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Degradation of selected pharmaceuticals in aqueous solution with UV and UV/H₂O₂

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ABSTRACT

The degradation of four pharmaceutical compounds (PhACs), ibuprofen (IBU), diphenhydramine (DP), phenazone (PZ), and phenytoin (PHT) was investigated via ultraviolet (UV) photolysis and UV/H₂O₂ process with a low-pressure (LP) UV lamp. For each PhAC tested, direct photolysis quantum yields at 254 nm were found to be ranging from 6.32×10^{-2} to $2.79 \times 10^{-1} \text{ mol E}^{-1}$ at pH 7. The second-order rate constants of the reaction between the PhACs and $\cdot\text{OH}$ were determined to be from 4.86×10^9 to $6.67 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ by using a competition kinetic model which utilized *para*-chlorobenzoic acid (pCBA) as a reference compound. The overall effect of $\cdot\text{OH}$ radical scavenging from humic acid (HA) and anions HCO_3^- , NO_3^- was measured utilizing $R_{\text{OH,UV}}$ method through examining the aqueous photodegradation of pCBA as a probe compound. Moreover, these fundamental direct and indirect photolysis parameters were applied in the model prediction for oxidation rate constants of the PhACs in UV/H₂O₂ process. It was found that the predicted oxidation rate constants approximated the observed ones. The results indicated that the new $R_{\text{OH,UV}}$ probe compound method was applicable for measuring background $\cdot\text{OH}$ radical scavenging effects in water treatment process of UV/H₂O₂. Furthermore, by GC–MS analysis, most of the intermediates created during the photodegradation of the selected PhACs in UV/H₂O₂ process were identified. For the photodegradation of PZ, a competition mechanism existed between the direct UV photolysis and the oxidation of $\cdot\text{OH}$. An appropriate dosage of H₂O₂ could hinder the occurrence of the direct photolysis.

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1. Introduction

Pharmaceutical compounds (PhACs) are developed and manufactured for specific biological effects, to improve human and animal health care, and livestock farming. PhACs are continuously introduced into the environment and are prevalent at small concentrations (Kolpin et al., 2002), which can affect water quality and potentially impact drinking water supplies, ecosystem and human health (Heberer, 2002b; Roefer et al., 2000; Trussell, 2001). Some of the adverse effects

caused by pharmaceutical pollution include aquatic toxicity, resistant development in pathogenic bacteria, genotoxicity, and endocrine disruption (Halling-Sørensen et al., 1998; Kümmerer, 2004; Sumpter, 1998). The presence of trace pharmaceutical and other xenobiotic compounds in finished drinking water is another public health concern, since little is known about potential chronic health effects associated with long term ingestion of mixtures of these compounds through drinking water (Kümmerer, 2001; Stackelberg et al., 2004). Thus, it is an emerging issue in environmental science and

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engineering to achieve effective removal of PhACs, along with other priority pollutants, from wastewaters before their discharge.

Various advanced treatment technologies have been studied to remove these kinds of pollutants in recent years, such as chemical oxidation using ozone and ozone/hydrogen peroxide (Ternes et al., 2002; Zwiener and Frimmel, 2000), membrane filtration (Hartig et al., 2001; Heberer, 2002a; Nghiem et al., 2004, 2005), and activated carbon adsorption (Hartig et al., 2001; Ternes et al., 2002). These available technologies also have some disadvantages. For example, the ozone-based advanced oxidation processes (AOPs) will form bromate ion (a suspected carcinogen) from bromide (Von Gunten and Hoigné, 1994). And there is a need to treat the off-gas and to strip VOCs. While the UV/H₂O₂ process, one of the UV-based AOPs, does not cause these problems. It is very effective in the oxidation and mineralization of most organic pollutants (Legrini et al., 1993), and has been used routinely worldwide for groundwater and drinking water remediation.

The goal of this study was to examine the potential effectiveness of UV/H₂O₂ as drinking water remediation technologies for the removal of PhACs. The PhACs selected in this study, ibuprofen, diphenhydramine, phenazone and phenytoin, occurred in the aquatic environment due to their high usage in the U.S. and Europe and their presence in wastewater (Ashton et al., 2004; Farr et al., 2001; Heberer et al., 2002; Kolpin et al., 2002). The fundamental parameters for all the targeted PhACs photolysis were determined. The overall effect of [•]OH radical scavenging from humic acid (HA) and anions HCO₃⁻, NO₃⁻ was examined by the new R_{OH,UV} probe compound method, developed by Rosenfeldt E. J. (Rosenfeldt and Linden, 2007). Based on the above data, using a steady-state [•]OH radical model, the oxidation rate constants of the selected PhACs were predicted for the UV/H₂O₂ process. By gas chromatography–mass spectroscopy (GC–MS) analysis, most of the intermediates during the degradation of the selected PhACs were identified. Especially, for significant direct photolysis of PZ in UV/H₂O₂ process, a photodegradation pathway was proposed to confirm the competition between the direct UV photolysis and the oxidation reaction of [•]OH.

2. Materials and methods

2.1. Reagents

The selected pharmaceuticals diphenhydramine hydrochloride (99%), phenytoin (99+%) and phenazone (99%) were purchased from Acros, while ibuprofen (98+%) was acquired from TCI, Japan. Their molecular structures are shown in Table 1. Humic acid (HA) and atrazine were obtained from Aldrich. *para*-Chlorobenzoic acid (*p*CBA) (98+%) and H₂O₂ (30% w/w) were supplied by Sinopharm Chemical Reagent Beijing Co. Ltd. HPLC grade acetonitrile and methanol were from Fisher Chemicals. All the other reagents were analytical grade and used as received. And all solutions were prepared with deionized (DI) water.

2.2. Analytical methods

A UV–vis spectrophotometer – U-3100 (Hitachi Co., Japan) was used to measure the aqueous solution absorbance and the decadic molar absorption spectra for each PhAC. Total organic carbon (TOC) was analyzed with TOC analyzer – Phoenix 8000 (Tekmar-Dohrmann Co., U.S.A.). The concentration of H₂O₂ was determined by the method of KMnO₄-titration (Klassen et al., 1994).

HPLC analyses were carried out using an Agilent 1200 series equipment with UV/vis detector, and a ZORBAX Eclipse XDB-C₁₈ column (4.6 × 150 mm, 5 μm); 20% acetonitrile with 80% water mobile phase was used. pH measurements were performed using a PHSJ-3F pH-meter (Shanghai Precision & Scientific Instrument Co. Ltd.).

For GC–MS analysis, the solutions at different reaction time were evaporated by freeze-dried method. Then the residue was trimethylsilylated with 0.1 mL of hexamethyldisilazane, and 0.05 mL of chlorotrimethylsilane at room temperature. GC–MS analysis was carried out on an Agilent 6890GC/5973MSD with a DB-5 MS capillary column.

2.3. Photochemical reactor

The reactor had a volume of 500 mL and was equipped with a 11 W low-pressure (LP) Hg vapor lamp (Institution of Light Source, Beijing) emitting essentially monochromatic UV light at 254 nm, with sleeves made of commercial grade quartz tubing. A small stir bar was placed at the bottom of the reactor to ensure homogeneous UV exposure.

UV fluence (mJ cm⁻²) was calculated as the average photon fluence rate multiplied by the exposure time. A photon fluence rate of 4.5 × 10⁻⁵ E m⁻² s⁻¹ (which corresponds to a power output of 2.12 mW cm⁻²) was obtained, using atrazine as the actinometer according to the procedures published (Canonica et al., 2008). The effective path length of the reactor was 1.9 cm determined by hydrogen peroxide actinometry (Beltrán et al., 1995).

2.4. UV photolysis experiments

UV photolysis of solutions containing individual PhAC was evaluated at different UV fluence to determine the degradation rate constants. To investigate the effects of HA and anions on PhACs photolysis, these tests were then repeated in the presence of HA (DOC 2 mg/L), HCO₃⁻ (2 mM), and NO₃⁻ (1.4 mg/L). Solution (500 mL) with an initial concentration of each PhAC (5 μM) was photolyzed at pH 7.0 in the photochemical reactor. At given time intervals, samples were withdrawn and analyzed immediately by HPLC.

2.5. UV/H₂O₂ advanced oxidation experiments

The UV/H₂O₂ advanced oxidation experiments were conducted under otherwise identical conditions, as described above for the UV photolysis experiments, with 0.29 mM or 1 mM H₂O₂ added just before exposure to UV radiation. A competition kinetic approach was used to determine the oxidation rate constants between the PhACs and [•]OH using *p*CBA as a reference compound. In the experiment, H₂O₂

Table 1 – Structures and therapeutic classes of selected PhACs.

Name	CAS-number	Chemical structure	Application
Ibuprofen	15687-27-1		Analgesic and anti-inflammatory
Diphenhydramine	147-24-0		Antihistamine
Phenazone	60-80-0		Analgesic and anti-inflammatory
Phenytoin	57-41-0		Antiepileptics

(1 mM) was presented in excess to ensure efficient $\cdot\text{OH}$ radical production, and the concentrations of pCBA and individual PhAC in solution were 5 μM , respectively.

3. Results and discussion

3.1. UV photolysis

The capacity of a compound absorbing photons of the incident light is an important factor for its photochemical reaction. The decadic molar absorption coefficient (ϵ) measures the probability that a compound will absorb light at a certain wavelength (λ). In this experiment, it was determined by measuring the absorbance (a) of solutions spiked with each PhAC at concentrations ranging from 10 μM to 100 μM using a 1 cm path length (z):

$$a = \epsilon \times [\text{PhAC}] \times z \quad (1)$$

Fig. 1 shows the decadic molar absorption coefficient for IBU, DP, PZ, and PHT at different wavelengths. As can be seen, all of them absorb light at wavelengths ranging from 200 to 275 nm. The ϵ obtained was 256 $\text{M}^{-1}\text{cm}^{-1}$ for IBU, 388 $\text{M}^{-1}\text{cm}^{-1}$ for DP, 8906 $\text{M}^{-1}\text{cm}^{-1}$ for PZ, and 1260 $\text{M}^{-1}\text{cm}^{-1}$ for PHT at $\lambda = 254$ nm. Among the four selected PhACs, PZ has the strongest absorption at 254 nm wavelength, while PHT has the second strongest absorption. IBU and DP absorb light mainly at lower wavelengths (in the range of 200–240 nm) and present absorbance minima at approximately 250 nm.

Therefore, degradation of PZ and PHT by LP/UV photolysis was expected to be high, while that of IBU and DP was lower.

Pseudo-first-order kinetics was observed for degradation of selected PhACs, as indicated by linear relations between $\ln([\text{PhAC}]/[\text{PhAC}]_0)$ versus UV fluence (Fig. 2), and these rate constants (k'_d) are presented in Table 2. Fig. 3 shows that when using an extremely high UV fluence of 1272 mJ cm^{-2} , only 27.40% of the initial 5 μM of IBU and 26.34% of DP were removed. However, under the same UV fluence, 95.78% and 87.75% degradation for PZ and PHT occurred. In the presence of HA , HCO_3^- and NO_3^- , the degradation of IBU, DP and PHT

Fig. 1 – Decadic molar absorption coefficient (ϵ) of the selected PhACs in aqueous solution.

Fig. 2 – Direct photolysis of the selected PhACs at pH 7 ([PhAC]₀ = 5 μM).

decreased, due to the competition of HA for the UV light, while the degradation of PZ increased a little, due to an indirect production of $\cdot\text{OH}$ from reaction of the UV light with HA and NO_3^- .

Besides the molar absorption coefficient, quantum yield (ϕ) is another fundamental parameter governing the rate of direct photodegradation, which could be calculated using Eqs. (2)–(4) (Schwarzenbach et al., 1993; Sharpless and Linden, 2003):

$$-\frac{d[\text{PhAC}]}{dt} = k'_d[\text{PhAC}] = k_{s,\text{PhAC}}\phi_{\text{PhAC}}[\text{PhAC}] \quad (2)$$

$$\phi_{\text{PhAC}} = \frac{k'_d}{k_{s,\text{PhAC}}} \quad (3)$$

where

$$k_{s,\text{PhAC}} = \frac{E_p^0 \epsilon_{\text{PhAC}} [1 - 10^{-az}]}{az} \quad (4)$$

In these equations, k'_d is the pseudo-first-order rate constant for direct photolysis of each PhAC (s^{-1}), $k_{s,\text{PhAC}}$ the specific rate of light absorption by the compound ($\text{E mol}^{-1} \text{s}^{-1}$) presented in Table 2. E_p^0 represents the incident photon irradiance ($4.5 \times 10^{-5} \text{ E m}^{-2} \text{s}^{-1}$), ϵ_{PhAC} the decadic molar absorption coefficient at $\lambda = 254 \text{ nm}$, a the solution absorbance at wavelength 254 nm, z the optical path length (1.9 cm), and ϕ_{PhAC} the quantum yield. Table 2 also displays the quantum yield of each PhAC under LP UV radiation.

3.2. UV/H₂O₂ advanced oxidation

As shown in Fig. 4, considerably higher removal of IBU and DP was obtained with the addition of 0.29 mM H₂O₂ compared to no addition. The increasing of removal of PZ and PHT was not as much as IBU and DP, because they were highly degraded by direct photolysis even at a low UV fluence. Further increasing H₂O₂ concentration to 1 mM, resulted in additional increase in the degradation of these four PhACs. Even though the removals obtained by UV/H₂O₂ advanced oxidation (0.29 mM H₂O₂) for all PhACs were less than 30% of the initial concentration at the lower UV fluence of 40 mJ cm^{-2} , all the compounds were reduced to levels below detection by UV/H₂O₂ at the higher UV fluence of 508.8 mJ cm^{-2} . The difference seen in destruction of the constituents with the addition of H₂O₂ is due to the fact that the dominant mechanism of PhACs destruction becomes $\cdot\text{OH}$ mediated advanced oxidation. Therefore, the rate of PhACs removal depends on the formation of $\cdot\text{OH}$ and the second-order rate for the reaction between $\cdot\text{OH}$ and PhACs. In this experiment, a competition kinetic method was used to determine the rate constants ($k_{\text{OH/PhAC}}$) between $\cdot\text{OH}$ radical and the PhACs. pCBA ($k_{\text{OH/pCBA}} = 5 \times 10^9 \text{ M}^{-1} \text{s}^{-1}$) (Buxton et al., 1988) was chosen as a reference compound, because it essentially does not undergo direct photolysis, and has been successfully applied in similar experiments (Pereira et al., 2007). Both degradation of PhAC and pCBA followed pseudo-first-order reaction kinetics, so the second-order rate constants ($k_{\text{OH/PhAC}}$) can be determined as Eq. (5):

$$\ln\left(\frac{[\text{PhAC}]}{[\text{PhAC}]_0}\right) = \ln\left(\frac{[\text{pCBA}]}{[\text{pCBA}]_0}\right) \frac{k_{\text{OH/PhAC}}}{k_{\text{OH/pCBA}}} \quad (5)$$

In UV photolysis, the rate constant for IBU was 0.0005 s^{-1} , and for DP was also 0.0005 s^{-1} (Table 2), which was less than those of PZ and PHT. The results indicated that direct photolysis of IBU and DP could be neglected in calculating $k_{\text{OH/PhAC}}$. However, the direct photolysis of both PZ and PHT should be taken into consideration in determining the intrinsic $\cdot\text{OH}$ radical rate constants, by subtracting the UV photolysis rate constants obtained for the PhACs from the UV/H₂O₂ oxidation rate constants. For the tested PhACs, the experimentally determined second-order rate constants ($k_{\text{OH/PhAC}}$) are shown in Table 3.

Second-order rate constants for different reactions of organic compounds with $\cdot\text{OH}$ typically vary between 10^6 and $10^{10} \text{ M}^{-1} \text{s}^{-1}$ and have been reported in the literature (Schwarzenbach et al., 1993). The selected PhACs can

Table 2 – LP specific rate of light absorption (K_s), quantum yield (ϕ), and pseudo-first-order rate constant of the selected PhACs in UV photolysis (k'_d); correlation coefficient (R^2) given in parenthesis.

Compound	k'_d^a (s^{-1})	k'_d^a ($\text{cm}^2 \text{mJ}^{-1}$)	k'_d^b (s^{-1})	k'_d^b ($\text{cm}^2 \text{mJ}^{-1}$)	K_s ($\lambda = 254 \text{ nm}$) ($\text{E mol}^{-1} \text{s}^{-1}$)	ϕ (mol E^{-1})
IBU	0.0005 (0.9931)	0.24×10^{-3} (0.9931)	0.0003 (0.9967)	0.14×10^{-3} (0.9967)	0.0026	0.1923
DP	0.0005 (0.9966)	0.24×10^{-3} (0.9966)	0.0003 (0.9894)	0.14×10^{-3} (0.9894)	0.0040	0.1250
PZ	0.0053 (0.9922)	2.50×10^{-3} (0.9922)	0.0055 (0.9911)	2.59×10^{-3} (0.9911)	0.0838	0.0632
PHT	0.0036 (0.9903)	1.70×10^{-3} (0.9903)	0.002 (0.9981)	0.94×10^{-3} (0.9981)	0.0129	0.2791

a Experiments performed in DI water.

b Experiments performed in the presence of HA (DOC 2 mg/L), HCO_3^- (2 mM) and NO_3^- (1.4 mg/L).

Fig. 3 – Percent destruction of the selected PhACs following UV fluences of 1272 mJ cm^{-2} via UV direct photolysis at pH 7 ($[\text{PhAC}]_0 = 5 \mu\text{M}$).

therefore be considered to be fast-reacting compounds. To our knowledge, this is the first report of the hydroxyl radical rate constant for DP, PZ and PHT. The experimental rate constant of $k_{\text{OH/IBU}}$ obtained in our study is $6.67 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, agreeing well with the value of $(7.4 \pm 1.2) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ in the Huber et al's., 2003 study.

3.3. Model predictions of UV/ H_2O_2 oxidation rate constants

In the presence of H_2O_2 , the overall degradation of PhACs will be contributed by both UV direct photolysis and UV/ H_2O_2 oxidation degradation (García Einschlag et al., 2002; Wu et al., 2007):

$$-\frac{d[\text{PhAC}]}{dt} = (k'_d + k'_i)[\text{PhAC}] \quad (6)$$

where k'_i is the pseudo-first-order initial rate constant for indirect photolysis (s^{-1}). It is a function of the second-order

Fig. 4 – Percent destruction of the selected PhACs following UV fluences of 40 mJ cm^{-2} via direct photolysis (0 mM H_2O_2) and UV/ H_2O_2 AOP (0.29 mM or 1 mM H_2O_2) at pH 7 ($[\text{PhAC}]_0 = 5 \mu\text{M}$; nd: not degraded).

Table 3 – Second-order rate constant of $\cdot\text{OH}$ with the selected PhACs; correlation coefficient (R^2) given in parenthesis.

Compound	Slope $\ln(\text{PhAC}/\text{PhAC}_0)$ versus $\ln(p\text{CBA}/p\text{CBA}_0)$	$k_{\text{OH/PhAC}}$ ($\times 10^9 \text{ M}^{-1} \text{ s}^{-1}$)
IBU	1.3335 (0.9982)	6.67
DP	1.0832 (0.9972)	5.42
PZ	0.9717 (0.9569)	4.86
PHT	1.2552 (0.9830)	6.28

reaction rate constant ($k_{\text{OH/PhAC}}$), and the steady-state concentration of $\cdot\text{OH}$ ($[\cdot\text{OH}]_{\text{ss}}$):

$$k'_i = k_{\text{OH/PhAC}}[\cdot\text{OH}]_{\text{ss}} \quad (7)$$

$[\cdot\text{OH}]_{\text{ss}}$ can be expressed by the ratio between the production rate and the depletion rate of $\cdot\text{OH}$ radical:

$$[\cdot\text{OH}]_{\text{ss}} = \frac{k_{\text{s,H}_2\text{O}_2} \phi_{\text{OH}} [\text{H}_2\text{O}_2] f_{\text{H}_2\text{O}_2}}{\sum k_{\text{OH/S}} [\text{S}]_i + k_{\text{OH/PhAC}} [\text{PhAC}] + k_{\text{OH/H}_2\text{O}_2} [\text{H}_2\text{O}_2]} \quad (8)$$

$$k_{\text{s,H}_2\text{O}_2} = \frac{E_p^0 \epsilon_{\text{H}_2\text{O}_2} [1 - 10^{-(a + \epsilon_{\text{H}_2\text{O}_2} [\text{H}_2\text{O}_2])z}]}{(a + \epsilon_{\text{H}_2\text{O}_2} [\text{H}_2\text{O}_2])z} \quad (9)$$

$$f_{\text{H}_2\text{O}_2} = \frac{\epsilon_{\text{H}_2\text{O}_2} [\text{H}_2\text{O}_2]}{\epsilon_{\text{H}_2\text{O}_2} [\text{H}_2\text{O}_2] + \epsilon_{\text{PhAC}} [\text{PhAC}]} \quad (10)$$

where ϕ_{OH} is the quantum yield describing the production of $\cdot\text{OH}$ by H_2O_2 photolysis (1.0 mol E^{-1}) (Rosenfeldt and Linden, 2007), $f_{\text{H}_2\text{O}_2}$ is the fraction of UV absorbed by H_2O_2 , $\sum k_{\text{OH/S}} [\text{S}]_i$ is the sum of the pseudo-first-order rates of reaction of $\cdot\text{OH}$ with scavengers (not including the contribution of PhACs and H_2O_2), and $\epsilon_{\text{H}_2\text{O}_2}$ is the molar absorption coefficient for H_2O_2 ($18.7 \text{ M}^{-1} \text{ cm}^{-1}$) (Bolton and Cater, 1994) at $\lambda = 254 \text{ nm}$.

AOPs that utilize the reaction between $\cdot\text{OH}$ radicals and substrates are subject to scavenging effects because $\cdot\text{OH}$ radicals are nonselective and can react with virtually any species present in aqueous solutions ($E_0 = 2.8 \text{ V}$) (Juang et al., 1998). Carbonate species (HCO_3^- , CO_3^{2-}), NOM and H_2O_2 can act as $\cdot\text{OH}$ radical scavengers and hence reduce the destruction rate of PhACs. The overall effect of these scavenging species ($\sum k_{\text{OH/S}} [\text{S}]_i$, not including the contribution of H_2O_2) was investigated by two kinds of methods. One is the traditional method, that utilizes DOC and alkalinity to calculate $\sum k_{\text{OH/S}} [\text{S}]_i$, as surrogate parameters for NOM and carbonate/bicarbonate species, respectively.

$$\sum k_{\text{OH/S}} [\text{S}]_i = k_{\text{OH/NOM}} [\text{NOM}] + k_{\text{OH/HCO}_3^-} [\text{HCO}_3^-] + k_{\text{OH/CO}_3^{2-}} [\text{CO}_3^{2-}] \quad (11)$$

where $k_{\text{OH/NOM}}$ is $2.5 \times 10^4 \text{ L mg}^{-1} \text{ s}^{-1}$ (Larson and Zepp, 1988); $k_{\text{OH/CO}_3^{2-}}$ is $3.9 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$, and $k_{\text{OH/HCO}_3^-}$ is $8.5 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ (Buxton et al., 1988). It is important to note that NOM was destroyed as the UV fluence increased, so the composition of the DOC is likely to change (Rosenfeldt and Linden, 2004), but the traditional method does not account for this. The modeled $\cdot\text{OH}$ radical concentration remains the same as if DOC were at its original concentration and composition, when in fact the $\cdot\text{OH}$ radical concentration may be increasing as the contribution of the dominant scavenger is deduced. Moreover, the contributions of species contributing to the formation of $\cdot\text{OH}$

radicals, such as nitrate and other species, were also missed by utilizing this traditional calculating method. All of these may cause the underestimation of the degradation of PhACs in UV/H₂O₂ process. But the other method, called as the new $R_{OH,UV}$ probe compound method, developed by Rosenfeldt E. J. (Rosenfeldt and Linden, 2007), handled this problem caused by the traditional method. The $R_{OH,UV}$ concept is defined as the experimentally determined $\cdot OH$ radical exposure per UV fluence, and it was determined by examining the aqueous photodegradation of pCBA as a probe compound.

$$R_{OH,UV} = \frac{\int_0^t [\cdot OH] dt}{E_0 t} = \frac{k_T^D - k_d^D}{k_{OH/pCBA}} \quad (12)$$

where k_T^D is the total observed pseudo-first-order fluence based rate constant for pCBA oxidation ($\text{cm}^2 \text{mJ}^{-1}$), k_d^D is the observed fluence based pCBA direct photolysis pseudo-first-order initial rate constant ($\text{cm}^2 \text{mJ}^{-1}$), E_0 is the photon fluence rate which is 2.12 mW cm^{-2} in this experiment.

In UV/H₂O₂ advanced oxidation, the direct photolysis of pCBA was negligible, and the steady-state $\cdot OH$ radical in the UV/H₂O₂ process could be calculated as Eq. (13):

$$[\cdot OH]_{ss} = \frac{E_0 \cdot \epsilon_{H_2O_2} [H_2O_2] \phi_{OH}}{U_{254} (\sum k_{OH/S} [S]_i + k_{OH/pCBA} [pCBA] + k_{OH/H_2O_2} [H_2O_2])} \quad (13)$$

where U_{254} is the energy per 1 mol of photons (Einstein) at 254 nm (J E^{-1}), and all the other parameters have been previously defined. Rearranging Eq. (13) results in Eq. (14):

$$\frac{E_0}{[\cdot OH]_{ss}} = \frac{U_{254} (\sum k_{OH/S} [S]_i + k_{OH/pCBA} [pCBA])}{\epsilon_{H_2O_2} \phi_{OH}} \left(\frac{1}{[H_2O_2]} \right) + \frac{U_{254} k_{H_2O_2, OH}}{\epsilon_{H_2O_2} \phi_{OH}} \quad (14)$$

$R_{OH,UV}$ and $[\cdot OH]_{ss}/E_0$ have the same units, that is $\text{M s cm}^2 \text{mJ}^{-1}$. From Eq. (14), it is easy to know that the inverse of the $R_{OH,UV}$ is plotted as a function of $1/[H_2O_2]$. Thus, a linear relationship with slope (m) and y-intercept (b) is observed. Further analysis of Eq. (14) indicates that $U_{254}/\epsilon_{H_2O_2} \phi_{OH}$ is a common term to both slope and y-intercept, so with combination and rearrangement of the terms, $\sum k_{OH/S} [S]_i$ can be measured as Eq. (15):

$$\sum k_{OH/S} [S]_i = k_{OH/H_2O_2} \frac{m}{b} - k_{OH/pCBA} [pCBA] \quad (15)$$

To check the accuracy of the two methods, in the presence of HA (DOC 2 mg/L), HCO_3^- (2 mM) and NO_3^- (1.4 mg/L), the overall scavenging effect of these three species ($\sum k_{OH/S} [S]_i$) was measured as $2 \times 10^3 \text{ s}^{-1}$ by the $R_{OH,UV}$ method, and calculated as $6.7 \times 10^4 \text{ s}^{-1}$ by the traditional one. Furthermore, the observed oxidation rate constants for the selected PhACs were compared with the predicted ones. Expectively, as shown in Fig. 5, for all the selected PhACs, the predicted oxidation rate constants by the steady-state $\cdot OH$ radical model were more approximative to the observed ones, when scavenging effects calculated by the new $R_{OH,UV}$ probe compound method. The results indicated that the $R_{OH,UV}$ method would be applicable for measuring background $\cdot OH$ scavenging effects in the process of UV/H₂O₂. The overall effect of scavenging species ($\sum k_{OH/S} [S]_i$) measured by the

Fig. 5 – Comparison of observed (black bars) and steady-state $\cdot OH$ radical model predicted oxidation rate constants utilizing scavenging factors calculated using the traditional method (gray bars) or as measured by the new $R_{OH,UV}$ probe compound method (white bars) (a) $\text{H}_2\text{O}_2 = 0.29 \text{ mM}$; (b) $\text{H}_2\text{O}_2 = 1 \text{ mM}$ (DOC = 2 mg/L, $\text{HCO}_3^- = 2 \text{ mM}$, $\text{NO}_3^- = 1.4 \text{ mg/L}$, $[\text{PhAC}]_0 = 5 \text{ }\mu\text{M}$, pH = 7).

$R_{OH,UV}$ method could be coupled as an input into the steady-state $\cdot OH$ radical model to predict oxidation of environmental pollutants in different waters during the treatment of UV/H₂O₂.

3.4. Photodegradation byproduct identification

GC–MS was used to monitor the generation of reaction intermediates during the photodegradation of the selected PhACs in the process of UV/H₂O₂, to gain an insight into the mechanism of the reaction. For all the selected PhACs, most of the intermediates belonged to hydroxylation products, mainly including benzoic acid, 1,4-benzenedicarboxylic acid, *m*-hydroxybenzoic acid, *para*-hydroxybenzoic acid and some aliphatic acids, etc. Moreover, with the increase of the reaction time, these intermediates would be mineralized by sequential hydroxylation. The results also verified that $\cdot OH$ radicals were the main reactive oxygen species in the reaction. However, the photodegradation pathway of PZ was different from the other

Table 4 – Main aromatic species formed in UV/H₂O₂ oxidation of PZ identified by GC–MS analysis.

Name and retention time (min)	Proposed structure	m/z (relative abundance %)
Anthranilic acid (RT = 34.829)		209(64), 195(63), 194(100), 150(31), 120(63), 119(59), 92(28)
2-Acetamidobenzoic acid (RT = 43.574)		194(100), 209(72), 119(53), 251(47), 120(33), 92(19), 75(19)
1,4-Benzenedicarboxylic acid (RT = 45.815)		295(100), 296(25), 221(21), 73(16), 103(12), 251(11)
Diantiprylmethane (RT = 82.002)		177(100), 56(72), 388(55), 201(44), 269(39), 268(301), 241(22), 77(21)

three PhACs. In UV photolysis of PZ, it was observed that the colour and the absorption of the solution at 254 nm increased with irradiation time. This phenomenon did not occur in UV direct photolysis of the other three PhACs. In UV/H₂O₂ process,

there was a competitive reaction between the direct UV photolysis and the oxidation of [•]OH during the photo-degradation of PZ. This point has been observed in the degradation of PZ at different dosage of H₂O₂. Different samples from

Fig. 6 – PZ degradation pathways induced by UV/H₂O₂ AOP ([PZ]₀ = 30 μM, H₂O₂ = 0.29 mM, pH = 7).

treating aqueous solutions of PZ at 30 μM concentration with 0.29 mM or 5 mM H_2O_2 under UV irradiation, at pH 7, were analyzed by GC–MS. All the identified compounds were unequivocally identified using the NIST98 library database with fit values higher than 90%. As shown in Table 4, for the reaction with 0.29 mM H_2O_2 , at a reaction time of 3 min, the main products included anthranilic acid, 2-acetamidobenzoic acid, 1,4-benzenedicarboxylic acid and diantipyrylmethane. The former three products were generated from hydroxylation of PZ, while diantipyrylmethane which was also detected in the direct photolysis of PZ, may be formed by the mechanism of dimerization or photoaddition involved in direct UV destruction. For the reaction of 15 min, the three aromatic acids disappeared, and some aliphatic acids were detected, while diantipyrylmethane still remained. The results indicated that diantipyrylmethane was very photostable for UV. However, for the reaction with 5 mM H_2O_2 , the diantipyrylmethane was not detected. PZ photodegradation proceeds first by the cleavage of the N–N bond of penta heterocycle leading to the formation of three aromatic acids, then followed by the opening of phenyl ring to form small molecular organic acids, and these organics may be decomposed further into CO_2 . According to the above results, an overall view of PZ degradation pathways is proposed in Fig. 6. The results indicated that an appropriate dosage of H_2O_2 could hinder UV direct photolysis to achieve more mineralization of pollutant.

In UV/ H_2O_2 process, it should be noted, although the organic substrates can easily be mineralized in most cases, but the complete mineralization of PhACs may be an uneconomical goal for treatment. So in further research, it would be paid more attention to toxicity measurements for the UV/ H_2O_2 process.

4. Conclusions

Pseudo-first-order kinetics was observed for IBU, DP, PZ, and PHT degradations both by direct photolysis and UV/ H_2O_2 advanced oxidation. Low rates of direct photolysis of IBU and DP were observed, while direct photodegradation of PZ and PHT occurred at a higher rate. Correspondingly, the quantum yields of the four PhACs were determined to be from 6.32×10^{-2} to $2.79 \times 10^{-1} \text{ mol E}^{-1}$. $\cdot\text{OH}$ radicals have high reactivity toward all of the selected PhACs, with $k_{\text{OH/PhAC}}$ values of $6.67 \times 10^{-9} \text{ M}^{-1} \text{ s}^{-1}$, $5.42 \times 10^{-9} \text{ M}^{-1} \text{ s}^{-1}$, $4.86 \times 10^{-9} \text{ M}^{-1} \text{ s}^{-1}$, and $6.28 \times 10^{-9} \text{ M}^{-1} \text{ s}^{-1}$ for IBU, DP, PZ, and PHT, respectively. The overall effect of $\cdot\text{OH}$ radical scavengers including HA, HCO_3^- and NO_3^- was calculated more accurately by the new ROH_{UV} probe compound method. Coupling this scavenging contribution into the steady-state $\cdot\text{OH}$ radical model, the oxidation rate constants of PhACs were predicted very well in UV/ H_2O_2 process. Furthermore, in the UV/ H_2O_2 process, most of the intermediates from PhACs photodegradation belonged to hydroxylation compounds, including benzoic acid, 1,4-benzenedicarboxylic acid, *m*-hydroxybenzoic acid, *para*-hydroxybenzoic acid and some aliphatic acids, etc. For the degradation of PZ in UV/ H_2O_2 , the byproduct of diantipyrylmethane was detected, which was produced from the direct photolysis. A competition mechanism was verified between the direct UV photolysis and the oxidation of $\cdot\text{OH}$ radical.

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