Efficacy of ultraviolet radiation and hydrogen peroxide oxidation to eliminate large number of pharmaceutical compounds in mixed solution

*R. R. Giri; H. Ozaki; Y. Takayanagi; S. Taniguchi; R. Takanami

Osaka Sangyo University, 3-1-1 Nakagaito, Daito City, 574-8530 Osaka, Japan

ABSTRACT: Ultraviolet photolysis and ultraviolet and hydrogen peroxide oxidation of fourteen commonly used pharmaceutical compounds and two personal care products in mixed solution using low pressure ultraviolet lamp was investigated in laboratory batch experiments. Removal of the compounds followed the first-order reaction kinetic. Three distinct impacts of hydrogen peroxide on ultraviolet and hydrogen peroxide oxidation of the compounds (positive, negative and no significant effect) were observed. Removal behavior of the several tested compounds in mixed solution varied significantly than their respective behavior in absence of coexisting compounds. Clofibric acid, diclofenac, fenoprofen, isopropylantipyrine, ketoprofen, phenytoin and triclosan were removed very efficiently (> 96 %) by ultraviolet photolysis alone. Residual hydrogen peroxide during ultraviolet and hydrogen peroxide oxidation was quantitated for the first time. Hydrogen peroxide addition to ultraviolet photolysis was not worthy for majority of the tested compounds as their removal did not increase significantly and very big fractions (> 85 %) of the added hydrogen peroxide (0.29 ~ 1.47 mM) remained unused presumably due to small fluence of the lamp, very small molar absorption for hydrogen peroxide at 254 nm (27.06 /M.cm) and acidic pH of reaction solution (< 5.7). Further exploration on ultraviolet and hydrogen peroxide oxidation with higher fluence lamp and alkaline solution pH will clarify usefulness of the method to treat pharmaceutical contaminated waters.

Keywords: *Hydroxyl radical; molar absorption; removal rate; residual hydrogen peroxide; ultraviolet photolysis*

INTRODUCTION

Ever increasing use of pharmaceutical compounds combined with inefficiency of conventional wastewater treatment methods to remove the compounds has resulted to their widespread detection in water environment. Oxidation of organic compounds in water using ultraviolet radiation and hydrogen peroxide (UV/H_2O_2) is widely investigated (Perkowski and Ledakowicz, 2002; Rauf *et al.*, 2005; Shu and Chang, *2006*; Abdullah *et al.*, 2007; Alshamsi *et al.*, 2007; Samarghandi *et al., 2007*), and the method is generally considered as a promising one (Lopez *et al.*, 2003; Vonga *et al.,* 2004; Pereira *et al.*, 2007a). Several literatures demonstrated degradations of commercial dyes by UV/H_2O_2 in aqueous solutions. Carmine degradation was enhanced at high pH in alkaline region, and presence of bromide, chloride, acetate, sulfate, silver and bicarbonate ions were found to have negative impact on safranin-O degradation by UV/H_2O_2 (Abdullah *et al.*, 2007). Enhanced efficiency of UV/H_2O_2 oxidation at alkaline pH region is attributed to hydroxyl radical formation (Qiao *et al.,* 2005; Giri *et al.,* 2010). Also, it is argued that decolorization of C. I. Acid Black 1 decreased with increasing solution pH due to decomposition of H_2O_2 into water and oxygen rather than hydroxyl radical formation (Shu and Chang, 2006; Igwe *et al.,* 2008; Shah *et al.,* 2009). A suitable H_2O_2 dosage showed enhanced performance of the process to degrade crystal violet (Alshami *et al.*, 2007). Vogna *et al.*, (2004) found UV/H_2O_2 to be an efficient process compared to ozonation to degrade diclofenac. Pseudo first-order degradation rates of some pharmaceutical compounds with UV/H_2O_2 increased significantly than those with UV photolysis alone (Kim *et al.,* 2008). Low pressure (LP) UV lamps with 254 nm wavelength emission were used in almost all the earlier investigations, while a couple of them (Pereira *et al.*, 2007b ; Canonica *et*

✉ *Corresponding Author Email: rabindra@cnt.osaka-sandai.ac.jp*
Tel.: +8172 875 3001

$al.$, 2008) argued that medium pressure (MP) lamps were more useful than LP lamps to effectively remove pharmaceutical compounds in water. Oxidation behaviors of an organic compound by UV and UV/H_2O_2 may not be the same as its oxidation behaviors in mixed solutions with several coexisting compounds due to wide variation in their physicochemical characteristics and some limiting conditions (available photon energy, other oxidizing species such as hydroxyl radical etc.). Large numbers of pharmaceutical compounds have been detected in sewage influents/effluents (Kasprzyk-Hordern *et al.*, 2009), and understanding their removal behaviors in mixed solutions can be very useful to estimate their fates in treatment facilities. But only few investigations (Kim *et al.,* 2008) on their degradation behaviors in mixed solutions have been published till to date. Degradation of organic compounds by UV and UV-based oxidation methods depends largely on UV absorption by the compounds. Therefore, matching between available UV wavelengths and wavelengths absorbed by the compounds is a fundamental technique to understanding their oxidation behaviors. Moreover, fate of H_2O_2 during oxidation of organic contaminants by UV/H_2O_2 can be a useful information to get better insight of their oxidation behaviors (Fagbote and Olanipekun, 2010; Aina *et al.,* 2009). However, almost no earlier investigations on UV/H_2O_2 process paid attention to fate of H_2O_2 in the system. Though Pereira *et al*., (2007a and b) mentioned about residual H_2O_2 measurement, no data is provided in the articles. This investigation aimed to elucidate removal characteristics of fourteen commonly used pharmaceuticals and two personal care products in mixed solutions in ultrapure water by UV/H_2O_2 method using a low pressure lamp in laboratory batch experiments. The investigated compounds and some of their physicochemical properties are illustrated in Table 1. TCC and TCS in the table belong to personal care products. No information on chemical interaction among the selected compounds is available till to date. Therefore, it is presumed that no chemical interaction among them takes place in their mixed solutions. As this is a fundamental investigation on usefulness of UV/H_2O_2 oxidation for removal of the compounds in mixed solution, no solution pH was adjusted in any of the experiments.

Several H_2O_2 doses were tested with the emphasis on removal of the compounds and fate of the added H_2O_2 during oxidation. This investigation was carried out in the laboratory of New Industrial R and D Center of Osaka Sangyo University, Japan between July 2009 and March 2010.

MATERIALS AND METHODS
Materials

IBP and TCC standards were purchased from Sigma-Aldrich Inc. and Tokyo Chemical Industry Co. Ltd., respectively. FEP, GFZ and CA standards were purchased from ICN Biomedicals Inc., LKT Lab Inc. and MP Biomedicals Inc., respectively. Standards of remaining compounds, aqueous H_2O_2 (30 % by weight) and Na_2SO_3 (for quenching residual H_2O_2 in samples) were purchased from Wako Pure Chemicals Ltd. Nanocolor Peroxide 2 test kit (Merck, Germany) was used to measure residual H_2O_2 in samples. A low power (10 W) low pressure tubular mercury lamp (UVL10D, 254 nm, Sen Light Corporation, Japan) emitting mainly 254 nm wavelength was the source of UV irradiation. Reactor design and details of the experimental setup are given elsewhere (Giri *et al.,* 2007). A recirculation cooler (CCA-111, Tokyo Rikakikai Co., Ltd.) was used for temperature control of reaction solution. A schematic diagram of the experimental setup is illustrated in Fig. 1.

Experimental

Stock solution of each compound (1.0 g/L) was prepared in ultrapure water and stored at 4 ^{o}C for future use. Mixed aqueous solutions (1.2 L) of the sixteen compounds (100 µg/L of each compound, i.e. $13.37×10^{-2}$ µM ~ 55.7910^{-2} µM) were prepared in ultrapure water using the stock solutions. Six initial H_2O_2 doses (0 ~ 1.47 mM) were selected in this investigation based on a series of preliminary test experiments. The reaction solution was continuously mixed ($\approx$ 300 rpm) using a magnetic bar and stirrer under controlled temperature (25±2 ^{o}C) in all the experiments. Solution pH was continuously monitored while the initial pH values in any of the experiments were not adjusted. Experiments were run for 30 min reaction time, samples were drawn at specified intervals for analysis. Residual H_2O_2 in samples were quenched using Na_2SO_3 solution (1.0 g/L). UV absorption

Table 1: Physicochemical characteristics of the investigated compounds

Name	Abbrev.	Mol. formula	MW	Type	Water solubility (mg/L)	pK_a	$logK_{ow}$
Clofibric acid	CA	$C_{10}H_{11}ClO_3$	214.65	Nonsteroidal/ anti-inflammatory	583.0	3.18	2.57
Clarithromycin	CAM	$C_{38}H_{69}NO_{13}$	747.95	Macrolide/ antibiotic	0.34	8.99	3.18
Carbamazepine	CBZ	$C_{15}H_{12}N_2O$	236.27	Analgesic/ anticonvulsant	17.7	2.30	2.45
Diclofenac	DCF	$C_{14}H_{10}Cl_2NNaO_2$	318.13	Nonsteroidal/ anti-inflammatory	2430.0	4.10	0.70
Fenoprofen	FEP	$C_{30}H_{26}O_6Ca$	522.60	Anti-inflammatory	-	7.30	3.90
Gemfibrozil	GFZ	$C_{15}H_{22}O_3$	250.33	Anti-cholesterol	10.9	4.75	4.77
Ibuprofen	IBP	$C_{13}H_{18}O_2$	206.28	Pain reliever	21.0	4.91	3.97
Indomethacin	IDM	$C_{18}H_{16}ClNO_4$	357.79	Nonsteroidal/ anti-inflammatory	0.94	4.50	4.27
Isopropylantipyrine	IPA	$C_{14}H_{18}N_2O$	230.31	Analgesic/ antipyretic	3.0×10^6	-	1.94
Ketoprofen	KEP	$C_{16}H_{14}O_3$	254.28	Nonsteroidal/ anti-inflammatory	51.0	4.45	3.12
Naproxen	NPX	$C_{14}H_{14}O_3$	230.26	Analgesic	15.9	4.15	3.18
Phenobarbital	PB	$C_{12}H_{12}N_2O_3$	232.24	Barbiturates	1110.0	7.30	1.47
Phenacetin	PNC	$C_{10}H_{10}O_2N$	179.22	-	766.0	-	1.58
Phenytoin	PNT	$C_{15}H_{12}N_2O_2$	252.27	Anti-convulsant	32.0	8.33	2.47
Triclocarban	TCC	$C_{13}H_9ON_2Cl_3$	315.58	Antimicrobial	0.024	-	4.90
Triclosan	TCS	$C_{12}H_7O_2Cl_3$	289.54	Antimicrobial	10.0	8.14	4.76

spectrum (200 ~ 800 nm) for each compound (1.0 mg/L) and H_2O_2 (9.79 mM) in ultrapure water were measured using U-3010 Spectrophotometer (Hitachi, Japan), and the corresponding molar absorption coefficient (ε) value at 254 nm were calculated based on Beer-Lambert equation:

$$\varepsilon = \frac{A}{cL} \qquad (1)$$

where, A: absorbance, c: concentration and L: path length.

Analyses

Remaining pharmaceuticals and personal care products in samples were analyzed using liquid chromatography tandem mass spectrometry (LCMS/MS, Applied Biosystems). A turbo ion spray interface was used as the ion source, and mass detection was carried out using multiple reactions monitoring (MRM) mode. Eleven compounds (CA, DCF, FEP, GFZ, IBP, IDM, NPX, PB, PNT, TCC and TCS) were scanned in negative ion mode while the remaining (CAM, CBZ, KEP, IPA and PNC) were scanned in positive ion mode. Nitrogen was used as collision and curtain gas. Air was used as nebulizer and dryer gas. Ion source voltages in negative and positive scan modes were -4500.0 and 5000.0 respectively, while dryer gas temperatures for the two cases were 400 and 500 ºC, respectively. The LC system consisted of a binary pump, an auto sampler and a degasser unit (Agilent 1100 series). Chromatographic separation was performed using ZORBAX Eclipse XDB-C18 column
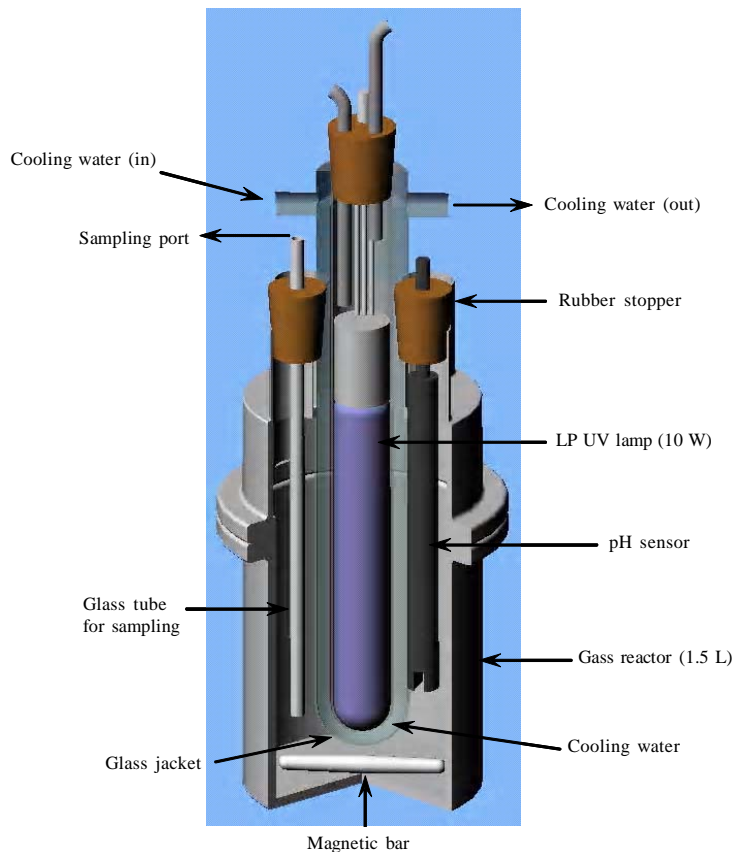
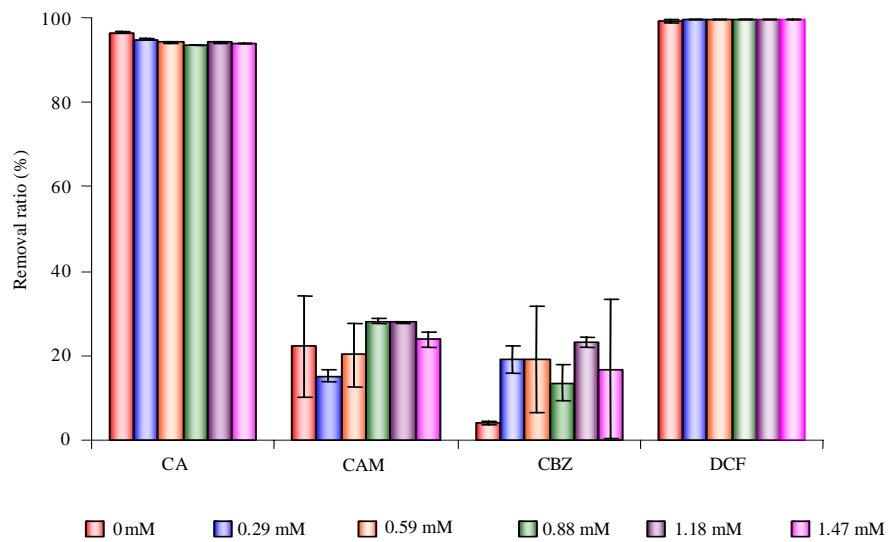Fig. 1: A schematic diagram showing reactor setup

Fig. 2: UV/H_2O_2 oxidation efficiencies for CA, CAM, CBZ and DCF (30 min reaction). The legend shows H_2O_2 concentrations
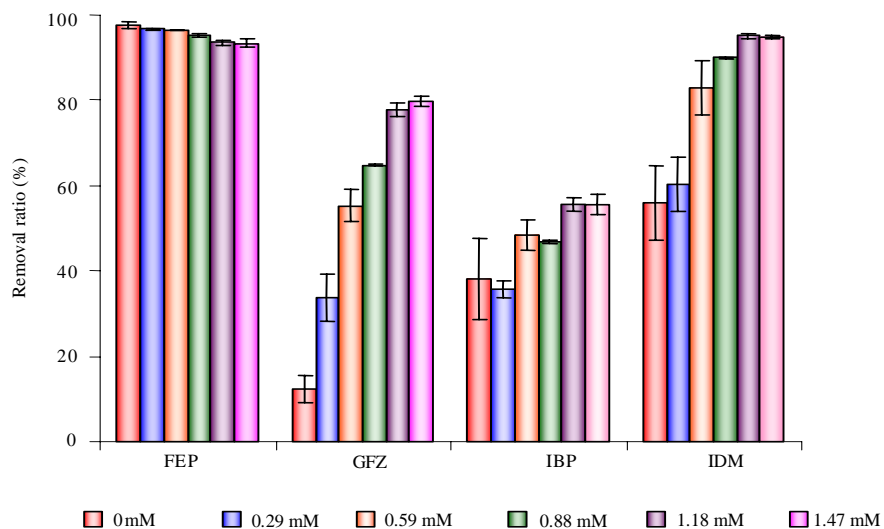
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Fig. 3: UV/H_2O_2 oxidation efficiencies for FEP, GFZ, IBP and IDM (30 min reaction). The legend shows H_2O_2 concentrations
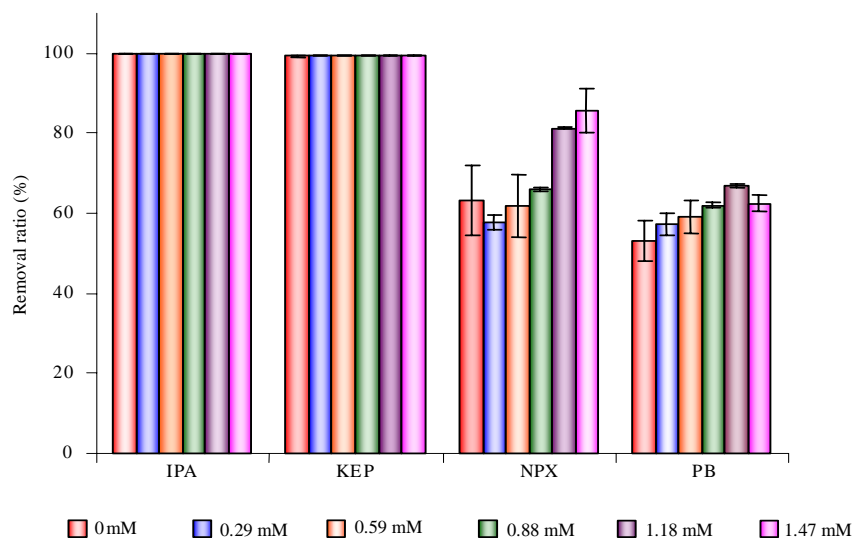

Fig. 4: UV/H_2O_2 oxidation efficiencies for IPA, KEP, NPX and PB (30 min reaction). The legend shows H_2O_2 concentrations

(2.1 × 150 mm, 3.5 μm) with 200 μL/min mobile phase flow rate, 10 μL sample injection volume and column temperature fixed at 40 °C. Mobile phases for negative scan mode were: 0.1 % (v/v) acetic acid in 2.0 mM ammonium acetate in ultrapure water (A) and acetonitrile (B), while 0.1 % (v/v) formic acid in ultrapure water and acetonitrile respectively were A

and B in case of positive scan mode. Flow rate for A was set to 90% from 0 to 2 min, which linearly decreased to 0 % at 7 min and the same continued until 15 min. Then the value increased again to 90 % at 15.1 min and continued the same until the end (i.e. 20 min). Residual hydrogen peroxide in samples was determined by photometric method using Nanocolor
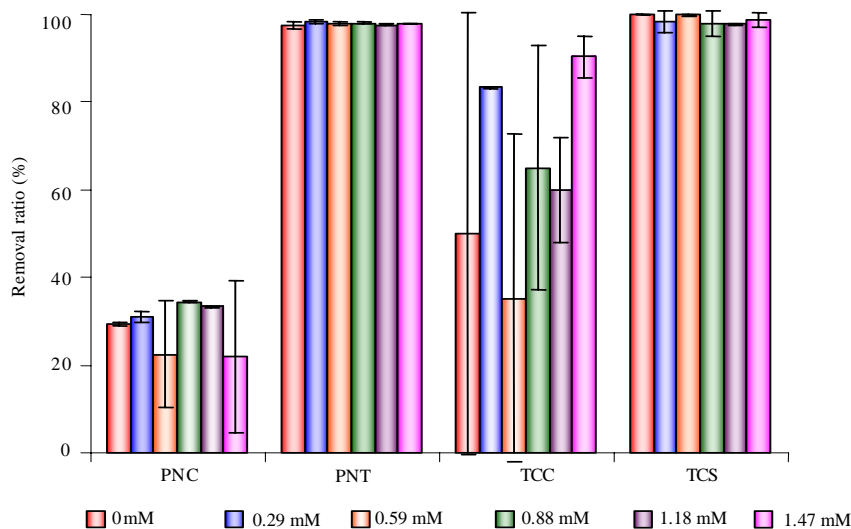
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Fig. 5: UV/H_2O_2 oxidation efficiencies for PNC, PNT, TCC and TCS (30 min reaction). The legend shows H_2O_2 concentrations

peroxide tube test kits and Odyssey DR/2500 spectrophotometer (HACH) at 620 nm UV wavelength. UV emission intensity of UV lamp was measured using UV Spectroradiometer (USR-30, Kansai Scientific Instruments Co. Ltd., Japan).

RESULTS AND DISCUSSION

All the results presented in this section are average values of at least three similar batch experiments, and the error bars in figures indicate standard variation of the results.

Removal of compounds

Preliminary degradation tests for the selected compounds by UV/H_2O_2 using a wide range of initial H_2O_2 doses were carried out first. Then six different H_2O_2 doses based on the observed removal performances in the preliminary tests were chosen for further tests. Average removal efficiencies for the compounds at the end of 30-min reaction time are illustrated in Fig. 2 through Fig. 5. The sixteen compounds can be divided into three distinct groups based on their removal efficiencies. The removals for CA, DCF, FEP, IPA, KEP, PNT and TCS were over 95 % irrespective of H_2O_2 doses. Negative impact of increasing H_2O_2 dosage was observed in case of CA and FEP removals. CAM, CBZ and PNC were very

difficult to degrade by both UV and UV/H_2O_2 (< 30 % removal efficiencies) within the range of tested H_2O_2 doses. Moreover, no specific trends in their removals were observed with increasing H_2O_2 dose. Removals of GFZ, IBP, IDM, NPX and PB varied between 40 % and 80 %. The removal efficiencies for these compounds, in general, increased with increasing H_2O_2 dose. No specific trend was observed in case of TCC removal. The initial TCC concentrations in mixed solutions were very low and not consistent in all the tests possibly due to very small water solubility of the compound, resulting to large errors in average removal efficiencies (Fig. 5).

UV photolysis of DCF in this investigation was very large (>95 %) compared to earlier reported values of 27 % (Canonica *et al.*, 2008) and 39 % (Vonga *et al.*, 2004) with similar experimental conditions. The extremely low UV photolysis of CBZ was consistent to earlier results (Vonga *et al.*, 2004; Pereira *et al.*, 2007a) while relatively small removals of the compound by UV/H_2O_2 (Fig. 2) may be attributed to low UV fluence (Pereira *et al.*, 2007a). Furthermore, the authors did not observe significant improvements in CA removals by UV/H_2O_2. More interestingly, CA removals decreased with increasing H_2O_2 doses in this investigation. IBP and PNT removals by UV photolysis in mixed solution in this

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Table 2: Apparent first-order removal rate (k) values for the selected compounds (concentration of each compound: 13.4×10^{-2} $\mu M \sim 55.8 \times 10^{-2}$ μM) in mixed solution by UV/H_2O_2 oxidation and corresponding molar absorption coefficient (ε) values at 254 nm

Compound	k values (/h) with initial H_2O_2 concentration (mM)						ε
	0	0.29	0.59	0.88	1.18	1.47	(/M/cm)
CA	6.80	6.00	5.74	5.55	5.78	5.61	-214.65
CAM	0.46	0.74	0.74	0.87	0.66	0.61	4487.70
CBZ	0.12	0.30	1.68	0.27	0.52	0.32	6143.02
DCF	44.39	43.90	46.50	48.35	45.16	47.70	3499.43
FEP	9.44	8.88	9.86	8.10	6.55	7.01	1045.20
GFZ	0.31	0.88	1.88	2.15	3.04	3.20	0
IBP	0.86	1.35	1.74	1.30	1.44	1.83	1237.68
IDM	1.36	2.35	4.81	4.59	6.28	7.08	16100.50
IPA	13.02	13.90	14.84	14.72	18.14	20.01	8291.16
KEP	149.36	149.63	144.17	145.10	142.88	149.67	16017.7
NPX	2.46	2.10	1.86	2.38	3.32	3.90	8519.62
PB	1.53	1.85	2.00	1.64	2.28	2.04	1625.68
PNC	0.70	0.74	0.62	0.85	0.80	0.62	1245.40
PNT	7.46	8.27	7.84	7.94	7.66	7.83	1261.35
TCC	5.23	4.32	1.16	2.56	2.59	5.83	1223.20
TCS	20.16	16.00	18.08	18.10	11.12	11.14	2605.86

investigation (38 % and 97 % respectively) were quite larger than the values (28 % and 87 % respectively) reported earlier (Yuan *et al*., 2009), where UV photolysis experiments were carried out with individual compounds (i.e. IBP and PNT separately). NPX and KEP removals by UV photolysis and UV/H_2O_2 oxidation were more or less consistent to the removals reported earlier.

Removal kinetic and behaviors

Removals of the selected compounds by UV and UV/H_2O_2 in mixed solutions were well-described ($R^2 \geq 0.98$) by the first-order reaction kinetic. The apparent first-order removal rate (k) values for the compounds are illustrated in Table 2. The k values for the sixteen compounds greatly varied. The compounds can roughly be grouped into two distinct categories based on the k values. CA, DCF, FEP, IPA, KEP, PNT and TCS exhibited significantly larger k values (up to 20-folds) than those of CAM, CBZ, GFZ, IBP, IDM, NPX, PB and PNC.

The k values for majority of the investigated compounds (e.g. CAM, CBZ, GFZ, IBP, IDM, NPX, PB, PNC, DCF and IPA) increased with increasing H_2O_2 doses. But, the values (excluding for GFZ, IBP, IDM, NPX and IPA) attenuated at larger H_2O_2 doses, which was consistent to an earlier report (Pereira *et al*., 2007b). Kim *et al*., (2008) reported significantly increased k values for FEP, NPX, CAM, KEP, DCF, IDM, CBZ and IPA with UV/H_2O_2 (0.14 mM initial H_2O_2 dose) compared to those with UV only. Moreover, decreased CBZ and NPX removal rates with larger H_2O_2 doses were also reported (Pereira *et al*., 2007b). But this tendency was observed in case of CA, FEP and TCS (Table 2) in this investigation. The decreased CA photodegradation and k value in presence of H_2O_2 was contrary to a result reported earlier (Andreozzi *et al*., 2003). No significant improvements in k values were observed for KEP and PNT with increasing H_2O_2 doses possibly due to more than 98 % removals of the compounds by UV photolysis alone (Fig. 4 and Fig. 5). But DCF and IPA exhibited different behaviors than those of KEP

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and PNT. The k values for DCF and IPA increased significantly with increasing H_2O_2 doses despite more than 99 % removals of the compounds by UV photolysis alone (Fig. 2 and Fig. 4). Consistent to an earlier report (Lin and Reinhard, 2005), KEP was the most easily photodegraded compound. The k values for NPX, CAM, DCF and CBZ in this investigation were similar to those of Kim *et al.*, (2008), but the values for KEP and IPA were very large. Yuan *et al.*, (2009) investigated photodegradation of PNT and IBP separately using a low pressure UV lamp with similar experimental conditions to those of this investigation. Though UV photolysis rate for PNT in this investigation (7.46 /h) was very close to the value (7.20 /h) reported in Yuan *et al.*, (2009), value for IBP in the literature (1.08 /h) was significantly larger than that observed in this investigation (0.86 /h). Pereira *et al.*, (2007a) also investigated degradation of six pharmaceutical compounds in mixed solution by UV photolysis and UV/H_2O_2 using low pressure UV lamp with similar experimental conditions. But they used only one H_2O_2 dose (0.29 mM) with UV/H_2O_2 process. The reported UV photolysis rate for CA (4.2 /h) in Pereira *et al.*, (2007a) was quite smaller than that observed in our experiments (6.8/h). Moreover, they found drastic increase in CA removal rate by UV/H_2O_2 (71.4 /h), while decreasing tendency in k value was observed in our case (Table 2). The UV photolysis rate for NPX in our experiments was almost 2.5-folds larger than the value (0.99 /h) reported in Pereira *et al.*, (2007a). Similar to CA, k value for NPX with UV/H_2O_2 (74.4/h) was very large than that with UV photolysis in the literature, while the value for NPX decreased in our experiments (Table 2). UV photolysis rate for CBZ in our experiments was almost 1.5-folds larger than the value (0.08/h) reported in Pereira *et al.*, (2007a). The k value for CBZ with UV/H_2O_2 (80.4 /h) was very large compared to its UV photolysis rate. But the k value for CBZ with UV/H_2O_2 was only 2.5-folds of the UV photolysis rate value in our experiments. UV photolysis rate for KEP in our experiments was about 1.9-folds larger than the reported value (76.8/h) in Pereira *et al.*, (2007a). The k value for the compound with UV/H_2O_2 is not given (due to its very fast disappearance) in Pereira *et al.*, (2007a), while no significant change in its k value with UV/H_2O_2 was observed in our case. It is apparent from this discussion that degradation behaviors of an organic compound with UV and UV/H_2O_2 in presence and absence of coexisting organic compounds significantly vary, and number of coexisting compounds and their physicochemical characteristics might play greater role on its degradation behaviors. Three distinct impacts of increasing H_2O_2 doses in UV/H_2O_2 oxidation system on removal efficiency and k value of the sixteen compounds using low power (10 W) low pressure UV lamp were observed in this investigation: (a) positive impact, (b) negative impact and (c) no significant impact. The enhanced removals and larger k values in UV/H_2O_2 system were attributed to formation of hydroxyl radical ($^{\cdot}OH$) and dominance of $^{\cdot}OH$-mediated oxidation (Pereira *et al.*, 2007b; Yuan *et al.*, 2009). The attenuation in removal efficiency and k value for some compounds with larger H_2O_2 doses was presumably due to scavenging action of excess H_2O_2 on UV energy and $^{\cdot}OH$ (Pereira *et al.*, 2007a). H_2O_2 absorbs a fraction of available UV energy, which would otherwise be available for UV photolysis of target compounds in UV/H_2O_2 system. UV photolysis of H_2O_2 produces $^{\cdot}OH$. However, if $^{\cdot}OH$ is not produced by some reason and/or when H_2O_2 (in excess) scavenges generated $^{\cdot}OH$, then the absorbed UV energy by H_2O_2 would not be useful to degrade target compounds resulting in smaller removal efficiencies.

Molar absorption vs. photodegradation

Molar absorption coefficient (ε) value for each of the sixteen compounds was evaluated based on their measured UV absorption at 254 nm, and the value was compared with corresponding apparent first-order removal rate value (Table 2) obtained from UV photodegradation experiments carried out in mixed solution. The ε values for CBZ and KEP obtained in this investigation were very close to the values (6070.0/M.cm and 15450.0 /M.cm respectively) given in Pereira *et al.*, (2007a). But our values for CA and NPX were very different than those (400.0 /M.cm and 4900.0 /M.cm respectively) given in the literature. The compounds with higher UV absorbance at 254 nm (i.e. ε value) in general exhibited larger k values (Table 2). But CA, CBZ, GFZ and IDM showed different behaviors. Despite negligibly small UV absorption by both CA (the negative value of ε essentially implies no UV absorption) and GFZ,
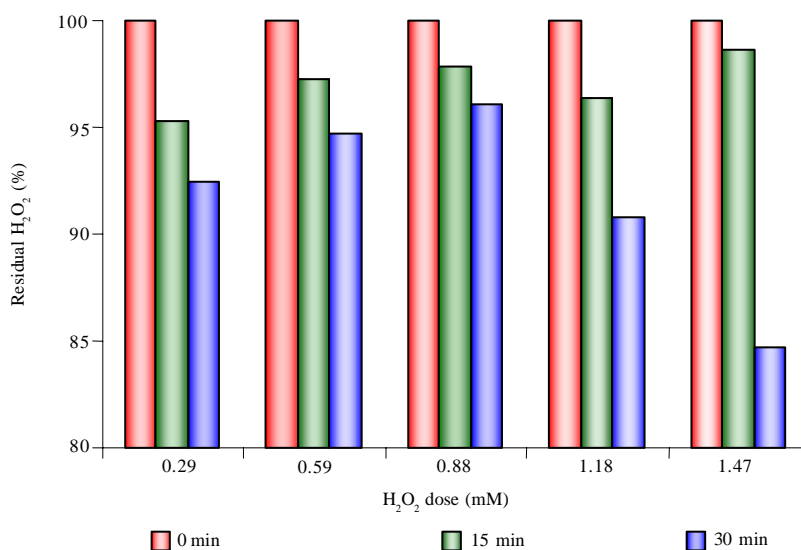
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Fig. 6: Residual H_2O_2 concentration during UV/H_2O_2 oxidation of pharmaceutical compounds in mixed solution
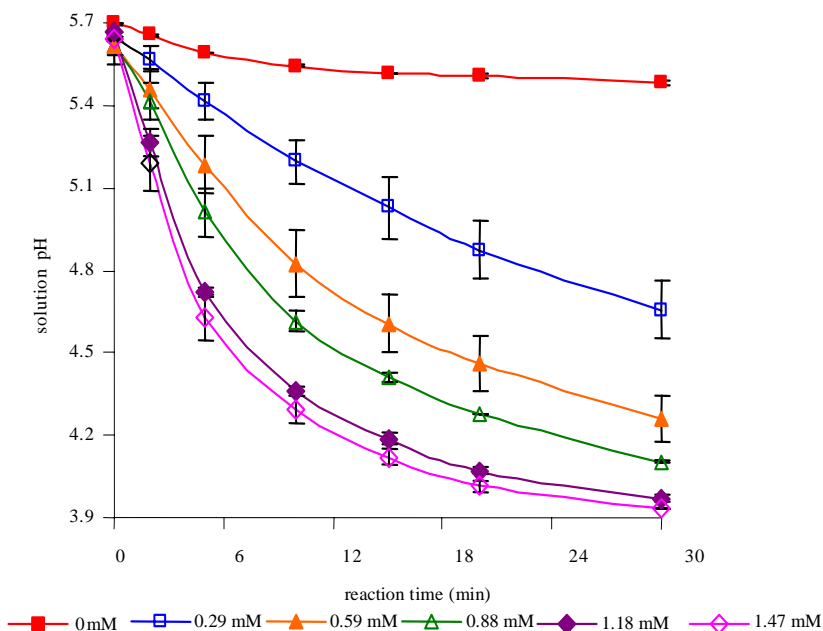

Fig. 7: Solution pH profiles during UV/H_2O_2 oxidation of pharmaceutical compounds in mixed solution. The legend shows H_2O_2 concentrations

k value for CA was very large while the value for GFZ was significantly larger than that of CBZ. Despite almost the same ε values for IDM and KEP, k value for the latter was more than one hundred folds of the former. Moreover, IBP, PNC, PNT and TCC exhibited very closer ε values, but k values for the latter two compounds were at least 6-folds larger than those for IBP and PNC (Table 2). With similar k

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values for both IDM and PB, ε value for the former was almost 10-folds larger than that of the latter. UV absorbance (at 254 nm) by H_2O_2 also was measured and the corresponding ε value was evaluated. The value (27.06 /M.cm) was very small compared to those of the investigated pharmaceutical compounds (excluding CA and GFZ). It is evident from the ε and k values in Table 2 that molar absorption coefficient alone does not necessarily reflect photodegradation of a compound as one hundred percent of the absorbed photon energy may not be useful for degradation, which is known as "quantum yield". Furthermore, molar absorption coefficient and quantum yield values of an organic compound in presence and absence of several coexisting organic compounds can be expected to vary greatly due to variation in physicochemical characteristics of the compounds and limitation of available photon energy. The very small molar absorption coefficient value of H_2O_2 at 254 nm (27.06 /M.cm) compared to those of the pharmaceutical compounds can be expected to decrease further in the mixed solution of sixteen compounds. Hydroxyl radical-mediated oxidation of organic compounds in UV/H_2O_2 system leads to its enhanced efficiency, but UV photolysis of H_2O_2 is the first step for ·OH generation. As molar absorption of H_2O_2 (27.06 /M.cm) was very small and the value presumably further decreased in mixed solution, formation of ·OH may not be a major reaction pathway with UV/H_2O_2 oxidation in this investigation. Moreover, H_2O_2 at large concentrations acts as ·OH scavenger in UV/H_2O_2 system (Pereira *et al.* 2007a). Therefore, ·OH-mediated oxidation might not be a major reaction mechanism for the compounds in our experiments. With this discussion, one naturally gets curious on the fate of H_2O_2 in UV/H_2O_2 system as no such information in our knowledge is available in published articles.

Fate of H_2O_2

Residual H_2O_2 concentrations at the beginning, middle and end of 30-min reaction time in UV/H_2O_2 oxidation system with five different initial H_2O_2 doses are illustrated in Fig. 6. The added H_2O_2 concentrations gradually decreased with reaction time, but no specific trends in H_2O_2 concentration decrease were observed among the tested H_2O_2

doses. Remaining H_2O_2 at 15 min were 95.3, 97.3, 97.9, 96.4 and 98.6 % respectively for 0.29, 0.59, 0.88, 1.18 and 1.47 mM of initial H_2O_2 doses, while the values at 30 min were 92.5, 94.7, 96.1, 90.8 and 84.7 %, respectively. The residual H_2O_2 concentration at 30 min with 1.47 mM H_2O_2 dose decreased drastically compared to those of the remaining cases. Only few authors simply mentioned about residual H_2O_2 with UV/H_2O_2 oxidation (Pereira *et al.,* 2007a and b), but fate of H_2O_2 and its significance in the system are not discussed so far. It can clearly be observed (Fig. 6) that only small fractions of the initially added H_2O_2 were used in UV/H_2O_2 oxidation during 30 min reaction period. For example, the highest H_2O_2 consumption in the system during the reaction period was with 1.47 mM H_2O_2 dose, and the value was only 15 % of the added H_2O_2. In other words, more than 85 % of the added H_2O_2 just remained in the system unused at the end of the reaction.

Pereira *et al.,* (2007a and b) illustrated the impact of UV fluence on UV/H_2O_2 oxidation of pharmaceutical compounds. Removal of pharmaceutical compounds in this investigation could possibly be enhanced further by using higher UV fluence values, but increasing UV fluence with the type of lamp we used (a standard LP/UV lamp) was not possible. The use of a fixed fluence UV lamp and the very large fractions of unused H_2O_2 (Fig. 6) indicated that available UV energy was possibly a limiting factor for UV/H_2O_2 oxidation of the compounds in this investigation. What were more important with reference to UV/H_2O_2 oxidation of the tested compounds that their removals were not in general significantly enhanced compared to their removals by UV photolysis and very large fractions of the added H_2O_2 remained unused by the end of 30 min reaction, which requires further treatment of the treated effluent before it is discharged to water bodies. An earlier investigation (Baumgarten *et al.,* 2007) also concluded that adding H_2O_2 to UV photolysis of pharmaceutical compounds using LP lamp was unworthy though no information on residual H_2O_2 was given.

Pereira *et al.,* (2007b) found medium pressure (MP) UV lamps to be more useful than LP lamps for efficient removal of pharmaceuticals by UV/H_2O_2. The enhanced removal efficiency with MP lamps was the result of several wavelengths (200 ~ 300 nm) emitted

by the lamps. But nothing is mentioned about fate of H_2O_2 in the system with MP lamps. It would therefore be worthy to explore on fate of H_2O_2 with UV/H_2O_2 using MP lamps for more insight.

Significance of solution pH

Solution pH is very important in photochemical reactions. Initial pH of reaction solutions in these experiments was not adjusted. Solution pH values during UV photolysis and UV/H_2O_2 oxidation of the compounds in mixed solutions are illustrated in Fig. 7. Initial solution pH values before switching the UV lamp on were between 5.62 and 5.70. The values gradually decreased with reaction time. Moreover, the decrease in solution pH was more significant with increasing H_2O_2 dose (Fig. 7). Enhanced efficiency of UV/H_2O_2 oxidation system is primarily attributed to ·OH-mediated reaction. But ·OH generation due to UV photolysis of H_2O_2 is favorable only in alkaline pH region (Qiao *et al.,* 2005). It is then apparent that the acidic solution pH values and their further decrease with time and larger H_2O_2 doses in UV/H_2O_2 system might have negatively affected ·OH generation in this investigation. Therefore, adjusting solution pH to larger values (alkaline region) would be a possible way to enhance H_2O_2 photolysis with UV/H_2O_2 oxidation.

CONCLUSION

UV photolysis and UV/H_2O_2 oxidation of the sixteen compounds in mixed solution followed the first-order reaction kinetic. Oxidation behavior (i.e. removal efficiency and rate) of the several tested compounds in mixed solution varied significantly from their respective behavior in absence of coexisting organic compounds presumably due to wide variation in their physicochemical characteristics and limitation of available UV photon energy in the system. Three distinct effects of H_2O_2 on UV/H_2O_2 oxidation of the compounds (positive, negative and no significant effect) were observed. CA, DCF, FEP, IPA, KEP, PNT and TCS were eliminated very efficiently (> 96 %) by UV photolysis alone, while H_2O_2 addition to UV was not very worthy to further enhancing removals of majority of the compounds. Residual H_2O_2 during UV/H_2O_2 oxidation was quantitated for the first time. Very large fractions (> 85 %) of the added H_2O_2 (0.29 ~ 1.47mM) in UV/H_2O_2 system remained unused presumably due to small UV

fluence of the LP lamp, very small molar absorption coefficient value for H_2O_2 at 254 nm (27.06 /M.cm) and acidic solution pH (< 5.7). Further tests with UV/H_2O_2 oxidation using higher UV fluence and alkaline solution pH are desirable to clarify usefulness of the method to treat pharmaceutical contaminated waters.

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AUTHOR (S) BIOSKETCHES

Giri, R. R., Ph.D. is a researcher in New Industrial R & D Center of Osaka Sangyo University, 3-1-1 Nakagaito, Daito City, 574-8530 Osaka, Japan. Email: *rabindra@cnt.osaka-sandai.ac.jp*

Ozaki, H., D. is a professor in Department of Civil Engineering of Osaka Sangyo University, 3-1-1 Nakagaito, Daito City, 574-8530 Osaka, Japan. Email: *ozaki@ce.osaka-sandai.ac.jp*

Takayanagi, Y. is an undergraduate student in School of Engineering of Osaka Sangyo University, 3-1-1 Nakagaito, Daito City, 574-8530 Osaka, Japan. Email: *takayanagi@sub.osaka-sandai.ac.jp*

Taniguchi, S., M. Eng. is a researcher in New Industrial R & D Center of Osaka Sangyo University, 3-1-1 Nakagaito, Daito City, 574-8530 Osaka, Japan. Email: *taniguch@cnt.osaka-sandai.ac.jp*

Takanami, R., M. Eng. is a researcher in New Industrial R & D Center of Osaka Sangyo University, 3-1-1 Nakagaito, Daito City, 574-8530 Osaka, Japan. Email: *r-nami@cnt.osaka-sandai.ac.jp*