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Kinetics and degradation mechanism of clofibric acid and diclofenac in UV photolysis and UV/H_2O_2 reaction

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ABSTRACT

In this study, we investigated the removal of the selected pharmaceuticals, clofibric acid and diclofenac, using UV photolysis and UV/H_2O_2 reactions. The degradation of diclofenac during UV photolysis reaction was faster than that of clofibric acid. Diclofenac was mainly removed by photolysis reaction; clofibric acid was more sensitive to OH radical. More effective removals of clofibric acid and diclofenac were observed when H_2O_2 was added in the UV photolysis reaction. The competition kinetics showed that the second-order rate constant between the OH radical and the pharmaceuticals was $5.57 \times 10^9\,M^{-1}\,s^{-1}$ for clofibric acid and $2.45 \times 10^9\,M^{-1}\,s^{-1}$ for diclofenac, respectively. The major reaction intermediates during the UV photolysis and UV/H_2O_2 reactions of clofibric acid were 4-chlorophenol and hydroquinone, and these intermediates were degraded as phenol with further reaction.

Keywords: Competition kinetics; OH radical; Hydroquinone; Phenol; Mineralization

1. Introduction

In recent years, it is reported that many pharmaceuticals occur in different aquatic environments [1–3]. The presence of pharmaceuticals in surface water is a public health concern, since little is known about the potential chronic health effects associated with long-term ingestion of the mixture of these pharmaceuticals through drinking water [4]. In addition, photo-excited pharmaceuticals can produce either singlet oxygen or superoxide radical, which are believed to be the major cause for phototoxicity, thus resulting in the production of organic compounds of higher toxicity [5,6].

Among the pharmaceuticals, clofibric acid and diclofenac are widely detected in the aquatic environment due to their incomplete removal during the wastewater treatment process, and thus have received increased attention as an emerging class of environmental pollutants (Fig. 1) [7]. Bioactive metabolites of clofibrate are widely used as blood lipid regulating drugs for decreasing the plasmatic concentration of cholesterol and triglycerides [8,9]. Diclofenac is a synthetic non-steroidal anti-inflammatory drug meant to reduce inflammation.

Clofibric acid has been detected in the range of $ng\,L^{-1}$–$\mu g\,L^{-1}$ in the influents and effluents of sewage treatment plants, lakes, rivers, and ground and drinking waters [8,10–12]. Diclofenac has been detected

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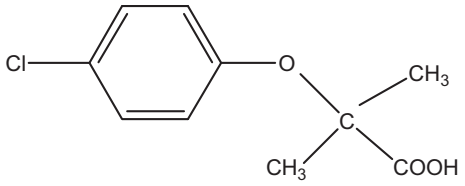
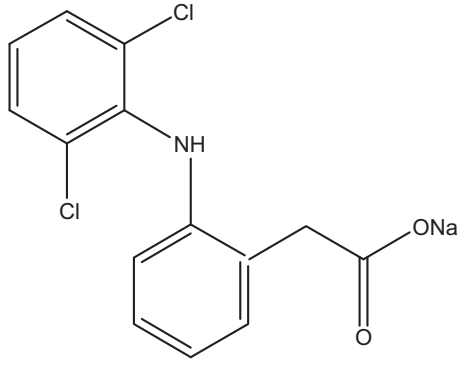


Clofibric acid



Diclofenac

Fig. 1. Molecular structures of clofibric acid and diclofenac.

up to 1.2 μg L^{-1} in Europe [13,14], and up to 0.13 μg L^{-1} in wastewater effluents and 0.7 ng L^{-1} in surface waters in Korea [1]. These pharmaceuticals are not effectively removed in the conventional water treatment [15,16]. Therefore, the alternative treatment processes are required to reduce their presence in the receiving environment [17,18].

Recently, the removals of clofibric acid have been studied using various AOP processes, such as ozonation, H_2O_2/UV [19,20], UV photolysis and sunlight [7], TiO_2/UV [21], and Fenton reaction [22,23]. Also, kinetic studies have been investigated for ozone/UV, H_2O_2/UV, photo-Fenton, and UV-C photolysis of diclofenac [24–28]. However, the detailed mechanism of clofibric acid and diclofenac degradation during AOP reactions need to be further studied.

The goal of this study is to examine the potential effectiveness of UV photolysis and UV/H_2O_2 for treating clofibric acid and diclofenac in water. We determined kinetic constants for clofibric acid and diclofenac during UV photolysis and UV/H_2O_2 reactions. We also identified the intermediates and ionic byproducts during degradation of clofibric acid and diclofenac using GC-MS. Finally, we suggested photodegradation pathways of direct UV photolysis and UV/H_2O_2 reactions.

2. Materials and methods

2.1. Reagents

Clofibric acid ($C_{10}H_{11}ClO_3$, 99%), diclofenac ($C_{14}H_{11}Cl_2NO_2$, 99%), hydrogen peroxide (H_2O_2, 30%), and *p*-chlorobenzoic acid (*p*-CBA), ($C_7H_5ClO_2$, 99%) were purchased from Sigma-Aldrich of highest purity. All other chemicals used were of analytical grade and used as received.

2.2. Photoreactor

The experiment was performed in a circulating photoreactor system. The reactor system has a reservoir consisting of a stirred 2-L glass bottle, a peristaltic pump (Master Flex model 7518-00, Cole-Parmer Instrument) for circulating the reactor contents, and a photoreaction chamber. The reaction chamber was connected to a flexible Teflon tubing. The reaction solutions were continuously circulated with a rotary pump at a flow rate of 1 L min^{-1}. The UV chamber is composed of six UV lamps (San-kyo electrics, 20 W) and six quartz columns (10 mm diameter, 650 mm length). The distance from the UV lamp to a quartz column was 20 mm. The intensity of a single UV lamp was measured by a radiometer (VLX-3W Radiometer 9811-50, Cole-Parmer Instrument) at a distance of 20 mm. Photolysis reaction was carried out at different UV wavelengths. The light intensity for one single lamp is 4.56 mW cm^{-2} at 365 nm and 2.12 mW cm^{-2} at 254 nm. The external surface of the reactor around the quartz columns was covered with aluminum foil for UV safety and energy consideration.

2.3. Analytical methods

Stock solutions of clofibric acid and diclofenac were prepared using deionized water obtained from a Millipore Milli-Q system (>18 MΩ), then were filtered with 0.45 μm PTFE filter (Advantec, Tokyo, Japan) to remove particle suspensions prior to the analysis.

Concentrations of clofibric acid and diclofenac were determined using HPLC equipped with a VWD-3100 detector (Ultimate-3000, Dionex Co., USA). Separation of peaks was achieved with C18 column (150 × 2.1 mm, i.d., 5-μm particles, Waters Atlantis) at a flow rate of 0.3 mL min^{-1}. The mobile phase consisted of an isocratic mixture of 70% acetonitrile and 30% water for clofibric acid and 60% acetonitrile and 40% water for diclofenac. The detection wavelength was set at 230 nm for clofibric acid and 220 nm for diclofenac. *p*-CBA was determined by using a mobile

phase consisting of a mixture of 50% acetonitrile and 50% water, and with detection wavelength of 234 nm using HPLC as well.

Chloride ion as an ionic byproduct was measured with a Dionex DX-120 ion chromatography (Dionex Co., USA). The column for chloride ion analysis was a Dionex Ion Pac AS14-HC column (4×250 mm). The eluent consisted of a mixture of 3.5 mM Na_2CO_3 and 1 mM $NaHCO_3$. Total organic carbon analysis was carried out using a TOC analyzer (Shimadzu, Tokyo, Japan).

Organic degradation byproducts during the reaction process were measured by a Hewlett-Packard (HP) 6890 gas chromatography mass spectroscopy (GC-MS) equipped with a HP-5MS 5% phenyl methyl siloxane capillary column (30×0.25 mm, i.d., 0.25 μm) and a HP 5973 mass selective detector. The flow rate of the helium as carrier gas was 1 mL min^{-1}. The temperature program was as follows: 80°C for 1 min, 7°C min^{-1} up to 150°C, hold time 5 min, and 7°C min^{-1} up to 200°C, hold time 5 min. The injector temperature was 250°C. The MS detector was operated in the EI mode and mass scan range of 40–300 *m*/*z*.

2.4. Competition kinetics in UV/H_2O_2 reaction

UV/H_2O_2 reaction was conducted in the same conditions with UV photolysis reaction, by adding 1 mM H_2O_2 before exposure to UV radiation. The competition kinetics experiment was conducted to determine the rate constants between selected pharmaceuticals and OH radical using *p*-CBA which is known to react fast with OH radical as a probe. In this study, the concentration of *p*-CBA was 4.67×10^{-5} M for clofibric acid and 3.14×10^{-5} M for diclofenac, respectively.

3. Results and discussion

3.1. Photolysis

The capacity of a compound to absorb photons from UV light irradiation is an important factor for its photochemical reaction. The molar absorption coefficient (ε) measures the probability of a compound to absorb light at a certain wavelength (λ). We can calculate the molar absorption coefficient by measuring the absorbance (A) of test solutions at different wavelengths ranging from 230 to 400 nm using a Beer-Lambert law, as shown in Eq. (1):

$$A = \varepsilon \times [\mathrm{PhAC}] \times z \quad (1)$$

where A is the absorbance at a certain wavelength (λ), z is the cell path length (in centimeters), and [PhAC] is the molar concentration of the pharmaceuticasl (4.67×10^{-5} M for clofibric acid, and 3.14×10^{-5} M for diclofenac, respectively).

Fig. 2 shows the change in the molar absorption coefficient (ε) of clofibric acid and diclofenac at different wavelengths. As shown in Fig. 2, both clofibric acid and diclofenac hardly absorbed light, especially in the range of 340–400 nm. The ε value, by using Eq. (1), and measured absorbance at 254 nm was 229 M^{-1} cm^{-1} for clofibric acid and 5,831 M^{-1} cm^{-1} for diclofenac, respectively. This result implies that the degradation of clofibric acid and diclofenac by UV-C photolysis is expected to be higher than by UV-A photolysis. Since diclofenac has stronger absorption than clofibric acid at 254 nm, it is expected that diclofenac will be more susceptible to UV-C photolysis than clofibric acid.

Fig. 3 shows the degradation of clofibric acid and diclofenac during UV photolysis under different wavelengths (UV-A (365 nm) and UV-C (254 nm)). While no degradation of clofibric acid and diclofenac was achieved under UV-A photolysis, both the clofibric acid and diclofenac were degraded over 90% within 60 min under UV-C conditions. Fig. 3 shows that diclofenac was more effectively degraded than clofibric acid. This is might be due to the higher molar absorption coefficient (ε) value of diclofenac compared to clofibric acid (Fig. 2).

Quantum yield (Φ) can also influence UV photolytic degradation of compounds in water. The quantum yield for degradation of each pharmaceutical can be determined by the ratio of photons which are used to degrade the pharmaceutical to photons absorbed by the pharmaceutical. Packer [7] reported that the quantum yield of pharmaceuticals under sunlight photoly-

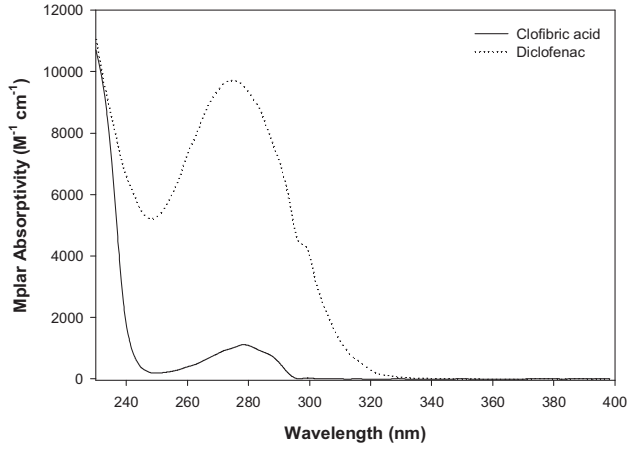


Fig. 2. Molar absorption coefficient (ε) scans of clofibric acid and diclofenac in aqueous solution. (pK_a is 3.18 for clofibric acid, 4.15 for diclofenac).

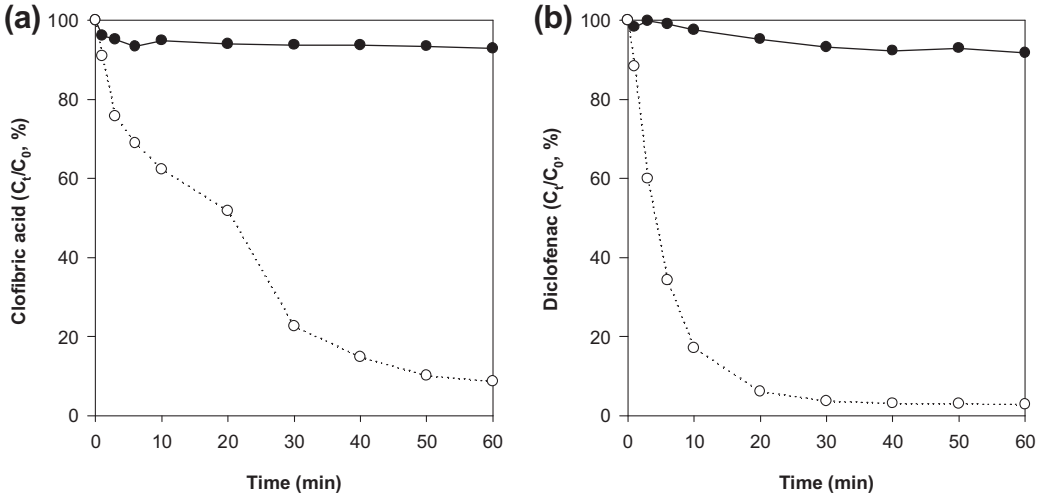


Fig. 3. Degradation of (a) clofibric acid (4.67×10^{-5} M), (b) diclofenac (3.14×10^{-5} M) by UV-only photolysis under different wavelengths (filled circles: UV-A, open circles: UV-C).

sis in distilled water is 0.002 mol einstein^{-1} for clofibric acid and 0.094 mol einstein^{-1} for diclofenac, respectively. According to the data of both the molar absorption coefficient (ε) and the quantum yield (Φ), photon-mediated degradation of selected pharmaceuticals, especially diclofenac, is a dominant mechanism in UV photolytic reaction.

3.2. Competition kinetics in UV/H_2O_2 reaction

Fig. 4 shows that more effective removals of clofibric acid and diclofenac were observed when H_2O_2 was added in UV-C photolysis reaction. This result is due to the effective production of OH radials. Interestingly, while increase in the removal of diclofenac by the addition of H_2O_2 was small, the removal of clofibric acid was significantly improved by the addition of H_2O_2 in UV-C photolysis reaction. This result implies that, while diclofenac is mainly removed by photon reaction, clofibric acid was more sensitive to the OH radical than diclofenac.

In the presence of H_2O_2, the degradation of pharmaceuticals is mediated by both the direct UV photolysis mediated by the photon and the indirect oxidation by OH radicals. The degradation rate of clofibric acid and diclofenac depends on the concentration of OH radical and the second-order rate for the reaction between OH radical and selected pharmaceuticals (PhACs). In order to calculate the second-order rate constants ($k_{OH/PhAC}$) between the

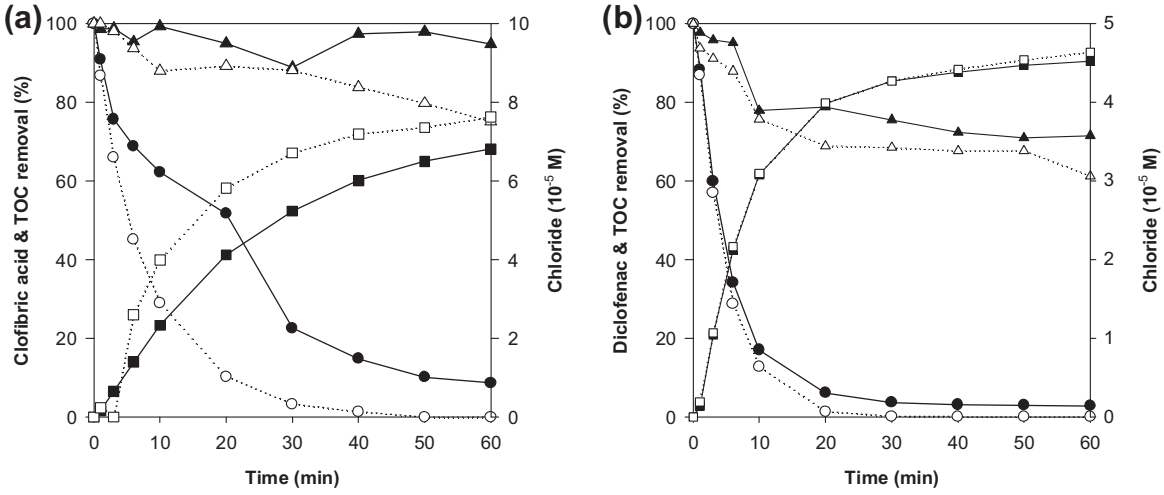


Fig. 4. Removal of (a) clofibric acid (4.67×10^{-5} M) (b) diclofenac (3.14×10^{-5} M), TOC, and chloride production by UV-C photolysis in the absence or presence of H_2O_2 (1.0×10^{-3} M). (full symbols = UV photolysis, empty symbols = UV/H_2O_2; circles = pharmaceutical removal; triangles = TOC removal; squares = chloride production).

OH radical and the pharmaceuticals, the competition kinetic method for simultaneous reaction of OH radical with PhACs and *p*-CBA was applied as described, as shown in Eq. (2) [29]:

$$\ln\left(\frac{[\mathrm{PhAC}]_t}{[\mathrm{PhAC}]_0}\right) = \ln\left(\frac{[p\mathrm{CBA}]_t}{[p\mathrm{CBA}]_0}\right)\frac{k_{\mathrm{OH/PhAC}}}{k_{\mathrm{OH}/p\mathrm{CBA}}} \quad (2)$$

where $k_{\mathrm{OH/PhAC}}$ and $k_{\mathrm{OH}/p_{\mathrm{CBA}}}$ are the second-order rate constants for the reaction of OH radical with the pharmaceuticals and the reference compound (*p*CBA), respectively. *p*-CBA was chosen as a reference compound, assuming the first-order kinetic dependence on each pharmaceutical and *p*-CBA, and the two reactions proceed independently in parallel [29–31]. The *p*-CBA essentially does not undergo direct photolysis and has been successfully applied in similar experiments [29,30].

The second-order rate constant ($k_{\mathrm{OH/PhAC}}$) with pharmaceutical compound can be determined as the slope of the plot of $\ln([\mathrm{PhAC}]_t/[\mathrm{PhAC}]_0)$ vs. $\ln([p\mathrm{CBA}]_t/[p\mathrm{CBA}]_0)$ and with previously known value of $k_{\mathrm{OH}/p\mathrm{CBA}}$ ($k_{\mathrm{OH/pCBA}} = 5 \times 10^9\,\mathrm{M^{-1}\,s^{-1}}$) [32,33]. Since UV-C photolysis reactions of both the clofibric acid and diclofenac are effective (Fig. 1), the disappearance of clofibric acid and diclofenac during UV-C/H_2O_2 reaction is due to both direct photolysis and OH radical attack, whereas in that of *p*-CBA only to the latter. In fact, the rate constant in UV-C photolysis for clofibric acid was $0.16\,\mathrm{min^{-1}}$, and for diclofenac it was $0.39\,\mathrm{min^{-1}}$ (Table 1), implying that UV photolysis of clofibric acid and diclofenac should be considered while calculating the second-order rate constants ($k_{\mathrm{OH/PhACs}}$) during the UV/H_2O_2 reaction. Therefore, the second-order rate constant ($k_{\mathrm{OH/PhAC}}$) with clofibric acid and diclofenac was determined by subtracting the contribution of UV-C photolysis during UV-C/H_2O_2 reaction [29].

Table 1
The rate constant during UV-C photolysis and UV-C/H_2O_2 reactions, slope in plot of ln ($[\mathrm{PhAC}]/[\mathrm{PhAC}]_0$) vs. ln ($[p\mathrm{CBA}]/[p\mathrm{CBA}]_0$), and the second-order rate constant of OH radical and with selected PhACs ($k_{\mathrm{OH/PhACs}}$)

	Chemical clofibric acid	Diclofenac
UV-C photolysis (k_d, $\mathrm{min^{-1}}$)	0.16	0.39
UV-C/H_2O_2 (k_i, $\mathrm{min^{-1}}$)	0.65	0.62
Slope[a] (R^2)[b]	1.11 (0.9889)	0.49 (0.9485)
$k_{\mathrm{OH/PhACs}}$ ($\times 10^9\,\mathrm{M^{-1}\,s^{-1}}$)	5.57	2.45

[a]Plot of ln ($[\mathrm{PhAC}]/[\mathrm{PhAC}]_0$) vs. ln($[p\mathrm{CBA}]/[p\mathrm{CBA}]_0$).
[b]R^2 is correlation coefficient for second-order fitting.

Table 1 summarizes the slope values and the second-order rate constants ($k_{\mathrm{OH/PhACs}}$) for clofibric acid and diclofenac. The resulting plot of $\ln([\mathrm{PhAC}]_t/[\mathrm{PhAC}]_0)$ vs. $\ln([p\mathrm{CBA}]_t/[p\mathrm{CBA}]_0)$ has a slope of 1.11 for clofibric acid and 0.95 for diclofenac and the rate constant of $k_{\mathrm{OH/clofibric\ acid}}$ for clofibric acid and diclofenac was 5.57×10^9 and $2.45 \times 10^9\,\mathrm{M^{-1}\,s^{-1}}$, respectively.

Schwarzenbach et al. [32] reported that the second-order rate constants for organic pollutants reacting with OH radical typically varied between 10^6 and $10^{10}\,\mathrm{M^{-1}\,s^{-1}}$. Comparing with the reported values, the rates of clofibric acid and diclofenac with the OH radical were comparable. The rate constant of $k_{\mathrm{OH/clofibric\ acid}}$ for clofibric acid in this study also agreed with the reported values of $5.72 \times 10^9\,\mathrm{M^{-1}\,s^{-1}}$ in Pereira's study [30] and $4.7 \times 10^9\,\mathrm{M^{-1}\,s^{-1}}$ in Packet's study [7].

3.3. Mineralization of clofibric acid and diclofenac

Fig. 4 shows the removal of TOC along with the removal of clofibric acid and diclofenac and chloride ion production during UV photolysis and UV/H_2O_2 reactions. In case of clofibric acid, while almost 90% of clofibric acid was degraded during 60 min of reaction in UV photolysis, TOC removal was negligible. This result indicates that mineralization of clofibric acid does not occur in UV photolysis reaction (Fig. 4(a)). In contrast, clofibric acid was completely degraded during 60 min of UV/H_2O_2 reaction. Interestingly, the extent of dechlorination during clofibric acid removal was 74%, whereas TOC removal was only 23%. This result implies that the major intermediates of clofibric acid in UV/H_2O_2 reaction do not contain chlorine atom in their molecular form.

In case of diclofenac, the complete removal of diclofenac was achieved within 60 and 30 min in UV photolysis and UV/H_2O_2 reactions (Fig. 4(b)). During UV/H_2O_2 reaction, almost 40% of mineralization of diclofenac with chloride production of almost 90% was achieved after 60 min (Fig. 4(b)). Compared to UV photolysis reaction, the mineralization and dechlorination extents were not significantly improved by the addition of H_2O_2 during UV/H_2O_2reaction. This result implies that direct photolysis reaction is important during diclofenac degradation, while OH radical-mediated reaction is important in clofibric acid degradation (Fig. 4(a) and (b)).

3.4. Characterization of degradation products of clofibric acid

The reaction intermediates during UV photolysis and UV/H_2O_2 reactions of clofibric acid were examined by GC-MS. The reaction intermediates were identified using a library database with values fitting

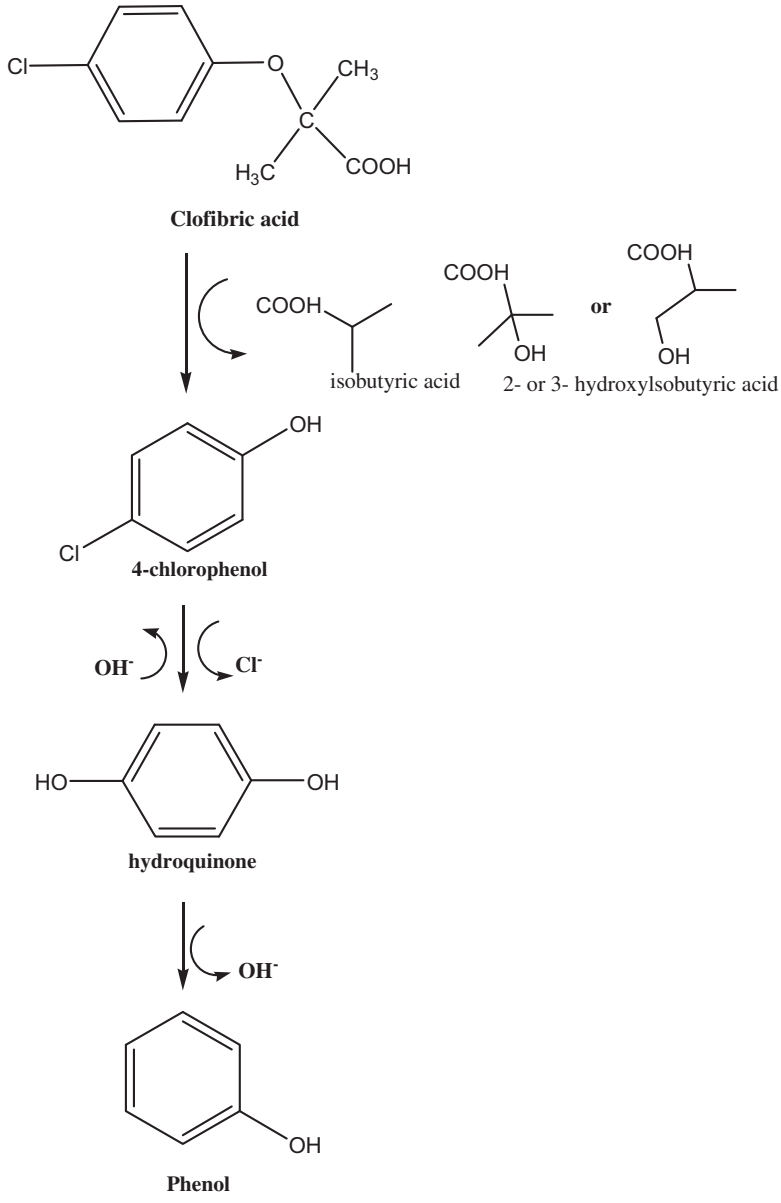


Fig. 5. Suggested simplified degradation pathway scheme of UV photolysis and UV/H_2O_2 degradation of clofibric acid.

higher than 90%. During UV-C photolysis reaction of clofibric acid, 4-chlorophenol ($m/z = 128$, $t_R = 11.77$ min) and hydroquinone ($m/z = 110$, $t_R = 12.79$ min) were identified within 30 min of reaction and phenol ($m/z = 94$, $t_R = 8.32$ min) was detected after 30 min of reaction. In contrast, during UV/H_2O_2 reaction of clofibric acid, 4-chlorophenol and hydroquinone were detected before 10 min of reaction and phenol was detected after 10 min of reaction.

Although the intermediate products of clofibric acid in UV/H_2O_2 reaction were detected at an earlier reaction time than in UV-C photolysis, 4-chlorophenol and hydroquinone were found to be the major intermediates of clofibric acid degradation during UV/H_2O_2 reaction. These intermediates were further degraded to phenol, which is the major byproduct of th reaction of clofibric acid. Based on the identification of the intermediate products, the possible degradation pathway schemes of UV-C photolysis and UV/H_2O_2 reaction of clofibric acid are proposed in Fig. 5.

Doll and Frimmel [20] proposed that clofibric acid degradation goes through two processes. One is the initial dechlorination of clofibric acid produced 2-(4-hydroxylpheonxy)-isobutyric acid, then a further breakdown into isobutyric acid, 2- or 3-hydroxyisobutyric acid, and hydroquinone. The other process is, first, breakdown of clofibric acid into isobutyric acid, 2- or 3-hydroxyisobutyric acid, and 4-chlorophenol, then

further dechlorination of 4-chloropheol into hydroquinone. In fact, Doll and Frimmel [20] used 20 times higher concentration of clofibric acid compared to our study. Since lower concentration of initial clofibric acid was applied in our study, it is unlikely that all the intermediate products, except 4-chlorophenol, hydroquinone, and phenol, would be identified in our study.

4. Conclusions

In this study, the kinetics and degradation mechanism of clofibric acid and diclofenac during UV photolysis and UV/H_2O_2 reactions were investigated. During UV-C photolysis reaction, the degradation of diclofenac was faster than that of clofibric acid, while clofibric acid degradation was faster than diclofenac during UV/H_2O_2 reaction. The second-order rate constant ($k_{OH/PhAC}$) of clofibric acid and diclofenac with OH radical was determined to be $5.57 \times 10^9\,M^{-1}\,s^{-1}$ for clofibric acid and $2.45 \times 10^9\,M^{-1}\,s^{-1}$ for diclofenac, respectively. During UV-C photolysis and UV/H_2O_2 reaction of clofibric acid, hydroquinone and 4-chlorophenol were produced as the major intermediates and phenol was identified as the major byproduct with further reaction.

Acknowledgments

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