Photo-degradation ibuprofen by UV/H₂O₂ process: response surface analysis and degradation mechanism

Mingguo Peng, Huajie Li, Xu Kang, Erdeng Du and Dongdong Li

ABSTRACT

The removal of ibuprofen (IBP) in aqueous solution using UV/H₂O₂ process was evaluated. The response surface methodology (RSM) and Box–Behnken design were employed to investigate the effects of process parameters on IBP removal, including the initial IBP concentration, H₂O₂ dosage, UV light intensity, and initial pH value of solution. The RSM model developed herein fits well with the experiments, and provides a good insight into the OH radical irritated degradation mechanisms and kinetics. High resolution accurate mass spectrometry coupled with liquid chromatography was used to identify the degradation intermediates. A total of 23 degradation products were identified, including mono-hydroxylated products and dihydroxylated products. A series of OH radical-initiated reactions, including hydroxylation, dihydroxylation, decarboxylation, demethylation, ring break, lead to the final mineralization of IBP to CO₂ and H₂O. UV/H₂O₂ technology could be a promising technology for IBP removal in aqueous solution.

Key words | degradation intermediates, ibuprofen, response surface methodology, UV/H₂O₂

INTRODUCTION

Currently, many water resources, including lakes, rivers, and water reservoirs, have become contaminated by emerging organic compounds characterized by low concentrations and high toxicities. Among these, pharmaceuticals and personal care products (PPCPs) are especially among the most important groups (Liu & Wong 2013). With universal production, use of PPCPs for human and animal applications, PPCPs and their metabolites are increasingly placed in the environment through direct and indirect pathways (Subedi et al. 2012). A wide range of PPCPs has been determined in surface water (Yu et al. 2011), groundwater (Peng et al. 2014), soil (Gottschall et al. 2012), and aquatic animals (Subedi et al. 2012) throughout the world, including the USA, China, and Europe (Ramirez et al. 2009; Yu & Chu 2009; Liu & Wong 2013; Ortiz de Garcia et al. 2013; Yu et al. 2013). It has been validated that PPCPs in the aquatic environment could be a potential risk to the ecological environment and human health (Ternes et al. 2004; Brooks et al. 2009; Schnell et al. 2009). Therefore, the detection and control technology of PPCPs in water have become an urgent and emerging problem faced by many countries and regions (Boxall et al. 2012).

Research has shown that existing wastewater treatment plants (WWTPs) cannot completely remove PPCPs in water, which persist with fluctuating concentrations in effluent (Kasprzyk-Hordern et al. 2009; Matamoros et al. 2009; Miege et al. 2009; Nelson et al. 2011). The removal of PPCPs by biological treatment processes, including conventional activated sludge, membrane bioreactors, sequencing batch reactors, sand filters, and constructed wetlands, are limited (Onesios et al. 2009; Hijosa-Valsero et al. 2010; Sui et al. 2011). The effluents of WWTPs are the major contributor to the aquatic environment, and the effect on the quality of the aquatic environment cannot be underestimated (Kasprzyk-Hordern et al. 2009; Laura Martin-Diaz et al. 2009).

Several technologies have been evaluated for the removal of PPCPs, including adsorption (Pan et al. 2009; Redding et al. 2009; Yang et al. 2011), land application (Sabourin et al. 2009), ferrate oxidation (Yang et al. 2012), Fenton oxidation (Li et al. 2012), and UV/H₂O₂ (Kim et al. 2009). Advanced oxidation processes (AOPs), based on hydroxyl radical reaction, are promising techniques to treat organic pollutants. As a type of AOP, the UV/H₂O₂ process has been tried and found effective in the degradation of PPCPs. The UV/H₂O₂ process degrades pollutants mainly by OH radical induced reactions (Yao et al. 2013). Several studies have been conducted to evaluate the removal of PPCPs in water (Yuan et al. 2012;
Eight kinds of PPCPs can be effectively removed by more than 90% under certain conditions (Shu et al. 2013; Li et al. 2013; Rahmah et al. 2013). Eight kinds of PPCPs can be effectively removed by more than 90% under certain conditions (Shu et al. 2013). Moreover, chloride could capture OH radicals to inhibit reaction. The co-existence of chloride and bromide also could produce ClBr—radicals to accelerate contaminants’ degradation in AOPs. Salinity in water plays multiple roles and imposes a broader impact on PPCPs’ removal by the UV/H2O2 process (Li et al. 2013).

Ibuprofen (IBP) is a nonsteroidal anti-inflammatory drug used for relieving pain, helping with fever, and reducing inflammation (Madhavan et al. 2010). The drug is extensively used through the world, and is ranked in 17th place on the list of the most prescribed drugs in the USA (Richards & Cole 2006). IBP was reported as being determined in the aquatic environment with a detectability frequency of 50–60% in China (Dan et al. 2014). Until now, research about IBP degradation by UV/H2O2 process has been limited, which inhibits the application of this technique in the treatment of wastewaters containing IBP.

Response surface methodology (RSM) is a particular collection of mathematical and statistical techniques, which can be used for experiment design, model building, parameter evaluation and optimization (Rezaee et al. 2014). It has been widely applied in chemistry, biochemistry, physics, environmental science research, particularly in situations where numerous variables influence the system feature (Kasiri & Khataee 2011).

IBP often occurs in the aquatic environment at ng/L or µg/L level, and its photodegradation in sunlight is also slow. The major goal of this study is to investigate the oxidation behavior of IBP degradation in aqueous solution by the UV/H2O2 process. The RSM method combined with an experimental design is used to investigate the main factors of the UV/H2O2 process, including UV light intensity, H2O2 dosage, initial IBP concentration, and initial pH value of solution. Additionally, the degradation intermediates are identified by LTQ-Orbitrap high-resolution mass spectrometer. Combined with chemical structure analysis, a degradation mechanism of IBP by the UV/H2O2 process is also proposed.

**MATERIALS AND METHODS**

**Materials and chemicals**

IBP (analytical grade) was bought from Energy Chemical Reagent Co., Ltd (Shanghai, China). 25 mg L⁻¹ original liquid of IBP was prepared by ultrapure water. Other different concentrations of IBP solution were prepared through dilution according to the actual needs. The chemical structure and basic characteristics of IBP are as shown in Figure S1 and Table S1 (available with the online version of this paper). Methanol (HPLC), hydrochloric acid, and sodium hydroxide were purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). Hydrogen peroxide (30% w/w analytical grade) was obtained from Lingfeng Chemical Company (Shanghai, China). The original liquid concentration of hydrogen peroxide (H₂O₂) solution used in the test is 0.1 M. The concentration of ammonium acetate (Aladdin, Shanghai) solution is 5 mM. All solutions were prepared using ultrapure water with the resistivity of 18.3 MΩ cm from a Milli-Q water purification system (Millipore, USA). Oasis HLB cartridge (Waters, 500 mg, 6 cc, USA) was used for solid phase extraction (SPE).

**Photoreactor and experimental methods**

The photodegradation experiment was performed in a homemade glass photoreactor with a volume of 200 mL and diameter of 10 cm. A stir bar was placed inside the reactor below the UV lamp to ensure the homogeneity of the solution. IBP solutions were irradiated with a 75 W mercury lamp emitting at 254 nm (Philips, Shanghai). IBP solution and H₂O₂ were added at a range of concentrations in the reactor. After the reaction started, IBP samples were collected every 5 min to determine the current IBP concentration by high-performance liquid chromatography (HPLC). In addition, according to the experimental design, several factors, including initial IBP concentration, H₂O₂ dosage, UV light intensity, and solution initial pH, were varied to investigate their effects on the degradation of IBP by the UV/H₂O₂ process.

The distance between the UV lamp and the water surface was adjusted to change the radiation intensity. The average UV light intensity was monitored using an ultraviolet meter (Model UV-B, Photoelectric Instrument Factory of Beijing Normal University, Beijing, China). The pH of the solutions was measured using a pH meter (PHS-3C, Shanghai REX, China) and adjusted with 0.1 mol/L hydrochloric acid and/or 0.1 mol/L sodium hydroxide prior to use.

**IBP and degradation intermediates analysis**

IBP concentration was determined by HPLC (LC-100), purchased from Wufeng Scientific Instruments Co., Ltd (Shanghai, China). The device is equipped with a UV
detector, and a C18 column (LK-C18, 4.6 × 150 mm, 5 μm) supplied by Kexiao Scientific Instrument Co., Ltd (Suzhou, China). The oven temperature was set at 30 °C with detection wavelength of 265 nm. The mobile phase was 60% methanol and 40% ammonium acetate solution (5 mM). Chromatogram retention time of IBP in HPLC was 5.7 min.

Fluorescence excitation-emission matrix spectroscopy (EEMs) was also employed to characterize the changes of IBP during the photodegradation process. EEMs was measured in a 1.0 cm quartz cell with a Varian Cary Eclipse spectrophotometer (Varian, USA). The relevant parameters are as follows: excitation wavelengths 220–450 nm in 5 nm intervals, emission wavelengths 280–500 nm in 2 nm intervals, scan rate 9,600 nm/min, slit width 5 nm, and photomultiplier tube voltage 700 V.

The SPE procedure was used for intermediates prepro-cess according to the US EPA method 1694 (EPA 2007). The procedure was as follows: hydrochloric acid was used to adjust IBP solution to pH = 2. SPE cartridge (Oasis HLB) was in turn activated by 20 mL methanol, 6 mL pure water, 6 mL acidified water (pH = 2), then IBP solution was percolated through the cartridge at the rate of 3 mL min⁻¹. The sorbent was washed with 10 mL water and dried under vacuum for 15 min. The sorbent was then eluted with 12 mL methanol, and 6 mL methanol/acetone mixture (volume 1:1) separately. The extract was evaporated under a stream of nitrogen and reconstituted in 1.0 mL of methanol.

LTQ-Orbitrap XL (Thermo Scientific, USA) was used to identify degradation intermediates. Chromatographic separation was performed using an HPLC equipped with a reversed phase column (Welch Ultimate Polar-RP C18, 100 × 2.1 mm, 3.0 μm particles). The liquid chromatography (LC) conditions were as follows: mobile phase (A) water, mobile phase (B) acetonitrile with 0.1% formic acid, flow rate 0.2 mL min⁻¹, injection volume 10 μL. The gradient elution program was used: 90% A at starting time, then linear decrease to 25% A over 35 min, 25% A for 5 min, then return to 90% A for 5 min. MS analysis was carried out with an electrospray ionization probe in the negative ion mode. Data-dependent analysis was performed with an electrospray ionization probe in the negative ion mode. Software Design Expert 7.1.3 (Student Version) was used to perform response surface analysis, optimize the reaction parameters, and construct RSM model.

RESULTS AND DISCUSSION

IBP degradation by single UV, single H₂O₂, and UV/H₂O₂ process

The removal of IBP was compared among single UV photoysis, single H₂O₂ oxidation, and UV/H₂O₂ processes. Figure 1 shows the changes of IBP concentration with reaction time in the three processes. The experimental conditions were as follows: H₂O₂ concentration 0.6 mM, UV intensity 850 mW cm⁻², and initial IBP concentration 15 mg L⁻¹. The initial pH value of the runs is 6.82. Figure 1...
shows that the IBP concentration was essentially unchanged by single H₂O₂ oxidation. This result indicates that H₂O₂ cannot basically break the chemical structure of IBP as H₂O₂ has a low oxidation-reduction potential of 1.77 V. Single UV photolysis process also cannot effectively treat IBP, with IBP removal of only 7.6% in a 30 min reaction. The results indicate that IBP is resistant to direct UV photolysis, similar to other PPCPs. However, the UV/H₂O₂ process performed well, with IBP removal of 82.4% in 30 min with an H₂O₂ dosage of 0.6 mM and a UV intensity of 850 mW cm⁻². Other research also illustrated that the UV/H₂O₂ process can effectively degrade IBP in aqueous solution (Iovino et al. 2014). IBP degradation by the UV/H₂O₂ process is mainly performed by OH radical generated from H₂O₂ photolysis excited by UV light (Yuan et al. 2016).

Pseudo-first-order reaction kinetics is usually used to describe the UV/H₂O₂ process (Li et al. 2015). Figure 1 also shows that pseudo-first-order reaction kinetics was successfully fitted with test results ($R^2 = 0.993$) with rate constant of 0.0362 min⁻¹, according to the kinetic model (Equation (2)):

$$\ln \frac{C_{[IBP]}}{C_{[IBP]₀}} = -K_{app}t$$  

where $C_{[IBP]₀}$ is the initial IBP concentration, $C_{[IBP]}$ is the IBP concentration at $t$ min, $K_{app}$ is the first-order rate constant, and $t$ is the reaction time.

EEM spectra and its changes were also illustrated to investigate IBP degradation by UV/H₂O₂ process (Figure 2). Figure 2(a) shows that there is a main fluorescent peak (approximately ex/em 220/280 nm) and a subordinate peak (approximately ex/em 260/280 nm). The intensity of the main fluorescent peak obviously decreases during the UV/H₂O₂ degradation process. Moreover, the subordinate peak even disappears after degradation of 15 min.

**Established RSM model and its validation**

According to the BBD experimental design, a total of 29 runs was performed. The reaction parameters and results are presented in Table 1. On the basis of the results obtained in each run (Table 1), two RSM models were constructed to explain the relationship of reaction parameters and results (rate constants $K$, and removal $\eta$), as follows:

$$K = 0.047 + 0.022x₁ + 0.031x₂ - 0.027x₃ + 0.005x₄$$
$$+ 0.012x₁x₂ - 0.018x₁x₃ + 0.002x₁x₄ - 0.012x₃x₅$$
$$+ 0.013x₂x₄ + 0.013x₃x₄$$

(3)

$$\eta = 64.86 + 16.07x₁ + 23.87x₂ - 16.13x₃ + 3.45x₄$$
$$+ 0.34x₁x₂ + 2.19x₁x₃ - 0.12x₁x₄ - 0.88x₃x₅$$
$$- 1.04x₂x₄ + 6.74x₃x₄$$

(4)
The analysis of variance (ANOVA) was also used to determine the significance and robustness of the established RSM models, as shown in Table 2. A p-value less than 0.0500 indicates the significance of the model (Li et al. 2013). The results of ANOVA showed that the two models were significant with a low p-value (<0.0001) and higher F value (>1). The two models were further validated by determination coefficients ($R^2$) of 0.8656 and 0.8188.

What is more, the robustness of the models were also investigated by diagnostic plots (Figure S2, available with the online version of this paper). Figure S2(a) illustrates the plot of normal probability and internally studentized residuals. The residuals explain the satisfaction of the model for the ANOVA assumptions, while the internally studentized residual is the residual divided by the estimated standard deviation (Rauf et al. 2013). The data points nearly scattering along the straight line in Figure S2(a) indicated that the normality is fine. Figure S2(b) shows the residuals and predicted rate constant plot. The random scattering distribution of data points means that the variance of the original observation is constant for all values of the response. Figure S2(c) shows the internally studentized residuals and the test runs plot. The normal standard residuals usually lie within the bound of $-3.50$ to $+3.50$, while the residuals outside this bound are odd with respect to observed response (Körbahti & Rauf 2008). The data points among the scope of $\pm 3.50$ represented the robustness and adequacy of the fitted model with no data recording error.

### Analysis of response surface

The 3D response surface graphs and contour plots of IBP degradation are shown in Figure 3, presenting the inner effects of four variables on first-order rate constant. It can be seen from Figure 3 that a strong interaction exists among UV light intensity, initial IBP concentration, H$_2$O$_2$ dosage, and initial pH value. UV light intensity and H$_2$O$_2$ dosage shows a positive effect on rate constant (Figure 3(a)–3(d)). In other words, higher light intensity and H$_2$O$_2$ dosage yield a higher rate constant. UV photons are the key factor for the OH radical production, which is primarily responsible for IBP degradation. The increase of UV photons (from 400 to 1,300 mW cm$^{-2}$) in the solution causes an increase of OH radical concentration, and thus accelerates the IBP degradation process (Equation (5)). It is also clear that H$_2$O$_2$ is an important source for OH radical production (Equation (5)). The addition of H$_2$O$_2$ could

### Table 1

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### Table 2

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Figure 3 | Response surface and contour plots that present the inner effects of four variables on first-order rate constant (K): (a) and (b) H2O2 dosage and UV intensity; (c) and (d) initial IBP concentration and UV intensity; (e) and (f) pH and H2O2 dosage; (g) and (h) initial pH and initial IBP concentration. The other factors are set as their central value in each surface plot.
produce more OH radical to speed up the degradation process. However, reports by other researchers showed that there is frequently the appearance of a maximum of degradation rate with increasing H2O2 dosage (Zuorro et al. 2013; Rezaee et al. 2014). The excessive concentration of H2O2 could capture produced OH radical, thus inhibiting IBP degradation efficiency, according to reactions of Equation (7). In the current test, H2O2 dosage represents the positive effect on rate constant from 0.1 mM to 0.6 mM. This means that H2O2 concentration has not yet reached the inhibition zone.

\[
\text{H}_2\text{O}_2 + \text{hv} \rightarrow 2 \bullet \text{OH} \quad (5)
\]

\[
\text{IBP} + \bullet \text{OH} \rightarrow \text{intermediates} \quad (6)
\]

\[
\text{H}_2\text{O}_2 + \bullet \text{OH} \rightarrow \text{H}_2\text{O} + \text{HO}_2\bullet \quad (7)
\]

Initial IBP concentration obviously illustrates the negative effect on rate constant (Figure 3(e)-3(h)). It means that higher initial IBP concentration could inhibit the degradation process. With the increase of initial IBP concentration (from 5 to 25 mg L⁻¹), IBP molecules could absorb higher amounts of UV photons, reduce the production of OH radical inspired by UV photons, and further decrease the degradation efficiency with rate constant from 0.015 to 0.097 min⁻¹. Another reason for the negative effect of higher initial IBP concentration lies in the fact that when initial concentration of IBP is high, the concentration of intermediates is also higher. These intermediates can act as scavengers of OH radical, react with OH radical, and further inhibit IBP attack. The effect of initial pH value on IBP degradation is limited in the current test. Many concomitant phenomena could perform different roles in the UV/H2O2 process, including pH-induced self-decomposition of H2O2, and the interaction of added CI⁻ or Na⁺ ions with radical species in the solution (Zuorro et al. 2013).

Response optimization and confirmation

The goal of optimization is to determine the optimum parameters of the UV/H2O2 process to achieve the highest degradation efficiency, i.e. highest degradation rate constant (Kasiri & Khataee 2011). The optimized reaction parameters were as follows: UV light intensity 1,285.50 mW cm⁻², H2O2 dosage 0.54 mM, initial IBP concentration 5.24 mg L⁻¹, and initial pH value 5.51. After verification by further experimental test with the optimized parameters, the maximal degradation rate constant was obtained, which was in good agreement with the predicted value. The established model is successful for investigating the reaction effects and predicting the degradation results.

Analysis of IBP molecular structure

Molecular orbitals, especially highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO), are the main orbital taking part in the chemical reaction (Figure 4). According to frontier orbital theory, for a radical reaction, the position where the highest density of the sum of each electron \((C_n^{\text{HOMO}})^2 + (C_n^{\text{LUMO}})^2\) occurs when they are, respectively, in the HOMO and LUMO (Fukui et al. 1952). Therefore, the radical FED \(f_r\) for the reaction initialized by OH radical, can be determined as follows:

\[
f_r = \sum_i (C_i^{\text{HOMO}})^2 + \sum_i (C_i^{\text{LUMO}})^2 \quad (8)
\]
where \( r \) is the number of atoms in \( i \): 2s, 2p\(_x\), 2p\(_y\), and 2p\(_z\) orbitals (Lee et al. 2001).

The radical frontier electron densities (\( f_r \)) of each atom are calculated and summarized in Table 3. The results show that the highest densities are 0.2492 and 0.2544 at the C5 and C6 positions. The second-highest densities are 0.0664, 0.0867, 0.0699, and 0.0575 at the C10, C11, C12, and C13 positions. Therefore, C5 and C6 are probably the most reactive positions most likely to be attacked by radical. C10, C11, C12, and C13 positions are also possibly vulnerable to being attacked. What is more, the energy difference between HOMO and LUMO (energy gap) is a critical parameter in evaluating electrical transport property of the title molecule (Senthil kumar et al. 2015). The HOMO–LUMO energy gap is calculated to be 7.829 eV, as shown in Figure 4.

Atom charges, including Mulliken atomic charges and CHELPG atomic charges, were also calculated, as shown in Table 3 and Figure 5. Atomic charges play an important role due to their effect on dipole moment, molecular polarization, and other properties of molecular systems (Issaoui et al. 2015). The Mulliken atomic charges are especially widely applied in research. The Mulliken atomic charges on carbon atoms ranged from –1.0288 to 1.6831. The atomic charges of C7 and C15 are positive with high values, due to the existing carboxyl group. C3 atomic charge, including the Mulliken charge and CHELPG charge, is also found to be positive. This is due to the attachment of negatively charged carbon C8 and C9. Moreover, O1 and O2 atoms are found to be negatively charged, as usual.

The Fukui function is usually an important concept, which has been used in prediction of reactive sites. The Fukui function is defined as:

\[
\psi(r) = \frac{\delta \rho(r)}{\delta N} r
\]

(9)

where \( \rho(r) \) is the electronic density, \( N \) is the number of electrons, and \( r \) is the external potential exerted by the nucleus (Shahidha et al. 2015). The Fukui function can be calculated.
unambiguously for the following situations:

Nucleophilic attack: $f^+ (r) = \rho_{N+1}(r) - \rho_N(r)$  \hspace{1cm} (10)

Electrophilic attack: $f^- (r) = \rho_N(r) - \rho_{N-1}(r)$. \hspace{1cm} (11)

The dual descriptor is another useful function used to reveal reactive sites. The definition of the dual descriptor $f^{(2)}(r)$ has a close relationship with the Fukui function, as follows:

$$f^{(2)}(r) = f^+ (r) - f^- (r)$$ \hspace{1cm} (12)

Unlike the Fukui function, both types of reactive sites can be revealed via $f^{(2)}(r)$ simultaneously. That is to say, if $f^{(2)}(r)>0$, then the site is favorable for a nucleophilic attack, while if $f^{(2)}(r)<0$, then the site is favorable for an electrophilic attack (Guegan et al. 2014). Dual descriptor has demonstrated to be a robust tool to predict specific sites of nucleophilic and electrophilic attacks. Electrophilic $f^-$ and nucleophilic $f^+$ condensed Fukui functions and dual descriptor $f^{(2)}(r)$ are also calculated and summarized in Table 3. It is found that C5 and C6 have the higher $f^-$ values of 0.0981 and 0.0964, which

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<td>221.11832</td>
<td>221.11842</td>
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<td>IM150</td>
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indicates the possible sites for electrophilic attack. Moreover, O2 is the possible reactive site for nucleophilic attack with an $f^+$ value of 0.0578. Based on the data of $f^{(2)}(r)$, dual descriptor predicts that the C15 position with $f^{(2)}(r)$ of 0.0394 will be the preferred site for nucleophilic attack. In contrast, there is a large negative value of $f^{(2)}(r)$ over C5, C6, C10, C11, C12, and C13, indicating these positions could possibly be the preferred sites for the electrophilic attack.

**Analysis of degradation intermediates**

A total of 23 intermediates (including isomers) were identified by means of LTQ-Orbitrap. HRMS and MS$^2$ spectra allowed us to obtain information useful to identify unknown intermediate products formed during the UV/H$_2$O$_2$ process. The molecular formula, retention time, high-resolution accurate masses ([M-H]$^-$) with errors ($\Delta$), and molecular structures for IBP and its degradation products are summarized in Table 4. The extracted-ion chromatogram (XIC) and MS$^2$ spectra of IBP obtained by LTQ-Orbitrap are presented in Figure 6. In the MS$^2$ spectrum of IBP, several product ions were detected with IBP appearance time of 28.46 min. The molecular ion of IBP is at 205.15964 m/z. The product ion at 161.13388 m/z was formed due to the loss of C$_2$H$_6$ from the side chain of IBP.

Four isobaric species at [M-H] 221.12 m/z and empirical formula C$_{13}$H$_{18}$O$_3$ were observed and attributed to the mono-hydroxylated IBP (named as IM222-A, IM222-B, IM222-C, IM222-D, respectively (Figure 7)). The appearance times were 22.85, 23.28, 23.93, and 26.52 min, respectively. Although HCD method was used to obtain more product ions of mass spectra, the spectra of IM222-A, IM222-B, IM222-C basically contains the same product ions, including 150.03, 164.04, 177.09, and 193.08 m/z. Based on the
Figure 7  XIC and MS² spectra of mono-hydroxylated IBP obtained by LTQ-Orbitrap: (a) XIC at 221.12 m/z; (b) HRMS spectrum of IM222-A; (c) HRMS spectrum of IM222-B; (d) HRMS spectrum of IM222-C; (e) HRMS spectrum of IM222-D.
discussion of IBP structure above and previous studies by other researchers (Collado et al. 2012; He et al. 2014; Li et al. 2014). OH radical could attack and add to the ring or the side chain of IBP, including C3, C4, C10, C11, C12, C13 positions, to yield a variety of hydroxylated IBP (Figure 7(a)). Taking the hydroxylated IBP products formed from OH radical attack to C4, C11, C13 positions as examples, the MS² spectra of these hydroxylated IBP products are analyzed and predicted (Figure 7(b)–7(d)). The predicted spectra agree with the determined spectra. Therefore, IM222-A, IM222-B, and IM222-C could not be identified and obtained the specific structure by the single MS² spectrum. The comparison with standard compounds, or LC-NMR technology, could be used in the future to achieve the final and definite structure of these three isobaric species.

For IM222-D, MS² spectrum exhibited three key fragments at 133.10227, 159.11813, and 177.12828 m/z. Spectrum analysis explains that OH radical attacks the C7 position of IBP and produces mono-hydroxylated IBP.

Two isobaric species at [M-H] 237.12 m/z and empirical formula C13H18O4 were detected and attributed to the dihydroxylated IBP (named as IM238-A, IM238-B, respectively) with the appearance time of 24.36 and 25.86 min, as shown in Figure 8. IM238-A exhibits three structural diagnostic ions at 165.11, 175.11, and 195.12 m/z. Combined with the research of other studies (Collado et al. 2012; He et al. 2014; Li et al. 2014), IM238-A was identified as 2-hydroxy-2-[4-(1-hydroxy-2-methylpropyl)phenyl] propionic acid, which is the formation of hydroxylation on C4 and C7 positions of the side chain. IM238-B is identified as
2-hydroxy-2-[4-(2-hydroxy-2-methylpropyl)phenyl] propanoic acid, which is the product of hydroxylation on C3 and C7 positions of the side chain with three main fragment ions at 149.10, 177.09, and 205.09 m/z.

OH radical could further attack hydroxylated IBP, and result in decarboxylation and demethylation on the side chains (Li et al. 2014). Smaller aromatic intermediates, including 4-acetylbenzoic acid, 4-hydroxyphenylpropionic acid, 1-(4-isobutylphenyl) ethanone, 1-(4-isobutylphenyl) ethanol, 1-[4-(1-hydroxy-2-methylpropyl)phenyl] ethanone, and 1-(4-acetylphenyl)-2-methylpropan-1-one were also observed in this study (Table 4). In the final stage of IBP degradation, the benzene ring could be broken by the continuous attack of OH radical, which leads to the formation of linear carboxylic acids (e.g. 3-methyl-4-oxopentanoic acid, 3-hydroxyvaleric acid).

In the initial stage of contaminant degradation, OH radical addition reaction or hydrogen-abstraction reaction can be two types of main reactions. The discussion regarding the IBP molecular structure above shows that the C atoms on the benzene ring could be the preferred sites for the electrophilic attack. OH radical is added to the C atom on the benzene ring to form unstable OH-addition intermediates. The unstable intermediates could easily lose an H atom through H-abstraction pathway, thus finally forming the hydroxylation product of IBP on the benzene ring. While on the side chain of the benzene ring, such as C4, C7, and C9, H-abstraction reaction possibly occurs. C atoms on the side chain may lose a proton, and further react with OH radical to finally form the hydroxylation product of IBP on the side chain. With the reaction process, hydroxylation and dihydroxylation products are gradually formed. Even if a simple IBP electronic structure is described, it is still hard to predict specifically reactive sites and the sequence of intermediates appearing in the

![Figure 9](https://iwaponline.com/wst/article-pdf/75/12/2935/452899/wst075122935.pdf)

**Figure 9** | Proposed reaction pathways for IBP degradation by UV/H2O2 process.
reaction. Quantum dynamics method and transition state theory could be used to analyze detailed mechanism and reaction rate in the future.

Based on the above information, there is a series of mainly OH radical-initiated reactions, including hydroxylation, dihydroxylation, decarboxylation, demethylation, and ring break. These reactions lead to the mineralization of IBP and finally the formation of CO$_2$ and H$_2$O. The plausible reaction scheme for IBP degradation by UV/H$_2$O$_2$ is proposed in Figure 9.

**CONCLUSIONS**

The results of this study indicate that the UV/H$_2$O$_2$ process is an effective method for water treatment containing IBP pollutants. Pseudo-first-order kinetic behavior was also observed for the degradation of IBP in the test. OH radical, produced from H$_2$O$_2$ and UV irradiation, reacts rapidly with IBP and accelerates the removal and mineralization of IBP.

The RSM approach allowed estimation of the influence of the main process parameters on IBP degradation, and provided useful guidance on the optimal reaction conditions which could be used in practice. The effect of the experimental parameters on IBP removal was established by the response surface. It was observed that higher H$_2$O$_2$ concentration, higher UV light intensity, and a lower initial compound concentration could have a positive effect on IBP degradation.

Based on mass spectrometry analysis, a total of 23 intermediates were identified, including mono-hydroxylated products and dihydroxylated products during the degradation process. There is a series of OH radical-initiated reactions, including hydroxylation, dihydroxylation, decarboxylation, demethylation, and ring break, which leads to the final mineralization of IBP to CO$_2$ and H$_2$O. The results suggest that UV/H$_2$O$_2$ technology is a promising technology for IBP removal in aqueous solutions.

**ACKNOWLEDGEMENTS**

This work was supported by the Key Special Program on the S&T for the Pollution Control and Treatment of Water Bodies (No. 2012ZX07301-001), National Natural Science Foundation of China (No. 51308078), Natural Science Foundation of Jiangsu Province, China (No. BK20130252), and Prospective joint research project of Jiangsu province, China (BY2016029-09). The chemical calculations and software services were also supported by the Supercomputing Center of Chinese Academy of Science, and High Performance Computing Cluster System of Changzhou University.

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