Application of UVC-LED/H$_2$O$_2$ in wastewater treatments: treatment efficacy on disinfection byproduct precursors and micropollutants

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Abstract

The applications of advanced oxidation processes (AOPs) for controlling microcontaminants are essential to meet the water quality criteria for potable or nonpotable water reuses. The objective of this study is to demonstrate the application of light emitting diode (LED) as a possible light source to substitute traditional low-pressure mercury lamp (LPUV) in UV/H$_2$O$_2$ processes in treating precursors of disinfection byproducts (DBPs) and pharmaceutical and personals care products (PPCPs) in wastewater. The results of this study revealed that UV fluence plays the most crucial role in the efficiency of UV/H$_2$O$_2$. At the same time, the initial concentration of H$_2$O$_2$, dissolved organic carbon (DOC), and turbidity had minimal effects, except that poor efficiency result of UV/H$_2$O$_2$ was observed at a solution with low DOC concentration (2.4 mg L^{-1}). Although the concentrations of organic matter decreased after UV/H$_2$O$_2$ treatment, the concentration of precursors of DBPs increased in the early stage of the photolysis process and decreased after that; moreover, the profiles of precursors for trihalomethanes and haloacetic acids were different. A comparison between LPUV and UVC-LED as light sources revealed that, at a fixed UV fluence input into the UV/H$_2$O$_2$ process, the trends and efficiencies in the degradation of organic matter and DBP precursors were similar. Meanwhile, the photoelectric conversion efficiency of UVC-LED should be improved for future applications in water treatment. Based on the UV/H$_2$O$_2$ treatment results on synthetic PPCPs wastewater solution, this study showed the effectiveness of UV/H$_2$O$_2$ to degrade micro organic contaminants.

Keywords Advanced oxidation process (AOPs), Light emitting diode (LED), Pharmaceutical and personals care products (PPCPs), Disinfection byproducts (DBPs)

1 Introduction

Advanced oxidation process (AOPs) is a promising technique for the wastewater treatment plants to meet the criteria and standards of water quality. AOPs are efficient in reducing the concentrations of organic compounds in wastewater, despite the defect of high maintenance cost of ultraviolet (UV) lamp illumination for AOPs which involve UV light. UV/H$_2$O$_2$ treatment process effectively removes certain organic contaminants, especially micropollutants [1, 2]. Currently, regulations and studies related to wastewater are more focused on outcomes such as chemical oxygen demand, biological oxygen demand, ammonia and pathogens reduction, formation of disinfection byproducts (DBPs) due to chlorination in the last stage of wastewater treatment are often neglected despite their toxicity effects to the aquatic system [3]. As many countries have carried out wastewater reclamation programs in coping with the growing water shortage

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crisis, the performances of wastewater treatment techniques to remove specific emerging contaminants and DBP precursors in wastewater should be assessed [4, 5]. Although UV/H_2O_2 process has shown prominent efficiency in organic contaminant degradation, the electrical cost for the generation of UV light is one of the issues for this technique not to be widely used in water/wastewater treatments; therefore, the rising technique of light-emitting diodes (LEDs) could be a solution for this technique to be more energy conserve and mercury-free eco-friendly in future [6, 7].

Chlorination is essential to inactivate pathogens in wastewater before its discharge into the aquatic environment or to be further reused [8]. Wastewater which comprises natural organic matter (NOM) and synthetic organic compounds such as pharmaceutical personal care products (PPCPs), could efficiently react with free chlorine to form DBPs or halogenated compounds [9]. Based on the different characteristics of municipal wastewater and wastewater treatment techniques, DBP formation potential (DBPFP) tests are tools to evaluate water treatments' effectiveness and predict the possible DBP species formed in a chlorination reaction [10]. Trihalomethanes (THMs) and haloacetic acids (HAA) are among the known major DBPs that can be detected in chlorinated water; many studies reported that THM precursors are more hydrophobic than HAA precursors, and water treatment techniques to remove hydrophilic or hydrophobic content are crucial to the proportion of THMs and HAAs formed [11].

UV/H_2O_2 process, with forming of hydroxyl radical (•OH) by direct photolysis of H_2O_2 with ultraviolet, these OH radicals are capable of degrading and mineralizing dissolved organic matters (DOM), which including DBP precursors and PPCPs in wastewater [12–14]. The performance of UV/H_2O_2 might be altered by the dose of H_2O_2, the irradiance of ultraviolet, pH, and turbidity of the matrix [15]. The complexity of wastewater elevated the challenges for UV/H_2O_2 to be applied in wastewater treatments; however, UV/H_2O_2 process effectively diminishes micropollutants, especially PPCPs, which are highly abundant in the wastewater [16, 17]. The removal efficacy of PPCPs in wastewater using UV/H_2O_2 can achieve up to 90% on average for PPCPs from the range of ng L^{-1} to mg L^{-1} in wastewater [15].

The vision to eliminate mercury products by the year 2020 based on the Minamata Convention on Mercury, had extensively promoted the rapid progress of LED manufacturing techniques in UVC region, becoming a possible substitute for mercury lamps [18, 19]. Numerous studies have used a UV-light emitting diode (LED) as the UV source alternative to the traditional mercury lamp, which also showed an equivalent effect as a mercury lamp in either chemical abatement or pathogen inactivation in water treatment processes [20–22]. The advantages of LED include a customized light bandwidth, no warm-up time, no mercury, reactor design flexibility owing to the small unit (chip) size, and simple DC power requirements, which allows the UV-LED to be driven by batteries or solar cells and extends its life [23].

Although many studies of UV-LED on water treatment have been reported, most of them have focused on microbial inactivation or on the degradation of specific contaminants coupled with chlorine (UV/Cl_2), study using UV-LED on UV/H_2O_2 is still limited. This study aims to assess the potential use of a UVC-LED as an alternative to a traditional low-pressure UV (LPUV) lamp in the UV/H_2O_2 treatment process for further purification of wastewater effluents. The efficiency of UV/H_2O_2 treatment on DOM, DBP precursors, and PPCPs were demonstrated.

2 Materials and methods
2.1 Sample collection
Water samples of unchlorinated secondary effluent were collected from a local municipal wastewater treatment plant in Taipei, Taiwan. The water samples were set still for 4 h in a laboratory, and the supernatant was collected and stored at 4 °C until further uses in UV/H_2O_2 processes.

2.2 Materials and methods
The UV/H_2O_2 system consisted of a 2 L glass reaction chamber and a UV light source. A designated amount of H_2O_2 was added to the samples before the samples were illuminated with UV light. The water samples were mixed homogenously with a stirrer during the UV photolysis. The image of the UV/H_2O_2 system used in this study is shown in Fig. S1 in the Supplementary Information (SI).

Three UV light sources were assessed in this study, including two LED modules [LED (A): 40 LEDs@280 nm; LED (B): 384 LEDs@275 nm] and a 15-W LPUV. The averaged irradiance [0.33 mW cm^{-2} for LED (A), 4.08 mW cm^{-2} for LED (B), and 14.8 mW cm^{-2} for LPUV] was measured using a radiometer (RM-12, OPSYTEC). Fluence (UV dose, mJ cm^{-2}) is used as a comparative illumination basis for different UV light sources due to accumulated UV dosages according to illumination time. LED (A) and LED (B) were used to perform the UV-LED/H_2O_2 experiment.

This study consisted of two parts: Part A demonstrated the overall efficacy of UV/H_2O_2 towards treatments of wastewater eluent with different operating variables. In contrast, Part B assessed the efficacy of UV/H_2O_2 towards PPCPs spiked solution. Overall, the standard operation parameters of the UV/H_2O_2 treatment process

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were as follows: reaction volume: 2 L, irradiance distance between the LED lamp and the sample surface: 4 cm, initial $[H_2O_2]$: 6.5 mM, and initial non-purgeable dissolved organic carbon [NPDOC]: 6.0 mg L^{-1}. The experimental variables for UV/H_2O_2 treatments in this study are listed in Table 1.

In Part A, the concentration of H_2O_2 selected was based on a previous study [24], as the NPDOC of wastewater collected was around 6 mg L^{-1}, hence 2.4, 4.5 mg L^{-1} of NPDOC was selected as dilution factor of 1/3 and 2/3. Kaolin was added to the reaction solution to simulate the actual turbidity in wastewater [25]. In Part B, simulated PPCPs solutions were used for the UV/H_2O_2 treatment. 15 PPCPs were employed in this study to investigate the extent to which they were removed after UV/H_2O_2 treatment. The PPCPs assessed were acetylsalicylic acid, naproxen, fenoprofen, methylparaben, ethylparaben, propylparaben, butylparaben, estrone, 17β-estradiol, 17α-ethynyl estradiol, estriol, benzophenone, oxybenzone, caffeine, and diethyltoluamide (DEET). These PPCPs were selected based on the results of a previous study, which provided fundamental information on the presence of PPCPs in Taiwan's river waters [26]. A 2500 ng L^{-1} dose of each PPCP standard were spiked into either Milli-Q water or wastewater to perform the UV/H_2O_2 test based on the previous study [27].

During the UV/H_2O_2 process, samples were collected at different reaction times. The samples were analyzed for NPDOC, H_2O_2 residual concentrations, and turbidity. For DBPFP tests, the bovine enzyme was added to samples to quench the remaining H_2O_2 residue. A sufficient amount of sodium hypochlorite was added and incubated at 25 °C for 7 d to perform the DBPFP tests before

Table 1 Experimental conditions for UV/H_2O_2 treatments in this study

	Parameters	Conditions
Part A	Initial H_2O_2, mM	4.9
		6.5
		10
	Initial DOC, mg L^{-1}	2.4
		4.5
		6.0
	Initial Turbidity, NTU	2
		8
		40
	UV Light source	LED A
		LED B
		LPUV
Part B	15 PPCPs	Spiked in Milli-Q water
		Spiked in wastewater

running for DBPs analysis. The samples were scanned with Excitation-Emission Matrix (EEM) fluorescence spectroscopy to evaluate the composite of the DOM. The concentration of PPCPs were analyzed for samples in Part B. Further details of the analytical method of NPDOC, H_2O_2 residual, EEM spectra, DBPs, and PPCPs are summarized in Supplementary information S2 (SI).

3 Results and discussions
3.1 Effects of initial H_2O_2 doses, DOM concentrations, and turbidities on the effectiveness of the UV-LED/H_2O_2 processes

The UV-LED/H_2O_2 processes were conducted with solutions prepared with different water quality statuses to assess the effects of the water quality parameters on the efficiency of the UV-LED/H_2O_2 processes; the parameters included the initial H_2O_2 concentrations, DOC concentrations, and turbidities. Each experiment was conducted in duplicate. The results of DOC mineralization and H_2O_2 degradation are shown in Fig. 1.

The UV-LED/H_2O_2 photolysis conducted with fixed initial DOC concentration but different initial H_2O_2 concentrations ($[H_2O_2]_o$ = 4.9, 6.5, 10.0 mM) did not show any significant different trend in H_2O_2 photolysis and DOM mineralization. With 16 h of UV-LED/H_2O_2 treatment (input of 18,916 mJ cm^{-2} UV dose), around 55% of the H_2O_2 has been consumed, and the organic content reduced by 26–31% (as DOC) after photolysis. These results showed that, with limited UV irradiation, the conversion efficiency of H_2O_2 into hydroxyl radials and results of DOC mineralization is relatively steady. H_2O_2 exhibited hydroxyl radical generation when irradiated with UV light; for steady photolysis of H_2O_2, enough inputs of photons from UV light sources are required [28].

For UV/H_2O_2 photolysis of solutions containing different initial DOC concentrations, which are 2.4, 4.5, and 6 mg L^{-1} of DOC, results showed that the DOC concentrations were reduced by 27 and 38% for solutions containing 6 and 4.5 mg L^{-1} of DOC, respectively, after 18,916 mJ cm^{-2} of UV fluence. As mentioned above, the decomposition of H_2O_2 greatly relies on the input of UV energy; therefore, the photolysis rate in the three compared groups is expected to be similar. However, with different initial DOC, the percentage degradation of solution with initial DOC of 4.5 and 6 mg L^{-1} are 38 and 27%, respectively; for the solution with 2.4 mg L^{-1} of DOC, the DOC concentration remained steady throughout the photolysis process without apparent mineralization. The decreasing of DOC concentration through the AOPs process is due to the conversion of DOC by hydroxyl radicals to CO_2; few studies reported that when the concentration of the DOM in the solution was relatively low, the
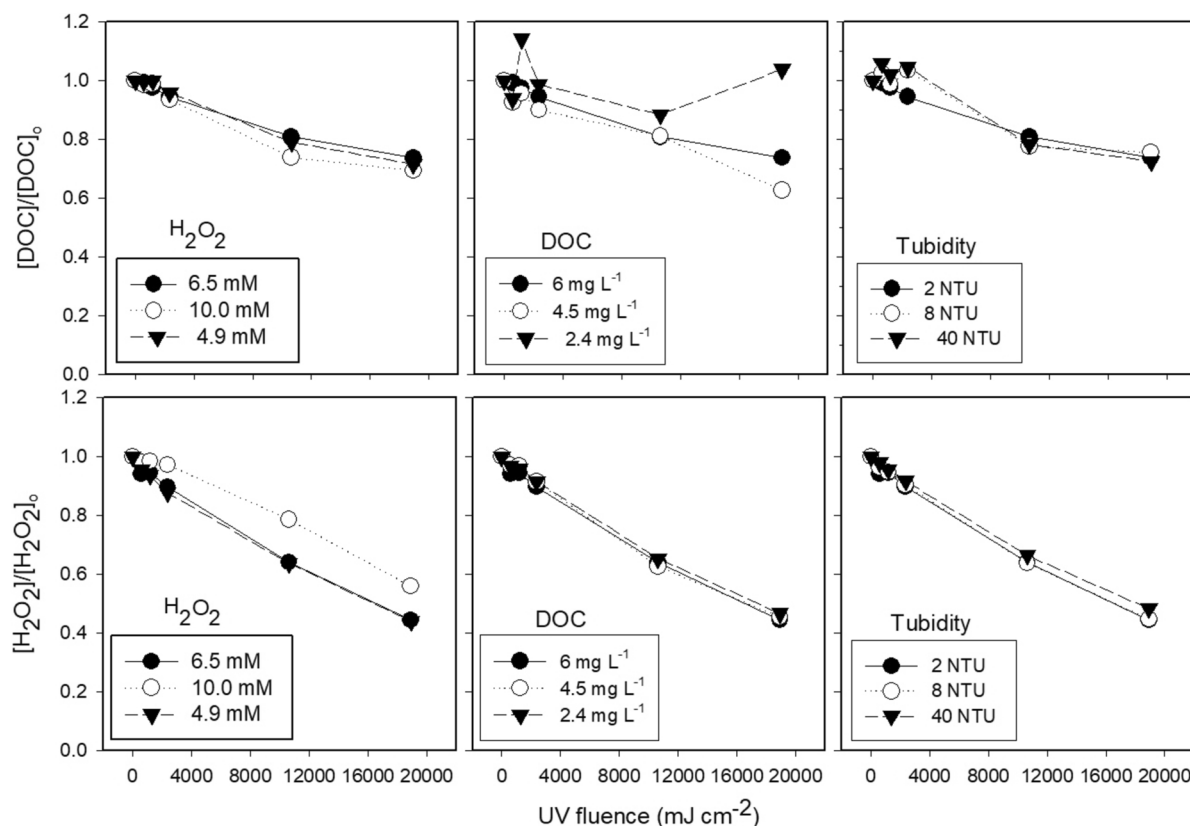
Fig. 1 Effects of initial concentrations of H_2O_2, DOC and turbidity on degradation of DOC (top) and H_2O_2 (bottom) under different experimental conditions. (Light source: LED (A); unless otherwise mentioned, $[H_2O_2]_o = 6.5$ mM, $[DOC]_o = 6$ mg L^{-1}, and $[Turbidity]_o = 2$ NTU.)

hydroxyl radicals generated from H_2O_2 appeared more likely to react with H_2O_2 itself, leading to poor DOM degradation [24, 29]. Dwyer also reported that the mineralization efficiency of DOM with low molecular weight compounds < 1 kDa was relatively low; therefore, the depletion of DOC in the 2.4 mg L^{-1} test group in the later stage was flat due to the remaining higher portion of low molecular weight compounds in the treated solution [30].

For the UV-LED/H_2O_2 process conducted with different initial turbidities (2, 8, and 40 NTU), the results of organic matter mineralization exhibited a fluctuating trend at the beginning (UV dose: 0 to 2364 mJ cm^{-2}) of photolysis, after which a rapid decline in DOC was observed after inputting 10,640 mJ cm^{-2} of UV doses. When the turbidity of the water sample reached 8 or 40 NTU, the degradation of DOM in the initial stage of photolysis (0 to 2,364 mJ cm^{-2} of UV irradiation) was significantly affected and exhibited an unstable DOM degradation trend owing to the presence of high particulate content. This observation has also been reported elsewhere [31, 32]. After a long photolysis time, a rapid decrease in DOM concentration was observed after 10,640 mJ cm^{-2} of UV irradiation was applied.

Overall, the trends of H_2O_2 degradation and DOC mineralization showed a similar way in three different turbidity solutions.

The results in this part revealed that, among the selected water parameters, only the UV irradiance has a prominent effect on the degradation of H_2O_2. Most of the experiment results exhibited consistent trends that ~ 60% of H_2O_2 degraded at the end of the photolysis process.

3.2 Efficacy of UV-LED/H_2O_2 on degradation of DBP precursors

In this set of experiments, solutions with different initial H_2O_2 concentrations ($[H_2O_2]_o = 4.9, 6.5, 10.0$ mM) were prepared for UV-LED/H_2O_2 photolysis, and the results on the outcome of DBPFP and DOC reductions are shown in Fig. 2. No significant difference was observed between the DOM mineralization for solutions containing different initial H_2O_2 concentrations during the UV-LED/H_2O_2 process. The DOC in water was reduced from 6 to approximately 4 mg L^{-1} after photolysis. The corresponding THM formation potential (THMFP) increased from 350 to 400 μg L^{-1} after UV irradiation with a UV fluence of 2364 mJ cm^{-2}, gradually decreasing from
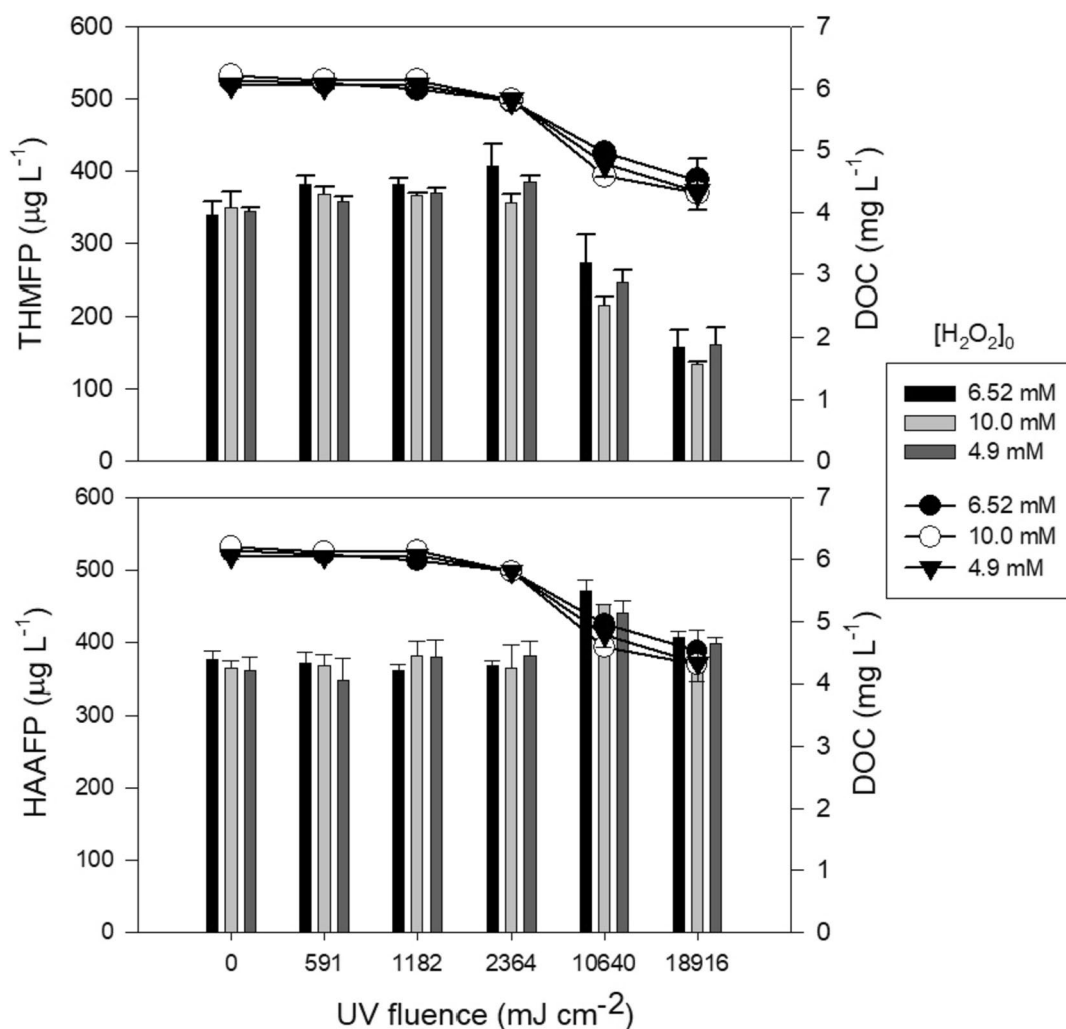
Fig. 2 Effects of initial H_2O_2 concentration on the degradation of dissolved organic matter (DOC) and DBP precursors. (Light source: LED (A), Bar charts: DBPFP, Symbols: DOC.)

400 µg L^{-1} to approximately 150 µg L^{-1} until the reaction terminated.

The initial THMFP increase was probably due to large-molecular-weight organic matter in the solution. The oxidation process often begins with the transformation of large molecules into small organic matter, and these small organic compounds usually act as the precursors for THMs during chlorination [33].

By contrast, the haloacetic acid formation potential (HAAFP) remained steady during the early stage of photolysis (up to 2364 mJ cm^{-2} of irradiation fluence) and was maintained at approximately 380 µg L^{-1} for a reaction time. When the reaction continued with 10,640 mJ cm^{-2} of UV irradiation fluence, an increase in the HAAFP was observed, from 380 to 450 µg L^{-1}, after which the concentration decreased to 400 µg L^{-1} after

exposure to an irradiation fluence of 18,916 mJ cm^{-2}. The results indicate that, at the early stage of UV/H$_2$O$_2$ photolysis, the precursor of THMs in water are first degraded, and the organic precursors are then degraded and converted into HAA precursors; eventually, both the THM and HAA precursors degrade in the later stage of UV/H$_2$O$_2$ photolysis when enough oxidizing capacity was applied [24]. Due to the limit UV dose input to the UV/H$_2$O$_2$ process, the outcome of DBPFP precursor degradation shows a similar trend in three solutions with different initial H$_2$O$_2$ concentrations.

In this section, solutions with different initial concentrations of DOM ([DOC]$_o$ = 6.0, 4.5, 2.4 mg L^{-1}) were also prepared for UV-LED/H$_2$O$_2$ photolysis. As shown in Fig. 3, the profiles of DOM mineralization were similar in solutions containing 6 or 4.5 mg L^{-1} of DOC. No apparent reduction in DOM mineralization was observed after
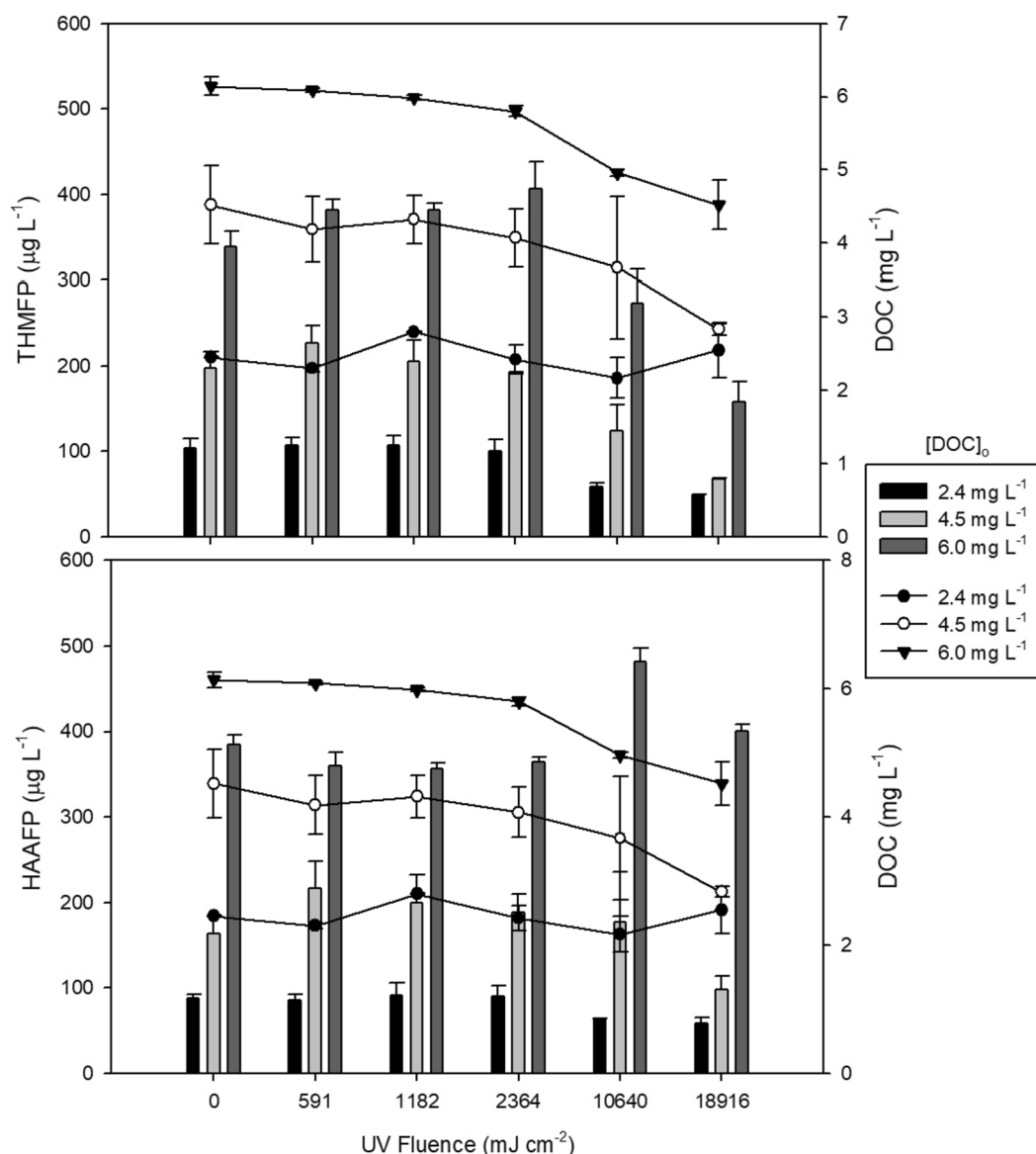
Fig. 3 Effects of initial DOC concentrations on the degradation of dissolved organic matter (DOC) and DBP precursors. (Light source: LED (A), UV light intensity = 0.33 mW cm^{-2}; Bar charts: DBPFP, Symbols: DOC.)

UV-LED/H$_2$O$_2$ photolysis compared with results with low DOM concentration (2.4 mg L^{-1} of DOC).

The solution with 4.5 mg L^{-1} of DOC showed an increasing THMFP after 591 mJ cm^{-2} of UV irradiation and gradually decreasing THMFP throughout the rest of the reaction. The HAAFPs also increased from 170 to 220 μg L^{-1} after 591 mJ cm^{-2} of UV irradiation, after which the HAAFP started to decrease to 100 μg L^{-1} at the end of the process [24].

For the solution with 2.4 mg L^{-1} of DOC, the THMFP level remained constant after 2364 mJ cm^{-2} of UV irradiation, after which the concentration was decreased to

60 μg L^{-1}. This result is probably due to the decrease in DOM concentration and the simultaneous transformation of large-size organic matter into small organic molecules during the photolysis throughout the reaction. The concentration of HAAFPs was maintained at 90 μg L^{-1} during the first 2 h of the contact time (2364 mJ cm^{-2} of UV irradiation), after which it was decreased to 60 μg L^{-1} at the end of the photolysis.

The results of DBPFP tests showed that, although the degradation of DOM in the solution is insignificant, the UV-LED/H$_2$O$_2$ process can still significantly degrade the DBP precursors during the photolysis. Since DBP
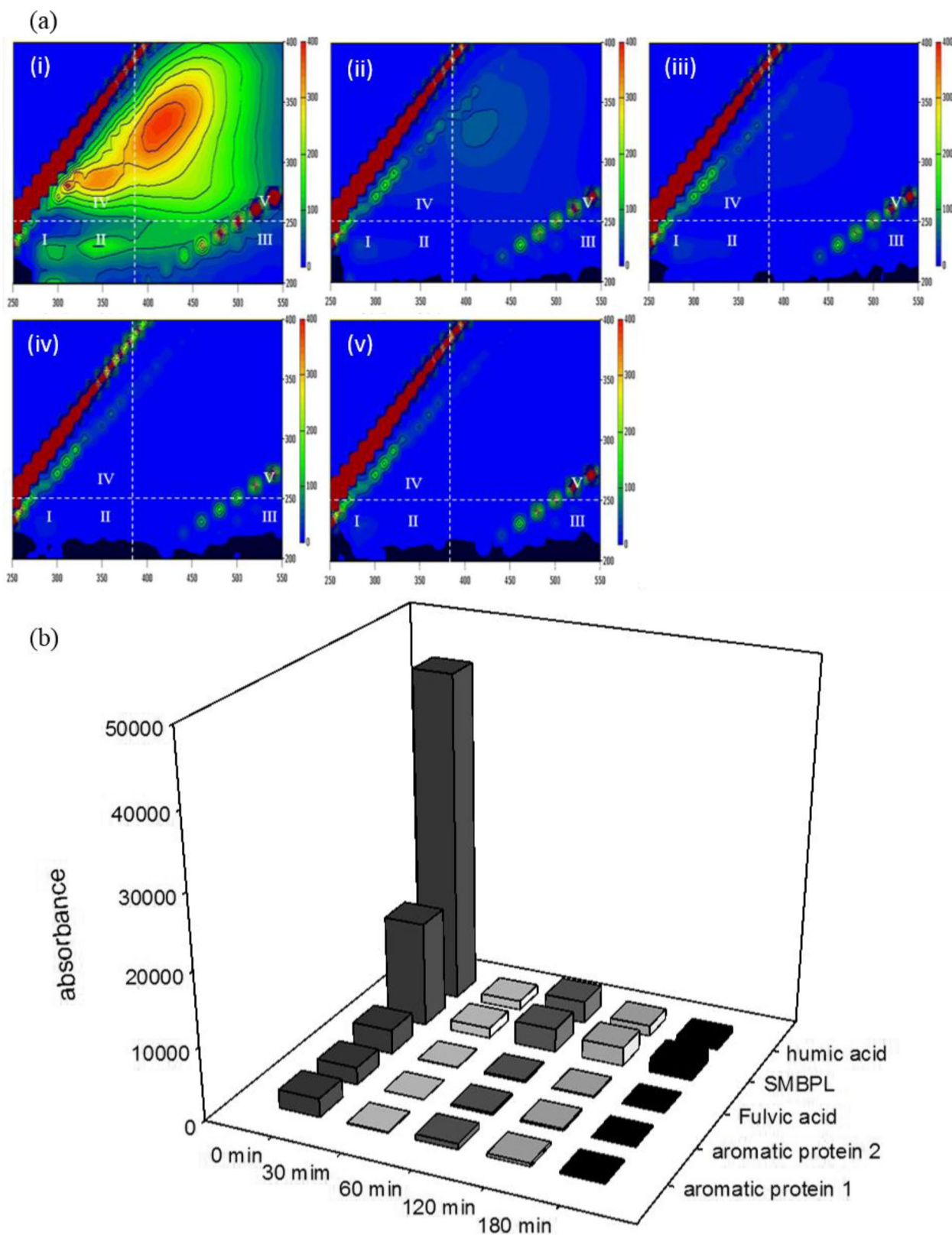
Fig. 4 Excitation–emission matrix (EEM) scanning results. **a** Spectrum for samples at (i) 0 h, (ii) 0.5 h, (iii) 1 h, (iv) 2 h, and (v) 3 h of reaction time. **b** Absorbance. (Light source: LED (B), light intensity = 4.08 mW cm^{-2}). The EEM spectra deconvolution was given in S2 of SI: EEM analytical method

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precursors are part of DOC, the results of DBPFP precursor degradation in three different initial concentrations of DOM showed the same scale as initial DOC.

The EEM spectrum showed that the DOM in water was mostly humic acid–like and soluble microbial byproduct–like (SMBPL), as shown in Fig. 4a. Regarding the UV fluence of each composition shown in Fig. 4b, the trend in SMBPL degradation was consistent with the trend in HAA formation, which implies that part of the precursor of HAAs was produced from the degradation of microbial cells. In addition, the EEM spectrum in Fig. 4a showed that the organic substances in the solution were mainly humic acid, and the humic acid substances decreased gradually as the UV/H_2O_2 treatment progressed.

3.3 Comparisons of UV light sources in UV/H_2O_2 processes

In this section, the treatment efficiencies of three different UV light sources were compared, which include an LPUV lamp and two UV-LED lamps provided by different manufacturers [LED (A) and LED (B)]. The three light sources were compared based on their irradiation fluence and electricity consumption.

Figure 5 shows the UV/H_2O_2 treatment efficiencies on the degradation of DOC and DBP precursors using different UV light sources. Due to the UV light intensity gap between the UV light sources, the maximum UV fluence inputs from LED A, LED B, and LPUV are 18,916, 44,064, and 160,055 mJ cm^{-2} for individual tests with different UV light sources. It can be seen that the three light sources posed a similar trend of DOC degradation. The DOC degradation with LED A and LED B is expected to be the same as the result with LPUV after the designated UV fluence was input in the UV/H_2O_2 process. The results observed from Fig. 5 indicated that the main factor affecting the UV/H_2O_2 efficiency between UVC-LEDs or LPUV is the input of UV dose.

The results of DBPFP tests indicate that the LPUV/H_2O_2 process reduces the THMFPs from 300 to 50 μg L^{-1} and that of HAAFPs from 400 to 100 μg L^{-1}. This indicates that UV/H_2O_2 first degrades the THM precursors in the solution, followed by the HAA precursors [24]. Because of the higher efficiency of LPUV/H_2O_2, it is difficult to observe the rising trend of DBPFPs as described in previous sections using UV-LED/H_2O_2. The degree of DOM degradation with LED (B) was higher than that with LED (A), owing to the difference in UV fluence. An increasing and gradually decreasing trend in the THMFP was observed when UV/H_2O_2 photolysis was conducted with LEDs; again, LED (B) degraded THM precursors more than LED (A) because of its higher UV fluence.

Figure 6 shows the UV/H_2O_2 process results for degradation of DOM and DBPFPs conducted with different UV light sources based on electricity consumption. Based
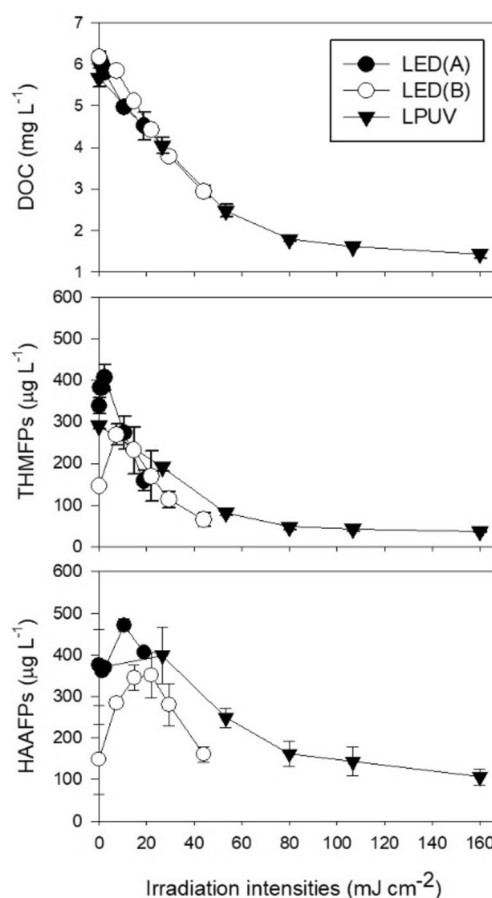

Fig. 5 Effects of different UV light sources (irradiation intensities) on the degradation of DOC and DBP precursors

on the electricity consumption, the LPUV lamp achieved a much higher DOM degradation efficiency than the other two UV-LED lamps. The LPUV consumed 0.007 kWh of electricity, whereas the other two UV-LEDs consumed 0.39 and 0.61 kWh to achieve the same degree of DOM degradation, from around 6 to 4 mg L^{-1} of DOC, as shown in Fig. 5. For the LPUV/H_2O_2 process, the DOC concentration in the solution decreased from 6 to 2.5 mg L^{-1} with 0.013 kWh of electricity consumption, and the DOC concentration decreased gradually with additional electricity consumption of 0.03 kWh (from 0.01 to 0.04 kWh of electricity consumption); the DOC concentration remained at 1.4 mg L^{-1} until the end of the reaction.

The results obtained in this study revealed that the LED lamps exhibit the same performance as LPUV lamps in degrading aqueous DOM. A comparison between the treatment efficiencies of the LPUV and UV-LED lamps indicated that the efficiencies of the three light sources are similar, and the same UV irradiation fluence and UV intensity of different light sources are the key to performance. However, the results also indicated that the
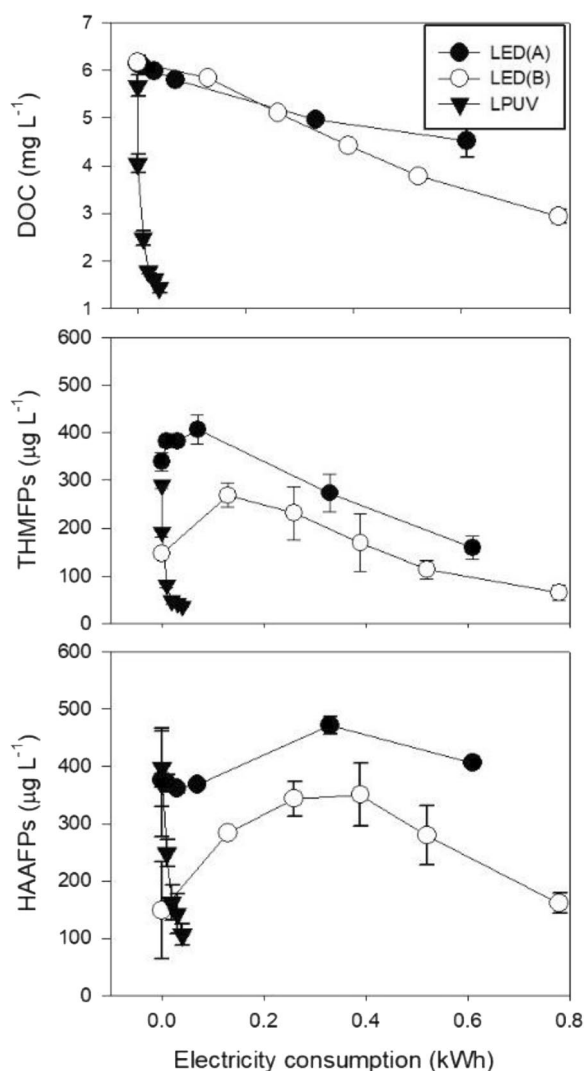
Fig. 6 Effects of different UV light sources (electricity consumption) on the degradation of DOC and DBP precursors. (LED (A): 0.33 mW cm^{-2}; LED (B): 4.08 mW cm^{-2}; LPUV: 14.8 mW cm^{-2})

current UV-LED source has low photoelectric conversion efficiency [34]; the energy transformation efficiency of LED sources should be improved to enhance their advantages, especially that of the UVC-LED. Although UV/H$_2$O$_2$ appears to be an effective technique for degrading organic matter, the results also indicate that some organic chemicals in water are persistent in UV oxidation.

The costs for different AOPs for water treatments depend on the quality of the water to be treated and the treatment requirements. The capital, operational, and management costs all increased with the removal efficiency of the system. However, comparing costs between different AOPs is difficult due to the complicated correlations between the surrogates to be removed, their

removal efficiency, and operating costs. Detailed discussions concerning the costs of AOPs for water and wastewater treatments have been reported in several works of literature [35, 36].

3.4 Efficacy of UV-LED/H$_2$O$_2$ on PPCP removals

PPCP standard solutions were spiked in Milli-Q water or wastewater eluent samples to simulate the conditions of natural water containing PPCPs and undergo UV-LED/H$_2$O$_2$ treatments. The results showed that UV-LED/H$_2$O$_2$ treatment efficiently removed the selected 15 PPCPs, as shown in Figs. 7 and 8. According to the removal efficiencies, the PPCPs were divided into two groups: the chemicals in Group 1 (Fig. 7) were quickly removed compared with those in Group 2 (Fig. 8) after UV-LED/H$_2$O$_2$ photolysis.

The chemicals in Group 1 (ketoprofen, fenoprofen, estriol, 17b-estradiol, 17a-ethynylestradiol, estrone, and benzophenone) were almost completely removed within 10 min in Milli-Q water, as shown in Fig. 7. The PPCPs in Group 2 (acetylsalicylic acid, naproxen, oxybenzone, methylparaben, ethylparaben, propylparaben, butylparaben, caffeine, and DEET) showed higher resistance to UV-LED/H$_2$O$_2$ photolysis, as it took more than
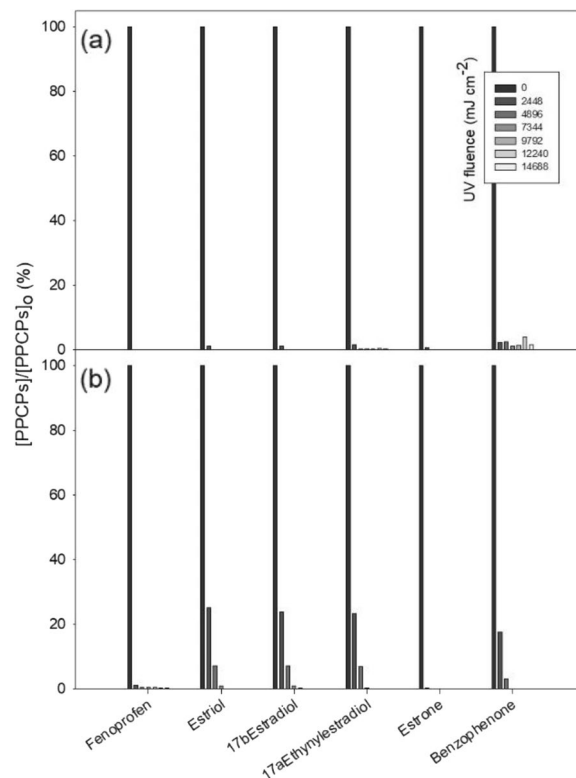

Fig. 7 Effects of UV/H$_2$O$_2$ on the degradation of Group 1 PPCPs in (**a**) Milli-Q water and (**b**) wastewater. (Light source: LED (B), light intensity = 4.08 mW cm^{-2}, [PPCP]$_o$ = 2500 ng L^{-1})
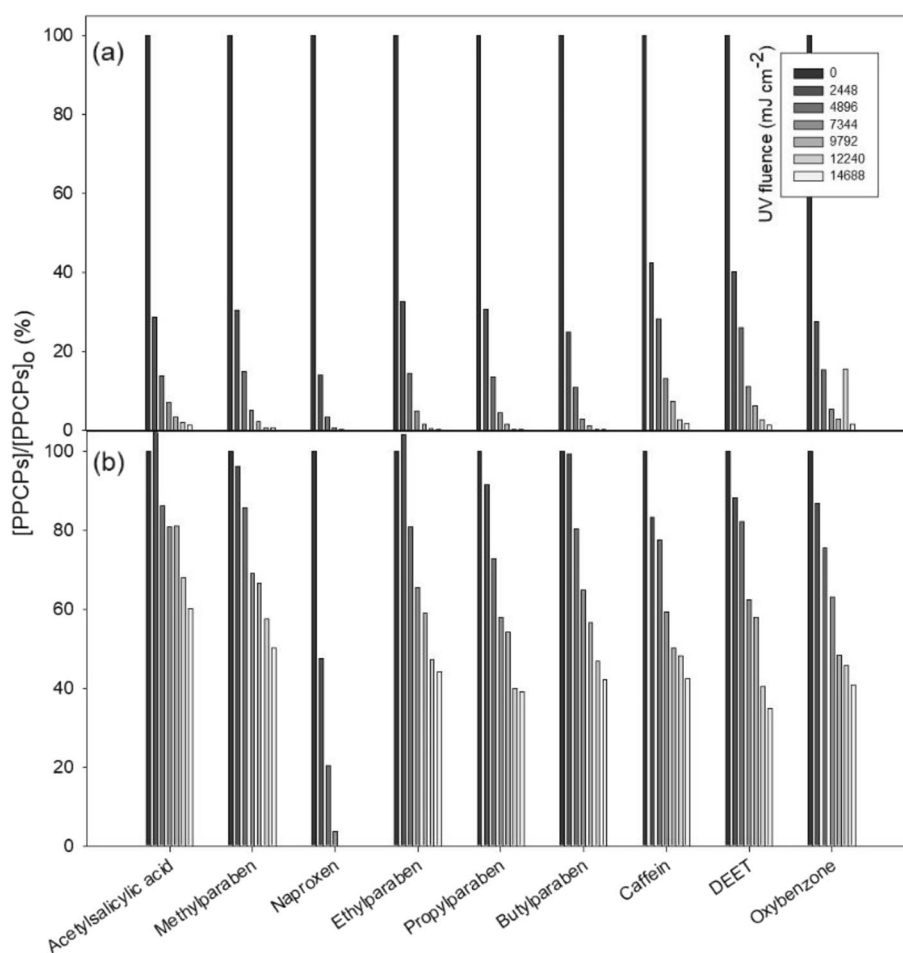
Fig. 8 Effects of UV/H_2O_2 on the degradation of Group 2 PPCPs in (**a**) Milli-Q water and (**b**) wastewater. (Light source: LED (B), light intensity = 4.08 mW cm^{-2}, [PPCP]$_o$ = 2500 ng L^{-1})

14,688 mJ cm^{-2} input of UV dose for them to be effectively removed, as shown in Fig. 8. The degradation efficiency of the micro-pollutants by UV/H_2O_2 process can be governed by constant reaction rates of hydroxyl radicals (k_{OH}) of each chemical compound; many k_{OH} values were reported in previous literature [37]. The predictions of the k_{OH} of micropollutants can be achieved by quantitative structure-property relationships modeling tool, which is a critical approach to be done in the future to understand the capability of each AOP to deal with degradations of micropollutants [38].

The trend of UV-LED/H_2O_2 treatment efficiency based on individual PPCP in wastewater was similar to those observed in Milli-Q water, in which the chemical compounds in Group 1 have much higher degradation rates than Group 2 chemicals. The lower degradation efficiency for PPCPs in wastewater was probably due to the presence of effluent organic matter (EfOM) and some inorganic ions (NH_4^+, NO_2^- and Br^-) in wastewater, which served as OH• scavengers with target PPCPs,

resulting in the poor degradation of PPCPs in wastewater comparing with those in Miili-Q. Some studies showed that EfOM scavenged over 75% hydroxyl radical [39]. Soluble microbial products in wastewater could be the main EfOM to react with hydroxyl radicals. Furthermore, the presence of particulate matter and DOM in wastewater reduced the probability of interactions between UV light and H_2O_2, and a longer UV irradiance time was necessary to improve the treatment efficiencies. Overall, UV/H_2O_2 show excellent efficiency in the degradation of PPCPs evaluated in this study, and some study supported that AOP is an effective way to decrease the toxicities of PPCPs and PPCP byproducts in the end-products of treatment [40].

4 Conclusions

This study showed that initial H_2O_2 dosage, DOC and turbidity have relatively minor effects to interfere with the overall performance of UV/H_2O_2 process, and the

input of UV dose has a prominent effect on the degradation of H_2O_2 and target organic contaminants. Most of the results exhibited consistent trends that ~60% of H_2O_2 degraded at the end of the photolysis process. For degradation of DBP precursors with UV/H_2O_2, the amount of THM precursors increases in the early stage of the treatment process and then decreases at the later stage of the reaction; however, HAA precursors require a longer oxidation time than THM precursors to achieve similar DBPFP removal. The results also showed that if the concentration of DOM in water is low (2.4 mg L^{-1} in this study), the treatment efficiency of UV-LED/H_2O_2 is lower than expected.

The removal efficiency of PPCPs varied. In this study, we found that UV/H_2O_2 has higher degradation efficiency for estrogens, fenoprofen, and benzophenone and lower degradation efficiency for acetylsalicylic acid, naproxen, oxybenzone, methylparaben, ethylparaben, propylparaben, butylparaben, caffeine, and DEET.

A comparison between LPUV and a UVC-LED revealed that when the same amount of electricity was provided, LPUV exhibited much higher treatment efficiency for organic matters; however, when the treatment efficiency was normalized based on the same amount of UV doses in UV/H_2O_2 processes, the profiles of DOM mineralization and reductions of DBP precursors were similar between the different UV sources. The results indicated that UVC-LED is useful for degrading organic matter and DBP precursors despite poor photoelectric conversion efficiency at the current moment. Based on the advantages of LED, that it is more portable and petite, LED shows excellent potential on smaller scale water treatment facilities, and further study on reaction chamber designing and operating parameters is recommended to boost the beneficial effect of UV-LED/H_2O_2.

Supplementary Information

The online version contains supplementary material available at https://doi.org/10.1186/s42834-023-00194-7.

Additional file 1.

Authors' contributions
Dexter Leong and Hao-Bin Chen provided conceptualization, validation, conduct experiments and writing - original draft. Gen-Shuh Wang provided writing - review and editing. All authors read and approved the final manuscript.

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