \( r_{\text{UV}} \) was less than 3%). The results support the previous conclusion that *OH play a major role in IBU degradation in the UV/H₂O₂ system.

Thus, under the same initial conditions, the secondary reaction rate constants of molecular and ionic IBU with *OH and the steady-state concentration of *OH determine the IBU degradation rate in the UV/H₂O₂ system. These also explain why the IBU degradation rate at pH = 7.55 is faster than at pH = 3.00 in UV/H₂O₂ 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 H₂O₂ dosage and NOM on IBU degradation in the UV/H₂O₂ system. Then the contributions of direct photolysis and *OH to IBU degradation (i.e. \( k_{\text{cal,UV}} \) and \( k_{\text{cal,OH}} \)) under various experimental conditions were calculated according to Equations (18) and (19), respectively.

\[
k_{\text{cal,UV}} = \varphi_{\text{IBU}} \times I_0 \times \frac{b \varepsilon_{\text{IBU}}}{A} \times (1 - 10^{-4}) \tag{18}
\]

\[
k_{\text{cal,OH}} = k_{\text{IBU,OH}} \times [\text{OH}]_{\text{SS}} \tag{19}
\]

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

\[
k_{\text{cal,obs}} = k_{\text{cal,UV}} + k_{\text{cal,OH}} \tag{20}
\]

**Effect of the initial H₂O₂ dosage**

The concentration of H₂O₂ in the UV/H₂O₂ system affected the degradation rates of IBU. As shown in Figure 4, the experimental results of the pseudo first-order rate constants for IBU degradation \( (k_{\text{exp,obs}}) \) increased from \( 2.25 \times 10^{-3} \, \text{s}^{-1} \) to \( 10.24 \times 10^{-3} \, \text{s}^{-1} \) when the H₂O₂ concentration increased from 45 to 375 \( \mu \text{M} \) (1.53 mg L⁻¹ to 12.75 mg L⁻¹) at pH = 7.55. This result could be well predicted by the kinetic model. In Figure 4, the \( k_{\text{exp,obs}} \) was consistent with the modeling results \( (k_{\text{cal,obs}}) \).

The calculated contributions of direct photolysis and *OH to IBU degradation are also shown in Figure 4. The *OH was the main reactive species in the UV/H₂O₂ system, whose contribution to IBU degradation \( (k_{\text{cal,OH}}) \) was always greater than 97% with the increase of H₂O₂ concentration from 45 \( \mu \text{M} \) to 375 \( \mu \text{M} \) (1.53 mg L⁻¹ to 12.75 mg L⁻¹) (i.e. the contribution of direct photolysis \( (k_{\text{cal,UV}}) \) was less than 3%). The calculated contributions of direct photolysis and *OH were 2.67% and 97.33% at the initial concentration of H₂O₂ (625 \( \mu \text{M} \)) at pH = 7.55, which were consistent with experimental data (Equation (17)). Guo et al. (2015) found that the apparent rate constant \( (k_{\text{app}}) \) of ciprofloxacin (CIP) increased from \( 0.39 \times 10^{-3} \, \text{s}^{-1} \) to \( 3.72 \times 10^{-3} \, \text{s}^{-1} \) when H₂O₂ 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 H₂O₂ further increased, but only when the concentration of H₂O₂ was above 10 mM, when the decreasing trend of \( k_{\text{cal,obs}} \) occurred (the inset in Figure 4). The possible explanation is that *OH could be scavenged by the excess H₂O₂ 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/H₂O₂ system at pH = 7.55 was studied by adding different concentrations of humic acid (0–2.87 mgC L⁻¹). Figure 5 shows that \( k_{\text{exp,obs}} \) decreased from 3.55 × 10⁻³ s⁻¹ to 1.79 × 10⁻³ s⁻¹ with humic acid concentration increasing from 0 mgC L⁻¹ to 2.87 mgC L⁻¹. 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/H₂O₂ 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 \( A = b(\epsilon_{\text{IBU}}[\text{IBU}] + \epsilon_{\text{H₂O₂}}[\text{H₂O₂}] + \epsilon_{\text{NOM}} \text{[humic acid]}) \), the \( \epsilon_{\text{NOM}} \text{[humic acid]} \) being 0.10 L mgC⁻¹ cm⁻¹ 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 \( \epsilon \) 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 \( \cdot \text{OH} \) (\( k_4 \) 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/H₂O₂ process. Even in the presence of humic acid, the calculated contributions of \( \cdot \text{OH} \) was still clearly higher than the direct photolysis (Figure 5). This phenomenon suggests that \( \cdot \text{OH} \) is still the most important candidate regarding IBU degradation.

**Effect of inorganic anions**

In aquatic environments, Cl⁻, SO₄²⁻, NO₃⁻ and HCO₃⁻ are common inorganic anions. Therefore, the effects of Cl⁻, SO₄²⁻, NO₃⁻ and HCO₃⁻ on IBU degradation in the UV/H₂O₂ 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 NO₃⁻. Xiao et al. (2015) found that NO₃⁻ can promote the degradation of CHCl₃ in UV/H₂O₂ system. The redox potentials of NO₃⁻/NO₂⁻ (2.3–2.6 V) is almost similar to that of \( \cdot \text{OH}/\text{H₂O} \) (2.39 V) (Xiao et al. 2015) in neutral conditions. Thus, NO₃⁻ reacts slowly with \( \cdot \text{OH} \) and its scavenging effect is limited. Nitrate also absorbs UV photons, and then \( \cdot \text{OH} \) can be generated at a low quantum yield during the photolysis of nitrate as shown in Equations (21)–(25) (Keen et al. 2012).

\[
\text{NO}_3^- + \text{h} \nu \rightarrow \text{NO}_2^- + \text{O}  
\]

\[
\text{NO}_3^- + \text{h} \nu \rightarrow \text{NO}_2^* + \text{O}^*  
\]

\[
2\text{NO}_2^- + \text{H}_2\text{O} \rightarrow \text{NO}_2^- + \text{NO}_3^- + 2\text{H}^+  
\]

\[
\text{O} + \text{H}_2\text{O} \rightarrow 2\cdot \text{OH}  
\]

\[
\text{O}^* + \text{H}_2\text{O} \rightarrow \cdot \text{OH} + \text{HO}^*  
\]
The degradation of IBU was not affected by adding SO$_4^{2-}$ and Cl$^-$ in the UV/H$_2$O$_2$ system. The results are consistent with the previous studies of Xiao et al. (2015) and Guo et al. (2013). In the presence of SO$_4^{2-}$ and Cl$^-$ with concentration ranging from 1 to 5 mM, Xiao et al. (2015) found that the degradation rates of CHCl$_2$I remained constant. Guo et al. (2013) reported that SO$_4^{2-}$ had no significant influence on CIP degradation. The redox potentials of SO$_4^{2-}$/SO$_4^{2-}$ (2.43 V) and Cl$^-$/Cl$^-$ (2.41 V) (Huie et al. 1999) are almost similar to that of *OH/H$_2$O (2.59 V) (Xiao et al. 2015) in neutral conditions. These indicate that the scavenging effect of SO$_4^{2-}$ can be ignored and the scavenging effect of Cl$^-$ is limited. However, previous studies reported that the fast reaction of *OH with Cl$^-$ yielded secondary reactive chlorine radical species such as Cl$^\bullet$, ClO$^\bullet^+$, and Cl$^{2\bullet}$ through complex chain reactions and ClO$^\bullet^+$ can convert to *OH and Cl$^-$ 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$_2$O$_2$ process in the presence of Cl$^-$. For instance, Cl$^\bullet$ is a highly selective oxidant (Grebel et al. 2010). Cl$^{2\bullet}$ and Cl$^\bullet$ 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$^-$ is offset by the release of *OH from the transient intermediate (ClO$^\bullet^+$) 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$_2$O$_2$ system at pH = 7.55 were not affected by the presence of Cl$^-$.

As reported in a previous study, HCO$_3^-$ is the predominant carbonate species in neutral conditions (Kwon et al. 2015). As shown in Figure 6, the presence of HCO$_3^-$ has an inhibitory effect on IBU degradation. The $k_{obs}$ of IBU decreased significantly when HCO$_3^-$ was present. When the initial concentration of HCO$_3^-$ was increased to 5 mM, the $k_{obs}$ of IBU was further decreased by 25%. The inhibitory effect of HCO$_3^-$ on other PPCPs degradation in the UV/H$_2$O$_2$ 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$_3^-$ ($k_{OH,HCO_3} = 8.5 \times 10^6 \text{ M}^{-1} \text{s}^{-1}$) (Buxton et al. 1988; Grebel et al. 2010).

In the UV/H$_2$O$_2$ 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$_2$O$_2$ 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$_2$O$_2$ system, the degradation rate of ionic IBU is also slightly faster than that of molecular IBU, and the main determinants are $k_{IBU,*OH}$ and $k_{*OH,SS}$. The effect of matrix components on IBU degradation in the UV/H$_2$O$_2$ 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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