Journal of Hazardous Materials 166 (2009) 1134–1140

Contents lists available at ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

Performance of UV and UV/H_2O_2 processes for the removal of pharmaceuticals detected in secondary effluent of a sewage treatment plant in Japan

Ilho Kim*, Naoyuki Yamashita, Hiroaki Tanaka

Research Center for Environmental Quality Management, Kyoto University, 1-2 Yumihama, Otsu, Shiga 520-0811, Japan

ARTICLE INFO

Article history:
Received 23 May 2008
Received in revised form 3 December 2008
Accepted 3 December 2008
Available online 7 December 2008

Keywords:
Pharmaceuticals
UV
UV/H_2O_2
AOPs
LC/MS/MS

ABSTRACT

The effectiveness of UV-based processes (UV and UV/H_2O_2) for the removal of pharmaceuticals in real wastewater using bench-scale experiment setup with a treatment capacity of 10 m^3/day was investigated. Forty-one kinds of pharmaceuticals including 12 antibiotics and 10 analgesics were detected in secondary effluent used for tested water. For UV process a good removal seems to be expected for just a few pharmaceuticals such as ketoprofen, diclofenac and antipyrine. Especially, the removal efficiencies of macrolide antibiotics such as clarithromycin, erythromycin and azithromycin for UV alone process were found to be very low even by the introduction of considerable UV dose of 2768 mJ/cm^2. For UV/H_2O_2 process, a 90% removal efficiency could be accomplished in 39 pharmaceuticals at UV dose of 923 mJ/cm^2, indicating that it will be possible to reduce UV energy required for the effective pharmaceuticals removal by the combination of H_2O_2 with UV process.

1. Introduction

Recently, much attention has been paid to the safety of tap water and wastewater treated water because of the lack of water resources and water reuse. While, there is a growing concern regarding the occurrence of pharmaceuticals in the aquatic environment [1,2]. These pharmaceuticals have been detected in samples from the aquatic environment such as river water, ground water and drinking water and the main source of them has been known as the effluent from wastewater treatment plant [3,4]. There are also several investigations showing that pharmaceuticals are not eliminated during wastewater treatment and also not biodegraded in the environment [5–8]. However, wastewater can be reclaimed after rigorous treatment at a wastewater treatment plant and piped to individual households for uses such as toilet flushing, garden watering and washing of cars and outdoor surfaces. So, high quality treated water after conventional wastewater treatment will be needed to satisfy wastewater reclamation in the future and, therefore, the safety evaluation and the removal of micropollutants such as pharmaceuticals should be studied.

UV process lacks applicability for the pharmaceuticals removal in wastewater treatment system. However, recently many studies on the removal of various organic pollutants such as *N*-nitrosodimethylamine (NDMA), pharmaceuticals, hydrocarbons and water soluble fraction of crude oil with UV treatment have been done because UV treatment does not form byproducts and has been known as an effective process for degrading organic matter when it is combined with O_3 or H_2O_2 [9–11]. A study on the UV and UV/H_2O_2 degradations of pharmaceutical intermediates in aqueous solution showed that two pharmaceutical intermediates (5-methyl-1,3,4-thiadiazole-2-methylthio and 5-methyl-1,3,4-thiadiazole-2thiol) degradation by photo-oxidation was always faster than by direct photolysis and during direct photolysis, a lower substrate initial concentration led to a faster and more efficient degradation [12]. UV/H_2O_2 process also could degrade carbamazepine very effectively, while UV alone process was not effective for reducing carbamazepine concentration [13].

To date, most of studies on pharmaceuticals degradation using UV have been done to investigate the reactivity of pharmaceuticals with UV and OH radicals. In addition, only few pharmaceuticals such as carbamazepine and diclofenac, etc. have been studied on their removal by physicochemical processes, and tested water spiked with a selected pharmaceutical has been used during almost all the studies. Therefore, limited information is available on the effectiveness of physicochemical processes such as UV-based processes for pharmaceuticals removal in real wastewater. The objective of this study is to investigate the effectiveness of UV and UV/H_2O_2 processes for the removal of pharmaceuticals in real wastewater using bench-scale experimental setup with a treatment capacity of 10 m^3/day.

* Corresponding author. Tel.: +81 77 527 6223; fax: +81 77 524 9869.
E-mail address: jinker123@gmail.com (I. Kim).

0304-3894/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.jhazmat.2008.12.020

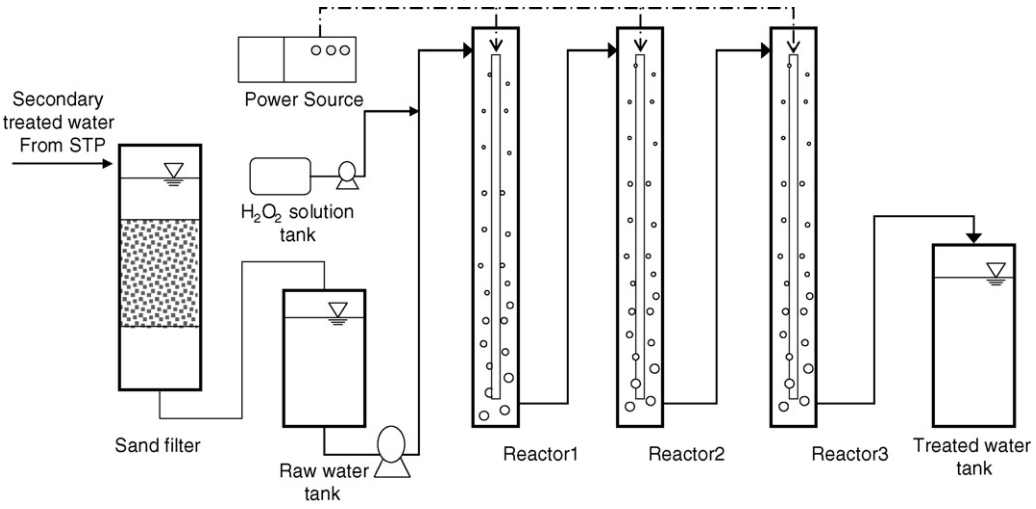

Fig. 1. Experiment setup for UV-based processes.

2. Materials and methods

2.1. Experimental setup

Experiment setup used in this study consists of three reactors (R1, R2 and R3) connected in series (Fig. 1). The effective volume and hydraulic retention time (HRT) of each reactor are 35 L and 5 min, respectively. Biologically treated water (i.e., effluent from secondary sedimentation tanks in a municipal wastewater treatment plant) filtered by sand filter was used as tested water. The pH, DOC and UV_{254} absorbance of the tested water ranged from 6.5 to 6.6, 3.3 to 3.7 mg/L and 0.0691 to 0.0702 cm^{-1}, respectively. In order to ensure stable state of UV irradiation, each process had been operated for more than 3 HRT (45 min) and then, samples were withdrawn at each sampling port.

UV process was operated using a 65 W low pressure mercury lamp with UV output of 21.8 W (UV wavelength: 254 nm, length of the lamp: 1556 mm, UV intensity: 1.025 mW/cm^2) and 3 UV lamps are placed inside each reactor. During UV process, tested water was aerated at an air flow rate of 0.5 L/min for efficient UV irradiation. For H_2O_2 process, H_2O_2 solution with the concentration of 1720 mg/L and tested water were supplied continuously to R1 at flow rates of 1.9 and 416.7 L/h, respectively, which resulted in initial H_2O_2 concentration of 7.8 mg/L in the tested water.

2.2. Pretreatment for pharmaceuticals quantification with LC/MS/MS

For pharmaceutical quantification with LC/MS/MS, each sample of 1000 mL were firstly filtered with GF/B (pore size: 1.0 μm) and then, 1 g EDTA was added to the filtrate to chelate heavy metals in the tested water. Afterwards, pharmaceuticals in the filtrate were concentrated in an Oasis HLB cartridge (Waters, 6 cm^3/100 mg) with the concentrator (Waters, Sep-Pak concentrator SPC-10). The Oasis HLB cartridge conditioned with 3 mL methanol and 6 mL distilled water in advance was used for concentration. After concentration, the cartridge was dehydrated by a pneumatic pump for 1 h in order to avoid the remaining of water in the cartridge, and 6 mL methanol was used for elution of pharmaceuticals from the dehydrated cartridge. The eluted solution was volatilized with N_2 gas and then, dissolved again with 1 mL mixed solution of 0.1% formic acid and methanol. This solution of 1 mL was used for pharmaceuticals quantification using LC/MS/MS.

2.3. Analytical methods

Selected pharmaceuticals were purchased from Wako, Japan except levofloxacin (Fluka) and ceftiofur (Hayasijyunyaku, Japan). Stock solutions of 1000 mg/L for each pharmaceutical were prepared and stored at 4 °C until use. The concentration of each pharmaceutical in samples was calculated from the standard curve which was made by standard solutions (0.5, 1, 5, 10, 25, 50 and 100 μg/L) for each pharmaceutical.

The concentrations of pharmaceuticals were measured simultaneously with LC/MS/MS. HPLC Alliance Waters2695 separation module was used for LC and Quattro micro API Tandem mass spectrometer for MS/MS. The control of LC/MS/MS system and the treatment of data acquired during operation of LC/MS/MS were managed by MassLynx™ Software (Waters). For simultaneous quantification of pharmaceuticals, gradient elution analysis method varying the polarity of mobile phase with time was adopted. Table 1 shows the measurement conditions of LC/MS/MS in details and ionization conditions, LOD and LOQ for 47 pharmaceuticals investigated in this study are shown in Table 2.

The values of limit of detection (LOD) and limit of quantification (LOQ) for simultaneous analysis of the 47 pharmaceuticals

Table 1
Measurement condition for LC/MS/MS analysis.

<HPLC: Waters 2659>
- Column: Waters SunFire C18 2.1 mm × 150 mm, 5 μm
- Column Temp.: 20 °C
- Flow rate: 0.2 mL/min
- Injection volume: 10 μL

- Mobile Phase:

	A MilliQ	B Methanol	C 1% Formic acid
- Gradient:			
Time (min)	A (%)	B (%)	C (%)
0	85	5	10
18	0	90	10
20	0	100	0
25	0	100	0
25.01	0	90	10
28	100	0	0
31	100	0	0
31.01	85	8	10

<MS/MS: Waters Quattro micro API>
- Ionization: Electrospray Ionization (ESI) Positive
- Capillary Voltage: 3.5 kV
- Capillary Temp.: 350 °C - Source Temp.: 120 °C

Table 2
Ionization conditions, LOD and LOQ for pharmaceuticals investigated.

PPCP	Parent ion	Product ion	Cone voltage (V)	Collision energy (V)	Retention time (min)	LOD (μg/L)	LOQ (μg/L)
2-QCA	175.0	128.9	20	15	17.2	0.18	0.60
Acetaminophen	152.0	109.8	25	16	10.6	0.27	0.89
Antipyrine	189.1	76.7	30	35	13.9	0.85	2.83
Atenolol	267.4	145.1	25	30	6.8	0.14	0.48
Azithromycin	749.5	591.4	40	25	12.0	0.36	1.18
Bezafibrate	362.4	276.2	20	15	22.3	0.07	0.23
Caffeine	195.3	138.0	35	18	13.3	0.15	0.49
Carbamazepine	237.1	194.0	25	20	19.4	0.14	0.48
Cetiofur	524.0	241.0	25	15	18.0	0.51	1.72
Chloramphenicol	323.4	275.0	20	14	17.2	0.19	0.62
Chlorotetracycline	479.3	462.0	25	15	13.3	6.18	20.62
Clarithromycin	748.9	157.9	30	20	17.7	0.12	0.41
Clenbuterol	277.0	202.9	20	15	10.6	0.16	0.53
Crotamiton	204.1	68.7	30	20	21.8	0.27	0.89
Cycolphosphamide	261.0	139.8	25	20	17.7	0.17	0.56
DEET	192.1	118.8	25	15	20.4	0.40	1.32
Diclofenac	296.1	214.9	20	20	24.0	0.17	0.58
Diltiazem	415.5	178.1	30	30	15.4	0.02	0.05
Dipyridamole	505.7	385.4	35	40	16.1	0.05	0.15
Disopyramide	340.2	239.0	20	15	11.3	0.30	1.01
Enrofloxacin	360.2	245.2	30	26	11.3	0.82	2.74
Erythromycin	717.0	158.1	15	30	16.8	0.14	0.46
Ethenzamide	166.0	148.9	15	10	16.8	0.13	0.44
Fenoprofen	243.1	196.9	15	10	23.1	0.10	0.33
Ifenprodil	326.2	308.1	30	20	13.6	0.23	0.75
Indomethacine	358.0	138.9	25	20	24.0	0.30	0.99
Isopropylantipyrine	231.1	184.9	20	15	22.0	0.13	0.44
Ketoprofen	255.1	209.0	25	15	21.4	0.10	0.33
Levofloxacin	362.1	318.0	30	20	10.6	0.11	0.37
Lincomycin	407.5	126.1	30	22	8.6	0.05	0.16
Mefenamic acid	242.1	224.0	25	20	25.2	0.37	1.24
Metoprolol	268.2	115.9	30	20	11.3	0.38	1.26
Nalidixic acid	233.2	215.1	35	14	18.9	0.23	0.77
Naproxen	231.1	188.9	35	20	19.2	0.08	0.26
Norfloxacin	320.2	276.2	25	18	11.0	0.84	2.79
Oxytetracycline	461.1	425.9	20	20	11.5	0.23	0.78
Prenzepine	352.4	113.0	30	22	10.0	0.12	0.40
Primidone	219.3	162.1	20	10	16.0	0.08	0.26
Propranolol	260.2	115.9	30	20	14.2	0.12	0.42
Sulfadimethoxine	311.0	155.9	30	20	16.7	0.20	0.65
Sulfadimizine	279.0	185.9	25	15	12.6	0.12	0.40
Sulfamethoxazole	254.0	155.9	25	15	14.3	0.16	0.54
Sulfamonomethoxine	281.0	155.9	25	15	14.7	0.15	0.50
Sulpiride	342.4	112.1	35	25	6.9	0.04	0.13
Tetracycline	445.1	409.9	20	20	11.0	0.41	1.38
Theophylline	181.0	123.8	30	20	12.2	0.08	0.28
Trimethoprim	291.4	230.2	35	20	9.5	0.13	0.42

were determined by measuring repeatedly standard solutions with the concentration of 0.5, 1, 5, 10 μg/L for individual pharmaceuticals with LC/MS/MS. From the values measured 5 times for each standard solution, average value and standard deviation value for each pharmaceutical were calculated. The two values were used for acquiring a coefficient of variation (CV), which is defined as a ratio of the standard deviation value to the average value. Based on the standard deviation (σ) of standard solution of the lowest concentration with CV of less than 20%, LOD (3σ) and LOQ (10σ) were calculated. Calculated LOQ ranged from 0.05 to 20.62 μg/L (average: 1.17 μg/L) and LOD from 0.02 to 6.18 μg/L (average: 0.35 μg/L). In this study, the removal efficiency was expressed as 100% when the concentration of a pharmaceutical decreased by below its LOD after treatments.

DOC (dissolved organic carbon) concentration was measured with a TOC analyzer (TOC-5000A, Shimadzu) and calculated from the difference of TDC (total dissolved carbon) and DIC (dissolved inorganic carbon). The absorbance at 254 nm (UV_{254}) was measured by a spectrophotometer (UV-16000, Shimadzu). DMP (2,9-dimethyl-1,10-phenanthroline) method was adopted for the measurement of H_2O_2 concentration in sample [14].

3. Results and discussion

3.1. Pharmaceuticals detected in the tested water

Fig. 2 shows average initial concentrations of individual pharmaceuticals detected in the tested water. As known in Fig. 2, the detected pharmaceuticals were 10 analgesics, 4 antiarrhythmic agents and 12 antibiotics. 15 others such as carbamazepine and primidone (anticovulsants), crotamiton (antiitch drug), cyclophosphamide (antineoplastic agent), sulpiride (antipsychotic drug), theophylline (bronchodilator), 2-QCA (carbadox intermediate), *N*,*N*-diethyl-m-toluamide (DEET, insect repellent), bezafibrate and clofibric acid (lipid modifying agent), ifenprodil (NMDA receptor antagonist), pirenzepine (peptic ulcer drug), caffeine (stimulant drug), and dipyridamole and diltiazem (vasodilators) also occurred in tested water. Concentrations of 10 analgesics ranged from 3 to 121 ng/L and especially, ketoprofen and fenoprofen were present at high concentrations of more than 100 ng/L. Among 4 antiarrhythmic agents, disopyramide showed the highest concentration of 499 ng/L. Antibiotics consisted mainly of macrolides (clarithromycin, erythromycin and azithromycin), sulfoamides

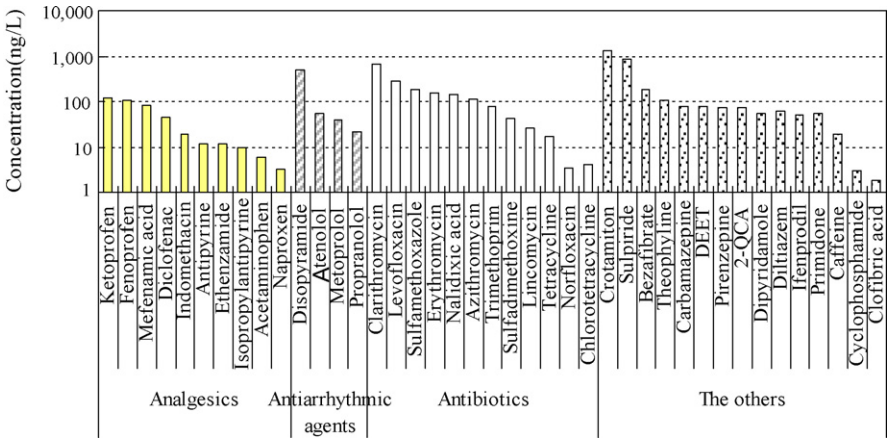

Fig. 2. Average initial concentrations of the 41 pharmaceuticals detected in the tested water.

(sulfamethoxazole and sulfadimethoxine), tetracyclines (tetracycline and chlorotetracycline) and quinolines (nalidixic acid and norfloxacin). The concentrations of macrolides, sulfonamides, tetracyclines and quinolines ranged from 110 to 656 ng/L, 42 to187 ng/L, 4 to 17 ng/L and 4 to 148 ng/L, respectively, showing that macrolides concentrations are comparatively high.

On the other hand, crotamiton (1359 ng/L) and sulpiride (857 ng/L) showed the highest concentration among 41 pharmaceuticals detected in the tested water, while 6 pharmaceuticals such as analgesics acetaminophen and naproxen, antibiotics norfloxacin and chlorotetracycline, antineoplastic agent cyclophosphamide and lipid modifying agent clofibric acid were present to very low concentrations of 2–6 ng/L. In particular, 13 pharmaceuticals including antiitch drug crotamiton, antipsychotic drug sulpiride and antibiotic clarithromycin exceeded 100 ng/L in their concentrations.

A study on the fate of pharmaceuticals in wastewater treatment system has reported that atenolol, acetaminophen, naproxen, DEET and ketoprofen were susceptible to biodegradation by activated sludge from their high removal efficiencies of more than 70% for biological process [15]. However, atenolol, DEET and ketoprofen were still present to high concentration of 58–104 ng/L in the tested water, biologically treated water. In addition, disopyramide and crotamiton classified to pharmaceuticals with low biodegradability in their study were also detected at quite high concentrations of 499 and 1359 ng/L, respectively. Another study on the removal efficiency of pharmaceuticals during wastewater process in Japan has showed that 26 pharmaceuticals including disopyramide, sulpiride and dipyridamole occurred at an order of ng/L to μg/L concentration [8]. The study also reported that during BNR (biological nutrient removal) process, 8 pharmaceuticals such as caffeine, theophylline, acetaminophen, ibuprofen, ketoprofen, dipyridamole, indomethacin and DEET were removed by 80%, while the removal efficiency of carbamazepine and crotamiton were limited only to 30% or less. It was also known in their study that ozonation following biological treatment process could reduce significantly concentrations of the pharmaceuticals. Consequently, it can be known that although biological process is effective for the removal of many pharmaceuticals, additional processes such as ozonation and advance oxidation processes (AOPs) should be followed after biological process in order to remove pharmaceuticals with low biodegradability effectively.

3.2. Pharmaceuticals removal by UV process

The performances of 2 UV-based processes (UV and UV/H_2O_2 processes) for pharmaceuticals removal were investigated using the experimental setup shown in Fig. 1. UV dose introduced during UV-based processes for 15 min was 2768 mJ/cm^2, which is much higher than 40–140 mJ/cm^2 required for typical disinfection.

Fig. 3 compares removal efficiency of the 41 pharmaceuticals at each reactor (R1, R2 and R3) during UV process. As seen in Fig. 3, 12 pharmaceuticals including antipyrine, chlorotetracycline, clofibric acid and norfloxacin showed the removal efficiency of more than 90% even at R1. However, it was quite difficult to get a good removal efficiency of more than 90% for each pharmaceutical despite the introduction of considerable UV dose (R1, R2 and R3: 923 mJ/cm^2, respectively), although removal efficiencies of most of pharmaceuticals increased with the increased contact time. In particular, 12 pharmaceuticals including erythromycin, clarithromycin and azithromycin (macrolide antibiotics), carbamazepine and primidone (anticonvulsants), sulpiride (antipsychotic drug), DEET (insect repellent) and pirenzepine (peptic ulcer drug) showed removal efficiency of less than 50% even for HRT of 15 min (until R3), resulting in low performance of UV process.

Comparatively good removals of sulfadimethoxine (antibiotic), isopropylantipyrine (analgesic), ifenprodil (NMDA receptor antagonist) and theophylline (bronchodilator) by UV process were also achieved. However, various pharmaceutical intermediates could be formed for the degradation of the pharmaceuticals by UV process and, therefore, further studies need to be done on the removal and toxicity of the intermediates.

On the other hand, removal efficiencies of 25 pharmaceuticals including acetaminophen, carbamazepine, clarithromycin, cyclophosphamide, DEET and indomethacine, etc. were in the very low range of 1% (acetaminophen) to 43% (indomethacine), showing that it will be difficult to accomplish their effective removals by UV alone process. It has been reported that clarithromycin and DEET were very resistant to UV and degradation reaction of ketoprofen, diclofenac and antipyrine with UV occurred very fast from UV treatment experiment carried out using pure water spiked with 30 kinds of pharmaceuticals [16]. In this study, ketoprofen, diclofenac and antipyrine were removed by more than 90% at R1, indicating that the 3 pharmaceuticals can be removed easily by UV process.

On the other hand, for antibiotics, sulfonamides such as sulfamethoxazole and sulfadimethoxine, and quinolines such as norfloxacin and nalidixic acid showed quite high removal efficiency in the range of 86–100% during UV process. In contrast to this, macrolides such clarithromycin, erythromycin and azithromycin were removed by 4–7% only, and showed removal efficiency of 24–34% even by UV irradiation for 15 min (R1, R2 and R3). Therefore, it was thought that macrolides should be paid much attention in wastewater treatment process in both aspects for their low degradabilities and high occurrence concentrations of more than 100 ng/L as mentioned above. Among tetracyclines, chlorotetracycline

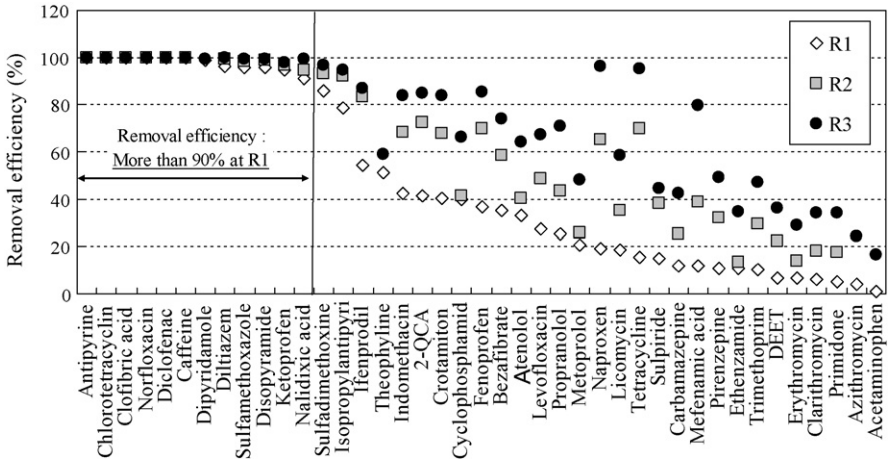

Fig. 3. Pharmaceuticals from each reactor during the UV process.

concentration decreased to less than LOD (6.18 μg/L) during UV process for 5 min, while only 15% removal efficiency was achieved for tetracycline. This can be explained by low molar extinction coefficient (4108 M^{-1} cm^{-1}) of tetracycline comparing to that (18,868 M^{-1} cm^{-1}) of chlorotetracycline. Their molar extinction coefficients were obtained by measuring UV_{254} absorbance of tested solution of each PPCP with a concentration of 10 mg/L. Generally, degradation of a compound by UV is affected by UV energy absorption and quantum yield of the compound. UV energy absorption by a compound is expressed as molar extinction coefficient, which is a measure of how strongly a chemical species absorbs light at a given wavelength. In other words, high molar extinction coefficient means that the compound can absorb much UV energy which could be utilized for its degradation. Therefore, a better removal efficiency was expected in chlorotetracycline than tetracycline.

3.3. Pharmaceuticals removal by UV/H_2O_2 process

A few studies have reported the effectiveness of H_2O_2 addition for pharmaceuticals removal during UV process. Lopez et al. [12] have studied on the UV and UV/H_2O_2 degradations of pharmaceutical intermediates in aqueous solution. They found that two pharmaceutical intermediates (5-methyl-1,3,4-thiadiazole-2-methylthio and 5-methyl-1,3,4-thiadiazole-2thiol) degradation by photo-oxidation was always faster than by direct photolysis and during direct photolysis, a lower substrate initial concentration led to a faster and more efficient degradation. Vogna et al. [13] have conducted a study on diclofenac oxidation with UV/H_2O_2 and O_3, showing that both ozonation and UV/H_2O_2 systems proved to be effective in diclofenac degradation. In other study, they have reported that UV/H_2O_2 process could degrade carbamazepine very effectively, while UV alone process was not effective for reducing carbamazepine concentration [17]. Therefore, the effect of H_2O_2 addition during UV process on the removal of pharmaceuticals in secondary effluent was examined.

Fig. 4 compares removal efficiency of the 41 pharmaceuticals obtained in UV and UV/H_2O_2 processes for HRT of 5 min (R1). In this study, a goal of 90% removal efficiency was set to compare the performance for pharmaceuticals removal of each process. During UV/H_2O_2 process, a 90% removal efficiency could be accomplished in most of the tested pharmaceuticals except norfloxacin (69%) and caffeine (67%) at R1 (Fig. 4), indicating that H_2O_2 addition contributed considerably to the removal of pharmaceuticals during UV process. The concentrations of norfloxacin and caffeine decreased by below LODs (0.84 and 0.15 μg/L, respectively) at R1 during UV alone process. However, the removal efficiencies of the 2 compounds were low to 69% and 67%, respectively at R1 during UV/H_2O_2 process. This might be due to the very low initial concentrations (initial concentration: 5 and 21 ng/L for norfloxacin and caffeine, respectively). In this study, each sample was concentrated by a factor of 1000 for pharmaceutical quantification with LC/MS/MS because of quite low concentration of ng/L order. This

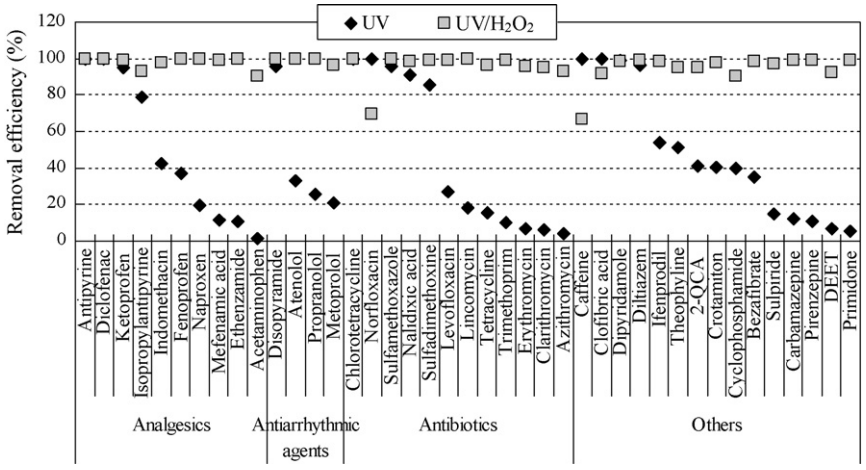

Fig. 4. Removal efficiency of the 41 pharmaceuticals detected during UV and UV/H_2O_2 processes for HRT of 5 min.

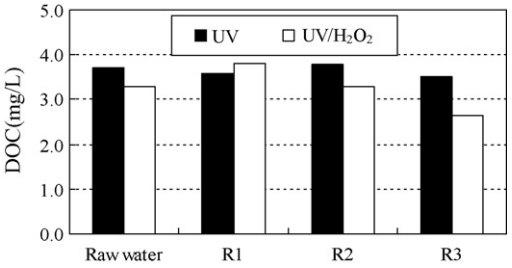

Fig. 5. Variation of DOC concentration during UV and UV/H_2O_2 processes.

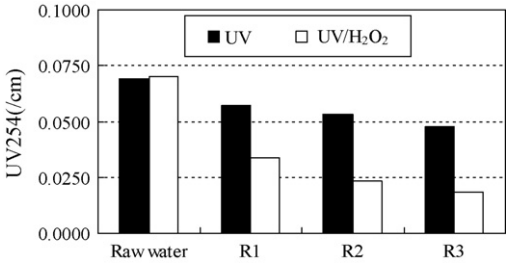

Fig. 6. Variation of UV254 during UV and UV/H_2O_2 processes.

high concentration ratio could cause analytical variation during the measurement of a compound's concentration, especially for compounds with very low concentrations. Consequently, it is thought that the analytical variation resulted in higher removal efficiencies of norfloxacin and caffeine for UV process than for UV/H2O2 process.

3.4. Variation of DOC, UV_{254} absorbance and H_2O_2 concentration during UV and UV/H_2O_2 processes

A little variation in DOC concentration (Raw water: 3.7 mg/L, effluent from R3: 3.5 mg/L) was found (Fig. 5), and UV_{254} absorbance also decreased slightly (Raw water: 0.0691 cm^{-1}, effluent from R3: 0.0480 cm^{-1}) during UV process (Fig. 6), implying that some other compounds including pharmaceuticals with unsaturated bonds still remain in the effluent from R3. Therefore, it can be said that considerable UV energy will be needed for good pharmaceuticals removal efficiency by UV process. While, it was observed that DOC concentration for UV/H_2O_2 process decreased more remarkably than for UV process (Raw water: 3.3 mg/L, effluent from R3: 2.6 mg/L) due to the contribution of OH radicals and direct UV photolysis (Fig. 5). For the UV/H_2O_2 process, UV_{254} absorbance values decreased significantly in comparison with for UV process (Raw water: 0.0702 cm^{-1}, Effluent from R1, R2 and R3: 0.0340, 0.0234 and 0.0182 cm^{-1}, respectively), and especially, even about 70% UV_{254} absorbance reduction was found at R1 (Fig. 6). This seems to be related to removal efficiency of more than 90% for most of pharmaceuticals at R1. Therefore, it was thought that the removal of pharmaceuticals in water might be related to the decrease of UV_{254} absorbance value. On the other hand, initial H_2O_2 concentration in tested water was 7.8 mg/L for the UV/H_2O_2 process. During the experiment, 1.6, 1.4 and 1.3 mg/L of added H_2O_2 were consumed in R1, R2 and R3, respectively, and finally 3.5 mg/L H_2O_2 remained in effluent from R3 (Fig. 7), which means that appropriate dose of H_2O_2 should be investigated in further studies for the reduction of H_2O_2 used in WWTP as well as the achievement of an effective pharmaceuticals removal efficiency.

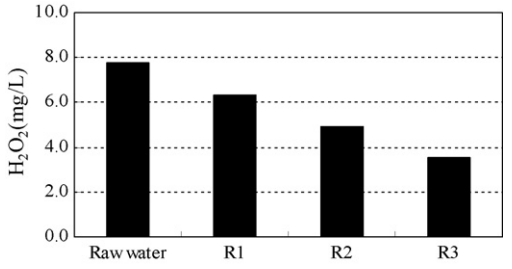

Fig. 7. Variation of H_2O_2 concentration during UV/H_2O_2 process.

4. Conclusion

The effectiveness of UV-based processes (UV and UV/H_2O_2) for the removal of pharmaceuticals in secondary effluent was investigated. 41 kinds of pharmaceuticals including 12 antibiotics and 10 analgesics were detected in secondary effluent used for tested water. Among 41 pharmaceuticals, 29 were not removed effectively in spite of considerable UV dose of 2768 mJ/cm^2 during UV process. Therefore, it was thought that a good pharmaceuticals removal can not be expected by UV process applied for the disinfection of treated water in wastewater treatment plants because UV doses of 40–140 mJ/cm^2 are usually used for the water disinfection as mentioned above. For UV/H_2O_2 process, 90% removal efficiency could be accomplished in 39 pharmaceuticals at UV dose of 923 mJ/cm^2. This means that it is possible to reduce UV energy required for the effective pharmaceuticals removal by the combination of H_2O_2 with UV process.

Acknowledgements

This study was funded by Ministry of Environment of Japan and Japan society for the promotion of science. The authors would like to thank Mr. Iwasaki, Mr. Yoshino and Mr. Takubo of Iwasaki Electrics for their cooperation.

References

[1] T. Heberer, Occurrence, fate and removal of pharmaceutical residues in the aquatic environment: a review of recent research data, Toxicol. Lett. 131 (2002) 5–17.
[2] T. Smital, T. Luckenbach, R. Sauerborn, A.M. Hamdoun, R.L. Vega, D. Epel, Emerging contaminants-pesticides, PPCPs, microbial degradation products and natural substances as inhibitors of multixenobiotic defense in aquatic organisms, Mutat. Res. 552 (2004) 101–117.
[3] B. Halling-Sørensen, S.N. Nielsen, P.F. Lanzky, F. Ingerslev, H.C.H. Lutzhoft, S.E. Jorgensen, Occurrence, fate and effects of pharmaceutical substances in the environment—a review, Chemosphere 36 (1998) 357–393.
[4] R. Kanda, P. Griffin, H.A. James, J. Fothergill, Pharmaceutical and personal care products in sewage treatment works, J. Environ. Monit. 5 (2003) 823–830.
[5] T.A. Ternes, Occurrence of drugs in German sewage treatment plants and rivers, Water Res. 32 (1998) 3245–3260.
[6] C.G. Daughton, T.A. Ternes, Pharmaceuticals and personal care products in the environment: agents of subtle hange? Environ. Health Persp. 107 (1999) 907–938.
[7] N. Nakada, T. Tanishima, H. Shinohara, K. Kiri, H. Takada, Pharmaceutical chemicals and endocrine disrupters in municipal wastewater in Tokyo and their removal during activated sludge treatment, Water Res. 40 (2006) 3297–3303.
[8] T. Okuda, Y. Kobayashi, R. Nagao, N. Yamashita, H. Tanaka, S. Tanaka, S. Fuji, C. Konishi, I. Houwa, Removal efficiency of 66 pharmaceuticals during wastewater treatment process in Japan, Water Sci. Technol. 57 (2008) 65–71.
[9] G. Mascolo, R. Ciannarella, L. Balest, A. Lopez, Effectiveness of UV-based advanced oxidation processes for the remediation of hydrocarbon pollution in the groundwater: a laboratory investigation, J. Hazard. Mater. (2007), doi:10.1016/j.jhazmat.2007.07.120.
[10] S. Canonica, L. Meunier, U.V. Gunten, Phototransformation of selected pharmaceuticals during UV treatment of drinking water, Water Res. 42 (2008) 121–128.
[11] M.H. Plumlee, M. Lopez-Mesas, A. Heidlberger, K.P. Ishida, M. Reinhard, *N*-nitrosodimethylamine (NDMA) removal by reverse osmosis and UV treatment and analysis via LC-MS/MS, Water Res. 42 (2008) 347–355.
[12] A. Lopez, B. Anna, M. Giuseppe, K. John, Kinetic investigation on UV and UV/H_2O_2 degradations of pharmaceutical intermediates in aqueous solution, J. Photochem. Photobiol. A 156 (2003) 121–126.
[13] D. Vogna, R. Marotta, A. Napolitano, R. Andreozzi, M. d'Ischia, Advanced oxidation of the pharmaceutical drug diclofenac with UV/H_2O_2 and ozone, Water Res. 38 (2004) 414–422.

[14] A.N. Baga, G.R.A. Johnson, N.B. Nazhat, R.A. Saadalla-Nazhat, A simple spectrophotometric determination of hydrogen peroxide at low concentrations in aqueous solution, Anal. Chem. Acta 204 (1988) 349–353.
[15] Y. Kobayashi, T. Okuda, N. Yamashita, H. Tanaka, S. Tanaka, S. Fuji, C. Konishi, I. Houwa, The occurrence of pharmaceuticals during advanced wastewater treatment, Environ. Eng. Res. Jpn. 43 (2006) 65–72.
[16] I.H. Kim, H. Tanaka, T. Iwasaki, T. Takubo, T. Morioka, Y. Kato, Classification of the degradability of 30 pharmaceuticals in water with Ozone, UV and H_2O_2, Water Sci. Technol. 57 (2008) 195–200.
[17] D. Vogna, R. Marotta, R. Andreozzi, A. Napolitano, M. d'Ischia, Kinetic and chemical assessment of the UV/H_2O_2 treatment of antiepileptic drug carbamazepine, Chemosphere 54 (2004) 497–505.