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Efficacies of UVC and VUV photolysis for mineralization of pharmaceutical compounds in mixed aqueous solution

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ABSTRACT

The usefulness of ultraviolet-C (UVC: 254 nm) and vacuum UV (VUV: 185 + 254 nm) photolysis for elimination and mineralization of four selected pharmaceutical compounds (PhCs) in mixed aqueous solution were tested in laboratory batch experiments. UVC photolysis was unable to eliminate moderate and refractory PhCs. Moreover, it was not at all useful for mineralization of the PhCs (<10% TOC removal, 30 min reaction) and longer reaction period (i.e. 60 min) had no significant positive impact on the mineralization efficiency. On the other hand, VUV photolysis eliminated the PhCs almost completely in a short reaction period irrespective of their nature, and 90% mineralization was achieved in an hour. The greatly enhanced elimination and mineralization efficiencies for VUV photolysis were attributed to accelerated direct and indirect photolysis reactions. Based on the results, it was concluded that VUV photolysis was very promising over UVC photolysis for mineralization of PhCs in mixed aqueous solution. However, more studies are necessary for practical applicability of the method in wastewater treatments.

Keywords: Direct photolysis; Hydroxyl radical; Kinetics; Reaction period; TOC removal

1. Introduction

Pharmaceutical compounds (PhCs) are ubiquitously found in wastewater streams, treated effluents particularly from conventional wastewater treatment plants, and receiving waters [1–5]. Unlike perfluorinated compounds, ever increasing production and uses of PhCs are expected to result in increasing loads of the compounds to wastewater treatment plants and down to receiving waters. A number of published articles [6,7] have indicated potential negative impacts of PhCs present in water environment to aquatic ecosystem and human/animal health.

Advanced oxidation technologies (AOTs) like ultraviolet (UV) photolysis and ozonation have been successfully used as secondary/tertiary treatments in conventional wastewater treatment plants in combating

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Presented at the 5th IWA-ASPIRE Conference, 8–12 September 2013, Daejeon, Korea the pollution problem [3,6,8–11]. Among the AOTs, UV photolysis has been extensively tested and employed in water and wastewater treatment processes [8,9,12–17]. Moreover, 254 nm (i.e. UVC) is the most commonly used wavelength in these applications due to relatively high absorption of the wavelength by a large number of organic micro-pollutants in aqueous solution and technological considerations. Although radiation in vacuum UV (VUV) region is expected to be more effective than UVC for the degradation, there are few published articles on VUV usage for such purposes [18–20] presumably due to technological and cost considerations. Therefore, efficacy of VUV photolysis for such purposes has remained largely unknown.

Mere elimination of parent organic compounds in treated effluents does not imply their mineralization. A number of intermediates are generated during UV photolysis of PhCs before they are completely mineralized to inorganic products. A few cases of intermediates from UVC photolysis of PhCs being more harmful than the parent compounds are also reported [13]. Therefore, mineralization of the target compounds should be the goal of UV photolytic degradation technology particularly as a tertiary treatment method. Despite increasing uses of UVC photolysis in wastewater treatment, its efficacy for mineralizing recalcitrant PhCs in treated effluents is hardly understood due to very low concentrations (e.g. ng/L) of the compounds and their residues, while toxicity tests are often conducted to assess safety of treated effluents [2,11,14].

In our earlier investigation, UVC (254 nm) and VUV (185 + 254 nm) photolysis tests, of 16 PhCs very frequently found in wastewater streams, treated effluents, and receiving waters, were conducted in mixed solutions in different waters (unpublished data). The tested compounds were grouped into four categories based on their removal efficiencies by UVC photolysis in pure water (removal > 90%: clofibric acid, diclofenac, fenofrofen, isopropylantipyrine, ketoprofen, phenytoin, and triclosan; 50% < removal < 90%: ibuprofen, indomethacin, and naproxen; 30% < removal < 50%: phenacetin and triclocarban; and removal < 30%: clarithromycin, carbamazepine, erythromycin, and gemfibrozil). However, their mineralization in terms of organic carbon removal was not assessed, because stock solutions of the compounds were prepared in methanol due to very small water solubility for some of them. Out of the 16 PhCs, four water soluble compounds (one from each group) were selected for mineralization tests in this study. The objective of this investigation is to compare usefulness of UVC and VUV photolysis for elimination and mineralization of the four selected PhCs in water as a continuation of our earlier investigation. Bench-scale laboratory tests on UVC and VUV photolysis of the four PhCs, in mixed solutions, in ultrapure water were carried out with organic carbon measurement.

2. Materials and methods

2.1. Standards and reagents

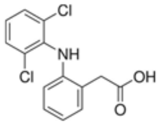
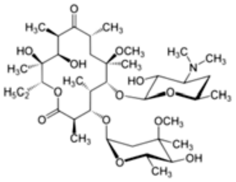
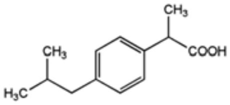
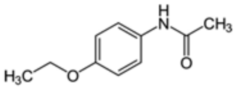
Names, acronyms, uses, and important physicochemical characteristics of the four tested PhCs are given in Table 1. Standards of the PhCs were purchased from Wako Pure Chemicals Ltd. All other necessary reagents like acetonitrile, formic acid, ammonium acetate etc. were also purchased from Wako Pure Chemicals Ltd. All the standards and reagents were used as received without further purification. Unlike in our earlier investigation, stock solutions of each of the PhCs (concentrations lower than the corresponding water solubility values, Table 1) were prepared separately in ultrapure water and stored in a refrigerator (≈4℃) for further use.

2.2. Irradiation source, reactor setup, and test procedure

A low pressure UV lamp (UVL20PS-6, 20 W, SEN Lights Corporation, Japan) emitting 185 and 254 nm wavelengths was used as irradiation source. The measured average intensities of the wavelengths at outer surface of the lamp were 5.05 and 9.15 $\mathrm{mW/cm^2}$, respectively.

Schematic diagrams of reactor setup and lamp sleeves used in this investigation are shown in Fig. 1. A cylindrical Pyrex glass reactor (ID: 9.8 cm, h: 20 cm, *V*: 1.5 L) with a circular central port and four surrounding small ports was used in all the photolytic degradation tests. A tubular lamp sleeve made of glass was inserted vertically down through the central port while the small size ports were used for other purposes. Two different types of lamp sleeves were used to control UV transmission into reaction solution. The first type of lamp sleeve was double-layered made of fused silica glass transmitting 254 nm wavelength only. Water was continuously circulated between the two layers to prevent 185 nm wavelength transmission (if any) into reaction solution and maintain reaction solution temperature. The second type of lamp sleeve was single-layered made of synthetic fused silica glass transmitting both 254 and 185 nm wavelengths to reaction solution. In this case, the solution temperature was maintained by circulating water through a tightly coiled thin rubber tube around the glass reactor. Additionally, cool air was blown down continuously from top of the reactor for maintaining reaction solution temperature in both cases.

Table 1
Tested PhCs, acronyms, and their properties

Compound	Diclofenac	Erythromycin	Ibuprofen	Phenacetin
Acronym	DCF	ERM	IBP	PNC
Type	Nonsteroidal	Antibiotic	Pain reliever	Antipyretic
MF	$C_{14}H_{10}Cl_2NNaO_2$	$C_{37}H_{67}NO_{13}$	$C_{13}H_{18}O_2$	$C_{10}H_{10}O_2N$
MW	318.13	733.93	206.28	179.22
WS	2430.0	1000.0	21.0	766.0
pK_a	4.10	8.90	4.91	2.20
$\log K_{ow}$	0.70	3.06	3.97	1.58
$\varepsilon 254$	3499.4	–	1237.7	1245.4
MS				

MF: molecular formula, MW: molecular weight (g/mol), WS: water solubility (mg/L), ε_{254}: molar extinction coefficient at 254 nm wavelength ($M^{-1}\,cm^{-1}$), and MS: molecular structure.

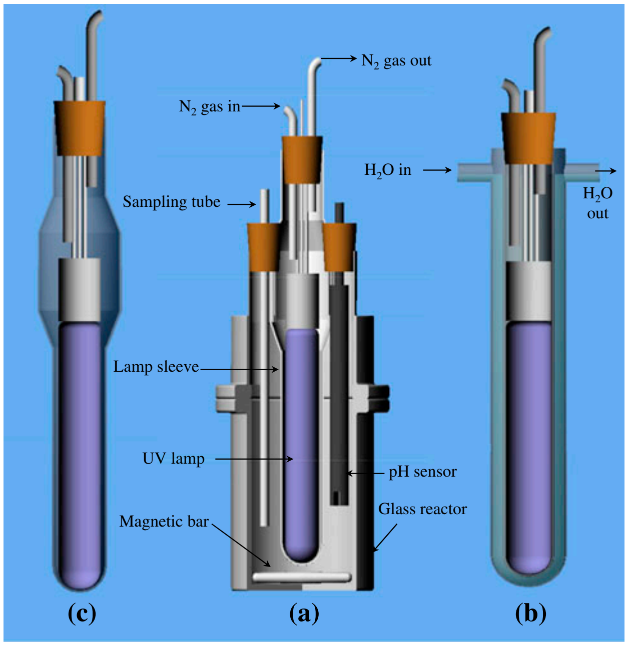


Fig. 1. Schematic diagrams of (a) reactor setup, (b) double-layered fused silica glass sleeve with water circulation between the layers, and (c) single-layered synthetic fused silica glass sleeve.

Mixed reaction solutions of the four PhCs (about 1.0 mg/L of each compound) were prepared in pure water using stock solutions of the compounds. About 1.4 and 1.2 L reaction solutions were used for the tests with single- and double-layered lamp sleeves, respectively. Each of the tests was carried out for 30 and 60 min reaction periods, and samples were drawn at selected time intervals for analysis. The reaction periods were decided based on preliminary photolysis test results. Solution pH was not adjusted in any of the tests while temperature of reaction solution was maintained between 20 and 23℃.

2.3. Analytical methods

Solution pH and temperature were continuously monitored using sensors (Mettler Toledo). Total organic carbon (TOC) contents in the samples were measured using a TOC analyzer (TOC-$V_{CSH/CSN}$, Shimadzu Corporation, Japan) with high sensitivity catalyst for low TOC samples. The lamp emission intensities for 185 and 254 nm wavelengths were measured using UV Power Meter C8026 (Hamamatsu Photonics K.K., Japan) with sensor heads H8025-185 and H8025-254, respectively.

Concentrations of PhCs in photolyzed water samples were determined by liquid chromatography coupled with tandem-mass spectrometry (LC-MS/MS, Applied Biosystems). A binary pump, autosampler and degasser units (Agilent 1100 series) constituted the LC system. Chromatographic separation was carried out using ZORBAX Eclipse XDB-C18 column (2.1 150 mm, 3.5 m) with 200 L/min mobile phase flow rate, 10 L sample volume, and 40℃ column oven temperature. The DCF and IBP were scanned in negative ion mode using 0.1% acetic acid (v/v) in 2.0 mM ammonium acetate in ultrapure water (A_1) and acetonitrile (B_1) as mobile phases in LC gradient elution. The measurement started with 95% of A_1 that remained unchanged until 0.5 min. It then decreased linearly to 2% at 7.0 min and remained so until 15.0 min. It then increased again to 95% at 15.1 min and remained so until 20 min ending the measurement. The ERM and PNC were scanned in positive ion mode using 0.1% formic acid (v/v) in ultrapure water (A_2) and acetonitrile (B_1) as mobile phases in LC gradient elution. The measurement started with 90% of A_2 that remained unchanged until 2.0 min. Then, it linearly decreased to 0% at 7.0 min and remained so until 15.0 min. It then increased again to 90% at 15.1 min and remained so until 20.0 min ending the measurement. A turbo ion spray was used as ion source and mass detection was performed in multiple reactions monitoring mode. The monitored mass numbers for DCF, ERM, IBP, and PNC were 295.8/251.5, 734.4/158.2, 205.0/160.9, and 180.1/110.0, respectively. The compounds were quantified using the corresponding five-point (0–100 g/L) linear calibration curves.

3. Results and discussion

Three replicate tests were conducted for each case, and their average value was taken as the final result. Two sets of UV wavelengths were utilized in these tests. The terms “UVC” and “VUV” used in the following sections represent the single wavelength (254 nm) and combined wavelengths (254 + 185 nm) respectively.

3.1. Characteristics of PhCs

The selected PhCs used in this study belong to different therapeutic groups (Table 1) and characterized by the presence of more than one functional group (e.g. ketone, carboxyl, hydroxyl, and methyl) in their molecules. The DCF and IBP, respectively, have the highest and lowest water solubility while the values for other two are moderate. The compounds are in general hydrophilic, DCF being the most hydrophilic followed by PNC among the four. The initial pH values of mixed solutions of PhCs in pure water varied between 5.6 and 5.7, which decreased to about 5.3 at the end of 60 min photolysis tests. The pK_a values (Table 1) indicate that the PhCs (excluding ERM) remained mostly in their undissociated states for the pH range observed during the tests.

3.2. Elimination of PhCs

Removal ratios for the selected compounds due to UV photolysis are shown in Fig. 2. In our earlier study (unpublished data), IBP and PNC (62.93 and 38.44% removal ratios for 30 min reaction) were grouped into two different categories as mentioned at the end of “Introduction” section of this article. But, IBP exhibited very similar removal ratio value to that of PNC for UVC photolysis in the present study (Fig. 2). It should be noted here that the experimental conditions in these two cases were same except the number of PhCs in mixed reaction solutions (sixteen in earlier study and four in the present) and presence of a very small fraction of methanol (<0.2% by volume) in mixed reaction solutions in the earlier study as stock solutions of the PhCs were prepared in methanol. The big difference in IBP removal ratios in these two cases could be the indication that interactions among organic compounds in mixed reaction solutions highly influence their photochemical behaviors during UV photolysis [14]. The DCF was eliminated completely by UVC photolysis in 30 min reaction. Doubling the UVC photolysis period increased the ratio values by 2.3, 1.8, and 1.8-folds respectively for ERM, IBP, and PNC. All the four PhCs were eliminated completely (>99.9%) irrespective of the two reaction periods in case of VUV photolysis. It is apparent that VUV photolysis was very effective than UVC photolysis to eliminate the target PhCs in mixed aqueous solutions in a short reaction time irrespective of their (PhCs) nature. But, nature of the target PhCs and reaction time were very important for their elimination by UVC photolysis.

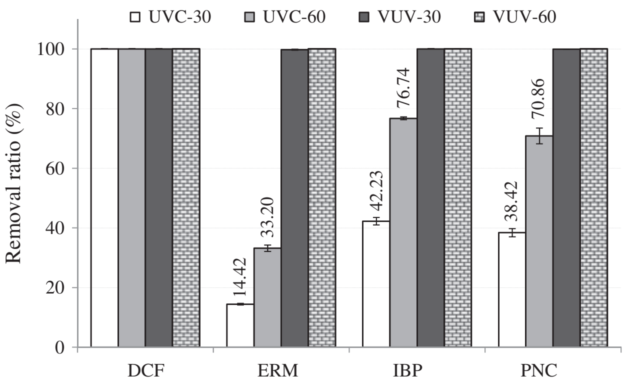


Fig. 2. PhCs removal efficiencies for UVC and VUV photolysis in ultrapure water (UVC: 254 nm, VUV: 185 + 254 nm, and the numbers “30” and “60” in legend represent reaction periods in minutes).

Reactor design, UV intensities, and other test conditions are key points that should be kept in mind while comparing results of different authors. An earlier investigation [16] on UVC photolysis of a mixture of PhCs achieved 27.4% of IBP removal (reaction time not mentioned), which is significantly smaller than the value observed in this study (42.2%). Kim and Tanaka

[19] also found VUV photolysis being superior to UVC photolysis in eliminating the tested PhCs (10 min reaction) in mixed solutions, and Clarithromycin and Carbamazepine were refractory to UVC photolysis.

3.3. Removal kinetics and rate

The eliminations of PhCs due to UV photolysis in this study were fitted to the zero, first, and second-order reaction kinetics. The zero-order kinetics described the eliminations very poorly ($R^2 < 0.70$) while the other two kinetics fitted well to the data ($R^2 \geq 0.90$). Similar to earlier investigation results [16,18,19], the first-order kinetics better described the eliminations, and hence it is used for discussing elimination behaviors of the PhCs in this article. The apparent first-order removal rate values for the PhCs are shown in Table 2. The ERM is the most refractory to UVC photolysis while DCF is the most easily eliminated one among the four PhCs. The removal rate values for VUV photolysis increased very significantly compared to those for UVC photolysis. The increments were about 104, 49, 50, and 2-folds, respectively, for ERM, IBP, PNC, and DCF. Moreover, increased reaction period enhanced the rate values (except for DCF) for both UVC and VUV photolysis, but the increments were about 1.3-fold only. This showed that selection of UV wavelengths is more critical than extended reaction periods for efficient elimination of PhCs by UV photolysis. The different behavior of DCF (i.e. decreased removal rate values for longer reaction period) is attributed mainly to very fast depletion of the compound in reaction solution and longer sampling interval in the beginning of 60 min reaction (0, 5, 10, 15, 20, 30, and 60) compared to that for 30 min reaction (0, 2, 5, 10, 15, 20, and 30). The observed first-order reaction rate values for UVC photolysis of IBP in this study ($1.06\,h^{-1}$, 30 min reaction) was very close to the value ($1.08\,h^{-1}$) obtained by Yuan et al. [16]. The results of this study demonstrated that VUV photolysis was far superior to UVC photolysis with extended reaction period to eliminate moderate and refractory PhCs in mixed aqueous solutions.

3.4. UV wavelength and PhCs mineralization

The VUV photolysis was far superior to UVC photolysis in eliminating moderate and recalcitrant PhCs in water in the results presented so far. The disappearance of parent PhCs in treated effluents doesn’t mean their mineralization while the final goal of wastewater treatment is mineralization of the target compounds. Fig. 3 shows organic carbon removal efficiencies for UVC and VUV photolysis of the four PhCs in terms of calculated organic carbon removal in parent PhCs and measured TOC values. Less than 50% of organic carbon in parent PhCs was removed during 30 min UVC photolysis reaction and the corresponding TOC removal was 9.3% only. Increasing reaction period by 200% increased the removal of organic carbon in parent PhCs by 1.5-fold, but the corresponding TOC removal did not increase very significantly (<1.0%). On the other hand, VUV photolysis removed organic carbon in parent PhCs almost completely in 30 min and the corresponding TOC removal was also about 6.5-fold of the UVC photolysis. Doubling the VUV photolysis period greatly enhanced TOC removal (about 8.9-fold of UVC-60 and 1.5-fold of VUV-30 cases). However, the PhCs were still not completely mineralized. There are only a few published data on mineralization of PhCs by UVC and VUV photolysis so far for comparison. Szabo [18] showed higher efficacy of VUV photolysis over UVC photolysis in terms of mineralization of two PhCs (IBP and KEP, high initial concentrations, 60 min reaction) in mixed solution. Rivas et al. [14] achieved 30 to 40% TOC removals for UVC/H_2O_2 and UVC/monopersulfate photolysis of six PhCs spiked in urban wastewater (each PhC = 5–15 ppm, 3-h reaction). Thus, it may be apparent that VUV photolysis could be a better alternative to UVC/H_2O_2 oxidation in terms of elimination and mineralization of PhCs. Szabo [18] illustrated VUV photolysis being superior to UVC photolysis for mineralizing IBP, KEP, and NPX in mixed solutions. The results of

Table 2
Average ($n = 3$) apparent first-order removal rates (h^{-1}) for UV photolysis of PhCs

	DCF		ERM		IBP		PNC	
Reaction time	UVC	VUV	UVC	VUV	UVC	VUV	UVC	VUV
30 min	66.53 (4.93)	160.21 (8.11)	0.31 (0.01)	32.41 (5.43)	1.06 (0.04)	52.11 (4.52)	0.91 (0.03)	50.56 (2.86)
60 min	62.33 (8.62)	85.22 (6.36)	0.40 (0.02)	41.77 (3.97)	1.39 (0.05)	79.09 (3.80)	1.17 (0.11)	58.66 (7.15)

UVC: 254 nm alone; VUV: 185 + 254 nm; and the values within parenthesis are standard deviations.

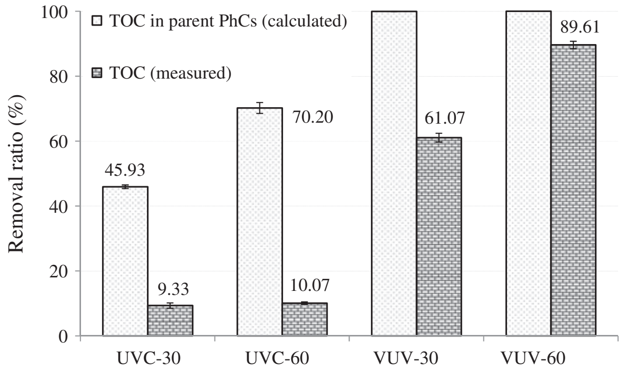


Fig. 3. Organic carbon removal efficiencies for UVC and VUV photolysis of PhCs in ultrapure water (UVC: 254 nm, VUV: 185 + 254 nm, and the numbers "30" and "60" in legend represent reaction periods in minutes).

this study unequivocally demonstrated that UVC photolysis was not useful for complete mineralization of the PhCs in water while VUV photolysis was very promising for that purpose.

It is generally accepted that two types of photolysis reactions are involved in UV oxidation of target/non-target organic compounds in water. Molecular bonds of the compounds are cleaved due to quantum energy transfer from UV photons to the molecules in direct photolysis reaction, while reactive radical species (e.g. hydroxyl radical: ${}^{\cdot}$OH) are generated due to UV energy absorption by water and photosensitive organic substances (e.g. natural organic matter: NOM), and those radical species react with the target/non-target molecules in indirect photolysis reaction as illustrated in the following equations.

$$\text{hv} + \text{PhCs} \rightarrow \text{Products (direct photolysis)} \quad (1)$$

$$\text{hv} + \text{H}_2\text{O} \rightarrow \text{HO}^{\cdot} + \text{H}^{\cdot} \quad (2)$$

$$\text{HO}^{\cdot} + \text{PhCs} \rightarrow \text{Products (indirect photolysis)} \quad (3)$$

A VUV (185 nm) photon contains 1.4-fold larger energy of a UVC (254 nm) photon. Therefore, it is more likely that direct photolysis of PhCs with VUV is considerably faster than with UVC. Moreover, VUV radiation is almost exclusively absorbed by water due to high VUV absorption cross-section of water resulting in formation of abundant ${}^{\cdot}$OH (Eq. (2)) and leading to enhanced indirect photolysis reaction. The relatively large removal of the tested compounds (33–99.9%, Fig. 2) and the corresponding very small TOC removal (~10%, Fig. 3) for UVC photolysis indicated formation of more resistant intermediates [2,13] although the intermediates were not analyzed and monitored in this study. The inefficiency of UVC photolysis reaction should be attributed to low photon energy of 254 nm wavelength coupled with lack of sufficient ${}^{\cdot}$OH generation in the reaction system. On the other hand, the, almost, complete removals and very high mineralization of the PhCs by VUV photolysis should be attributed to accelerated direct and indirect photolysis reactions. With these results, it is apparent that VUV photolysis is very promising than UVC photolysis for elimination and mineralization of PhCs in wastewater treatment. Nevertheless, more studies are necessary to assess its suitability for practical applications.

4. Conclusions

The conclusions of this study are as follows:

(1) The competitive interaction among co-existing PhCs in simulated mixed reaction solution possibly influenced photochemical behaviors of the compounds particularly in UVC photolysis.
(2) UVC photolysis in general was useful in eliminating PhCs. But, it could not efficiently degrade moderate (e.g. ibuprofen) and refractory (e.g. erythromycin) PhCs.
(3) Despite relatively higher efficiencies of UVC photolysis in eliminating the PhCs, the corresponding mineralization efficiency was extremely low (<10% TOC removal, 30 min reaction), while longer reaction period (e.g. 60 min) did not have a significant positive impact on the mineralization efficiency.
(4) On the other hand, VUV photolysis very easily degraded the PhCs in a short reaction period irrespective of their nature, and about 90% mineralization was achieved within an hour.
(5) The greatly enhanced elimination and mineralization efficiencies with VUV photolysis were attributed to high photon energy of 185 nm wavelength and formation of abundant hydroxyl radicals due to very high VUV absorption cross-section of water leading to accelerated direct and indirect photolysis reactions, respectively.
(6) The results demonstrated that VUV photolysis would be very promising than UVC photolysis for elimination and mineralization of various types of PhCs in mixed aqueous solution. However, more studies are required

to assess practical applicability of VUV photolysis in wastewater treatments.

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