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Improving UV/H_2O_2 performance following tertiary treatment of municipal wastewater†

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The ability of UV/AOP to treat trace organic contaminants (TOrCs) in wastewater is inhibited by (1) UV light-absorbing species and (2) hydroxyl radical ($^{\bullet}$OH) scavenging species. We address these challenges by investigating four diverse technologies, single-stage biofiltration, sequential biofiltration, coagulation–flocculation–sedimentation–filtration (CFSF), and nanofiltration, as options for improving water quality conditions just prior to UV treatment, with and without added hydrogen peroxide (H_2O_2). By evaluating UV_{254} transmittance (UVT), $^{\bullet}$OH scavengers, and $^{\bullet}$OH steady-state concentrations, we found nanofiltration treatment to produce the most favorable pre-UV and UV/H_2O_2 water quality conditions. In comparing CFSF, single-stage biofiltration and sequential biofiltration treatment, CFSF treatment resulted in the highest increase in UVT and all three technologies reduced the scavenging capacity by ~24% despite differences in removal of typical $^{\bullet}$OH scavengers. UV and UV/H_2O_2 performance were evaluated by tracking the degradation rates of 11 targeted TOrCs for each pre-UV/H_2O_2 treatment scenario. Applying the additional treatment, average pseudo first-order degradation rates of TOrCs under UV/H_2O_2 increased by 20 to 92%, informing potential strategies to increase the oxidation potential of UV/AOP systems applied to wastewater.

Water impact

Converting UV disinfection systems into UV/AOP systems is a potential strategy to decrease the concentration of trace organic contaminants discharged into natural water systems by municipal WWTPs. This study investigates the use of tertiary and advanced treatment processes to improve the water quality prior to, and increase the oxidation potential during, UV/AOP treatment of wastewater effluents.

1 Introduction

Numerous research studies[1–5] have demonstrated that conventional municipal wastewater treatment plants (WWTPs), consisting of preliminary treatment (screening and grit removal), primary treatment (sedimentation), secondary treatment (biological treatment like activated sludge), and tertiary treatment (filtration), are ineffective at removing pharmaceutical residuals, endocrine disrupting compounds and other pollutants that have low sorption coefficients and are recalcitrant to biodegradation.[2,6] Despite the increased toxicity and concentration of pollutants entering municipal WWTPs,[6] most countries require secondary treatment as the final treatment step prior to discharging into surface water.[7,8] Subsequently, discharging wastewater effluent into natural water systems has resulted in adverse health effects of aquatic ecosystems,[6] dispersion of trace-levels (ng L^{-1} to μg L^{-1}) of various contaminants of emerging concern[9] and compromised source water for drinking water treatment facilities located downstream of wastewater discharges.[10]

To decrease the concentration of pollutants in wastewater effluent, implementing advanced treatment technologies might be a viable option for existing and future WWTPs. A class of treatment technologies well-recognized for their ability to destroy a wide range of organic pollutants are advanced oxidation processes (AOPs). AOPs are defined by their capacity to generate powerful (2.8 eV) and reactive (10^8 to 10^{10} M^{-1} s^{-1}) $^{\bullet}$OH *in situ*.[11] The most common industry-used AOPs for advanced wastewater treatment are ozone or UV coupled with an added oxidant, which is commonly H_2O_2.[12] An advantage of ozone- and UV-based AOPs is their ability to simultaneously destroy TOrCs and inactivate microorganisms.

Today, there are over 7300 UV systems installed at WWTPs in the United States and over 12 600 UV systems installed

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worldwide. Although the UV dose required for disinfection (~30 to 40 mJ cm^{-2}) is significantly lower than design doses for UV/AOP applications (>500 mJ cm^{-2}), most UV reactors have the capacity to increase their UV intensity up to 4 times during average daily flow conditions. This is because UV reactors are often designed to achieve disinfection doses for peak flow conditions. Alternatively, increased UV intensity can be achieved by adding banks of lamps or another UV reactor in series (information above provided through personal correspondence with three independent UV manufacturers). Thus, there is opportunity to convert UV disinfection systems operating at WWTPs into UV/AOP systems which could result in capital cost savings compared to installing a new UV/AOP system or an alternative AOP system.

While it is common practice for municipalities to disinfect wastewater with UV light, UV/AOPs are not typically utilized for treatment of conventionally treated municipal wastewater effluent. Compared to drinking water sources, wastewater effluents contain higher concentrations of UV-absorbing species and $^{\bullet}OH$ scavengers which can decrease the performance of UV/AOP and result in increased operating costs. Low UVT conditions can inhibit the photolysis of UV-degradable contaminants and H_2O_2. The latter results in the reduction of $^{\bullet}OH$ production. Additionally, the ability of $^{\bullet}OH$ radicals to react with target pollutants can be inhibited by the competing reactions (scavenging) of $^{\bullet}OH$ with organic and inorganic constituents, such as dissolved organic matter (DOM), carbonate species, and NO_2^-.

The effect of water quality on $^{\bullet}OH$ scavenging has extensively been investigated,[13–15] and UV and UV/AOP performance has been evaluated in diverse effluents collected from established water and wastewater treatment processes (*e.g.*, CFSF, activated sludge, moving bed bioreactor, ion exchange, filtration and others).[16–18] However, few studies have evaluated the effect of treatment processes added post conventional tertiary filtration treatment as strategies to increase the oxidation potential of subsequent UV/AOP systems in WWTPs even though evidence suggests that UV/AOP systems are a viable solution to reduce pollutant discharge.[17,19] For example, a recent study conducted by Hofman-Caris *et al.*[17] reported that the addition of an anion exchange system before UV/H_2O_2 treatment increased the UVT from 38% to 85% and decreased the humic acid fractions of DOM which enabled the degradation of pharmaceutical compounds at UV doses <300 mJ cm^{-2}.

For this study, a single batch of tertiary-treated wastewater effluent collected from the WWTP in Garching, Germany was further treated with four technologies, single-stage biofiltration, sequential biofiltration, CFSF and nanofiltration, to improve water quality prior to UV and UV/H_2O_2 treatment. These treatment technologies were selected because they utilize different processes (*e.g.*, biological, physical and chemical) to remove organic matter and absorbing constituents that affect UV and UV/AOP efficiency. Wastewater effluents were compared before and after treatment of the tertiary effluent by quantifying changes in UVT, $^{\bullet}OH$ scavenging rates, and steady-state $^{\bullet}OH$ concentrations. The efficiency of UV and UV/H_2O_2 following post-treatment of tertiary effluent was evaluated by determining the degradation rates of 11 spiked TOrCs with varied susceptibility to photolysis and oxidation. TOrC removal was investigated over a range of UV doses, including well below those typically used for UV/H_2O_2 application.

2 Experimental methods

2.1 Wastewater effluent collection

A single 3 m^3 batch of wastewater effluent that was collected after tertiary filtration at the Garching WWTP, Germany which served as the test water for all bench-scale experiments. This WWTP employs conventional biological nutrient removal with full nitrification and denitrification and tertiary filtration. During the period from May to September, when this study was conducted, the plant operates a seasonal UV system (~50 mJ cm^{-2}) to provide disinfection prior to discharging to the Isar river. Minimal differences in water quality before and after UV disinfection were observed (data not provided). While the biological nutrient removal system is designed to achieve nitrogen concentration <10 mg L^{-1}-N, low-levels of nitrite were occasionally measured (<0.2 mg L^{-1}-N) in tertiary effluent (Table 1).

2.2 Post-treatment of tertiary effluent

A two-stage sequential biofiltration system comprised of an anthracite filter followed by a sand filter was operated under saturated top-down flow conditions with tertiary effluent (see Müller *et al.* (2017)[20] for detailed description of the system). Samples were collected after the first stage anthracite filter (empty bed contact time (EBCT) = 90 min, single-stage biofiltration) and after the second stage sand filter (EBCT = 200 min, sequential biofiltration). The first-stage effluent was aerated prior to sand filtration to promote aerobic biofilm growth at the surface of the sand media with the goal of improving DOC removal. The system was operated for approximately 2 years before sampling.

The CFSF treatment was simulated using a programmable jar tester (Microfloc Pty Ltd, Australia) with aluminum sulfate ($Al_2(SO_4)_3 \cdot 16\ H_2O$, Sigma Aldrich, Germany). After testing a range of alum concentrations (100–240 mg L^{-1}), a dose of 160 mg L^{-1} was determined as an optimum dose for DOC removal. (Mixing conditions are presented in the ESI,† Table S1.) The supernatant was filtered through a 0.45 μm filter (Sartorius AG, Germany) prior to water quality analysis and UV and UV/H_2O_2 experiments to remove particulates and simulate water quality conditions after rapid sand filtration.

Nanofiltration experiments were performed using a bench-scale cross-flow nanofiltration system (Sepa II, Osmonics), equipped with a feed tank, sensors to monitor conductivity, pressure and temperature, and a heat exchanger used to maintain a temperature of 20 °C. A flat-sheet test cell encased a nanofiltration membrane (NF270, Dow Filmtec™), with an active membrane area of 139 cm^2 and a cross sectional area

Table 1 Water quality characteristics of water matrices prior to UV and UV/H_2O_2 experiments

Parameter	Units	Tertiary	Single-stage biofiltration	Sequential biofiltration	CFSF	Nanofiltration
COD	mg L^{-1}	16.5	11.9	10.4	9.8	2.4
DOC	mg L^{-1}	5.3	4.0	4.0	4.2	0.3
NO_3^-	mg L^{-1} as N	10.8	11.5	11.4	10.7	9.7
NO_2^-	mg L^{-1} as N	0.110	DL[a]	DL[a]	0.021	0.019
UV_{254} (UVT)	m^{-1} (%)	13.0 (74.1)	11.3 (77.1)	10.8 (78.0)	8.3 (82.7)	1.0 (97.7)
SUVA	L mg_C^{-1} m^{-1}	2.5	2.8	2.7	2.0	3.3
HCO_3^-	mg L^{-1} as $CaCO_3$	231	231	231	155	119
CO_3^{2-}	mg L^{-1} as $CaCO_3$	2.12	2.38	3.50	0.33	0.83
pH	—	8.19	8.21	8.20	7.25	7.80

[a] DL of NO_2^- is 0.015 mg L^{-1}-N.

of 0.92 cm^2. Tertiary effluent was fed to the system at a cross-flow velocity of 0.22 m s^{-1} across the membrane surface and a flux of 20 L m^{-2} h^{-1} was maintained during permeate collection. The test unit was monitored and controlled using LabVIEW™ software.

2.3 UV and UV/H_2O_2 treatment

A 1 L sample from each pre-UV treated water matrix was spiked with TOrCs (discussed in section 2.5) to achieve a concentration of 1 μg L^{-1} of each TOrC. The purpose of spiking in TOrCs rather than using native TOrCs (additional information on native TOrC concentrations in this wastewater effluent can be found elsewhere[20] was to achieve an initial concentration well above the instrument limit of detection. This allowed for TOrCs measurement after UV exposures >1200 mJ cm^{-2} which was used to develop degradation curves. Water quality was measured prior to UV and UV/H_2O_2 experiments to ensure it was not changing over holding times of <3 days.

Bench-scale UV and UV/H_2O_2 irradiation experiments were performed using a collimated beam device equipped with three low-pressure UV lamps (15 W, UV Technik Meyer GmbH, Germany) emitting at 254 nm. An incident irradiance of 1.1 mW cm^{-2} was consistently measured before and after exposure using a UV-C surface radiometer (sglux GmbH, Germany). 30 mL aliquots of wastewater effluent were continuously mixed (~200 rpm) in a 100 mm glass Petri dish (Petri factor > 0.9) to ensure uniform sample irradiation. The delivered UV fluence was determined following protocols outlined in Bolton and Linden (2003).[21] A total of nine discrete samples were taken for each pre-UV treated water matrix at fluence values ranging from 0 to 1200 mJ cm^{-2} (up to 1180 s exposure time). Directly before UV/H_2O_2 treatment, H_2O_2 was added at a concentration of 10 mg L^{-1}. Based on previous studies,[19,22] 10 mg L^{-1} H_2O_2 in the absence of UV irradiation was assumed to have minimal (0 to <10%) impact on TOrC degradation at the exposure times studied herein.

2.4 Determination of scavenging rate, pseudo first-order degradation rate constants, and $^{\bullet}OH$ steady-state concentration

To quantify the reaction potential of $^{\bullet}OH$ with scavengers (*e.g.*, DOC, HCO_3^-, CO_3^{2-}, and NO_2^-) for each pre-UV treatment scenario, the scavenging rate (SR) was estimated by multiplying the scavenger concentration by established second order $^{\bullet}OH$ reaction rate constants ($k_{^{\bullet}OH}$) as shown in eqn (1).

$$SR = \sum k_{^{\bullet}OH,\text{scavenger}}[\text{Scavenger}] \tag{1}$$

The following $k_{^{\bullet}OH}$ values were used: $k_{^{\bullet}OH,DOC} = 5.8 \times 10^8$ M^{-1} s^{-1} for DOC,[23] $k_{^{\bullet}OH,HCO_3^-} = 8.5 \times 10^6$ M^{-1} s^{-1} for HCO_3^-,[24] $k_{^{\bullet}OH,CO_3^{2-}} = 3.9 \times 10^8$ M^{-1} s^{-1} for CO_3^{2-},[24] and $k_{^{\bullet}OH,NO_2^-} = 1.0 \times 10^{10}$ M^{-1} s^{-1} for NO_2^-.[24]

The degradation of target compounds was assessed by determining the pseudo first-order rate constant (k') which is the slope of the natural logarithm of the ratio of the compound concentration at an exposure time (t) to the concentration at t = 0, $\ln\left(\frac{C}{C_0}\right)$ plotted against exposure time (t) (eqn (2)). The k' plots were developed using seven discrete samples (Table S4†) taken at fluence values ranging from 0 to 1200 mJ cm^{-2} for each pre-UV treated water matrix.

$$k' = \frac{\ln\left(\frac{C}{C_0}\right)}{t} \tag{2}$$

The formation and scavenging of $^{\bullet}OH$ was evaluated in each water matrix by applying eqn (3) to determine the steady-state concentration of $^{\bullet}OH$, $[^{\bullet}OH]_{ss}$.

$$[^{\bullet}OH]_{ss} = -\frac{k'}{k_{^{\bullet}OH}} \tag{3}$$

Probe compounds carbamazepine and primidone were selected because of their low quantum yields and fast second-order rate of reaction with $^{\bullet}OH$ (Table 2).

2.5 TOrC selection

Selection of TOrCs was based on their presence and persistence in municipal wastewater[3,25–29] as well as analytical capabilities. TOrCs were grouped according to Miklos *et al.* (2018)[19] and categorized based on their sensitivity to

Table 2 Kinetic parameters of selected TOrCs. Standard deviation is given in parentheses as reported

Group	TOrC	$\Phi_{254} \times 10^{-2}$ (mol Einstein^{-1})	$\varepsilon_{254} \times 10^3$ (M^{-1} cm^{-1})	$k_{\cdot OH} \times 10^9$ (M^{-1} s^{-1})
Photo-susceptible	Diclofenac	23 (±1.6)[a]	6.8 (±0.27)[a]	8.2 (±2.6)[a]
	Iopromide	3.9[b]	21[b]	3.3[c]
	Sulfamethoxazole	8.4 (±0.95)[a]	13 (±0.097)[a]	6.3 (±0.55)[a]
Moderately photo-susceptible	Benzotriazole	1.6[d]	6.14 (±19)[d]	8.34 (±0.37)[d]
	Caffeine	0.18[e]	3.92[e]	6.4 (±0.71)[e]
	Metoprolol	6.6 (±4.7)[a]	0.33 (±0.0011)[a]	8.1 (±0.98)[a]
	Phenytoin	27.9[e]	1.26[e]	6.28[e]
	Venlafaxine	9.7 (±5.7)[a]	0.38 (±0.019)[a]	8.8 (±1.5)[a]
Photo-resistant	Carbamazepine	0.33 (±0.1)[a]	5.8 (±0.0089)[a]	9.5 (±1)[a]
	Gabapentin	—	—	9.1[f]
	Primidone	8.2[e]	0.22[e]	6.7[e]

[a] Wols *et al.* (2014).[52] [b] Canonica *et al.* (2008).[53] [c] Huber *et al.* (2003).[54] [d] Bahnmüller *et al.* (2015).[55] [e] Wols and Hofman-Caris (2012).[34] [f] Lee *et al.* (2014).[56]

degradation by photolysis (Φ_{254}) and $^{\bullet}OH$ oxidation ($k_{\cdot OH}$): photo-susceptible (diclofenac, iopromide, and sulfamethoxazole), moderately photo-susceptible (benzotriazole, caffeine, metoprolol, and venlafaxine), and photo-resistant (carbamazepine, gabapentin, and primidone) compounds (Table 2).

2.6 Analytical methods

The H_2O_2 (Bernd Kraft GmbH, Germany) concentration was verified before and after UV/H_2O_2 treatment using the titanium IV oxysulfate (Sigma-Aldrich) colorimetry method (DIN 38 409, part 15, DEV-18). The following methods and instruments were used to measure bulk water quality parameters: Hach cuvette tests for nitrate (LCK 340), nitrite (LCK 341/342), and acid capacity $K_{a4,3}$ (LCK 362), DR6000 UV/vis spectrophotometer (Hach Lange, Germany) for UVT_{254} measurement, and varioTOC cube (Elementar Analysensysteme, Germany) for DOC measurement of 0.45 μm cellulose nitrate membrane (Sartorius AG, Germany) filtered samples.

Samples collected for TOrC analysis were filtered through 0.22 μm PVDF syringe filters (Berrytec, Germany) and stored in amber glass vials at 4 °C before analysis. TOrC measurement was performed using a high performance liquid chromatography (Knauer PLATINBLUE UHPLC) coupled with tandem mass spectrometry (LC-MS/MS) (SCIEX QTRAP 6500) with direct injection as described in Müller *et al.* (2017).[20] Analytical grade TOrCs and isotope labelled standards were used.

3 Results and discussion

3.1 Effect of tertiary treatment on UV transmittance and scavenging rate

Table 1 presents the relevant water quality data of water types used for the UV and UV/H_2O_2 experiments. The UV transmittance (% UVT = $100 \times 10^{-UVA_{254}}$) and scavenging rate were the selected parameters to compare the water quality after treatment of tertiary effluent (Fig. 1) because of their impact on UV and UV/H_2O_2 performance. For example, absorbing species, including suspended solids and DOM, can shield UV light and inhibit the photolysis of target pollutants and H_2O_2, which results in decreased $^{\bullet}OH$ production. Radical scavengers consume generated $^{\bullet}OH$ and, subsequently, decrease the reaction potential of $^{\bullet}OH$ with target pollutants.

Overall, nanofiltration treatment resulted in the most improved water quality conditions, producing water with a 98% UVT and decreasing the scavenging rate by 86%. CFSF treatment increased the UVT by 12% while UVT was only marginally improved (4–5%) after biofiltration treatment (single-stage and sequential). The scavenging rates of CFSF and biofiltration (single-stage and sequential) treatment were similar and ranged from 2.27×10^5 s^{-1} to 2.44×10^5 s^{-1} (Fig. 1).

To further analyze the scavenging rate results, the percent contribution of individual scavengers to the overall scavenging rate was evaluated (Fig. 2). The radical scavengers evaluated in this study were: $k_{\cdot OH,DOC} = 5.8 \times 10^8$ M^{-1} s^{-1}, $k_{\cdot OH,NO_2^-} = 1.0 \times 10^{10}$ M^{-1} s^{-1}, and $k_{\cdot OH,CO_3^{2-}} = 3.9 \times 10^8$ M^{-1} s^{-1} and $k_{\cdot OH,HCO_3^-} = 8.5 \times 10^6$ M^{-1} s^{-1}. The contribution of NO_3^- to the overall scavenging demand was found to be negligible which is explained by its low reaction rate with $^{\bullet}OH$ ($k_{\cdot OH,NO_3^-} < 1.0 \times 10^5$ M^{-1} s^{-1} (ref. 30)). Although chloride and sulfate are often present in wastewater and known scavengers of $^{\bullet}OH$ ($k_{\cdot OH,Cl^-} = 4.3 \times 10^9$ M^{-1} s^{-1} (ref. 31) and $k_{\cdot OH,SO_4^-} = 1.0 \times 10^{10}$

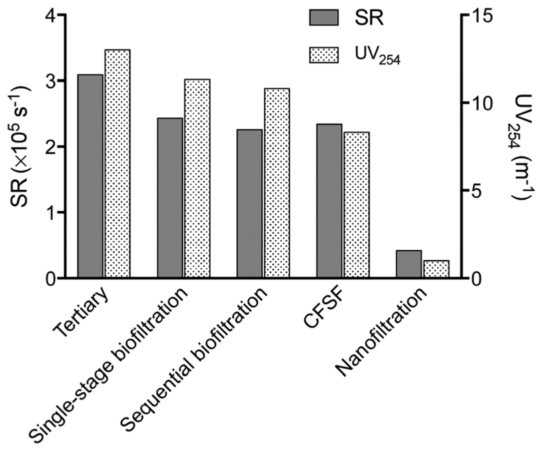

Fig. 1 Scavenging rate (primary *y*-axis) and UV absorbance (secondary *y*-axis) of pre-UV/H_2O_2 water quality scenarios.

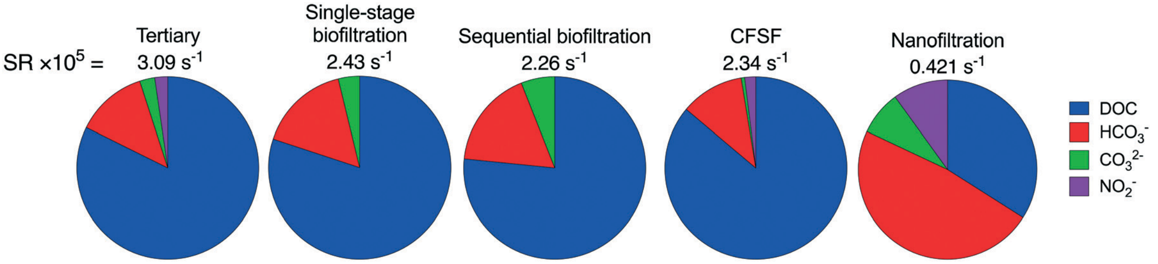

Fig. 2 Percent contribution of individual scavengers to the overall scavenging demand. SR × 10^5 values represent the total scavenging capacity of the water matrix. Scavenging by DOC is calculated using rate constant from literature which may not represent reactivity in every post-treated effluent as explained in section 3.1.

M^{-1} s^{-1} (ref. 32)), their scavenging potential has been shown to be offset by the production of radicals through intermediate reactions. Liao *et al.*[33] explains that at a pH >6 (for all wastewaters the pH was >7) the $^{\bullet}$OH scavenged by Cl$^-$ is replaced by $^{\bullet}$OH generated during the dissociation of HOCl$^{\bullet-}$ (ref. 33) thus is inconsequential at the pH of the wastewater in this study. Photolysis of sulfate generates the sulfate radical which is more selective then $^{\bullet}$OH but has similar oxidizing power.[33] Therefore, chloride and sulfate were not considered major scavengers of $^{\bullet}$OH.

Within the literature, there is a high variance between $k_{^{\bullet}\mathrm{OH,DOC}}$ values reported ranging from 3.5 × 10^8 M^{-1} s^{-1} to 9.2 × 10^8 M^{-1} s^{-1}.[34] This is because $^{\bullet}$OH reactivity with DOC is a function of organic matter composition, and organic matter present in aqueous environments is continuously changed from natural and anthropogenic inputs and processes. The $k_{^{\bullet}\mathrm{OH,DOC}}$ (5.8 × 10^8 M^{-1} s^{-1}) value used to calculate the scavenging rate was previously determined for WWTP effluent[23] and, therefore, was assumed to be a good representative of the tertiary-treated WWTP effluent used for this study. Because differences in organic matter composition have been shown to affect the reactivity of $^{\bullet}$OH,[35,36] it is important to consider that the $k_{^{\bullet}\mathrm{OH,DOC}}$ used to determine the scavenging rate of tertiary effluent may not accurately represent the reactivity of $^{\bullet}$OH with DOC in every post-treated tertiary effluent. While $k_{^{\bullet}\mathrm{OH,DOC}}$ values were not experimentally determined in this study, section 3.3 investigates whether the reactivity of organic matter is changed as a result of treatment of tertiary effluent by comparing modeled and experimentally-determined $^{\bullet}$OH steady state concentrations.

Interestingly, CFSF and biofiltration (single-stage and sequential) treatment achieved similar DOC removal (21 to 24%) which resulted in comparable calculated scavenging rates (Fig. 2). This result was unexpected since CFSF and biofiltration utilize different mechanisms for DOC removal: CFSF combines chemical and physical processes to remove organic matter whereas biofiltration simultaneously removes organic matter through adsorption, filtration and biodegradation. However, analysis of specific UV absorbance at 254 nm (SUVA, calculated by dividing the 254 nm absorbance (UVA$_{254}$) by DOC) values reveal CFSF and biofiltration treatment may have preferentially removed different organic matter components. CFSF treatment decreased the SUVA value by 20% indicating larger molecular weight or aromatic DOC fractions were removed, which has been observed in previous coagulation work.[37,38] In comparison, SUVA was increased by 15 and 8% after single-stage and sequential biofiltration, respectively, indicating preferential biodegradation of aliphatic and lower molecular weight compounds.[39,40]

In comparing single-stage and sequential biofiltration, the removal of DOC was not enhanced by the additional biofiltration step. Similar results were observed in a recent study by Müller *et al.* (2017)[20] where it was explained that the first biofiltration stage likely consumed the readily available organic substrate and the second biofiltration stage resulted in minor structural changes as well as minimal mineralization of the remaining slowly biodegradable organic substrate.

Removal of carbonate species and NO$_2^-$ was shown to vary with treatment. While alkalinity was unchanged after biofiltration (single-stage and sequential) treatment, CFSF and nanofiltration treatment removed 33% and 49%, respectively. It was also observed that CFSF treatment decreased the pH from 8.2 to 7.3 which resulted in the shift of carbonate (CO$_3^{2-}$) to bicarbonate (HCO$_3^-$) and an overall reduction in carbonate scavenging potential. In contrast, oxic biofiltration (single-stage and sequential) removed NO$_2^-$ to levels below the method detection limit (<0.015 mg L^{-1}-N) likely due to biological oxidation of NO$_2^-$ to NO$_3^-$. These findings demonstrate that biofiltration treatment, while maintaining oxic conditions, can be an effective barrier for NO$_2^-$ when WWTPs are experiencing sporadic elevated NO$_2^-$ emissions from secondary treatment.

Because nanofiltration treatment reduced the DOC concentration to <0.3 mg L^{-1}, the contribution of HCO$_3^-$ (48%) and NO$_2^-$ (10%) were found to have a higher impact on the scavenging rate as compared to the other wastewater effluents (Fig. 2). Nanofiltration systems have been shown to physically reject compounds with a molecular weight compounds down to 200 Da through repulsive forces at the membrane surface.[41–43] However, inorganic nitrogen molecules have been shown to pass through nanofiltration membranes.[43]

3.2 Degradation rates of TOrCs

Presented in Fig. 3 are time-based pseudo first-order degradation kinetics (noted as k') of selected TOrCs. Time-based units were selected because they do not correct the fluence for absorbance and water depth (embedded in Beers law) and therefore illustrate the impact of UV transmittance on UV degradation. For instance, for an exposure of 600 s the delivered fluence was 606 mJ cm^{-2} for tertiary effluent and 674 mJ cm^{-2} for nanofiltration permeate (irradiance was constant at 1.1 mW cm^{-2} for all experiments).

With respect to individual treatment technologies, average TOrC degradation rates ($n = 11$) were improved by 27%, 18%, 30%, and 98% after single-stage biofiltration, sequential biofiltration, CFSF, and nanofiltration treatment, respectively. Although a consistent trend of $k'_{\text{nanofiltration}} > k'_{\text{CFSF}} > k'_{\text{single-stagebiofiltration}} > k'_{\text{sequentialbiofiltration}} > k'_{\text{tertiary}}$ for average k' values of TOrCs can be observed for most compounds (Fig. 3), k' values generated for single-stage biofiltration, sequential biofiltration and CFSF were not statistically different ($p > 0.05$, one-tailed student's *t*-test) which corroborates scavenging rate results.

Resulting from treatment of tertiary effluent, the average TOrC degradation rates of photo-resistant compounds ($n = 3$) were most improved (75% ± 33%, reported as averages followed by the standard error of the mean), followed closely by moderately photo-susceptible compounds ($n = 5$) (71% ± 26%) and finally photo-susceptible compounds ($n = 3$) which were least improved (34% ± 21%). With relatively low quantum yields or molar absorption coefficients (Table 2), moderately photo-susceptible and photo-resistant compounds degrade primarily through $^{\bullet}OH$ oxidation and are therefore more sensitive to changes in $^{\bullet}OH$ scavengers.

The changes in scavenging capacity and UVT from tertiary treatment on TOrC degradation rates can be investigated by comparing fluence-based k' values to time-based k' values (Table S3†). UV-fluence-based pseudo first-order degradation kinetics correct the fluence for absorbance and depth effects, therefore normalizing differences between waters,[21] however, the impact of the water matrix on scavenging of $^{\bullet}OH$ radicals is present in both time and fluence based units.[21] To illustrate this point, the variability (based on the standard deviation, $n = 4$) of time-based k' values ($s = 4.29 \times 10^{-4}$ s^{-1}) after treatment was almost double that of fluence-based k' values ($s = 2.62 \times 10^{-4}$ cm^2 mJ^{-1}) for the photo-amenable compound iopromide. In comparison, the variability of time- and fluence-based k' after treatment were similar ($s = 6.29 \times 10^{-4}$ s^{-1} and 5.14×10^{-4} cm^2 mJ^{-1}) for photo-resistant compound Primidone, and the variability of fluence-based k' values is notably higher than Iopromide. Similar trends were observed for the other photo-susceptible and photo-resistant compounds studied. Overall, these results show that photo-amenable compounds are primarily affected by absorbing species,[44] as demonstrated by the relatively low variability of fluence-based degradation rates after treatment, whereas nonphoto-amenable TOrCs will not only be affected by absorbing species, but also vary because of treatment due to known and unknown effects of scavenging as well as other radicals that may form during UV photolysis.

3.3 Hydroxyl radical production

To compare the oxidation potential of water quality conditions prior to UV/H_2O_2 treatment, steady-state $^{\bullet}OH$ concentrations, $[^{\bullet}OH]_{ss}$, were determined. As shown in Fig. 4, treatment of tertiary effluent significantly increased the $[^{\bullet}OH]_{ss}$ by 55% for single-stage biofiltration, 36% for sequential biofiltration, 59% for CFCF and 164% for nanofiltration. $^{\bullet}OH$ production is a function of the UVT since UVT controls the rate of light absorption by H_2O_2. Therefore, it is not surprising that the $[^{\bullet}OH]_{ss}$ level correlated well with the TOrC degradation rates and scavenging rates (inversely correlated) for each pre-UV/H_2O_2 water quality scenario.

As discussed in section 3.1, differences in SUVA values (Table 1) indicate organic matter composition was changed as a result of tertiary effluent treatment. While $^{\bullet}OH$ are widely recognized as a non-selective oxidant, studies have observed that $^{\bullet}OH$ react more quickly with electron rich carbon–carbon double and triple bonds, as compared to aliphatic structures[24] and, in general, $^{\bullet}OH$ reaction rates increase with increasing SUVA and molecular size of DOM.[36] To understand if $^{\bullet}OH$ reactivity changed after tertiary effluent treatment, modeled $[^{\bullet}OH]_{ss}$ were calculated from literature $k_{^{\bullet}OH}$ values of scavengers and probe compounds (additional information provided in ESI†), and compared to the experimentally-determined $[^{\bullet}OH]_{ss}$ (Fig. S1†). Experimental $[^{\bullet}OH]_{ss}$ values of sequential biofiltration and CFSF aligned well with the modeled $[^{\bullet}OH]_{ss}$ (<7% difference between experimental and

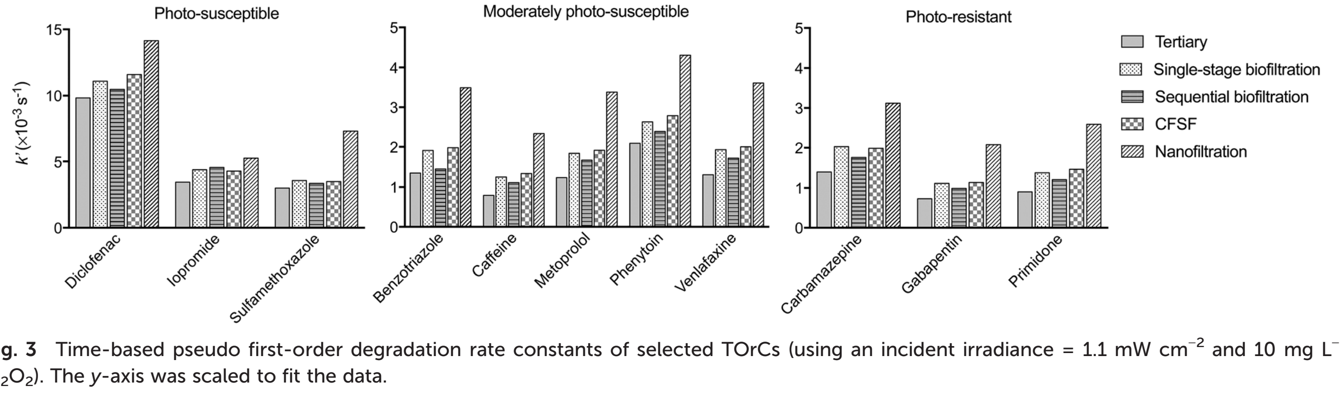

Fig. 3 Time-based pseudo first-order degradation rate constants of selected TOrCs (using an incident irradiance = 1.1 mW cm^{-2} and 10 mg L^{-1} H_2O_2). The *y*-axis was scaled to fit the data.

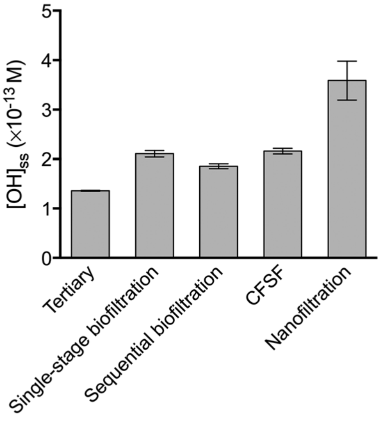

Fig. 4 Steady-state $^{\bullet}OH$ production determined using probe compounds primidone and carbamazepine with 10 mg L^{-1} H_2O_2. Error bars represent the standard deviation between probe compound results.

modeled values) and were below the percent difference (13%) between modeled and experimental $[^{\bullet}OH]_{ss}$ values for tertiary effluent. However, modeled $[^{\bullet}OH]_{ss}$ of single-stage biofiltration and nanofiltration were respectively 26% higher and 36% lower than experimental $[^{\bullet}OH]_{ss}$. These results suggest that organic matter reactivity, $k_{^{\bullet}OH,DOC}$, may have increased after nanofiltration, as indicated by the 32% increase in SUVA, and decreased after single-stage biofiltration.

Whether the organic matter reactivity was changed as a result of treatment cannot be reliably determined from this analysis; in future work, it would be valuable to study organic matter reactivity as a function of wastewater treatment by employing more advanced characterization techniques (such as ^{13}C-NMR, FT-IR spectroscopy).

3.4 Comparison of UV and UV/H_2O_2 treatment

TOrC degradation was evaluated at UV exposure times (100 s and 600 s) resulting in UV doses of 100 ± 3 mJ cm^{-2} to 600 ± 20 mJ cm^{-2}, well below those typically used for UV/AOP applications. 100 mJ cm^{-2} represents a UV dose achievable by existing UV disinfection systems during average daily flow conditions and 600 mJ cm^{-2} represents the lower limit of UV design doses for UV/AOP applications. In Fig. 5, the average percent degradation of TOrCs after 100 s and 600 s of UV exposure, with and without H_2O_2 addition of 10 mg L^{-1}, is depicted for photo-susceptible, moderately photo-susceptible and photo-resistant compounds. Results from individual compounds are illustrated in Fig. S2.†

Treatment of tertiary effluent simultaneously reduced the concentration of $^{\bullet}OH$ scavengers and increased the UVT which resulted in improvement of the percent degradation of TOrCs by direct photolysis and oxidation. For example, after 100 s of UV exposure and with added H_2O_2, treatment of tertiary effluent increased the TOrC degradation by 77% ± 14% for photo-susceptible compounds, 89% ± 30% for moderately photo-susceptible compounds and 95 ± 40% for photo-resistant compounds (Fig. 5).

As expected and observed in past work,[16,18,45] photo-susceptible compounds were degraded more efficiently by UV photolysis than moderately photo-susceptible and photo-resistant compounds. After only 100 s of exposure, compounds were degraded by 29 to 43% and increased UV exposure (600 s) resulted in up to 100% degradation. In contrast, UV alone was not sufficient to degrade compounds with relatively low quantum yields or molar absorption coefficients (Table 2). Moderately photo-susceptible compounds were

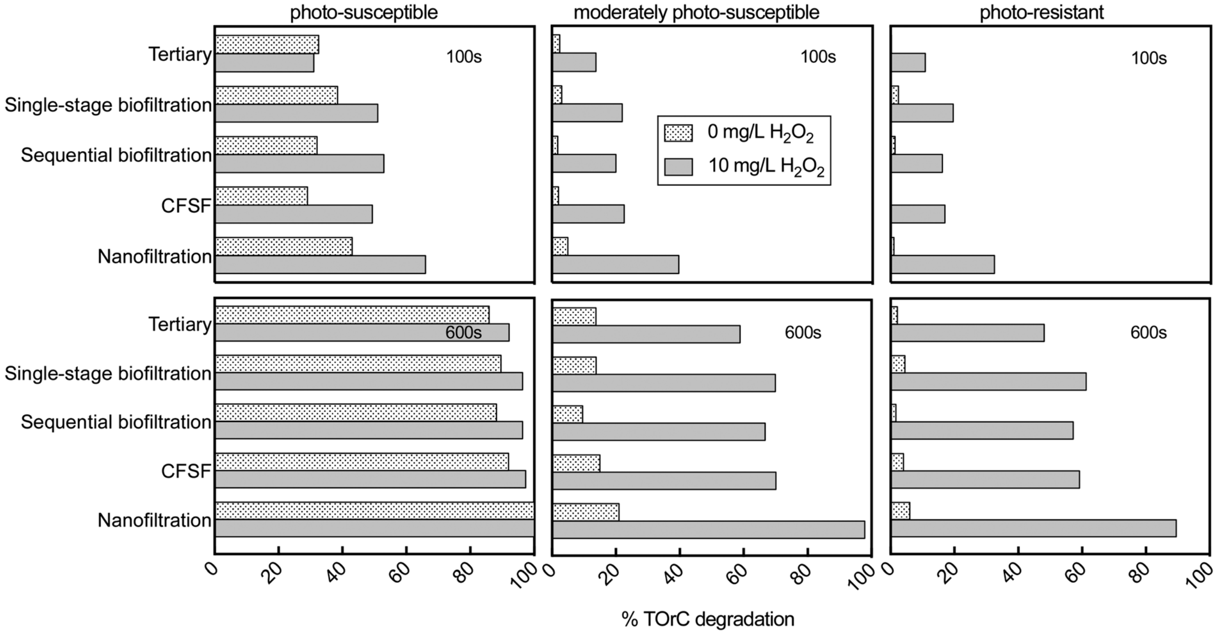

Fig. 5 Average percent degradation of TOrCs after 100 s and 600 s of UV exposure (incident irradiance 1.1 mW cm^{-2}) with and without 10 mg L^{-1} H_2O_2.

minimally degraded (<5% after 100 s, <21% after 600 s) and photo-resistant compounds were not removed. While past work[46] has demonstrated that the photolysis of DOM can produce $^{\bullet}OH$, our results indicate $^{\bullet}OH$ were not being produced at detectible levels during UV exposure following any of the treatments, based on decay results for non-photolyzable compound gabapentin (additional information provided in ESI†). In addition to $^{\bullet}OH$, other reactive intermediates (*e.g.* singlet oxygen and excited triplet state DOM) can be generated during DOM photolysis,[47] however, these radicals were not measured in this study.

What can clearly be seen in Fig. 5 are the significant increases in the degradation profiles of moderately photo-susceptible and photo-resistant compounds because of $^{\bullet}OH$ produced from the added H_2O_2. Importantly, without added H_2O_2, and at the exposure times studied herein, photo-resistant compounds would not have been significantly degraded. Lastly, few studies have evaluated the efficiency of low-pressure UV/H_2O_2 to degrade TOrCs in municipal wastewater using fluence values <300 mJ cm^{-2}.[17] While full degradation of the TOrC would require much higher UV doses, our results show that UV doses as low as 100 mJ cm^{-2} with added H_2O_2 can partially photolyze selected TOrCs in diverse wastewater matrices, produce $^{\bullet}OH$ and potentially improve the treatment of tertiary effluent *via* TOrC degradation by UV/H_2O_2.

4 Broader impact

Apart from improved efficiency of UV/AOP for the degradation of TOrCs, there are several other advantages of 1) adding a treatment step prior to UV/AOP and 2) operating UV system at doses >100 mJ cm^{-2}. Additional treatment steps, such as biofiltration, CFSF, and nanofiltration, would provide another barrier against TOrCs and pathogens and thereby reduce their presence in wastewater effluent. From a regulatory standpoint, increasing the UV dose to above 186 mJ cm^{-2} can meet a 4 log virus requirement;[48] and filtration followed by UV disinfection at a design dose (often based on MS2 bioassay results) of 100 mJ cm^{-2} can meet California's Title 22 water recycling disinfection criteria of 5-log inactivation of viruses.[49] Lastly, improved water quality as a result of added treatment processes would potentially decrease operating costs of UV/AOP systems as shown in previous work.[17] In future studies, it would be worthwhile to conduct an economic analysis to determine if the savings in UV/AOP energy costs offset the cost of energy, chemicals, installation and equipment required for an additional treatment step before the UV/AOP system.

While the focus of this study was on evaluating strategies to improve UV/H_2O_2 performance in municipal wastewater, it is important to consider that toxicity levels may change after UV/H_2O_2 treatment of TOrCs and effluent organic matter. Reports on toxicity levels post UV/H_2O_2 treatment have been shown to vary based on the toxicity test used and site-specific water quality conditions.[50,51] Whether toxicity levels are decreased or increased from advanced oxidation treatment is under active investigation.

5 Conclusion

This study evaluated four treatment technologies as strategies to improve water quality for, and TOrC degradation during, UV and UV/H_2O_2 processes for TOrC degradation. Overall, treatment of tertiary effluent increased the UVT and decreased the concentration of radical scavengers which resulted in improved $^{\bullet}OH$ production and degradation of targeted TOrCs. In comparing the four pretreatment technologies, nanofiltration treatment achieved the highest UVT, lowest scavenging demand and, subsequently, the highest $^{\bullet}OH$ production and TOrC degradation rates. The scavenging rates of biofiltration and CFSF treatment were similar despite preferentially removing different scavengers: CFSF treatment reduced carbonate scavengers where as biofiltration decreased NO_2^- to levels below detection. Differences in SUVA values and modeled and experimental $[^{\bullet}OH]_{ss}$ indicate treatment of tertiary effluent changed the organic matter composition and reactivity with $^{\bullet}OH$, however, more research is required to fully understand $^{\bullet}OH$ reactivity of organic matter as a function of treatment. Finally, treatment of tertiary effluent helped increase removal of all TOrCs at UV doses well below those typically used for UV/AOP applications.

Conflicts of interest

There are no conflicts to declare.

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