EFFECTIVE CONTROL OF PHARMACEUTICALS IN WATER USING OXIDATION TECHNOLOGIES

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ABSTRACT

In recent years, there has been growing concern about the appearance of pharmaceuticals in surface water as their uses increase. Even though the toxicological effect of low concentrations of pharmaceuticals in drinking water is not yet fully understood, these compounds should be minimized to reduce the risk of unpredictable long term effects based on the precautionary principles. Therefore, ozonation and copper catalyzed Fenton and photo-Fenton are discussed to be potential methods for effective control of pharmaceuticals in this study. In order to establish a practical and mechanistic database for pharmaceutical compounds using these methods, the following issues were investigated in this study.

Firstly, the oxidative degradation of pharmaceutical compounds is demonstrated during ozonation of different water samples in Ulsan. Diclofenac, carbamazepine, bezafibrate, and ibuprofen were selected as surrogate pharmaceutical compounds, and ozonation experiments were performed using four different water samples; Surface water samples (Hoeya Dam and Sayeon Dam) are the source of drinking water production in Ulsan. In addition, raw water and water after filtration were collected from the treatment process of Hoeya drinking water plant. Diclofenac and carbamazepine which have high reactivity with molecular ozone showed higher removal efficiencies than bezafibrate and ibuprofen during ozonation. The addition of *tert*-butanol, a hydroxyl radical scavenger, increased the removal efficiencies of diclofenac and carbamazepine by increasing the ozone exposure. However, the oxidation of bezafibrate and ibuprofen was inhibited by the presence of *tert*-butanol due to the suppression of the exposure to hydroxyl radical. The elimination of the selected pharmaceuticals could be successfully predicted by the kinetic model base on the R_{ct} concept. Depending on the experimental condition, R_{ct} values were determined to be $(1.54\sim3.32)\times10^{-7}$ and $(1.19\sim3.04)\times10^{-7}$ for the Sayeon Dam and the Hoeya Dam waters, respectively. Relatively high R_{ct} values indicate that the conversion of O_3 into $^{\cdot}OH$ is more pronounced for surface waters in Ulsan compared to other water sources. Furthermore, model prediction of 19 pharmaceutical compounds including diclofenac, carbamazepine, bezafibrate, and ibuprofen was conducted in investigated water samples with various concentrations of ozone dose.

Secondly, the degradation of diclofenac and carbamazepine by the copper-catalyzed Fenton and photo-Fenton systems was investigated with respect to several reaction parameters such as pH, scavenger and catalyst concentration. The removal rates of targeted pharmaceutical compounds by the $Cu(II)/H_2O_2$ system were found to be gradually increased with rising pH from 3 to 8, but decreased at more alkaline

pH. The possible mechanism was discussed based on Fenton chemistry, and two factors are recommended to be attributable for. First, the reduction reaction of Cu(II) is accelerated by the H_2O_2 and Cu(II) complexation, which favors the reaction of HO_2^- with Cu(II). Second, oxidants produced by the Cu(II)/H_2O_2 system are likely shifted from $^{\cdot}OH$ to Cu(III) as pH increases up to the alkaline region, and the oxidants responsible for the degradation of diclofenac and carbamazepine was not Cu(III) but $^{\bullet}OH$. On the other hand, the rate of pharmaceutical compounds removal by the Cu(II)/H_2O_2 system were monitored under UV irradiation, and a significant enhancement was observed in the degradation rates at a range of pH (3-10). It is believed that the decomposition of pharmaceuticals is leveled up because of the Cu(II) reduction by $HO_2^{\bullet}$ which is produced from H_2O_2 photolysis. The evidences was shown in the comparison of Cu(II) and H_2O_2 absorbance at λ_{max} = 365 nm and measurement of Cu(I) conversion rates.

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Chapter 1. Introduction

I. Research background

Micropollutants, such as endocrine disrupting compounds (or EDCs), pharmaceuticals, and personal care products have been a worldwide issue for the past several years because of potential adverse health effects via the consumption of drinking water. However, conventional drinking water treatment (coagulation/flocculation, filtration, chlorination) shows insufficient removal of emerging contaminants due to persistence in the aquatic environment by their chemical structure. Therefore, a number of studies for effective control of emerging contaminants including pharmaceuticals compounds have been reported.

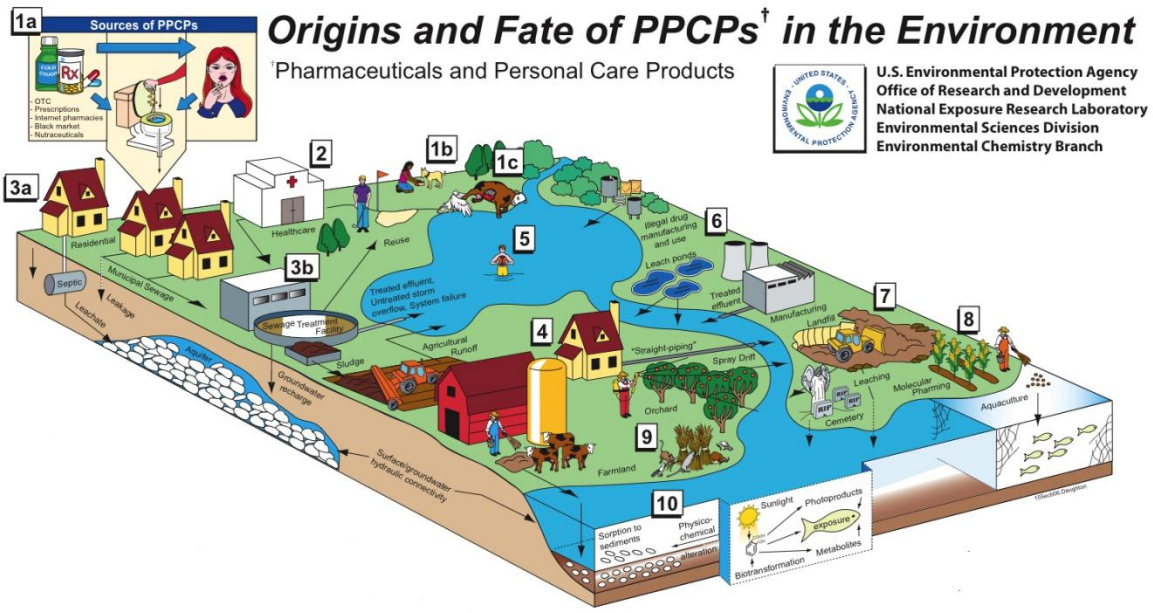


Figure 1. Origins and Fate of PPCPs in the Environment

(http://www.epa.gov/ppcp/)

Especially, researches concerning pharmaceutical compounds are newly highlighted since various pharmaceuticals are commonly used with development of modern pharmaceutical industry. Several studies have reported that pharmaceuticals in the nanogram per liter range are routinely detected in

surface waters (Santos et al., 2010), many of them mainly released from undegradable substance from the waste treatment process (Ternes, 1998). Even though the toxicological effect of low concentrations of pharmaceuticals in drinking water is not yet fully understood yet, these compounds should be minimized to reduce the risk of unpredictable long term effects based on the precautionary principles. It has been proven that conventional processes of drinking water treatment are fairly ineffective to completely remove several pharmaceuticals (Ternes et al., 2002). In contrast, a large number of studies have demonstrated that chemical oxidation using ozone, UV radiation, Fe(II)/H_2O_2 and other methods is an effective treatment process for organic micropollutants including pharmaceuticals (Benitez et al., 2011; Lee and von Gunten, 2010).

1.1. Oxidative degradation of pharmaceutical compounds during ozonation

A large number of studies have demonstrated validation of the ozone process to oxidative decomposition of pharmaceutical compounds among the advanced oxidation technologies (Huber et al., 2003; Deborde et al., 2005; Broseus et al., 2009). Previous studies reported that pharmaceutical compounds with high reactivity to ozone, such as carbamazepine, ethinylestradiol, diclofenac, sulfamethoxazole, and roxithromycin, were completely removed with more than 1 ppm of ozone injection. Cases such as ibuprofen and iopromide, which have less reactivity to ozone, also shows acceptable removal efficiency by employing the O_3/H_2O_2 process. Effective decomposition of pharmaceuticals by ozonation has been reported in waste water treatment plants as well as drinking water treatment plants (Huber et al., 2005; Dodd et al., 2006; Lee and von Gunten, 2010). An extensive database related to the decomposition of pharmaceuticals was mainly investigated in developed countries including Switzerland and the United States.

Domestically, a number of studies regarding the ozone process have been reported (Rhim, 2003; Kang et al., 2005), and several researches were also conducted to provide removal efficiency of the pharmaceuticals during ozonation (Son et al., 2009; Kim, 2010). However, there is insufficient information about the characteristic behaviors of ozone decomposition affecting the pharmaceuticals removal efficiency. In particular, no study concerning quantitative prediction based on removal kinetics of pharmaceutical and oxidants (ozone and hydroxyl radical) utilized in the ozonation process has been published.

Decomposition of organic contaminants during the ozone process occurs by the direct reaction with ozone and indirect reaction with hydroxyl radical. Therefore, a prediction for removal efficiency of

targeted organic contaminants can be made as far as concentration change and rate constants of ozone with organic contaminants and hydroxyl radical are known (Elovitz and von Gunten, 1999). Removal efficiency of the ozone process is influenced by several factors such as concentration and characteristics of natural organic matter, reactivity of targeted organic contaminants with ozone and so on (Elovitz et al., 2000; von Gunten, 2003).

This study investigated the removal efficiency of pharmaceuticals in river waters of Ulsan during the ozonation. In addition, the removal efficiency of pharmaceuticals was predicted based on the R_{ct} value involving the ratio of the OH radical exposure to the ozone exposure and rate constants.

1.2. Oxidaition of pharmaceutical compounds by copper-catalyzed Fenton and photo-Fenton systems

The advanced oxidation processes that employ hydrogen peroxide (H_2O_2) and iron have been widely utilized as methods for the oxidation of recalcitrant contaminants in drinking water, industrial wastewater, and soils (Pignatello et al., 2006). In spite of the volume of work published on Fenton processes (Fe^{2+}/H_2O_2), there appears to be a lack of information concerning the usage of other transition metals with hydrogen peroxide to treat organic contaminants. Among the transition metals, copper has been discussed as a potentially promising catalyst by demonstrating that copper presumably undergoes a similar reaction with H_2O_2 as iron does.

It is well known that the typical Fenton reaction occurs only at acidic pH which limits its application because of the low solubility of iron as a catalyst. To the contrary, copper as a catalyst enables activity in a wider range of pH due to the better solubility of copper ions than iron ions at neutral pH (Masarwa et al., 1988; Yip et al., 2005). On the other hand, copper has been proved to be an effective catalyst for oxidizing a range of organic compounds, for example p-coumaric acid, phenol, benzoic acid, humic acid and so on, owing to its relatively high solubility at neutral pH, considerable efficiency at low concentration, and little requirement of post processing after treatment (Liao et al., 2001; Mantzavinos et al., 1996; Mantzavinos, 2003; Santos et al., 2001).

However, there are only a few studies related to the usage of copper catalysts to degrade pharmaceutical contaminants (Sires et al., 2006; Sun et al., 2011), and the underlying mechanism is also little known. Kinetics and the reaction pathway in the decomposition of H_2O_2 catalyzed by Cu(II) is available in previous literature (Moffett and Zika, 1987; Luo et al., 1988), but most of the earlier work has

been carried out in a limited pH range or discussed apart from decomposition of organic compounds. This research attempts to examine the degradation efficiency of pharmaceuticals by a copper-catalyzed Fenton-like reaction and photo-Fenton-like reaction under various conditions of copper concentration, solution pH, and UV irradiation. A series of experiments performed to elucidate the mechanism through which the pharmaceuticals are oxidized in the Fenton-like systems, and the results are also discussed with those of the respective Fenton system.

II. Objectives of the study

In the study presented here after, two specific objectives were sought:

1. To assess the validity of model prediction for oxidation of pharmaceuticals and to discuss characteristic behaviors of ozone decomposition in the river waters of Ulsan:

For this purpose, the R_{ct} value is determined to predict oxidation kinetics of pharmaceuticals during the ozonation of river waters in Ulsan, and the R_{ct} concept was adapted to make a prediction. A characteristic behaviors of ozone decomposition is discussed by hiring a radical scavenger and comparison with previous studies.

2. To examine the degradation efficiency of pharmaceuticals by copper-catalyzed Fenton-like reaction and photo-Fenton-like reaction and to elucidate the mechanism through which the pharmaceuticals are oxidized in the Fenton-like systems:

For this purpose, carbamazepine and diclofenac were selected as surrogate pharmaceutical compounds, and the effects of copper dose and pH of the solution were studied in the absence and presence of UV irradiation. The mechanism involved in degradation of selected pharmaceuticals is experimentally identified.

Chapter 2. Materials and Methods

I. Characteristic behaviors of ozone decomposition and oxidation of pharmaceuticals during ozonation of water samples in Ulsan

1.1. Reagents

Carbamazepine, Diclofenac, Mefenamic acid and Lincomycin were obtained from Sigma-Aldrich with purity higher than 99%. Stock solutions of these pharmaceuticals were prepared with Milli-Q purified water (Millipore). All of the chemicals used for solutions (buffer, eluents, etc.) were reagent grade and used without further purification. Ozone stock solutions (~30 ppm) were produced by sparging O_3-containing oxygen through Milli-Q water that was cooled in an ice bath, and daily prepared.

1.2. Natural water samples

To simulate real treatment conditions, experiments were performed using natural waters that differed in dissolved organic carbon content (DOC) and alkalinity. Surface water samples (Hoeya Dam and Sayeon Dam) are the source of drinking water production in Ulsan. In addition, raw water and water after filtration was collected from the treatment process of Hoeya drinking water plant (HY WTP). Major water quality parameters of the tested water are indicated in Table 1. All waters were filtered (0.45-μm Nylon membrane) upon arrival and stored at 4 ℃ until use.

Table 1. Water quality parameters of the tested water

Water type	pH	TOC (mgL^{-1})	Alkalinity ($mgL^{-1}CaCO_3$)
Hoeya Dam	7.2	2.6	18
Sayeon Dam	7.4	3.0	31
Raw water (from HY WTP)	7.6	2.3	40
Water after filtration (from HY WTP)	7.5	2.1	33

1.3. Experimental procedure and analytic methods

All the experiments were performed in a batch system using a 100 mL Pyrex flask open to the atmosphere at room temperature (22 ± 2 ◦C). Desired concentration of pharmaceuticals was intentionally injected to the natural water samples for degradation experiments. Concentration of ozone stock solution was spectrophotometrically determined by measuring the absorbance at 260 nm (3000 M-1 cm-1) and diluted to desired concentration. Experiments were conducted with different concentrations of ozone (0.5, 1.0, 1.5, 2.0 ppm). Sampling was done at 20, 40, 60, 120, 180, 240, 300, and 600 sec after initiation of reaction, and sodium sulfite solution was used to remove ozone in the sampled solution. Variation of pH in the reaction solution was minimized by employing 10 mM phosphate buffer.

All pharmaceuticals were determined by high-performance liquid chromatography (HPLC, Agilent, 1200 series). Depending on the compounds and experiments, isocratic elutions were used with varying eluent ratios, and 100μL of the sample volumes were injected. Detailed information of analysis conditions for pharmaceuticals by HPLC is given in Table 2 (column: Inertsil ODS-4, 5-μm C18), and all the calibration curves reveal a good correlation coefficient ($R^2 > 0.98$) in a range of concentrations (0.05~1 μM).

The R_{ct} concept was suggested by Elovitz & von Gunten to describe characteristic behaviors of ozone decomposition in investigated water, and it is defined as the ratio of the OH radicals exposure to the ozone exposure (Elovitz and von Gunten, 1999). Dissolved ozone was determined with the indigo method (Bader and Hoigne, 1982), concentration of hydroxyl radical was calculated from measuring the decomposition rate of p-chlorobenzoicacid (pCBA). Initial concentration of pCBA was 0.5 μM, and analyzed by HPLC.

Table 2. HPLC analytical conditions for pharmaceutical compounds

		Carbamazepine	Diclofenac	Bezafibrate	Ibuprofen
Flow rate		0.8 mL/min	1.0 mL/min	1 mL/min	1 mL/min
Eluent	10 mM CH_2O_2	50%	40%	40%	40%
	Acetonitrile	50%	60%	60%	60%
Run time		10 min	10 min	10 min	10 min
Retention Time		4.623 min	5.569 min	3.601 min	6.354 min
Detection λ		285 nm	277 nm	226 nm	215 nm

II. Oxidation of Carbamazepine and Diclofenac by Copper-Catalyzed Fenton and Photo-Fenton Systems

2.1. Reagents

All chemicals were of reagent grade and used without further purification. All pharmaceuticals and chemicals including carbamazepine (CA), diclofenac (DF), copper sulfate ($CuSO_4$), hydrogen peroxide (H_2O_2), *tert*-butyl alcohol- (*tert*-BuOH) and ethylenediaminetetraacetic acid (EDTA) were obtained from Sigma–Aldrich except for acetonitrile from J.T. Baker and 2,9-Dimethyl-1,10-phenanthroline (DMP) from TCI. All the stock and buffer solutions were prepared in 18 MΩ Milli-Q water from a Millipore system. Stock solutions of H_2O_2 (10.2 M), carbamazepine (0.1 mM), and diclofenac (1 mM) were prepared prior to experiments.

2.2. Experimental apparatus and procedure

All the experiments were performed in a batch system using a 100 mL Pyrex flask open to the atmosphere at room temperature (22 ± 2 ◦C). Photochemical experiments were conducted in a dark chamber equipped with 4 W Black Light Blue (BLB) lamps (Philips. Co; λ_{max} = 365 nm), a sampling port, a stirrer, and a cooling fan. The incident photon flow (light intensity) of the setup for the photochemical experiments was measured to be 1.06×10^{-6} (2 Lamp); 3.42×10^{-6} (6 Lamp) Einstein L^{-1} s^{-1} by ferrioxalate actinometry (Hatchard and Parker, 1956). No pH buffer was used for reactions at pH 3-5, while 1 mM phosphate buffer and 1 mM borate buffer were employed for experiments at the pH range of 6-7 and pH 8-10 respectively. The initial pH of solutions was correspondingly adjusted with 0.1 N NaOH and 0.1 N HCl after adding catalysts and pharmaceuticals, and the pH variation was monitored at the end of the reaction. The reaction was initiated by adding H_2O_2 (simultaneously starting the UV irradiation in the case of photochemical experiments); 1 mL samples withdrawn at a predetermined time intervals were immediately quenched by 20 µL of 200mM EDTA which was priorly prepared. The samples were then analyzed by high performance liquid chromatography (HPLC, Agilent 1200) at 285 and 277 nm to detect the level of carbamazepine and diclofenac, respectively. Separation was performed on an Inertsil® ODS-4 C18 column (150 mm × 4.6 mm, 5 µm), using water with 10 mM formic acid and acetonitrile with varying eluent ratios. All the experiments were carried out at least in duplicate and average values and the standard deviations are presented.

2.3. Analytical methods of Cu(I) and H_2O_2

The concentration of Cu(I) was determined by the spectrophotometric method using a S-3100 UV/vis spectrophotometer (Scinco Co.) to measure copper complex with neocurpoine as described elsewhere (Eaton et al., 2005) with a slight modification. Hydroxylamine-hydrochloride, a substance that reduces cupric ions [Cu(II)] into cuprous [Cu(I)] ions, was not applied and excess DMP concentration (0.5 mM) was employed to prevent rapid oxidation of Cu(I) to Cu(II) in the presence of oxygen. Meanwhile, the titanium sulfate method was applied to measure the level of H_2O_2 absorbance at 405 nm by UV/vis spectrophotometer (Eisenberg, 1943).

Chapter 3. Results and Discussion

I. Characteristic behaviors of ozone decomposition and oxidation of pharmaceuticals during ozonation of water samples in Ulsan

1.1. Determination of R_{ct} values in water samples of Ulsan

The R_{ct} value was calculated to verify characteristic behaviors of ozone decomposition under the various concentrations of ozone prior to assessment for removal efficiency of selected pharmaceutical compounds during the ozonation. The R_{ct} value (Elovitz and von Gunten, 1999) is defined as the ratio of the OH radicals exposure to the ozone exposure in Eq. (3.1).

$$R_{ct} = \int[^{\cdot}OH]_t dt / \int[O_3]_t dt \qquad (3.1)$$

The ozone exposure ($\int[O_3]_t dt$) is calculated by measuring the concentration of dissolved ozone as a function of time, and the OH radicals exposure ($\int[^{\cdot}OH]_t dt$) is calculated from the decomposition results of pCBA by employing pCBA as a probe compound (Eq. 3.2, 3.3). $k_{\cdot OH,\, pCBA}$ in Eq. (3.2, 3.3) is 5×10^9 $M^{-1}s^{-1}$ (Buxton et al., 1988) as a rate constants of pCBA with hydroxyl radical in a second-order reaction.

$$\ln([pCBA]/[pCBA]_0) = - k_{\cdot OH,\, pCBA} \int[^{\cdot}OH]_t \, dt \qquad (3.2)$$

$$\int[^{\cdot}OH]_t \, dt = -\ln([pCBA]/[pCBA]_0) / k_{\cdot OH,\, pCBA} \qquad (3.3)$$

The R_{ct} value is described as a (Eq. 3.4) from (Eq. 3.1) and (Eq. 3.3). Finally, the R_{ct} value is determined by the linear slope, which is obtained from plotting of $\ln([pCBA]/[pCBA]_0)$ and $\int[O_3]_t dt$, divided by $-k_{\cdot OH,\, pCBA}$.

$$R_{ct} = -\ln([pCBA]/[pCBA]_0) / (k_{\cdot OH,\, pCBA} \int[O_3]_t dt) \qquad (3.4)$$

Plotting of $\ln([pCBA]/[pCBA]_0)$ and $\int[O_3]_t dt$ in various conditions of ozone concentrations is illustrated in Figure 3 and Figure 4, using Hoeya Dam and Sayeon Dam waters samples respectively, and

also described employing raw water and water after filtration (Figure 5, Figure 6). Decomposition of ozone and pCBA can be classified as two steps. In the first step, ozone is rapidly consumed to produce hydroxyl radicals by the Instantaneous Ozone Demand (IOD) of natural organic matter in water. Therefore, it leads to instantaneous decomposition of ozone and pCBA. Gradual decomposition of ozone and pCBA occurs after the first step consuming IOD, thus two different value of R_{ct} can be determined at each steps as shown in Figure 3-6. For the case in which the initial concentration of ozone is too low, the R_{ct} value in the second step could not be decided since the injected ozone was all consumed by the IOD (Figure 2). For instance, complete ozone depletion at the initial step reveals in 0.5 ppm of ozone injection for Hoeya Dam (Figure 2, (a)) and 0.5, 1 ppm of ozone injection for Sayeon Dam (Figure 3, (a, b)). Prominent ozone depletion was observed in Sayeon Dam according to the relatively higher concentration of DOM, because IOD increases as natural organic matters in water increases in general (Cho et al., 2003).

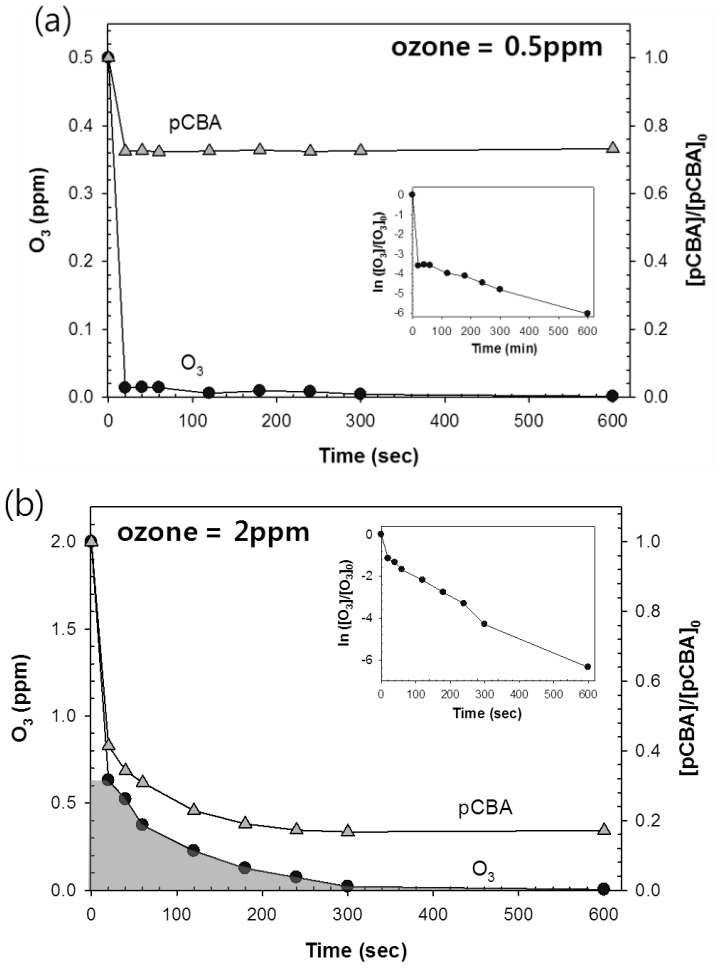


Figure 2. Depletion of ozone and pCBA as a function of reaction time

($[O_3]0$ = 0.5 ppm(a), 2 ppm(b); pCBA = 0.5 μM)

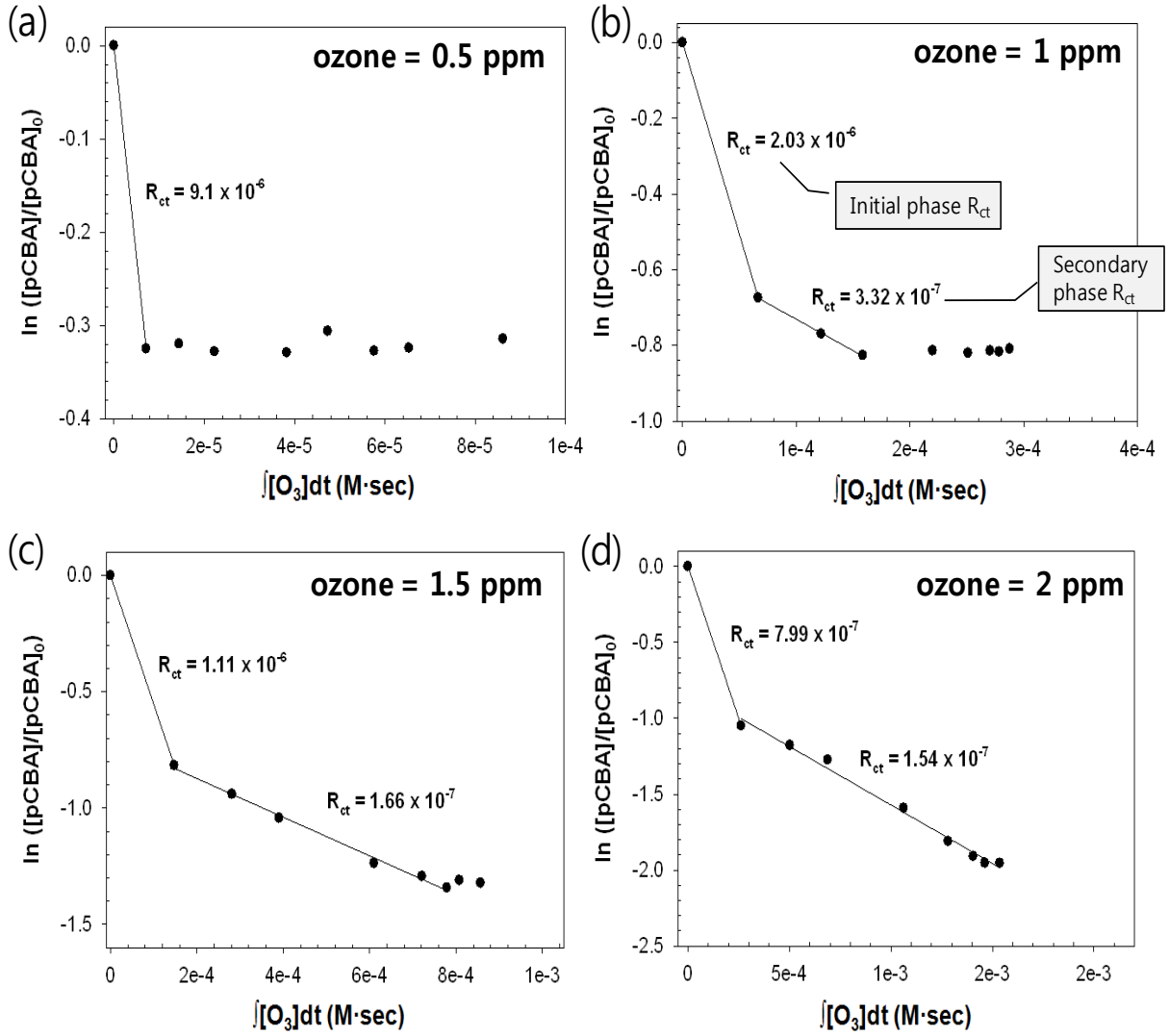


Figure 3. Plots of ln([pCBA]/[pCBA]$_0$) versus the ∫[O_3]$_t$dt for calculating R_{ct} values in the Hoeya Dam water

([O_3]0 = 0.5 ppm(a), 1 ppm(b), 1.5 ppm(c), 2 ppm(d); pCBA = 0.5 μM)

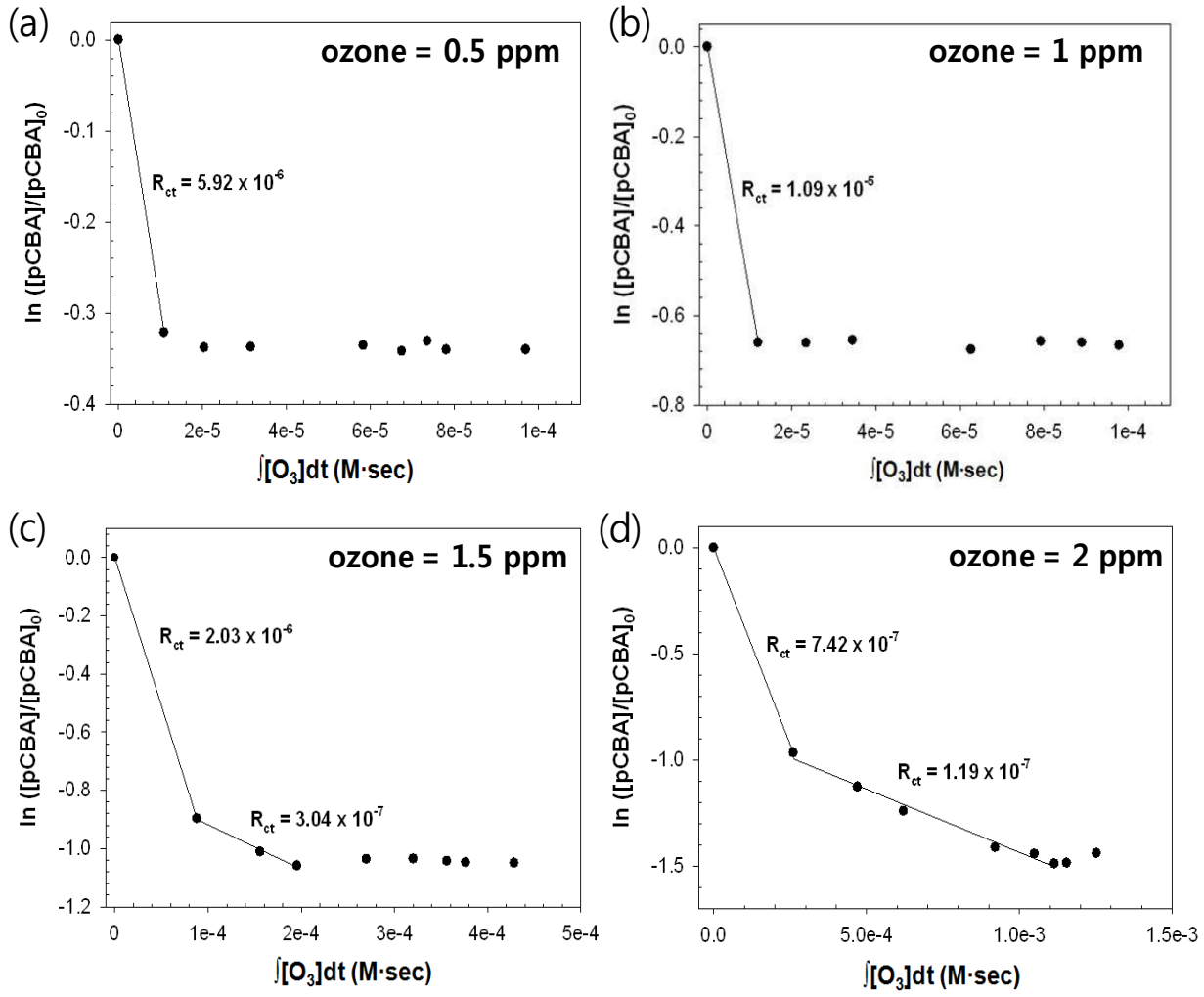


Figure 4. Plots of ln([pCBA]/[pCBA]$_0$) versus the ∫[O_3]$_t$dt for calculating R_{ct} values in the Sayeon Dam water

([O_3]$_0$ = 0.5 ppm(a), 1 ppm(b), 1.5 ppm(c), 2 ppm(d); pCBA = 0.5 μM)

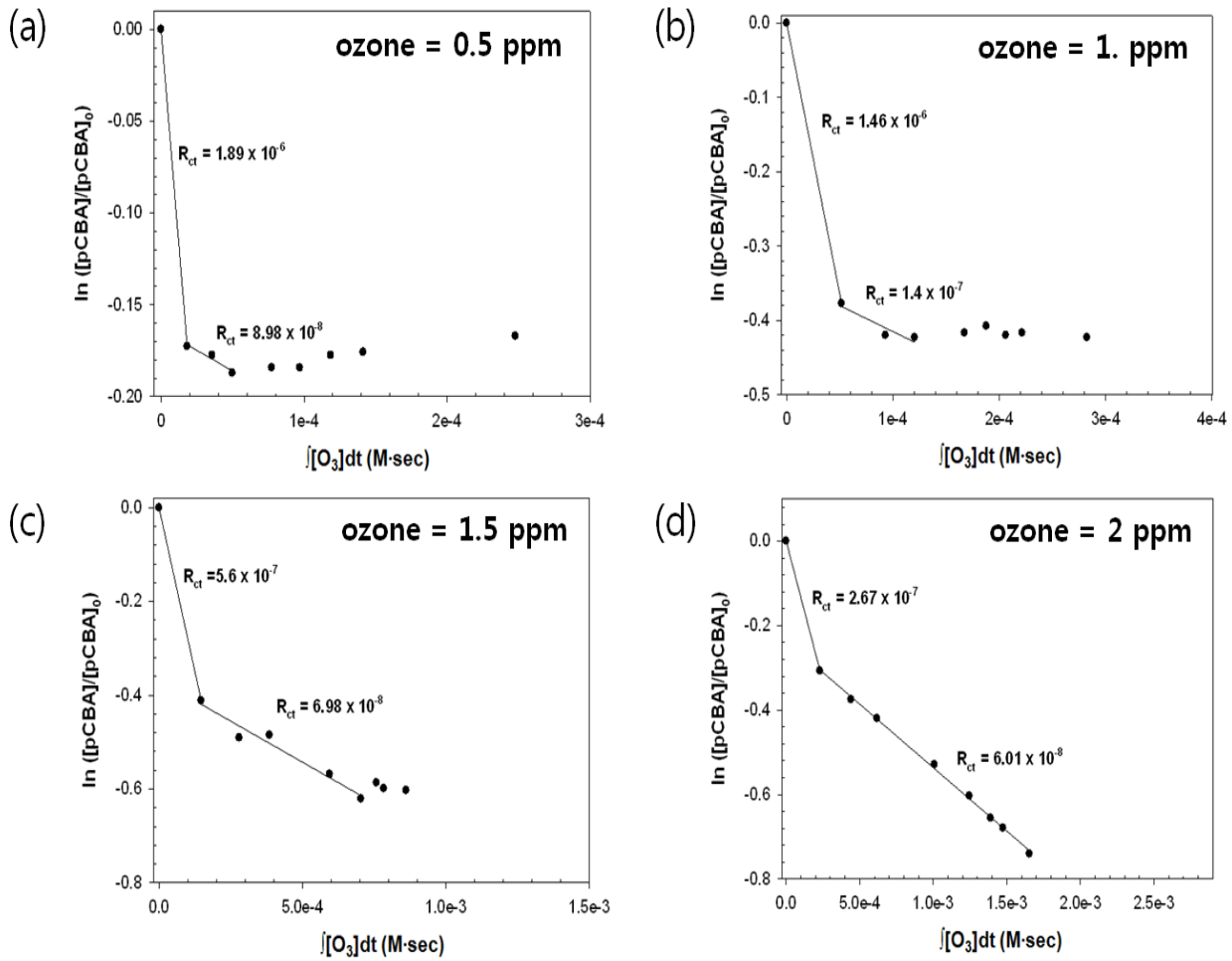


Figure 5. Plots of ln([pCBA]/[pCBA]$_0$) versus the ∫[O_3]$_t$dt for calculating R_{ct} values in Raw water

([O_3]$_0$ = 0.5 ppm(a), 1 ppm(b), 1.5 ppm(c), 2 ppm(d); pCBA = 0.5 μM)

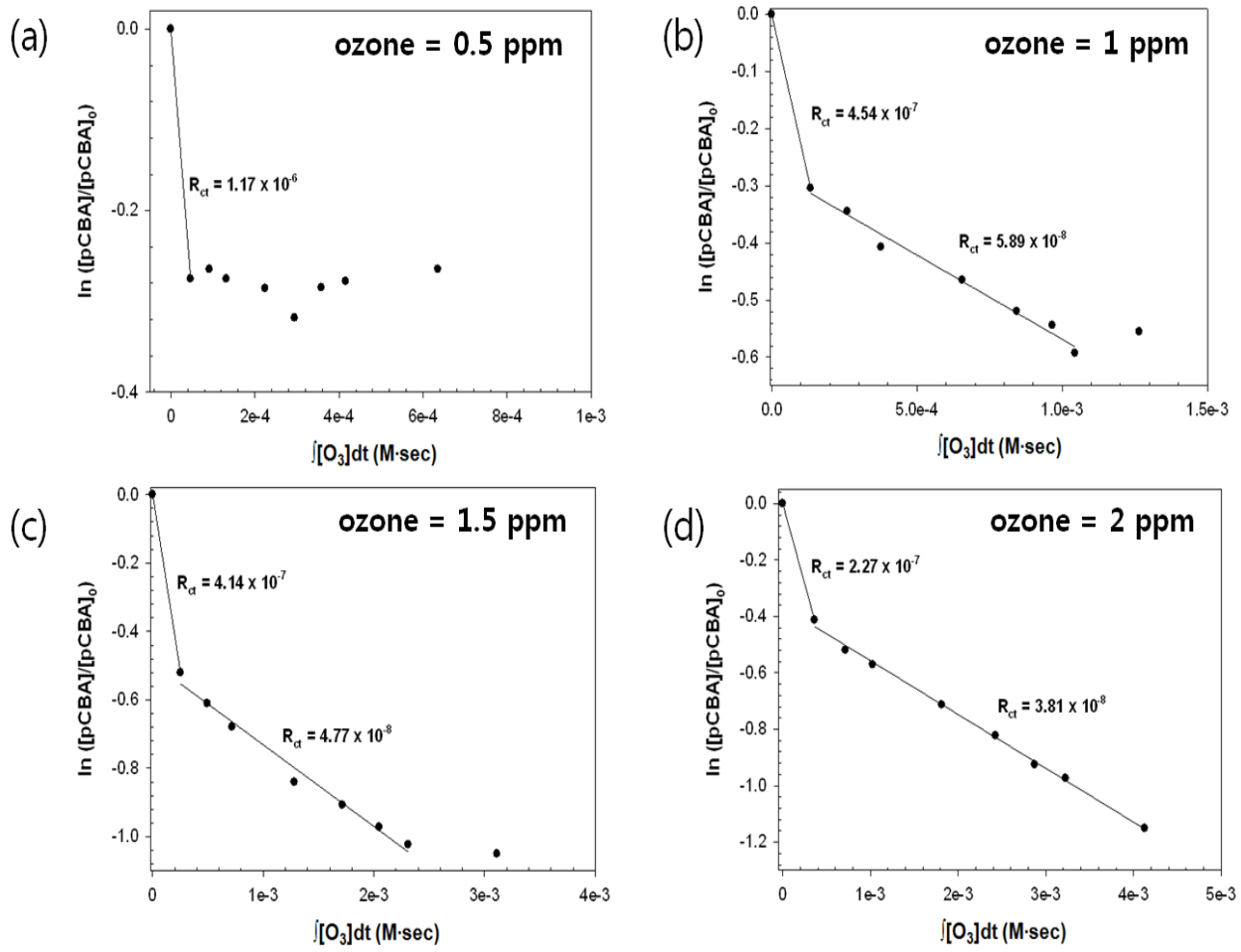


Figure 6. Plots of ln([pCBA]/[pCBA]$_0$) versus the $\int[O_3]_t dt$ for calculating R_{ct} values in Water after filtration

($[O_3]_0$ = 0.5 ppm(a), 1 ppm(b), 1.5 ppm(c), 2 ppm(d); pCBA = 0.5 μM)

Determined R_{ct} values at the second step show a similar figure; (1.54~3.32)×10^{-7} for Hoeya Dam and (1.19~3.04)×10^{-7} for Sayeon Dam. Comparison was made between the second step R_{ct} values obtained from surface waters of Ulsan in the present study and reported values from different water samples (Table 3). R_{ct} values in surface waters of Ulsan were calculated as ((1.2~1.5)×10^{-7}) at 2 ppm of injected ozone; it is approximately two times higher than (4.6×10^{-8}) in Han river of Seoul under the given conditions. Furthermore, the R_{ct} values in this study are about 10 times higher than the determined R_{ct} values ((1.8~1.9)×10^{-8}) in the other water samples. A high R_{ct} value indicates that the generation reaction of hydroxyl radical reaction is favored by deposition of ozone. Conventionally, addition of H_2O_2 (O_3/H_2O_2) is applied to achieve an increase of hydroxyl radical production, but determined R_{ct} values in the surface

waters of Ulsan shows significantly high values without the addition of H_2O_2 (O_3/H_2O_2) which was comparable to the value in the O_3/H_2O_2 obtained from Lake Zurich water, Switzerland (Table 3).

Table 3. Comparison of R_{ct} values determined during ozonation of natural waters

	No.	Conditions	R_{ct}	Reference
1	Surface waters of Ulsan, Korea	ozone, $[O_3]_0$ = 2 ppm	$(1.2\sim1.5)\times10^{-7}$	This study
2	Han River of Seoul, Korea	ozone, $[O_3]_0$ = 1.56 ppm	4.6×10^{-8}	Cho et al., 2003
3	North Saskatchewan River water, Canada	ozone, $[O_3]_0$ = 5 ppm	1.8×10^{-8}	Chelme-Ayala et al., 11
4	Lake Zurich water, Switzerland	ozone, $[O_3]_0$ = 2 ppm	$1.9\times10\text{-}^{8}$	Lee et al., 2007
5	Lake Zurich water, Switzerland	O_3/H_2O_2, $[O_3]_0$ = 2 ppm	7.8×10^{-7}	Lee et al., 2007

1.2. Degradation of pharmaceutical compounds during ozonation of water samples in Ulsan

Elovitz and von Gunten (Elovitz and von Gunten, 1999) developed the R_{ct} concept to predict the oxidation of a micropollutant. The R_{ct} concept is an experimental approach to calibrate ozonation processes and ozone-based AOPs with respect to ozone and OH radical exposure, because the oxidation of a micropollutant can occur due to either ozone or OH radicals. This calibration is done by determining the ratio of the OH radicals exposure to the ozone exposure in investigated water. After an initial phase, the R_{ct} value remains constant for the rest of the ozonation process and therefore, also represents the ratio of OH radicals concentration to ozone concentration. Consequentially the R_{ct} concept allows the prediction of the time-dependent transformation of a compound based on rate constants and oxidant behavior. As shown in (Eq. 3.5-3.7), decomposition of particular pharmaceuticals (P) during the ozonation can be predicted by utilizing determined R_{ct} values in each water samples under the different concentrations of ozone.

Selected pharmaceuticals (P) decomposed by reaction with ozone and hydroxyl radical, thus concentration change can described as (Eq. 3.5). Eq 3.6 is obtained by the integration of (Eq. 3.5), and here we apply the R_{ct} concept to get (Eq. 3.7) that decomposition of P is defined as ozone exposure. Eventually, decomposition of P can be predicted by measuring the concentration change of ozone as a

function of time. k_{O3} and $k_{\cdot OH}$ are rate constants of P with ozone and hydroxyl radical in a second-order reaction respectively, and literature values of selected pharmaceuticals in this study are listed in Table 4.

$$-d[P]/dt = k_{O3}[P][O_3] + k_{\cdot OH}[P][^{\cdot}OH] \quad (3.5)$$

$$\ln([P]/[P]_0) = -(k_{O3}\int[O_3]dt + k_{\cdot OH}\int[^{\cdot}OH]dt) \quad (3.6)$$

$$\ln([P]/[P]_0) = -(k_{O3} + R_{ct}\,k_{\cdot OH})\int[O_3]dt \quad (3.7)$$

Table 4. Second-order rate constants for the reactions of selected pharmaceuticals with molecular ozone and hydroxyl radical (Huber et al., 2003)

Compound	k_{O3} (M^{-1} s^{-1})	$k_{\cdot OH}$ (M^{-1} s^{-1})
Ibuprofen	9.6	7.4×10^9
Bezafibrate	5.9×10^2	7.4×10^9
Carbamazepine	3×10^5	8.8×10^9
Diclofenac	10^6	7.5×10^9

Decomposition experiment of pharmaceuticals (Diclofenac, Carbamazepine, Bezafibrate, Ibuprofen) was performed under the conditions of 0.5 ppm, initial injected ozone concentration (Figure 7 and Figure 8). Removal predictions of selected pharmaceuticals are illustrated in solid lines, and measured values are represented as symbols. Comparison between prediction and measured data was made to assess the validity of the prediction model based on the R_{ct} concept. Diclofenac and carbamazepine, which have relatively higher rate constants with ozone, mainly oxidize through direct reaction with the ozone, whereas removal of bezafibrate and ibuprofen due to the relatively slower rate constants with ozone largely depends on reaction with OH radicals. Therefore, diclofenac and carbamazepine show higher removal efficiency than ibuprofen and benzafibrate in all the investigated water samples (Figure 7 and Figure 8). This tendency is fairly consistent with modeling results using Eq. 3.7. Particularly modeling results for Hoeya Dam (Figure 7, (a)) shows well matching with measured results, whereas modeling results for Sayeon Dam (Figure 7, (b)) reveal differences from measured results in some parts. We suppose that this deviation came from low concentration of residential ozone due to the rapid ozone depletion in Sayeon Dam. When it is considered along with the detection limit (0.01 ppm) of the indigo method which is used for measuring the concentration of residential ozone, a low concentration of

residential ozone generates deviation in measurement of the ozone exposure ($\int[O_3]dt$) to apply (Eq. 3.7). On the other hand, the R_{ct} concept was successfully applied to the prediction of the oxidation of pharmaceuticals for the cases of raw water and water after filtration, exhibiting only a little difference between measured data and the predictions of the model. Higher removal efficiency of pharmaceutical degradation regarding water after filtration was observed in comparison between raw water and water after filtration (Figure 8), and this result indicates that putting the ozone process after the filtration is preferred for the better removal efficiency of pharmaceutical compounds.

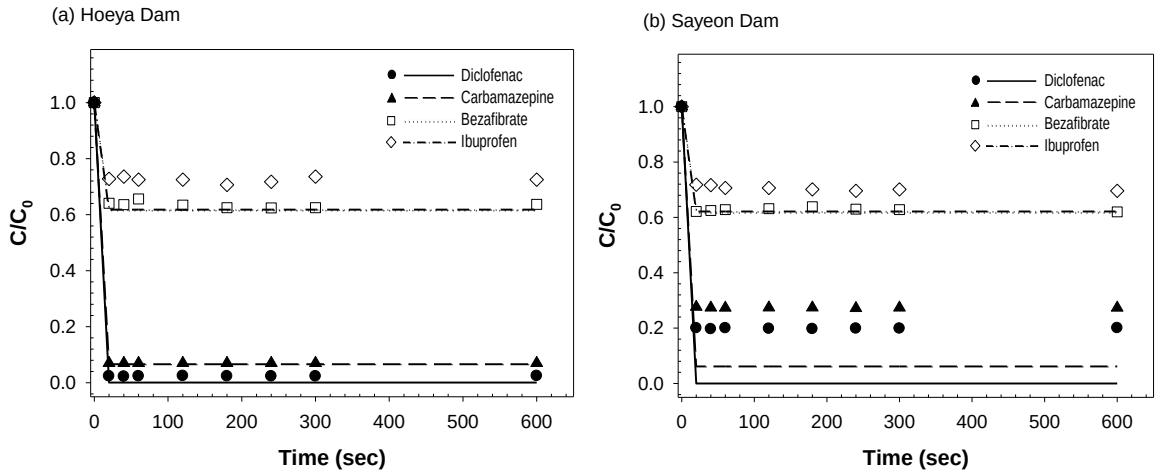


Figure 7. Oxidation of pharmaceutical compounds in the Hoeya Dam water (a) and the Sayeon Dam water (b)

(Symbols and solid lines indicate measured data and model predictions, respectively; $[O_3]_0$ = 0.5 ppm; [Carbamazepine, Bezafibrate, Ibuprofen]$_0$ = 1 μM; [Diclofenac]$_0$ = 0.5 μM)

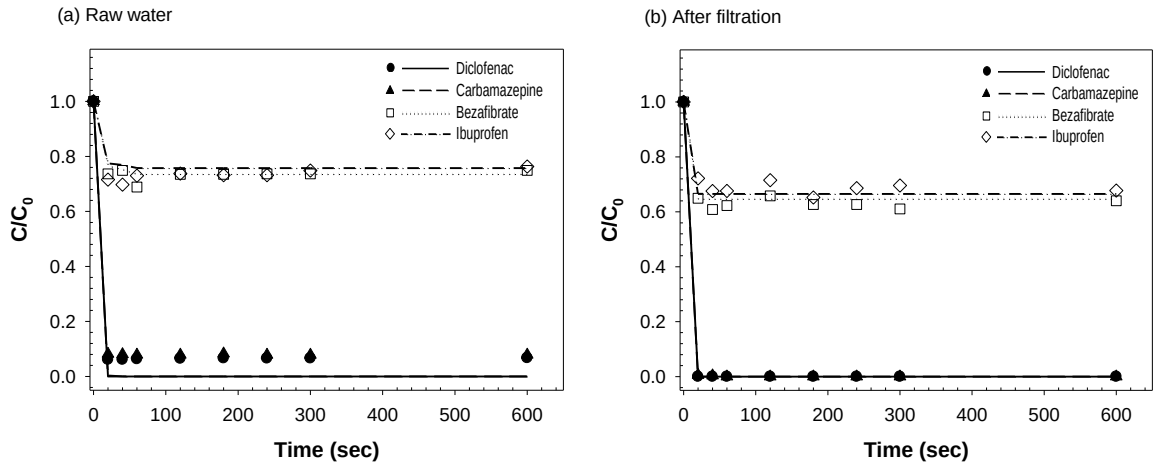


Figure 8. Oxidation of pharmaceutical compounds in the raw water (a) and the water after filtration (b)

(Symbols and solid lines indicate measured data and model predictions, respectively; $[O_3]_0$ = 0.5 ppm; [Carbamazepine, Bezafibrate, Ibuprofen]$_0$ = 1 μM; [Diclofenac]$_0$ = 0.5 μM)

1.3. Effect of hydroxy radical scavengers

The effect of hydroxyl radicals on the decomposition of ozone and selected pharmaceuticals was investigated by hiring excess amounts of *tert*-butanol (20 mM), well known as a scavenger of hydroxyl radicals. It is found that some portion of IOD was reduced in the reaction with *tert*-butanol (20 mM) as shown in Figure 9, and this result is contrasted to the previous study using Han river water (Cho et al., 2003). No change of IOD was observed in the Cho et al. (2003) results regardless of the existence of *tert*-butanol. Consequently, this observation regarding a decrease of IOD in the presence of *tert*-butanol could be evidence for the contribution of hydroxyl radical, which is generated during the rapid decomposition of ozone at the initial step, to the acceleration of ozone depletion.

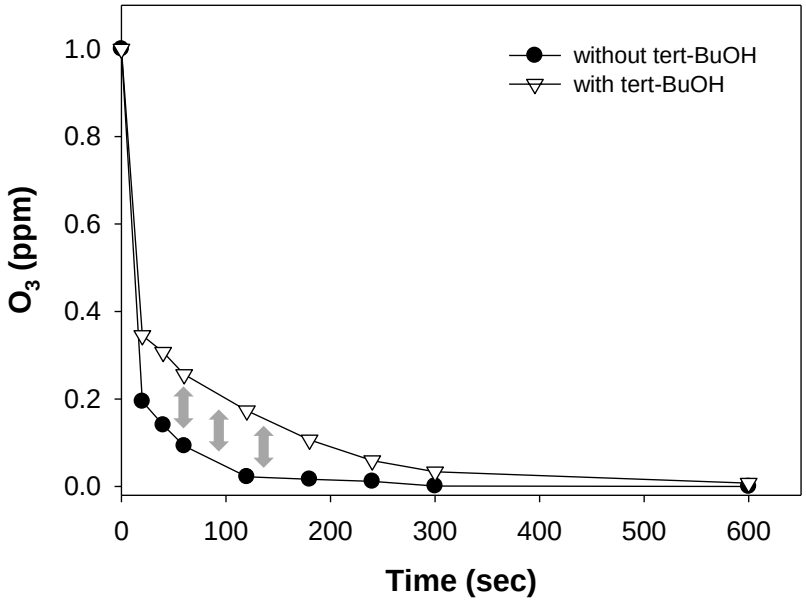


Figure 9. Effect of *tert*-butanol on decomposition of ozone in the Hoeya Dam water
($[O_3]_0$ = 1 ppm; pCBA = 0.5 μM; tert-BuOH = 20 mM)

On the other hand, Figure 10 shows the effect of *tert*-butanol on the decomposition of pharmaceutical compounds. Removal efficiency of diclofenac and carbamazepine is increased in the presence of *tert*-butanol (Figure 10, (a)), whereas the case of bezafibrate and ibuprofen reveals a decrease of removal efficiency (Figure 10, (b)). For diclofenac and carbamazepine, a rapid direct reaction occurs with ozone in the presence of *tert*-butanol, and removal reaction is accelerated by the increase of ozone exposure as shown in Figure 4. However, the decomposition rate of bezafibrate and ibuprofen, which have less reactivity to ozone, is inhibited by the existence of *tert*-butanol. These results explain that decomposition

of compounds with high reactivity to ozone can be favored when numerous substances that work as a scavenger of hydroxyl radical appear in natural water samples, though it can be a disadvantage for decomposition of the compounds that have less reactivity to ozone.

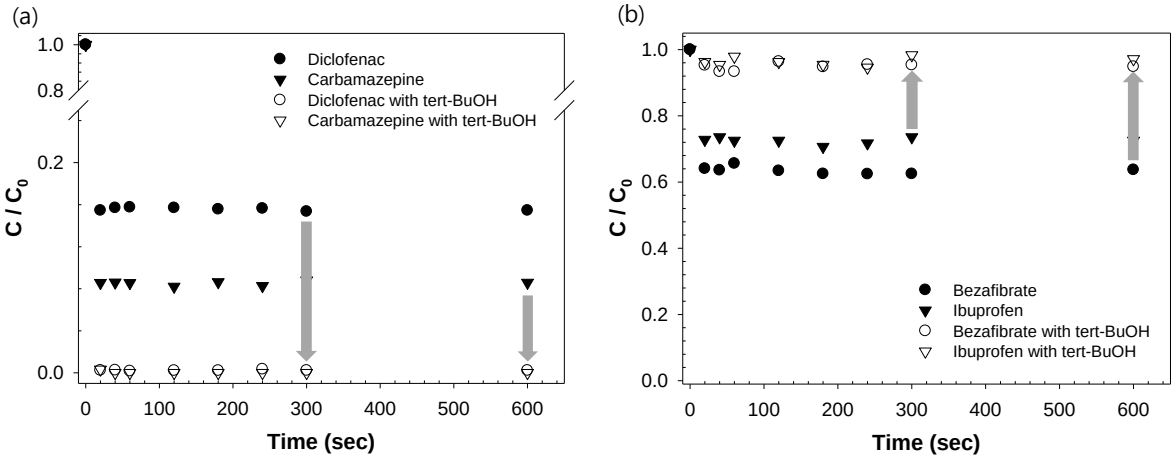


Figure 10. Effect of *tert*-butanol on oxidation of pharmaceutical compounds in the Hoeya Dam water

($[O_3]_0$ = 0.5 ppm; [Carbamazepine, Diclofenac]$_0$ = 1 μM(a); [Bezafibrate, Ibuprofen]$_0$ = 1 μM(b))

1.4. Modeling for parmaceuticals degradation

Modeling was conducted for 19 listed pharmaceuticals, whose constants are already known (Table 5), including carbamazepine, diclofenac, bezafibrate and ibuprofen (Table 4), and we classify the pharmaceuticals into 7 groups based on differences of rate constants to compare the importance of reaction with the ozone and OH radicals as shown in Figure 11. Since $k_{O3,}\ k_{\cdot OH}$ is a constant, the prediction for a micropollutant depends on the ozone and OH radicals exposure based on Eq. 3.5.

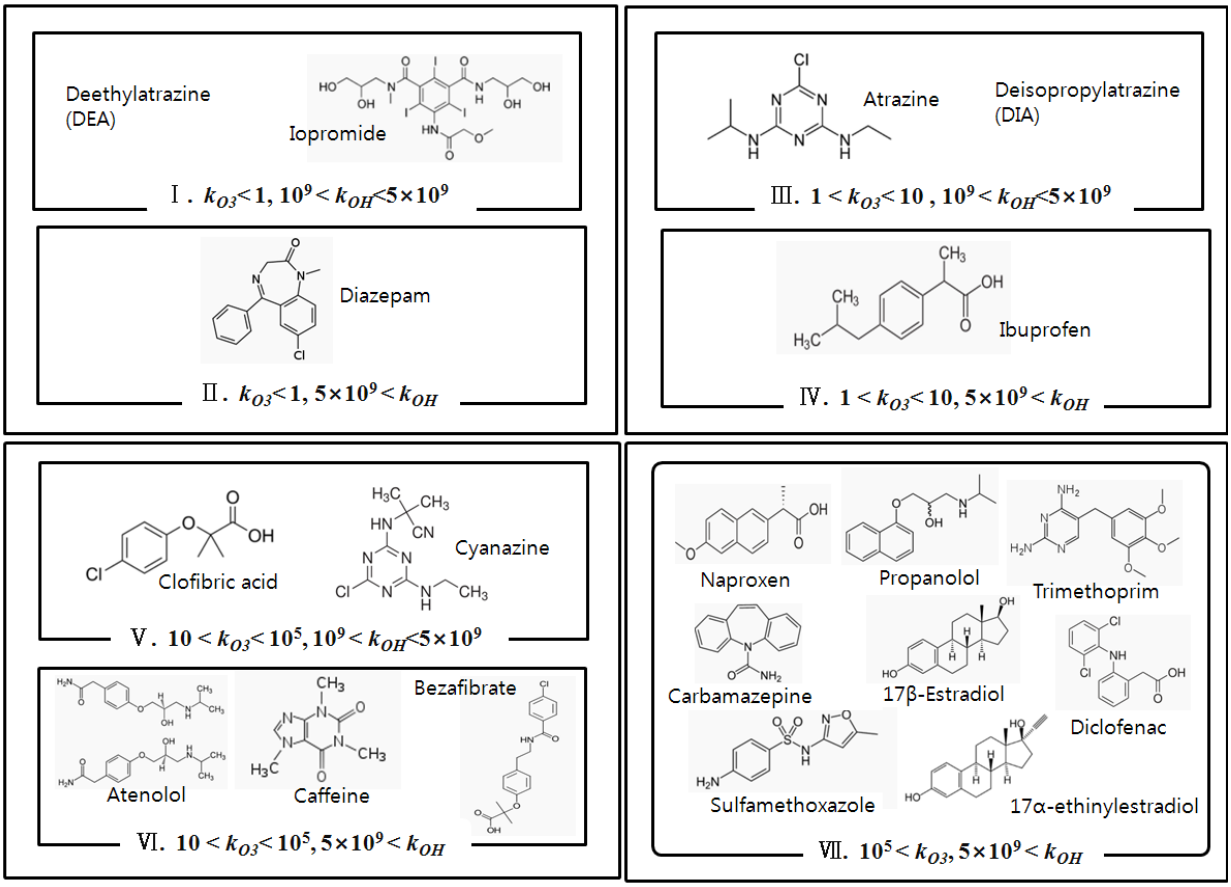


Figure 11. Grouped pharmaceuticals according to rate constant with O_3 and OH radicals

The prediction model of grouped pharmaceuticals removal efficiency was made in 0.5 ppm of ozone dose (Figure 12). Group II appears higher elimination efficiency than group I due to the faster rate constant with hydroxyl radical, when group I and group II are considered. The same results are also revealed in group III and group IV. It is meaningful that surface waters (Hoeya Dam and Cheonsang Dam) show superior removal efficiency compare to the others (raw water and water after filtration) according to

the significantly high R_{ct} values in surface waters from group I to group VI. For group VII, 100 % removal efficiency is achieved in raw water and water after filtration, whereas some pharmaceutical compounds were not degraded completely by the low residential ozone concentration. Elimination of pharmaceutical compounds is enhanced as injection of ozone dose increases (Figure 13). Specifically, 5-15% and 15-20% of improvement was observed in groups I and III, and groups II and IV respectively. On the other hand, efficiency enhancements are got clearer in groups V and VI by rising injected ozone concentration. Prediction modeling was conducted as a function of ozone dose (0.5 ppm – 2ppm), it is then possible to evaluate the effect of ozone dose on decomposition of each compounds (Figure 14). The modeling result clearly shows that eliminations of group I – VI constantly increases as the ozone dose increases until 1.5 ppm, whereas there are no remarkable differences when the 1.5 ppm of ozone dose changes to 2 ppm. Compounds that have a high rate constant ($5\times10^9 < k_{OH}$) for groups II, IV, and VI show more or less similar results meaning their removal efficiency mostly depends on OH radicals. However, an ozone dose of 0.5 ppm was sufficient to achieve elimination of >99% for group VII.

Table 5. Second-order rate constants for the reaction of ozone with the investigated pharmaceuticals

Compound	pKa	k_{O3} ($M^{-1}s^{-1}$)	$k_{\cdot OH}$ ($M^{-1}s^{-1}$)
Deethylatrazine (DEA)	1.4	0.2 (R.Broseus et al., 2009)	2×10^9 (R.Broseus et al., 2009)
Diazepam	-	0.75 (Hubber et al., 2003)	7.2×10^9 (Hubber et al., 2003)
Iopromide	-	< 0.8 (Hubber et al., 2003)	3.3×10^9 (Hubber et al., 2003)
Atrazine	-	6-7.9 (R.Broseus et al., 2009)	$2.4\text{-}3.0\times10^9$ (R.Broseus et al., 2009)
Deisopropylatrazine (DIA)	1.5	7.5 (R.Broseus et al., 2009)	2.1×10^9 (R.Broseus et al., 2009)
Clofibric acid	-	<20 (Huber et al.,2005)	4.7×10^9 (Huber et al.,2005)
Cyanazine	1.1	7.34-61.8 (R.Broseus et al., 2009)	1.9×10^9 (R.Broseus et al., 2009)
Atenolol	-	110 (Benner et al., 2008)	7.05×10^9 (Song et al., 2008)
Caffeine	10.4	650 (R.Broseus et al., 2009)	$5.9\text{-}6.9\times10^9$ (R.Broseus et al., 2009)
Propanolol	-	1×10^5 (Benner et al., 2008)	1×1010 (Benner etal., 2008)
Naproxen	4.15	$\sim2\times10^5$ (Huber et al.,2005)	9.6×10^9 (Huber et al.,2005)
Trimethoprim	7.12	2.7×10^5 (R.Broseus et al., 2009)	6.9×10^9 (R.Broseus et al., 2009)
17β-Estradiol	-	10^6 (R.Broseus et al., 2009)	1.41×1010 (R.Broseus et al., 2009)
Sulfamethoxazole	5.7	$\sim2.5\times10^6$ (Hubber et al., 2003)	5.5×10^9 (Hubber et al., 2003)
17α-ethinylestradiol	10.4	$\sim7\times10^9$ (Hubber et al., 2003)	9.8×10^9 (Hubber et al., 2003)

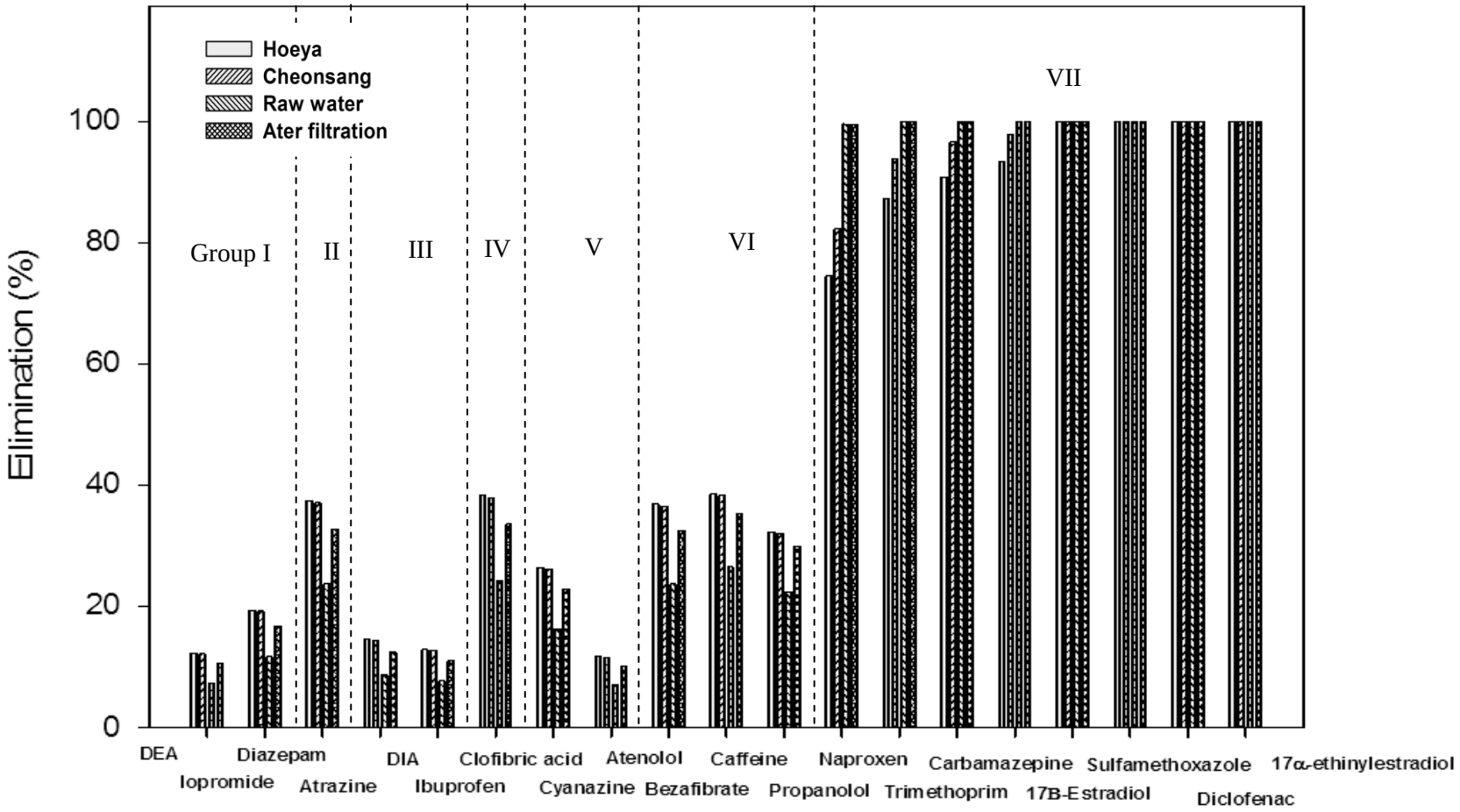


Figure 12. Predicted oxidation of grouped pharmaceuticals in 0.5 ppm of ozone dose

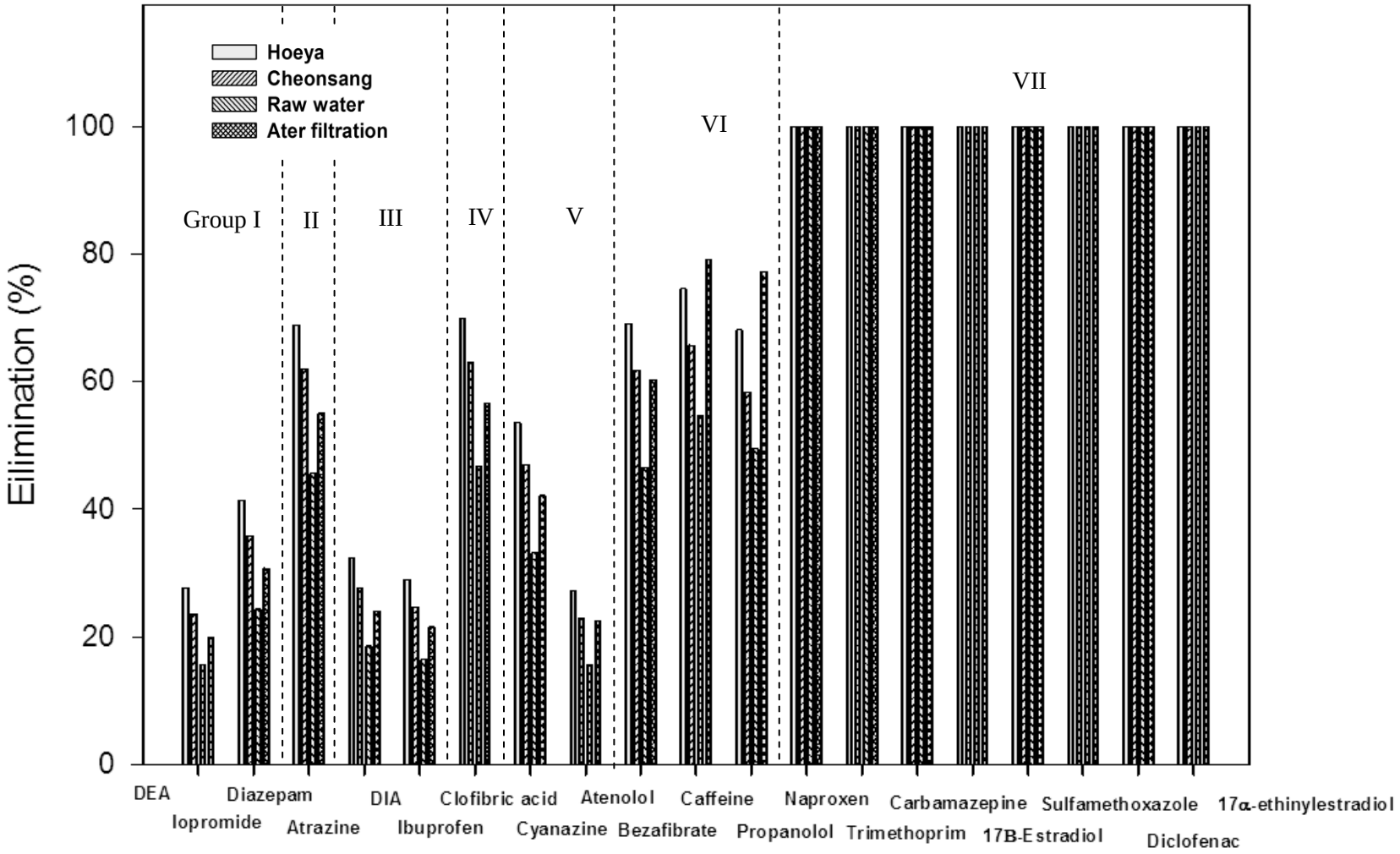


Figure 13. Predicted oxidation of grouped pharmaceuticals in 1 ppm of ozone dose

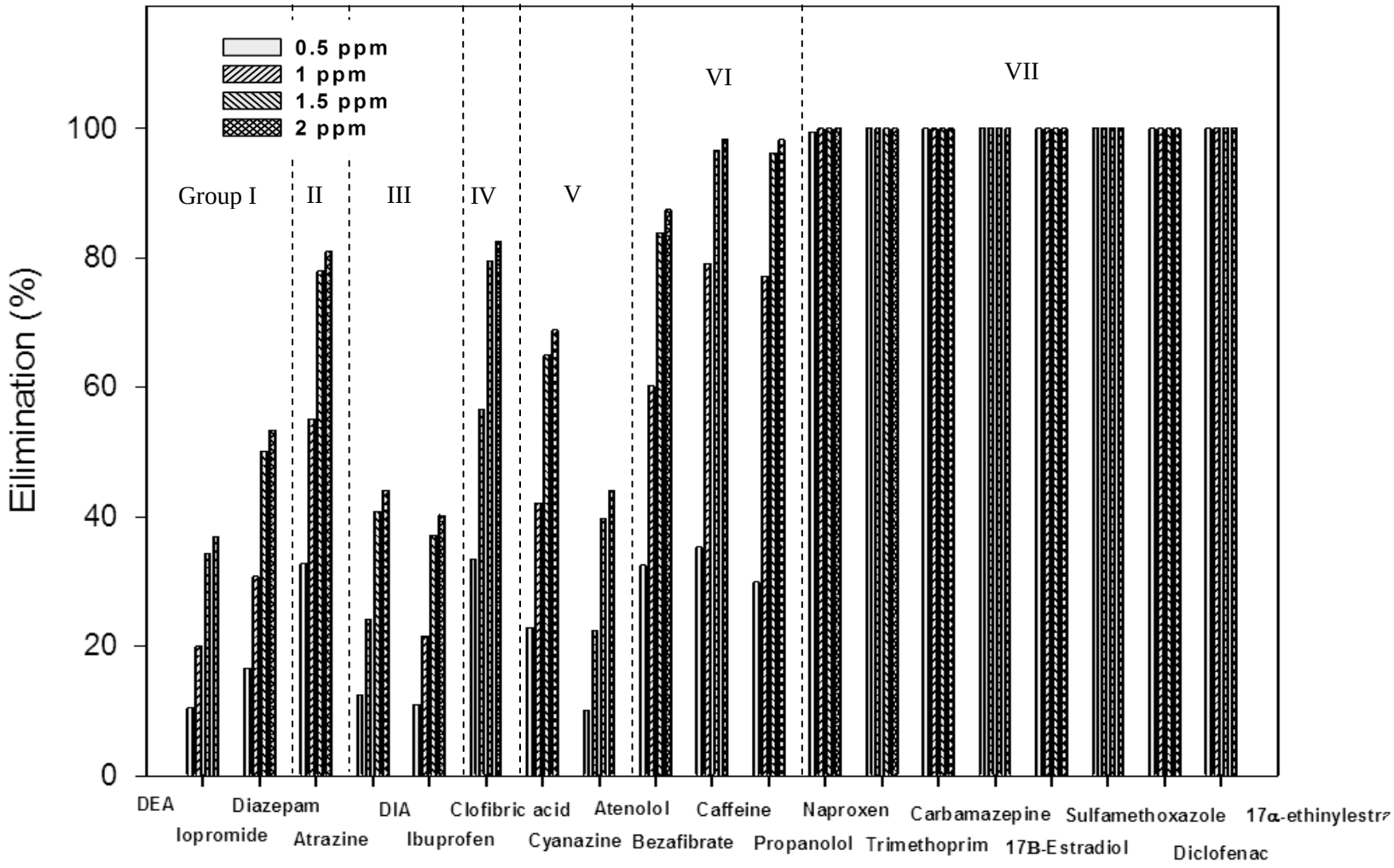


Figure 14. Predicted oxidation of grouped pharmaceuticals as a fuction of ozone dose

II. Oxidation of carbamazepine and diclofenac by copper-catalyzed Fenton and photo-Fenton systems

2.1. Effect of Cu(II) concentration and the solution pH on oxidation of pharmaceuticals

The effect of Cu(II) concentration was investigated on pharmaceutical degradation at pH 3 and pH 7. As shown in Figure 15, (a), the concentration of carbamazepine was gradually decreased by the Cu(II)/H_2O_2 system over 240 min at both pH 3 and pH 7. Removal of carbamazepine at pH 7 was slightly faster than at pH 3. The carbamazepine decomposition rate obeyed pseudo-first-order kinetics and the observed rate constant of carbamazepine, $k_{obs,\ Carbamazepine}$ (s^{-1}), can be readily determined by Eq. (3.8). As was the case with carbamazepine, the oxidation of diclofenac was also successfully expressed as pseudo-first-order kinetics.

$$-\frac{d\ln[\text{Carbamazepine}]}{dt} = k_{obs,\text{Carbamazepine}} \qquad (3.8)$$

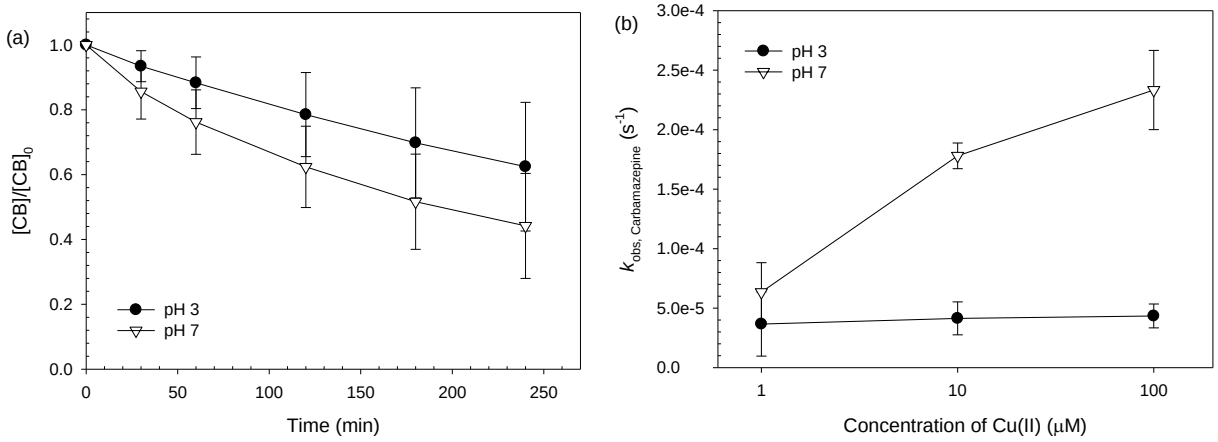


Figure 15. Removal of carbamazepine by Cu(II)/H_2O_2 system as a function of Cu(II) concentration at acidic pH and neutral pH

([Cu(II)]$_0$ = 1 μM for (a); [Cu(II)]$_0$ = 1, 10, 100 μM for (b); [CA(carbamazepine)]$_0$ = 1 μM; [H_2O_2]$_0$ = 10 mM; [phosphate buffer] = 1 mM at pH 7; reaction time = 4 hr)

Figure 15, (b) describes the effect of initial Cu(II) concentration on the carbamazepine decomposition rate over the range of Cu(II) concentration of 1-100 μM. The linear increase of $k_{obs,\ Carbamazepine}$ is observed

with respect to the increase of Cu(II) concentration at pH 7, whereas $k_{obs,\ Carbamazepine}$ at pH 3 remains fairly constant regardless of Cu(II) concentration. Likewise, the oxidation of diclofenac shows similar trends of concentration-dependency with carbamazepine (Figure 16). The enhancement of removal rate by the increase of copper concentration is more rapid from 1 μM to 10 μM than from 10 μM to 100 μM.

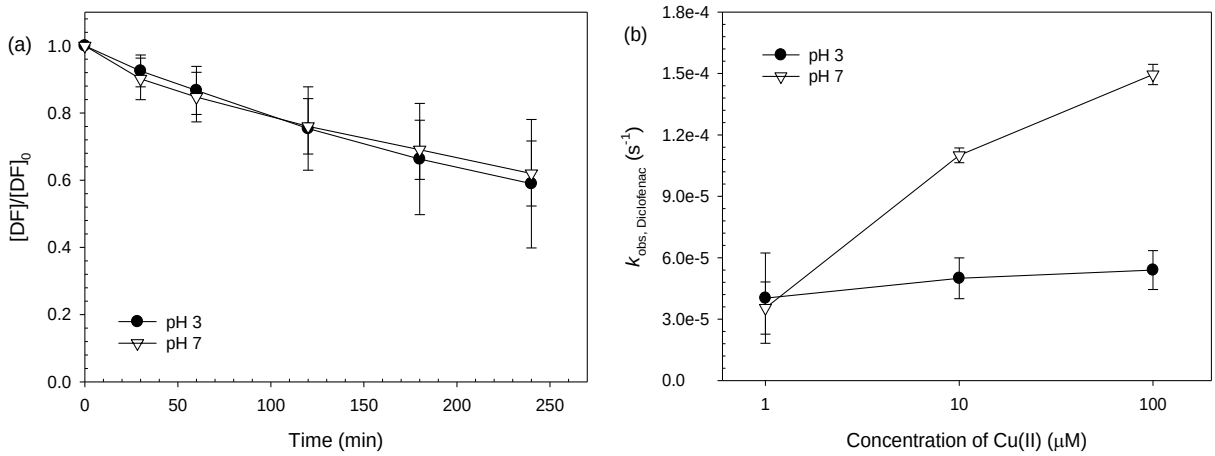


Figure 16. Removal of diclofecnac by Cu(II)/H_2O_2 system as a function of Cu(II) concentration at acidic pH and neutral pH

([Cu(II)]$_0$ = 1 μM for (a); [Cu(II)]$_0$ = 1, 10, 100 μM for (b); [DF(diclofenac)]$_0$ = 1 μM; [H_2O_2]$_0$ = 10 mM; [phosphate buffer] = 1 mM at pH 7; reaction time = 4 hr)

In the Cu(II)/H_2O_2 system, effects of the solution pH on oxidation of carbamazepine and diclofenac were monitored from pH 3 to 10 (Figure 17). The removal rate was optimized at around pH 8 for both carbamazepine and diclofenac, exhibiting substantial decrease in acidic and alkaline conditions except at pH 3 where somewhat affect enhancement. In the whole range of pH, the rate constant of carbamazepine keeps a higher position than diclofenac; in addition, it even reaches a rate approximately double that of diclofenac at the points where the maximum k_{obs} show. It has been shown that the maximum decomposition rate of both target compounds occurs around pH 8 in the Cu(II)/ H_2O_2 system due to increasing reduction rates of Cu(II) by H_2O_2 as pH increases from 3 to 8. However, the decrease of the removal rate above pH 8 suggests that less $^{\bullet}OH$ is produced. Here we propose the mechanism change to be the formation of an alternate oxidant at elevated pH values, such as Cupryl [Cu(III)] ion. Further experiments have provided to gather evidence about the increasing and deceasing decomposition rates as a function of pH except pH 3.

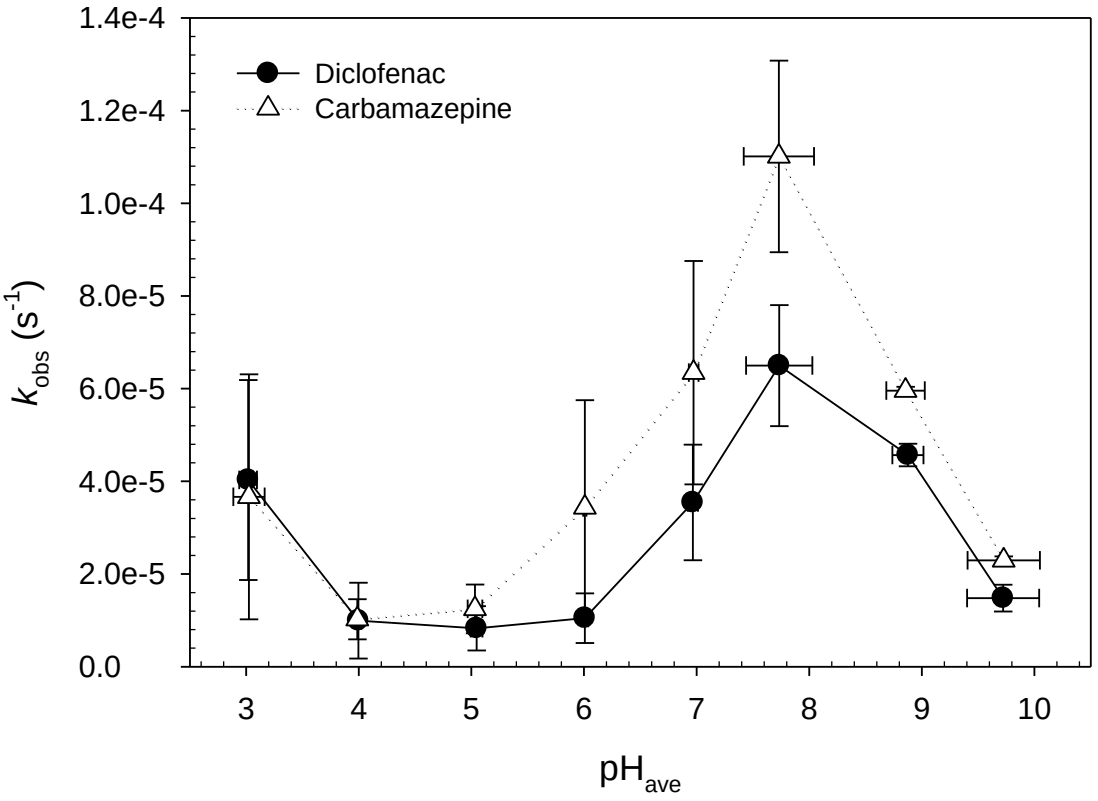
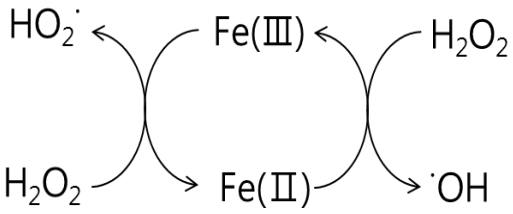


Figure 17. Removal of diclofenac and carbamazepine by Cu(II)/H_2O_2 system as a function of pH ([carbamazepine]$_0$ = [diclofenac]$_0$ = 1 μM; [Cu(II)]$_0$ = 1 μM; [H_2O_2]$_0$ = 10 mM; [phosphate buffer] = 1 mM at pH 6-7; [borate buffer]$_0$ = 1 mM at pH 8-10; reaction time = 4 hr)

2.2. Cu(I) production by reactions at Cu(II)/H_2O_2

The pH dependency of Cu(I) production by the Cu(II)/ H_2O_2 system can be explained by comparison with the Fe(III)/ H_2O_2 system based on the similarity of iron and copper ions. As described in the scheme 1 and 2, Cu(I) and Fe(II) oxidize to Cu(II) and Fe(III) to produce the most powerful oxidant $^{\bullet}OH$ by reaction with H_2O_2. Conversely, reduction of Cu(II) and Fe(III) occurs by reaction with H_2O_2 and follows the formation of $HO_2^{\bullet}$. It is noteworthy that the former oxidation reaction is significantly faster than the latter reduction reaction, thus the latter reaction becomes the rate determination step for both iron and copper (Table 6).

Scheme 1. Haber-Weiss Mechanism



Scheme 2. Mechanism of copper/H_2O_2

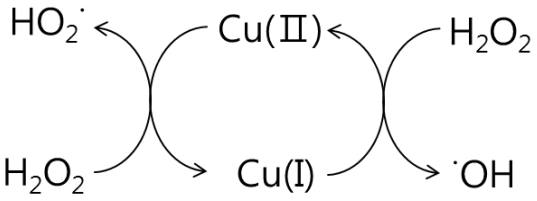


Table 6. Mechanism of H_2O_2 decomposition with iron and copper catalyst

Haber-Weiss mechanism	**k ($M^{-1}s^{-1}$)**	**reference**
$Fe(II) + H_2O_2 \rightarrow Fe(III) + {}^{\bullet}OH + OH^-$	6.3×10	De Laat and Gallard, 1999
$Fe(III) + H_2O_2 \rightarrow Fe(II) + HO_2^{\bullet} + H^+$	1.0×10^{-2}	Walling and Goosen, 1973
Mechanism of copper/H_2O_2	**k ($M^{-1}s^{-1}$)**	**reference**
$Cu(I) + H_2O_2 \rightarrow Cu(II) + {}^{\bullet}OH + OH^-$	1.0×10^{4}	Sharma and Millero, 1988
$Cu(II) + H_2O_2 \rightarrow Cu(I) + HO_2^{\bullet} + H^+$	$2.2\text{-}2.8 \times 10^{-5}$	Perez-Benito, 2004

The work of Gallard et al.(1999) has demonstrated that the reduction reaction of Fe(III) by H_2O_2 is enhanced with pH increase in the pH range 1-3 by the formation of a Fe-(III)-hydroperoxy complex formulated as $Fe^{III}(HO_2)^{2+}$. In the presence of an excess amount of H_2O_2, complexation in which the reaction of H_2O_2 with Fe^{3+} leads to the formation of a Fe-(III)-hydroperoxy complex formulated as $Fe^{III}(HO_2)^{2+}$ occurs, and $Fe^{III}(HO_2)^{2+}$ is produced more as pH increases according to the equilibrium constant with protonated and deprotonated H_2O_2 in a range of pH < 3 (ferric ion in homogeneous aqueous solution) (Table 7). No previous studies provide evidence for a copper complexation reaction in the presence of an excess amount of H_2O_2. However, this mechanism is more likely plausible relying on the

fact that it will go through a similar reaction as iron, although clear experiment data has not yet been provided for supporting such complex mechanisms. The decomposition rate of H_2O_2 and the production rate of Cu(I) measured in this study provide evidence of the complexiation reaction of Cu(II) by H_2O_2.

Table 7. Equilibrium constants of Fe^{III}-hydroxy complexes (Gallard et al., 1999)

Complexation reactions of Fe^{III} by H_2O_2	
$(Fe^{III})^{3+} + H_2O_2$ $(Fe^{III})^{3+} + HO_2^-$ $\leftrightarrow [Fe^{III}(HO_2)]^{2+} \leftrightarrow Fe^{2+} + HO_2^{\cdot}$	
Equilibrium constant of reaction * **H_2O_2 (pKa = 11.75)**	**K**
$(Fe^{III})^{3+} + H_2O_2 \leftrightarrow [Fe^{III}(HO_2)]^{2+}$	$3.1(\pm 0.4)\times 10^{-3}$
$(Fe^{III})^{3+} + HO_2^- \leftrightarrow [Fe^{III}(HO_2)]^{2+}$	1.74×10^{9}

Several important remarks on the Cu(II) reduction by pH dependence can be made on the basis of the results in Figure 18 and Figure 19. As motioned above, it is apparent that pH increase has affected the reaction of Cu(II)/ H_2O_2. Therefore, the experiment was conducted to measure the decomposition rate constant of H_2O_2 by Cu(II) from pH 3 to 10. The range of pH from 3 to 7 was found to approximately double the rate constant despite the fact that it shows only observable enhancement compared to the increase at pH 8-10. On the other hand, the H_2O_2 decomposition rate is noticeably increased from pH 8 to 10, and particularly the rate constant at pH 10 was observed to be 2-fold higher than the one at pH 3. This pH effect results on the Cu(II) catalyzed decomposition of hydrogen peroxide shows agreement with the work of Perez-Benito (2001), showing that a pH increase from 6.2 to 7.1 resulted in a 7 times increase of the hydrogen peroxide initial decomposition rate under the given experimental condition. H_2O_2 decomposition by copper gets clearer from pH 7 because the reaction is going to be faster with the increase of deprotonated H_2O_2 until pKa of H_2O_2 which is 11.75 (Table 7) like the complexation reaction with iron.

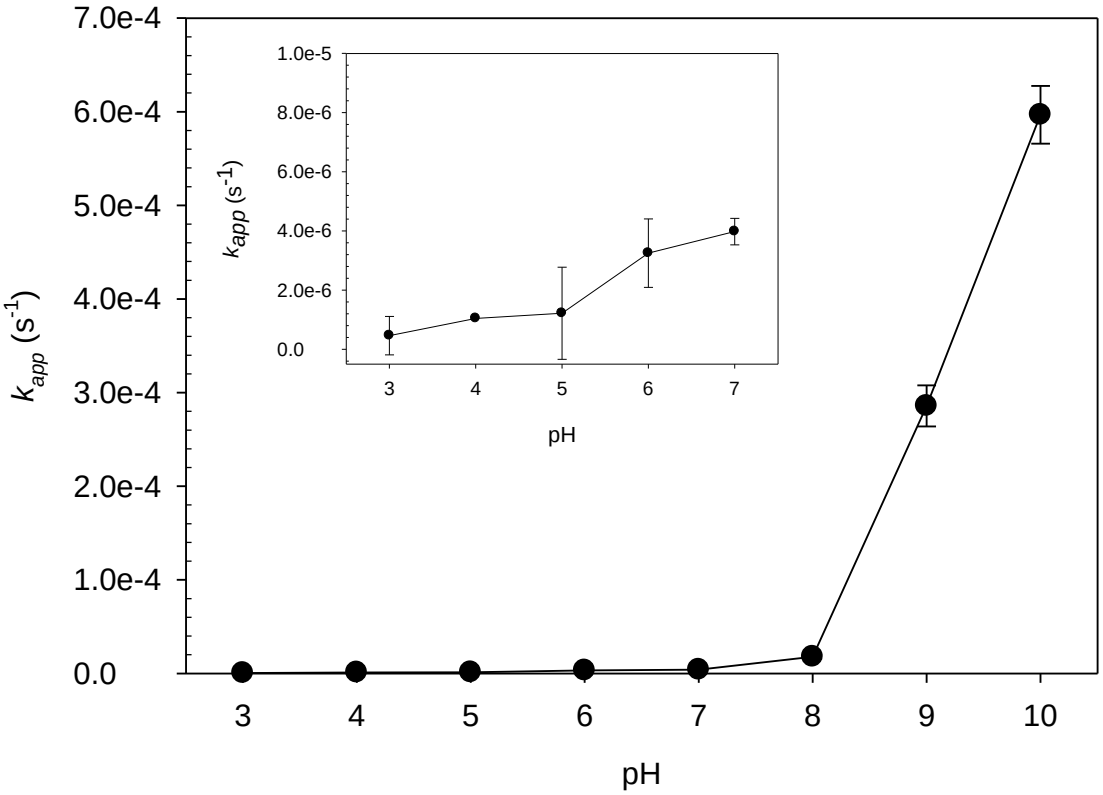


Figure 18. Decomposition rate of H_2O_2 by Cu(II)/H_2O_2 system as a function of pH

($[Cu(II)]_0$ = 10 μM; $[H_2O_2]_0$ = 1 mM; [phosphate buffer] = 1 mM at pH 6-7; $[\text{borate buffer}]_0$ = 1 mM at pH 8-10; reaction time = 2hr)

The Cu(I) conversion rate (Figure 19) reveals a good consistency with the result of the decomposition rate of H_2O_2 in improvement of reaction rate over the pH range; the Cu(I) production rate, which is the determination step in a cycle of the Fenton-like reaction by the Cu(II)/H_2O_2 system is continuously increased when the pH increases as shown in Figure 17. The production rate of Cu(I) by the reduction of Cu(II) with H_2O_2 gradually increased over the whole pH 5-11 range, although the reaction was too slow to measure at low pH (3-4). The kinetic data of the Cu(I) production rate along with catalytic decomposition of H_2O_2 by Cu(II) as a function of pH indicate that this reaction follows a rather complex mechanism. It appears that the nonprotonated form of H_2O_2, which is the predominant species present over the range of pH of 2-11 in aqueous solution, is responsible for the reduction of Cu(II). Perez-Benito (2004) and Berdnikov (1973) also suggested the possibility of a complex mechanism for copper ions with H_2O_2.

Controversy, the other literature reported that $Cu(OH)_2$ is the reactive species to reduction (Millero et al., 1992).

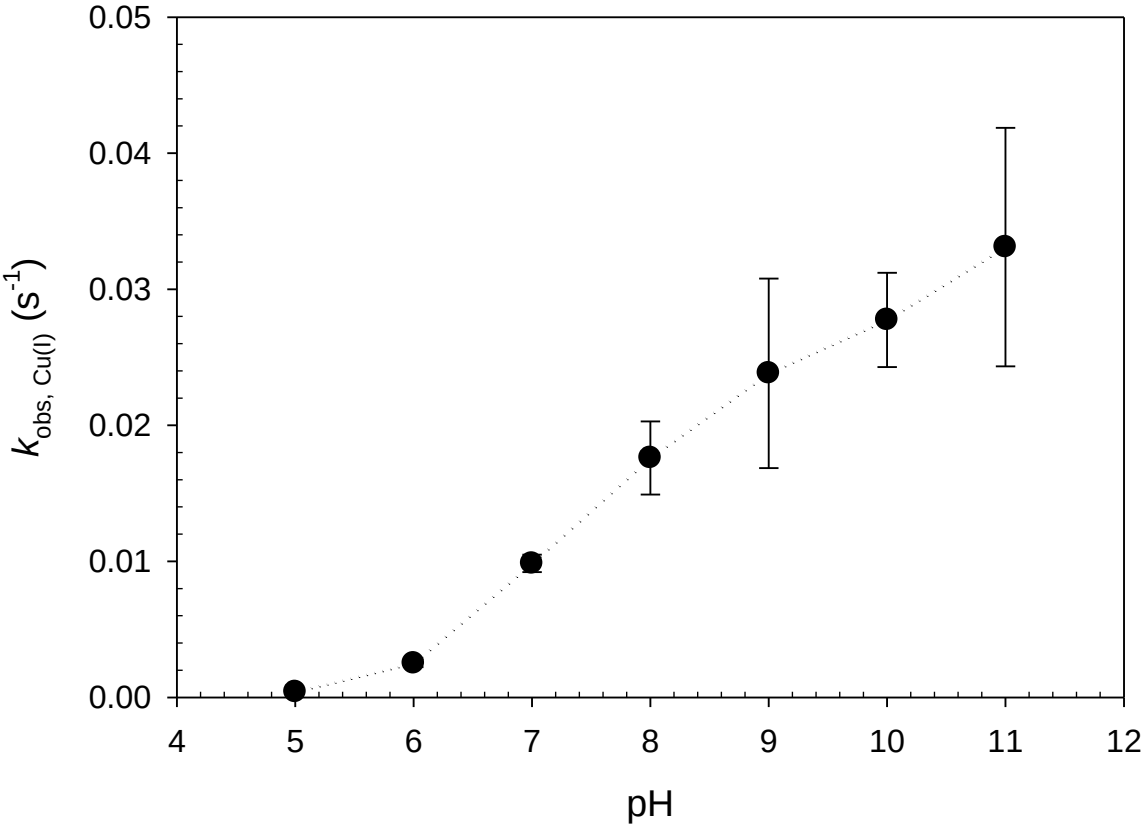


Figure 19. Cu(I) conversion rate by Cu(II)/H_2O_2 as a function of pH

($-\ln(1-[Cu(I)]/[Cu(II)]_0) = kt$; $[Cu(II)]_0$ = 10 μM; $[H_2O_2]_0$ = 1 mM; [phosphate buffer] = 1 mM at pH 6-7; $[\text{borate buffer}]_0$ = 1 mM at pH 8-10; $[DMP]_0$ = 0.5 mM)

2.3. Identity of oxidants by the Cu(II)/H_2O_2 system as a function of pH

The study conducted to elucidate oxidants that are produced by the Cu(II)/H_2O_2 system as a function of pH by employing the well known OH radical scavenger *tert*-BuOH. As shown in Figure 20, the pharmaceutical removal reaction totally stops in the presence of *tert*-BuOH throughout all the pH range. This result indicates that the OH radical is the only oxidant responsible for degradation of selected pharmaceuticals and suggests the formation of a different oxidant, most likely the cupryl ion (Cu[III]) as pH increases. We supposed that the mixture of OH radical and Cu(III) is produced by the Cu(II)/H_2O_2 system, and a larger amount of Cu(III) is produced rather than OH radical with increase of pH. This assumption is supported by demonstrating the formation of Cu(III) for a decrease of removal rate in pharmaceuticals at alkaline pH. The formation of alternative oxidants, such as Cu(III) appears in comparison of experimental results between selected pharmaceuticals and RB5 (Figure 20). In addition to *tert*-BuOH, the oxidation reaction of RB5 is maintained though it exhibits a minor inhibition over the pH range as shown in Figure 20. RB5 can decompose easily by relatively weak oxidants contrary to selected pharmaceuticals in which are only oxidized by OH radical. Decolorization of RB5 in the presence of an $^{\bullet}OH$ scavenger is constantly achieved, including alkaline pH in where pharmaceuticals removal starts to decrease, and it would be expected by the generation of Cu(III) which is a weak oxidant. Similarly, the Fenton reaction (i.e., Fe(II)/ H_2O_2) rapidly converts H_2O_2 into a stoichiometric amount of hydroxyl radical ($^{\bullet}OH$) under acidic conditions (Table 1). However, at circumneutral pH there are several reports that demonstrate evidence of Fe(IV) generation, which is a weaker oxidant than $^{\bullet}OH$. Fe(IV) is able to decompose a selection of compounds, bulky things such as RB5. Likewise, at acidic pH the Cu(II)/ H_2O_2 system produces strong oxidant hydroxyl radical ($^{\bullet}OH$). However, as pH increases up to the alkaline region, the major oxidants produced by the Cu(II)/ H_2O_2 system is likely shifted from hydroxyl radical ($^{\bullet}OH$) to Cu(III). By the means of generation of different oxidants in alkaline pH, it also reveals a possible usage of selectivity for a target compound. The possible mechanisms of Cu(III) formation have been reported in previous studies (Johnson et al., 1988; Meyerstein, 1971) similar to the appearance of Fe(IV) by the Fe(III)/ H_2O_2 system at neutral pH. Compared to the active researches about Fe(IV) (Lee et al. 2008a, b; Pang et al., 2011; Remucal et al., 2011), Cu(III) needs more research to assess the origin of oxidants in the Cu(II)/ H_2O_2 systems.

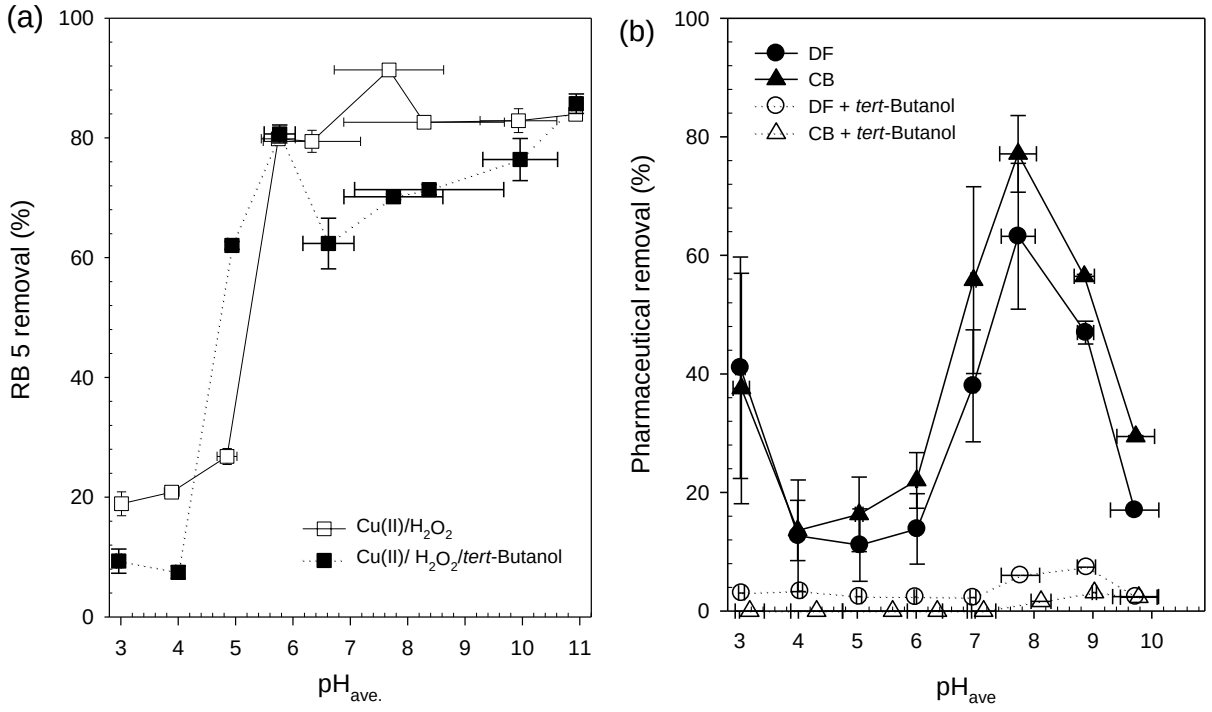


Figure 20. Removal of (a) RB 5 and (b) pharmaceuticals by Cu(II)/H_2O_2 in the presence and absence of *t*-BuOH

((a): $[RB\ 5]_0$ = 0.01 mM; $[Cu(II)]_0$ = 0.1 mM; [*tert*-BuOH] = 100 mM; $[H_2O_2]_0$ = 10 mM; reaction= 1 hr; (b): $[CA(carbamazepine)]_0$ = $[DF(diclofenac)]_0$ = 1 μM; $[Cu(II)]_0$ = 1 μM; [*tert*-Butanol] = 10 mM; reaction= 1 hr; $[H_2O_2]_0$ = 10 mM; [phosphate buffer] = 1 mM; [borate buffer] = 1 mM)

2.4. Enhanced degradation of pharmaceuticals in the presence of UV

The effect of ultraviolet (UVA) irradiation in the Cu(II)/H_2O_2 system was investigated in the degradation of diclofenac and carbamazepine during a period of 60 min. Several combination of the experiment with UV were conducted to assess enhancement of the Cu(II)/H_2O_2 system in the presence of UV (Figure 21). Only UV and UV/Cu(II) show a negligibly slower removal rate than the Cu(II)/H_2O_2 system, whereas UV/H_2O_2 reveals a considerably high rate constant. However, the greatest removal rate is shown under the coexistence of Cu(II) and H_2O_2 with UV for both diclofenac and carbamazepine. In addition, the degradation rate reveals a constant increase as Cu(II) concentration increases, and it drops with lower concentrations of H_2O_2 (Figure 22).

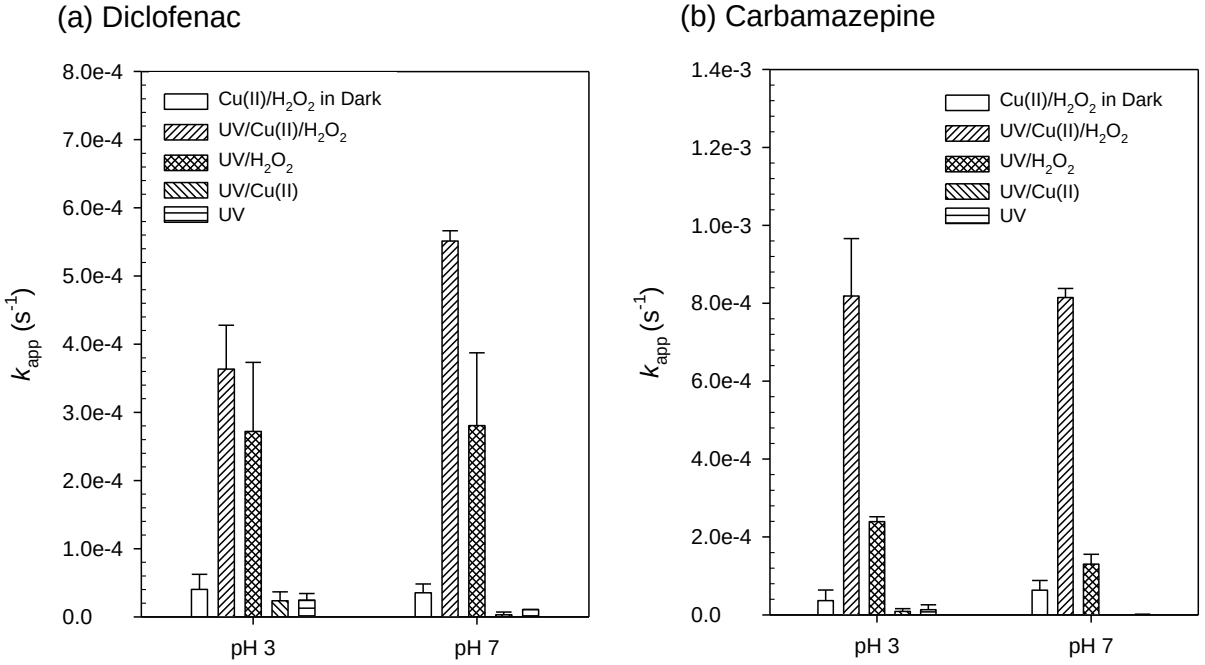


Figure 21. Removal of declofenac and carbamazepine by various combinations of Cu(II) ion, H_2O_2 and UV at acidic pH and neutral pH

([carbamazepine]$_0$ = [diclofenac]$_0$ = 1μM; [Cu(II)]$_0$ = 1μM; [H_2O_2]$_0$ = 10 mM; [phosphate buffer]$_0$ = 1 mM at pH 7; reaction time = 1 hr; 6 Lamp)

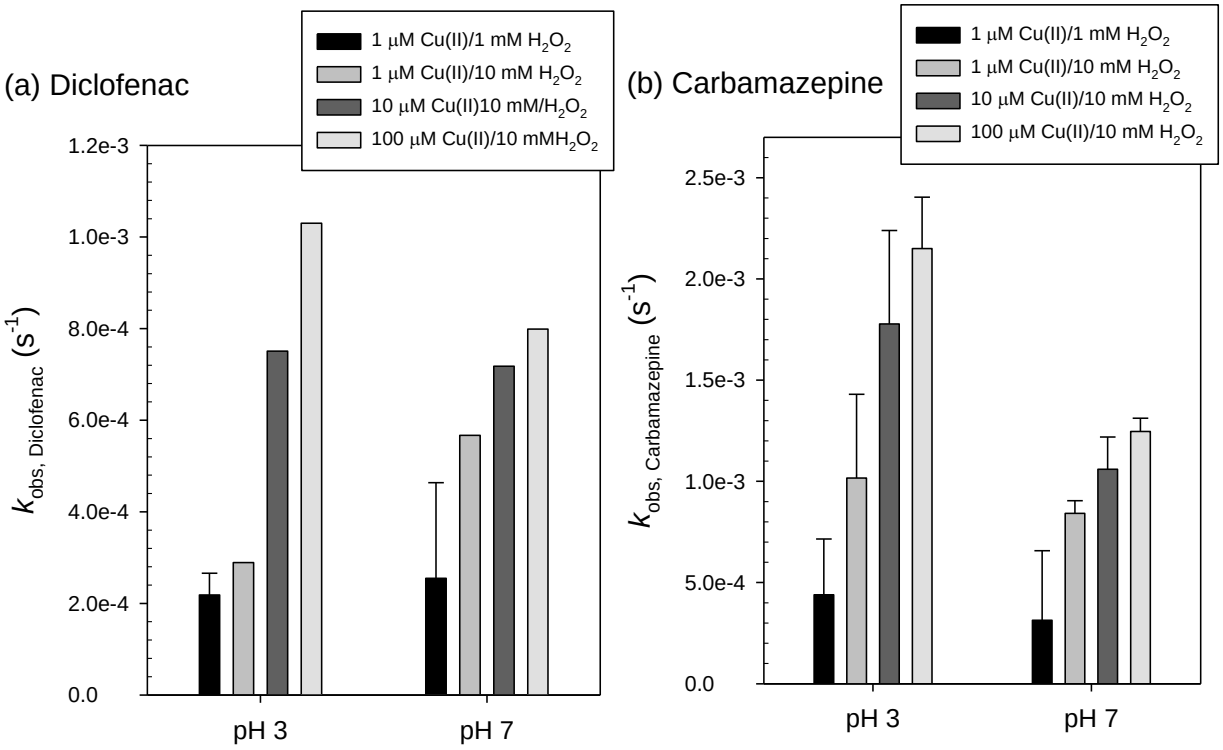


Figure 22. Removal of pharmaceuticals as Cu(II) doses in the Cu(II)/H_2O_2/UV system at acidic pH and neutral pH

([diclofenac]$_0$ = [carbamazepine]$_0$ = 1μM; [Cu(II)]$_0$ = 1, 10, 100 μM; [H_2O_2]$_0$ = 1,10 mM; [phosphate buffer]$_0$ = 1 mM at pH 7; Reaction time = 1 hr; 6 Lamp)

It was found that degradation of pharmaceuticals by the Cu(II)/H_2O_2 system was enhanced throughout the pH range in the presence of UV compared to the one in the absence of UV (Figure 23). The highest apparent rate constant of diclofenac and carbamazepine in the UV/Cu(II)/ H_2O_2 system was observed near neutral pH with approximately 3×10^{-4} (s^{-1}) at pH 7 and 6×10^{-4} (s^{-1}) at pH 6 (Figure 23), and it decreased in acidic and alkaline pH. Notably, an extreme decrease of the degradation rate under alkaline conditions is consistent with previous experiments with Cu(II)/H_2O_2 due to the formation of alternative oxidants. This similar trends in pH dependence regardless of UV suggests that the Cu(II)/H_2O_2 reaction predominantly produces different oxidants, likely Cu(III), in the alkaline pH range, although the removal rates were significantly higher relative to the one in the absence of UV.

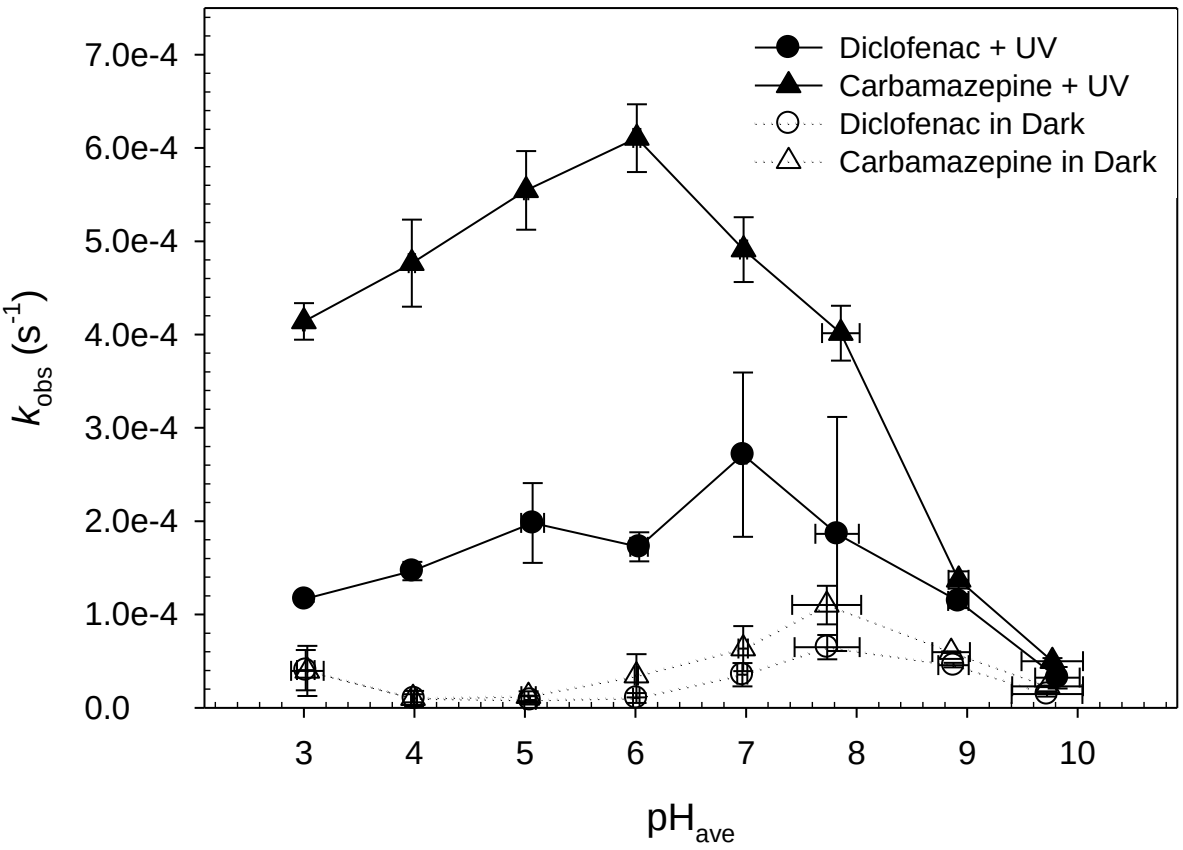


Figure 23. Removal of declofenac and carbamazepine by the Cu(II)/H_2O_2 system and UV/Cu(II)/H_2O_2 system as a function of pH

([carbamazepine]$_0$ = [diclofenac]$_0$ = 1 μM; [Cu(II)]$_0$ = 1 μM; [H_2O_2]$_0$ = 10 mM; [phosphate buffer] = 1 mM at pH 6-7; [borate buffer]$_0$ = 1 mM at pH 8-10; reaction time = 4 hr for The Cu(II)/H_2O_2 system; reaction time = 1 hr (2 Lamp) for The Cu(II)/H_2O_2/UV system)

2.5. Mechanism of oxidant production from the UV/Cu(II)/H_2O_2 system

Absorbance of Cu(II) and H_2O_2 was monitored to clarify the main product that absorbs the UV light (Figure 24). 10 mM H_2O_2 shows relatively higher absorbance than 1 μM Cu(II) at 365 nm where λmax appears from the lamp, thus H_2O_2 absorbed UV light accounts for the enhancement of the removal rate. We suppose H_2O_2 absorbs UV light to produce OH radicals, which can involve the cycle reaction by reduction of Cu(II) to Cu(I) with $HO_2^{\bullet}$ as shown in reaction (3.11), and the rate constant of the reduction reaction by $HO_2^{\bullet}$ is 12 orders of magnitude higher than the reaction by H_2O_2 (Table 6). This presumable assumption has also been supported in a previous study (Kozlov and Berdnikov, 1973), but no clear data was provided.

$$H_2O_2 + h\nu \rightarrow 2^{\bullet}OH \qquad (3.9)$$

$$H_2O_2 + {}^{\bullet}OH \rightarrow HO_2^{\bullet} + H_2O \qquad (3.10)$$

$k = 3.3 \times 10^7\ M^{-1}\ s^{-1}$ (Christensen et al., 1982)

$$Cu(II) + HO_2^{\bullet} \rightarrow Cu(I) + O_2 + H^+ \qquad (3.11)$$

$k = 5 \times 10^7\ M^{-1}\ s^{-1}$ (Bielski et al., 1985)

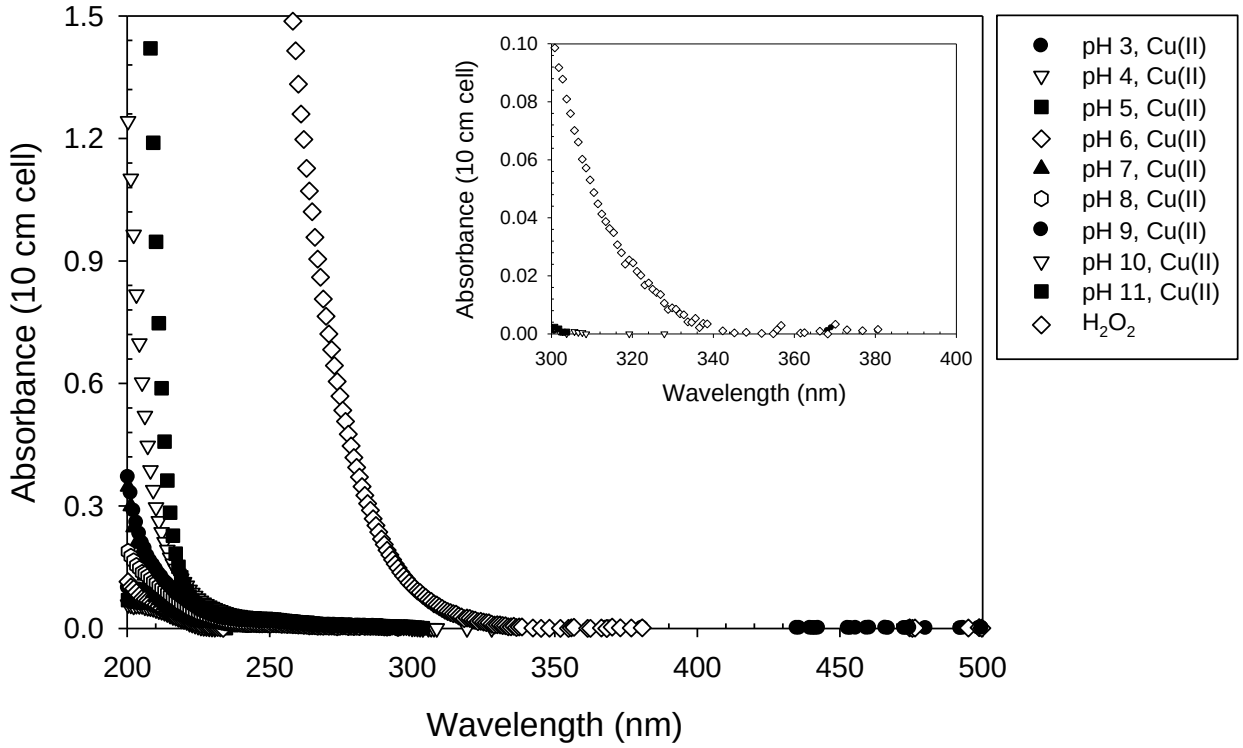


Figure 24. UV/vis absorption spectra of 1 µM Cu(II) at pH 3-11 and 10 mM H_2O_2

($[Cu(II)]_0$ = 1 µM; $[H_2O_2]_0$ = 10 mM; $[\text{phosphate buffer}]_0$ = 1 mM at pH 6-7; $[\text{borate buffer}]_0$ = 1 mM at pH 8-10)

The Cu(I) conversion kinetics of different combinations of Cu(II), H_2O_2, and UV were investigated at pH 3 and 5 (Figure 25). The kinetic data shows a big difference of Cu(I) conversion rate between the UV/Cu(II) system and the UV/Cu(II)/H_2O_2 system. In other words, H_2O_2 is involved in the reaction for generating Cu(I). This result verifies the reduction mechanism that we suggested above: the enhanced reduction of Cu(II) by $HO_2^{\cdot}$ produced from the H_2O_2 photolysis. As with the monitoring results of absorbance, mediator from H_2O_2 is likely involved in the reduction; the reduction reactions of Cu(II) by UV irradiation were much slower than UV/Cu(II)/H_2O_2 at pH 3 and pH 5, 15 times and 21 times respectively. This results are very different from the photo-Fenton reaction related to the irradiation of solutions with UV light to favor the regeneration of Fe^{2+} from additional photoreduction of $Fe(OH)^{2+}$ (Reaction 3.12) (Lee and Yoon, 2004).

$$Fe(OH)^{2+} + h\nu \rightarrow Fe^{2+} + {}^{\bullet}OH \quad (3.12)$$

Reduction reactions in each system accelerated with pH increase, from 3 to 5, despite the fact that the gap between pH 3 and pH 5 in the UV/Cu(II) system is smaller than the one in the UV/Cu(II)/H_2O_2.

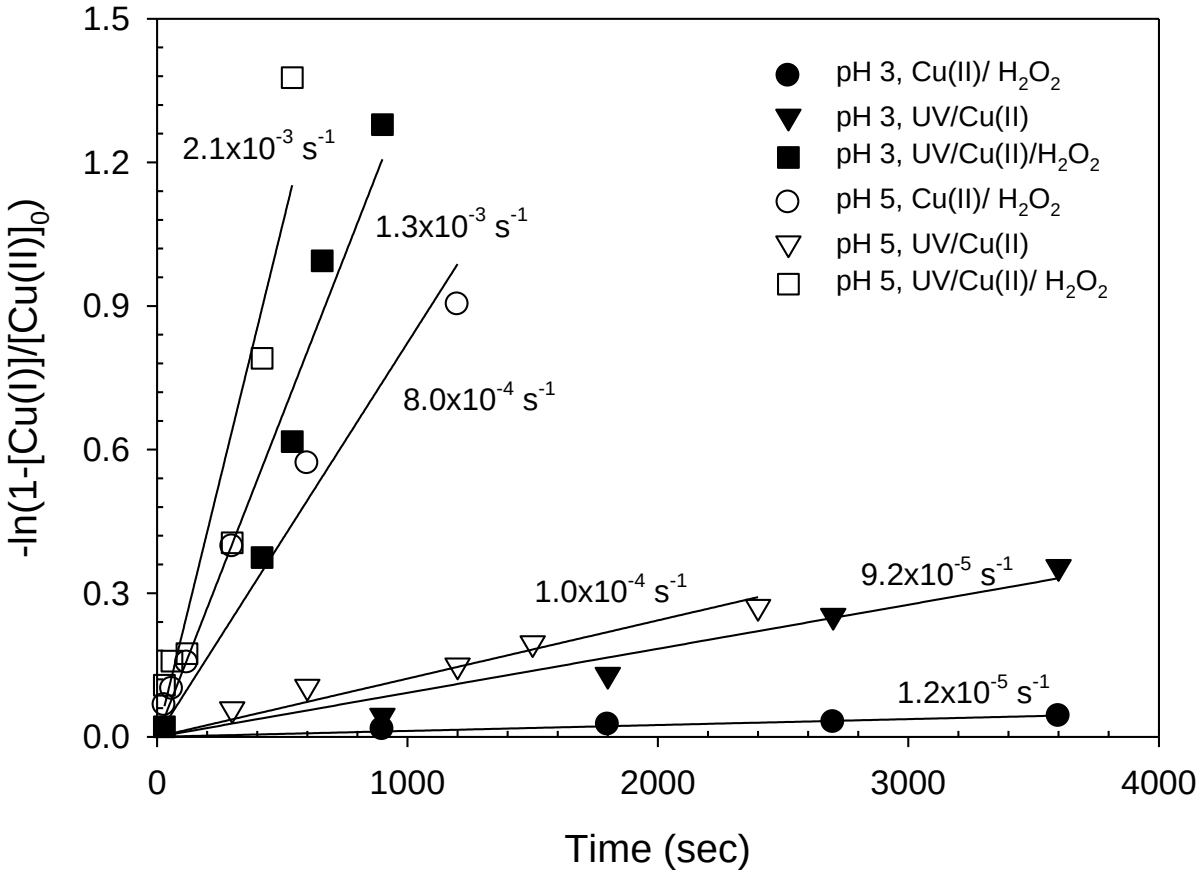


Figure 25. Cu(I) conversion rate from the Cu(II)/H_2O_2 and Cu(II)/H_2O_2/UV systems

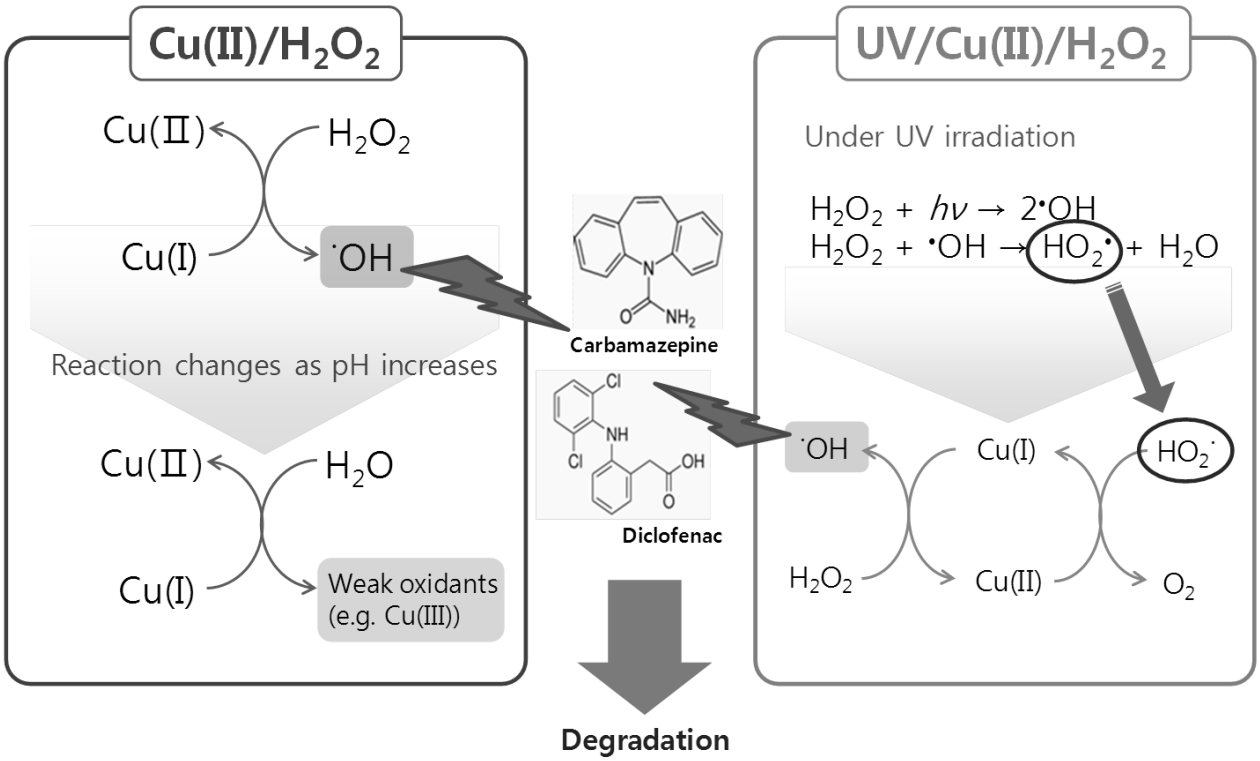
([Cu(II)]$_0$ = 10 μM; [H_2O_2]$_0$ = 10 mM; [DMP]$_0$ = 0.5 mM ; 6 Lamp)

Chapter 4. Conclusions

The first part of this study was concerning to a quantitative prediction base on the removal kinetics of pharmaceuticals and oxidants (ozone and hydroxyl radical) utilized in ozonation to discuss the characteristic behaviors of ozone decomposition and the oxidation of pharmaceuticals during ozonation of water samples in Ulsan. The conversion of O_3 into $^{\cdot}OH$ was more pronounced in the surface waters of Ulsan than other natural waters. That appears to be caused by as a relatively high R_{ct} value which is in the range 0.78 ~ 1.5×10^{-7} and a relatively high inhibitor effect of $^{\cdot}OH$ scavengers. It is expected that decomposition of organic contaminants which have less reactivity with molecular ozone is favored over the contaminants which rapidly react with ozone, owing to the fast conversion from ozone to hydroxyl radical. The efficacy of the ozonation process for the removal of pharmaceuticals was investigated in different water samples in Ulsan, and experiments demonstrated that the model calculation by the R_{ct} concept was feasible to predict the oxidation of pharmaceuticals. Modeling of the pharmaceuticals removal was evaluated in terms of rate constant with O_3 and OH radicals by grouping each compound. It is possible to predict removal efficiency of any pharmaceuticals as long as its rate constants is known since the results show that overall removal efficiency of the pharmaceuticals was fairly consistent in each group.

Secondly, the reactive oxidant produced by the Cu(II)/H_2O_2 system and the UV/Cu(II)/H_2O_2 system effectively oxidized pharmaceuticals. The observed rate constants for each system were monitored at various pH in given experimental conditions, and an additional experiment was conducted to demonstrate the working mechanisms we suggest. The pH dependence of the reactive oxidant in the Cu(II)/H_2O_2 system can be explain by two factors: production of reactive oxidants grows as pH increases due to raising of the Cu(II) reduction rate. In addition, formation of a weaker oxidant, likely Cu(III), at alkaline pH causes a decline of the removal rate for declofenac and carbamazepine. The UV/Cu(II)/H_2O_2 system shows much higher efficiency than the Cu(II)/H_2O_2 system, which is attributable to the enhanced reduction of Cu(II) by $HO_2^{\cdot}$ produced from the H_2O_2 photolysis. The principal results obtained in this study are illustrated in Scheme 3.

Scheme 3 Reaction pathways of oxidation of organic compounds in the Cu(II)/H_2O_2 system and UV/Cu(II)/H_2O_2 system



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감사의 글

먼저 무엇보다도 부족한 저를 지도해주신 이창하 교수님께 진심으로 감사 드립니다. 또한, 학위논문을 위해 여러 조언을 해주신 권영남 교수님과 이창수 교수님께 깊은 감사를 드립니다.

저와 2 년을 같이 연구실에서 고생해주고 도와준 우리 랩 멤버들, 실험적으로나 인생선배로나 항상 쓴 소리를 아끼지 않아주신 아이디어뱅크 홍신 선배, 동갑이지만 배울게 많은 우리랩 살림꾼 형은 선배, 키는 작지만 배포는 큰 COOL THUY (타칭자칭베프), 그리고 일찍 좋은 사람 만나 결혼해서 부러운 꼬마신랑 민식이, 마지막으로 우리랩 패셔니스타 막내 지원이, 모두 감사합니다. 그리고 중간 중간 실험을 도와줬던 학부실험보조 친구들, 희정이와 학현이 감사합니다.

저에게 항상 아낌없는 지원을 해 주시는 부모님과 이제는 듬직한 동생 진형이에게도 감사합니다. 아직 학생이라고 만날 때마다 밥와 커피을 사줬던 최고의 고등학교 친구들, 이주연, 이지, 장쥬 고맙다. 그리고 매번 서울출장 갈 때마다 연락해도 늘 반갑게 맞아주고 잠자리를 제공해준 베스트 안지 고맙다. 매번 맛집에 데려가 주고 나 만나러 울산까지 와주는 직장인 5 년차 베테랑 석진언니, 4 년간 맨날 붙어 다녀서 더 보고 싶은 노갱, 그리고 유지, 안나, 혬, 태송 모두 고맙습니다. 또한, 주일마다 만나서 담소를 나눠준 사촌동갑친구 지혜에게도 감사의 말을 전합니다.

학위기간 동안 힘들 때도 있고 좌절할 때도 있었지만 모두의 도움이 있었기에 이겨내고 해낼 수 있었습니다. 마지막으로 제가 가는 모든 길을 함께해 주시고 도와주시는 하나님께 감사 드립니다.