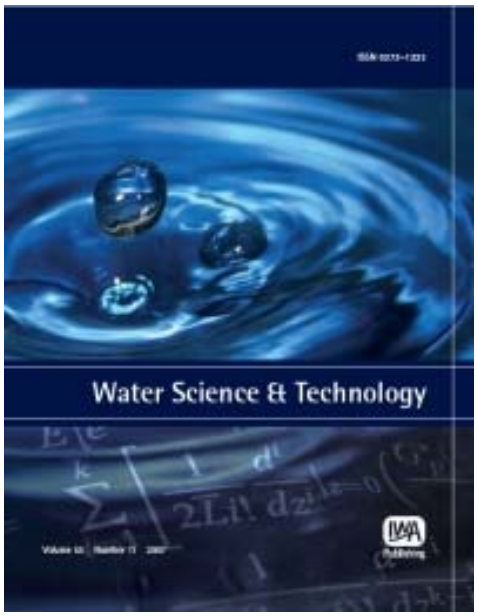

Removal of pharmaceuticals using combination of $UV/H_2O_2/O_3$ advanced oxidation process

Y. Lester, D. Avisar, I. Gozlan and H. Mamane

ABSTRACT

Water and wastewater effluents contain a vast range of pharmaceutical chemicals. The present study aims to determine the potential of the advanced oxidation technology $UV/H_2O_2/O_3$ and its sub-processes (i.e. UV, UV/H_2O_2, UV/O_3, O_3 and H_2O_2/O_3) for the degradation of the antibiotics ciprofloxacin (CIP) and trimethoprim (TMP), and the antineoplastic drug cyclophosphamide (CPD) from water. Creating AOP conditions improved in most cases the degradation rate of the target compounds (compared with O_3 and UV alone). H_2O_2 concentration was found to be an important parameter in the UV/H_2O_2 and H_2O_2/O_3 sub-processes, acting as $^{\bullet}OH$ initiator as well as $^{\bullet}OH$ scavenger. Out of the examined processes, O_3 had the highest degradation rate for TMP and H_2O_2/O_3 showed highest degradation rate for CIP and CPD. The electrical energy consumption for both CIP and CPD, as calculated using the E_{EO} parameter, was in the following order: $UV > UV/O_3 > UV/H_2O_2/O_3 > O_3 > H_2O_2/O_3$. Whereas for TMP O_3 was shown to be the most electrical energy efficient. Twelve degradation byproducts were identified following direct UV photolysis of CIP.

Key words | advanced oxidation, byproducts, EEO, ozone, pharmaceuticals, photodegradation photolysis

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INTRODUCTION

Chemicals such as prescription drugs, contraceptive pills, household chemicals, detergents and cosmetics are excreted or discharged by humans as wastewater contaminants. Commonly used wastewater treatments do not sufficiently remove these contaminants, thus they may still remain in trace concentrations in the treated effluents. As a result, effluents containing micro-pollutants like pharmaceuticals enter rivers, groundwater and drinking water by direct discharge, irrigation or artificial recharge. Several studies conducted world-wide have confirmed the occurrence of pharmaceutical residues in wastewater treatment plants (WWTPs) (e.g. Hirsch *et al.* 1999), water streams (e.g. Kolpin *et al.* 2002), surface and ground-waters (e.g. Avisar *et al.* 2009).

The acute and chronic effects of pharmaceutical compounds on the ecosystem and on human health are not yet fully understood, yet the problem remains worrisome, due to many concerns as the possible development of antibiotic-resistance bacteria. Other concerns rise from the presence of toxic pharmaceuticals as antineoplastic drugs that are used in cancer chemotherapy. These drugs, typically originated from hospital wastewater, even though detected in the environment at much lower concentrations in relation to other drugs, cannot be excluded as potential environmental contaminants due to their often carcinogenic and mutagenic properties (Kummerer 2001).

An attractive technology for the treatment of pharmaceuticals in water is the advanced oxidation process (AOP), where pollutants are chemically oxidized by a process that produces hydroxyl ($^{\bullet}OH$) free radicals. The hydroxyl radicals can be generated, for example, by the combined application of ozone/hydrogen peroxide (O_3/H_2O_2), ultraviolet radiation/ozone (UV/O_3), UV/titanium dioxide (UV/TiO_2) or UV/H_2O_2. Rosal *et al.* (2008) found AOP technologies (e.g. O_3/H_2O_2) to be efficient in the degradation of 33 organic compounds, treating effluent from two municipal WWTPs. Other researches have demonstrated the potential of UV/H_2O_2 (Vogna *et al.* 2004; Lester *et al.* 2010) and UV/O_3 (Peyton & Glaze 1988) for the removal of different pharmaceuticals and other micro-pollutants from water and wastewater effluents. Among the O_3- and UV-based AOPs, the combination of UV, O_3 and H_2O_2 ($UV/H_2O_2/O_3$), which employs several direct and indirect degradation

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mechanisms, may present an attractive option for the degradation of a wide range of refractory pollutants. Several studies have already demonstrated the advantage of UV/H_2O_2/O_3 over other AOPs in the degradation of phenol (Kusic *et al.* 2006) and 2-propanol (Wu *et al.* 2008) from water. However, information on this complex process and its potential in degrading pharmaceutical compounds is still lacking. Therefore, the objective of the current research is to determine the potential of the UV/H_2O_2/O_3 process for the degradation of commonly used pharmaceuticals, the antibiotics ciprofloxacin (CIP) and trimethoprim (TMP), and the antineoplastic drug cyclophosphamide (CPD). More specifically, this study aims to evaluate the efficiency of each of the sub-processes composing the UV/H_2O_2/O_3 process, namely: UV, O_3, UV/H_2O_2, UV/O_3, H_2O_2/O_3 and UV/H_2O_2/O_3, on the degradation of the selected pharmaceuticals.

METHODS

Chemicals

Pharmaceutical standards (>99% purity) were obtained from Sigma-Aldrich, ULC grade acetonitrile and water from Bio-Lab Ltd. (Jerusalem, Israel). All chemicals were used as obtained and pharmaceutical stock solutions were prepared by dissolving the compounds in deionized water (Direct-Q3 UV system, Millipore-France) at a concentration of 100 mg/L. H_2O_2 (30% w/w, extra pure) was obtained from Merck (Germany). Unless otherwise mentioned, all experiments were conducted in 2.5 mM phosphate buffer saline (PBS) at pH 7.

Experimental setup

UV Collimated Beam Apparatus (CBA)

A bench scale CBA was used to study the UV/H_2O_2 process (described in detail elsewhere; Lester *et al.* 2010). In the CBA experiments, UV light is directed through a collimated tube to dose a sample solution. Experiments were carried out using a 0.45 kW medium-pressure (MP) polychromatic UV lamp emitting wavelengths at the range of 200–300 nm and above (Ace-Hanovia Lamp). The spectral incident irradiance obtained from a calibrated spectroradiometer (USB4000, Ocean Optics, FL, USA) was used to calculate the average irradiance and UV fluence (Bolton & Linden 2003).

UV/H_2O_2/O_3 batch reactor

UV, O_3, UV/O_3, H_2O_2/O_3 and UV/H_2O_2/O_3 experiments were performed in a temperature controlled (25 °C) 1 L glass cylindrical batch reactor. The center of the reactor is occupied with a quartz tube in which a 0.45 kW UV MP lamp is placed vertically (Ace-Hanovia). Average irradiance in the reactor was calculated to be 6.7×10^{-6} einstein/L s, using the NO_3^- actinometer (Goldstein & Rabani 2008). Ozone is generated from pure oxygen (>99.9%) through an ozone generator (2–5 g/h, OZO-1VTT, Ozomax, Canada) and introduced into the aqueous solution using a diffuser located at the bottom of the reactor, while another tube carries the off-gases from the headspace of the reactor to the ozone destructor. The solution is continuously mixed with a magnetic stirrer. Dissolved ozone was quantified using the Indigo method (Bader & Hoigne 1981).

Determination of pharmaceutical rate constants with O_3

Two different approaches were applied to determine the second-order rate constant values of the pharmaceuticals with molecular ozone ($k_{O3,C}$, 1/M s). For CPD, with an expected low reactivity toward O_3, experiments were conducted in the 1 L reactor in a full batch mode using O_3 in excess. Ozone was initially diffused into a solution containing *t*-butanol – an $^{\bullet}OH$ radical scavenger (10 mM) until the dissolved O_3 concentration reached 5 mg/L. Ozone diffusion was then stopped and CPD was injected (1 mg/L). Samples were withdrawn at appropriate time intervals, quenched with sodium thiosulfate, and analyzed with HPLC/MS. The rate constant of CPD with ozone was obtained by using the equation below:

$$-\frac{d[CPD]}{dt} = k_{O3,CPD}[O_3] \times [CPD]$$

$$\Longrightarrow \mathrm{Ln}\frac{[CPD]_t}{[CPD]_0} = -k_{O3,CPD}\int_0^t [O_3]dt \quad (1)$$

where, $[CPD]_0$ and $[CPD]_t$ are initial CPD concentrations (M) and its concentration after exposure time t (s), $k_{O3,CPD}$ is the second-order rate constant of CPD with molecular ozone (1/M s) and the time integral over O_3 concentration is the measured ozone exposure (M s).

For the highly ozone reactive CIP and TMP, competition kinetic (CK) procedure was used, where carbamazepine (CBZ) was selected as a reference compound due to its known rate constant with O_3 ($k_{O3,CBZ}$ =

3×10^5 1/M s; Huber *et al.* 2003). In the CK experiments, different understoichiometric doses of O_3 (at a range of 0.6–3.8 μM) were added separately to samples containing *t*-butanol (10 mM) and equal concentrations of the target and the reference compound (~4.5 μM each). The samples were continuously mixed during the experiments and the remaining concentrations of the target and reference compounds were analyzed by HPLC/MS. The second-order rate constants with ozone were then calculated as described below (Huber *et al.* 2003):

$$\mathrm{Ln}\frac{[C]_H}{[C]_0} = \mathrm{Ln}\frac{[\mathrm{CBZ}]_H}{[\mathrm{CBZ}]_0} \times \frac{k_{O3,C}}{k_{O3,CBZ}} \quad (2)$$

where, $k_{O3,CBZ}$ (3×10^5 1/M s, Huber *et al.* 2003) and $k_{O3,C}$ are the rate constants of O_3 with CBZ and the target compound, respectively. H represents the different applied O_3 doses.

Determination of pharmaceutical rate constants with ·OH

The second-order rate constant of the pharmaceuticals with ·OH radical ($k_{\cdot OH,C}$, 1/M s) was calculated in the UV/H_2O_2 CBA using the CK procedure (Elovitz *et al.* 2008), where *p*-chlorobenzoic acid (*p*CBA) was used as a reference compound due to its low direct photolysis rate. In brief, a mixture of the target pollutant and reference compound (at 1 mg/L each) was exposed to UV irradiation with and without H_2O_2 (50 mg/L). Samples were withdrawn at two minute intervals for HPLC/MS analysis. In cases where the reaction with ·OH is the only degradation process (no direct photolysis), CK was used in its simplest form (Equation (2)). However, when direct photolysis played a significant role in the pollutant's UV/H_2O_2 degradation, a correction was made to subtract the loss of the compound due to direct photolysis (Equation (3); Elovitz *et al.* 2008).

$$k_{\cdot OH,C} = \frac{\left(k_{obs,C} - \left[E_{avg(H_2O_2)}/E_{avg(w/o\ H_2O_2)}\right] \times k_{d,C}\right)}{k_{obs,pCBA}} \times k_{\cdot OH,pCBA} \quad (3)$$

where, $k_{d,C}$ is the pollutant's time-based pseudo-first-order direct photolysis rate constant (1/s), $k_{obs,C}$ and $k_{obs,pCBA}$ are the observed (total) time-based pseudo-first-order rate constants (1/s) for degradation of the target pollutant and *p*CBA respectively. $k_{\cdot OH,C}$ *and* $k_{\cdot OH,pCBA}$ are the second-order rate constants of the target pollutant and *p*CBA with ·OH ($k_{\cdot OH,pCBA} = 5 \times 10^9$ 1/M s; Buxton *et al.* 1988). $E_{avg}(H_2O_2)/E_{avg}$(w/o H_2O_2) is the ratio of the average fluence rate with and without H_2O_2. This term is basically a weighting factor correcting for the pollutant's direct photolysis in the presence of H_2O_2.

Pharmaceutical degradation experiments

UV/H_2O_2 experiments using the CBA

The tested pharmaceuticals were prepared in 100 mL at an initial concentration of 1 mg/L. Different concentrations of H_2O_2 were added to generate the AOP process. Irradiation was performed with gentle stirring in a 7×5 cm crystallization dish open to the atmosphere. Samples of 0.5 mL were withdrawn at appropriate intervals for HPLC/MS analysis.

UV/H_2O_2/O_3 experiments using the 1 L batch reactor

All experiments were conducted in a semi-batch mode, where the ozone stream was continuously introduced into the aqueous solution. Initial pharmaceutical concentration was 1 mg/L. For the UV alone experiments, the UV lamp was preheated for 2 min before injecting the target compound. In O_3 and H_2O_2/O_3 experiments, steady dissolved O_3 concentration was initially achieved prior to injection of the target compound and H_2O_2. For the UV/O_3 and UV/H_2O_2/O_3 experiments, steady dissolved O_3 concentration was achieved prior to preheating UV lamp and injection of the target compound and H_2O_2. Samples (2 mL) were taken periodically after an initial mixing time of ~10 s, using a 20 cm syringe, quenched immediately with excess of sodium thiosulfate to decompose residual O_3 and analyzed chromatographically.

Analytical methods

All pharmaceuticals were detected and quantified by HPLC-UV Agilent, model 1100 (ACE-RP C18 column 2.5 mm × 250 mm) and mass spectrometer (MS) detector (Finnigan LCQ). The HPLC consisted of a binary pump, microvacuum degasser, diode array detector and thermostatic column compartment. The column temperature was 32 °C, flow rate of 0.5 mL/min and injection volume of 100 μL. Positive electro-spray ionization MS mode was used where probe temperature was 220 °C. The flow from the HPLC was passed through a split connector with 60 μL/min of effluent introduced into the MS interface. Ions in the range 200–400 m/z were registered in the conventional scanning mode. For CIP and TMP, the HPLC mobile phase conditions were adapted from Lester *et al.* (2010)

with minor modifications. For CPD the mobile phase was ammonium formate 0.05 M (A) and methanol (B), at pH 5. The mobile phase eluent gradient started with 50% of eluent A followed by a 2.5-min linear gradient to 30% of eluent A, 3 min isocratic elution and a 2 min linear gradient back to 50% of eluent A, maintained for 4 min to equilibration time. For the detection of the CIP photo-products, irradiated samples were pre-concentrated by factor of 10 using lyophilization.

RESULTS AND DISCUSSION

Determination of pharmaceutical rate constants with O_3 and $^{\bullet}OH$

Table 1 summarizes the measured rate-constants for the three pharmaceuticals with O_3 and $^{\bullet}OH$ and the used methods. Of the three compounds, TMP exhibits the highest reaction rate constants with both O_3 and $^{\bullet}OH$, while CPD reacts slowest.

The measured rate constants in the present study agree well with previously published results. The difference in rate constants between the three pharmaceuticals is due to basic structural differences. For example, the high rate constant of TMP with molecular O_3 is attributed to the presence of several amino moieties which react rapidly with O_3 (Huber *et al*. 2003).

Pharmaceutical degradation by UV/H_2O_2

Time-based degradation of the studied pharmaceuticals by UV/H_2O_2 using the CBA, with and without addition of 50 mg/L H_2O_2, is shown in Figure 1. The direct photolysis fluence-based rate constants were additionally calculated to be 5.8×10^{-3}, 3.4×10^{-4} and 2.3×10^{-5} cm^2/mJ for CIP, TMP and CPD respectively. Under direct UV light (no H_2O_2) CIP degradation rate was highest, while CPD only slightly degraded with UV. The differences in direct photodegradation rates are due to the magnitude of the compound's molar absorption coefficients and its overlap with the emission spectra of the UV lamp, as well as differences in the compounds quantum yields.

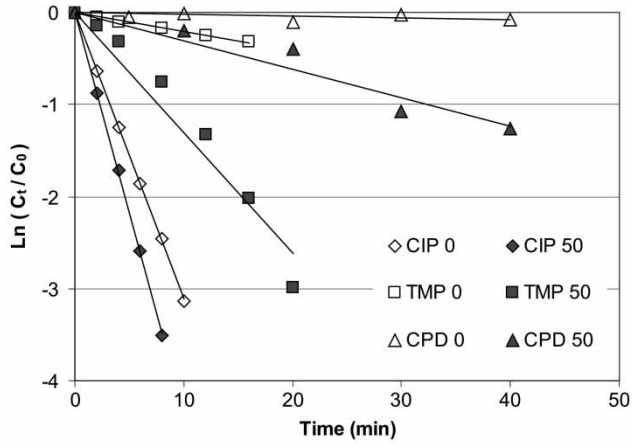


Figure 1 | Degradation of CIP, TMP and CPD by UV/H_2O_2 vs. time using the CBA, in PBS (2.5 mM, pH 7), with and without addition of 50 mg/L H_2O_2. Numbers in the legends (0 and 50) refer to H_2O_2 concentration in mg/L.

As expected, addition of 50 mg/L H_2O_2 to the photolysis process increased the degradation rate of all examined compounds, thus, the combined UV/H_2O_2 process is more effective than UV alone, presumably due to $^{\bullet}OH$ radical formation. Degradation of CPD in the UV/H_2O_2 process was previously examined by Kim *et al*. (2009). Their study showed that addition of 6 mg/L H_2O_2 to the photolysis process in pure water (using monochromatic UV lamp at 254 nm) increased the CPD degradation rate constant by factor of 12. For comparison, in the present study, addition of 50 mg/L H_2O_2 to the photolysis process of CPD increased its degradation rate constant by a factor of ~90.

H_2O_2 concentration is an important operating parameter in the UV/H_2O_2 process. Figure 2 presents the UV/H_2O_2 time-based degradation rate constants (k_{app}, 1/min) of the studied compounds as a function of H_2O_2 initial concentration, in the range of 0–200 mg/L. The degradation rate of

Table 1 | Rate constants for the examined pharmaceuticals with $^{\bullet}OH$ and O_3

	$^{\bullet}OH$ Method	Measured $k_{\bullet OH,C}$ (1/M s)	Literature $k_{\bullet OH,C}$ (1/M s)	O_3 Method	Measured $k_{O3,C}$ (1/M s)	Literature $k_{O3,C}$ (1/M s)
CIP	CK mod.[a]	5.0×10^9	4.1×10^{9c}	CK[b]	2.2×10^4	1.9×10^{4c}
TMP	CK[b]	6.4×10^9	6.9×10^{9c}	CK[b]	4.5×10^5	2.7×10^{5c}
CPD	CK[b]	1.3×10^9	2×10^{9d}	O_3 in excess	2.5	3.3[d]

[a]Competition kinetic modified for direct photolysis (Equation (3)).
[b]Competition kinetic.
[c]Dodd *et al*. (2006).
[d]Garcia-Ac *et al*. (2010).

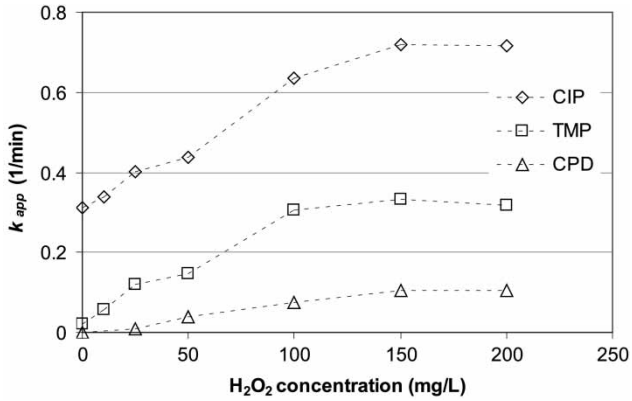


Figure 2 | UV/H_2O_2 time-based degradation rate constants (k_{app}) of CIP, TMP and CPD, in PBS (2.5 mM, pH 7), at different initial H_2O_2 concentrations.

CIP, CPD and TMP with UV was steadily increased with addition of H_2O_2 at concentrations up to 150 mg/L. However, further increase in H_2O_2 concentration above 150 mg/L, did not improve the degradation rate of the selected compounds. The tailing observed at H_2O_2 concentrations higher than 150 mg/L is a well-documented phenomenon (e.g. Aleboyeh *et al.* 2004; Lester *et al.* 2010) and can be explained by the H_2O_2 scavenging effect on $^{\bullet}OH$ and by the pharmaceuticals UV light screening due to H_2O_2 light absorbance, both occur predominantly at high H_2O_2 concentration. As a control experiment, the impact of H_2O_2 alone was evaluated on the degradation of CIP, TMP and CPD (without UV light). No degradation of the compounds was observed when H_2O_2 was used at concentration of 200 mg/L and contact times up to 48 h.

$^{\bullet}OH$ radicals were previously indirectly quantified using the *p*CBA method (Lester *et al.* 2010). These results indicate a steady increase in $^{\bullet}OH$ radical concentration from 2.9×10^{-14} to 4.7×10^{-13} M when increasing H_2O_2 initial concentration from 10 to 150 mg/L. A further increase in H_2O_2 concentration to 200 mg/L had almost no effect on $^{\bullet}OH$ concentration (i.e. 4.8×10^{-13} M).

Pharmaceutical degradation by UV/H_2O_2/O_3

In the UV/H_2O_2/O_3 treatment, $^{\bullet}OH$ radicals are generated through several different processes where each can operate as an independent AOP (Glaze *et al.* 1987), namely: (a) O_3 reaction with OH^-, (b) UV photolysis of H_2O_2, (c) the combined application of ozone and hydrogen peroxide and (d) UV photolysis of ozone, generating $^{\bullet}OH$ through a sequence of reactions, initiated by the formation of H_2O_2. In addition, direct degradation of the target pollutant may occur by UV photolysis and direct oxidation by ozone. In order to better understand the UV/H_2O_2/O_3 mechanism, each of the above processes was examined separately.

Degradation by O_3-based processes

Figure 3 illustrates the degradation of the pharmaceuticals in the ozone process, for different initial dissolved ozone concentrations (0.1–1 mg/L). Results for TMP were not plotted, as TMP completely degraded at the lowest ozone concentration of 0.1 mg/L, in less than 1 min. In all cases, a first order kinetic was observed, up to 30 min. For both CIP and CPD, degradation rate increased with an increase in initial ozone concentration. CPD showed the slowest degradation rate, at any ozone concentration, while TMP degraded the fastest. The observed degradation rates correlate well with the compound's calculated rate constants with O_3 and $^{\bullet}OH$, as presented in Table 1. Previous studies have already demonstrated the low O_3 degradability of CPD (Kim *et al.* 2008) and the quick reaction of TMP and CIP with O_3 (Dodd *et al.* 2006).

Addition of H_2O_2 to the ozone process creates AOP conditions and may enhance the degradation of the pharmaceuticals. Table 2 presents the pseudo-first-order time-based degradation rate constants of CIP and CPD, by the H_2O_2/O_3 process ($[O_3]_0 = 0.5$ mg/L), without H_2O_2 and with the addition of H_2O_2 at concentrations 0.17 and 0.35 mg/L. Results for TMP were not presented due to immediate O_3 degradation, as stated above. The degradation rate of CPD steadily increased with increase in H_2O_2 concentration, while the degradation rate of CIP increased at low concentration of H_2O_2 but decreased at the higher H_2O_2 level. CIP reacts relatively fast with molecular O_3 ($k_{O3,CIP} = 2.2\times10^4$ 1/M s), therefore, H_2O_2 which competes with

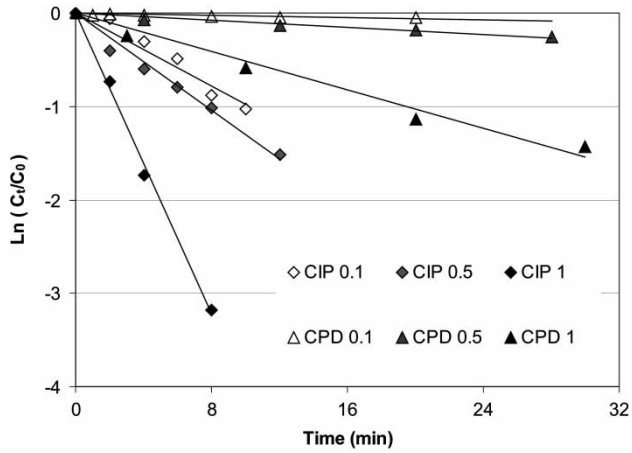


Figure 3 | Degradation of CIP and CPD with time at different initial dissolved O_3 concentrations in PBS (2.5 mM, pH 7). Numbers in the legends refer to initial O_3 concentration in mg/L.

Table 2 | H_2O_2/O_3 time-based degradation rate constant (k_{app}, 1/min) of CIP and CPD at different H_2O_2 initial concentrations. Initial O_3 dissolved concentration 0.5 mg/L

H_2O_2 concentration (mg/L)	0	0.17	0.35
CIP	0.113	0.171	0.121
CPD	0.008	0.0164	0.0227

CIP over O_3, may ultimately reduce its degradation rate. For CPD, direct reaction with O_3 is negligible, thus increasing H_2O_2 concentration (within the tested range) will increase $^{\bullet}OH$ formation, resulting in a higher degradation rate of CPD.

Kim *et al.* (2008) found that the addition of 2.3 mg/L H_2O_2 to the O_3 process slightly improved the degradation rate of CPD, while De Witte *et al.* (2009) reported an improvement in degradation rate of CIP from water by O_3 with the addition of up to 1.7 mg/L H_2O_2. In contrast, Vasconcelos *et al.* (2009a) found that the H_2O_2/O_3 process was slower than O_3 alone for the removal of CIP from wastewater effluent. Their results may be explained not only by the fast direct reaction of CIP with O_3, but also by the scavenging effect of constitutes in the wastewater effluent on $^{\bullet}OH$ radicals.

Degradation by UV-based processes

Time-based degradation of CIP and CPD by the UV, UV/O_3 and UV/H_2O_2/O_3 processes (in the 1 L batch reactor) are presented in Figure 4. Initial concentration of dissolved O_3 (before pollutant's injection) was 0.5 mg/L (for UV/O_3 and UV/H_2O_2/O_3) and initial H_2O_2 concentration was 2 mg/L (for UV/H_2O_2/O_3). At conditions studied, direct UV showed the slowest degradation rate for both compounds. For CPD, degradation rate decreased as follow: UV/H_2O_2/O_3 > UV/O_3 > UV. While for CIP the UV/O_3 and UV/H_2O_2/O_3 processes showed almost similar degradation rate, thus the addition of H_2O_2 to the UV/O_3 process have practically no additional value on the degradation rate of CIP.

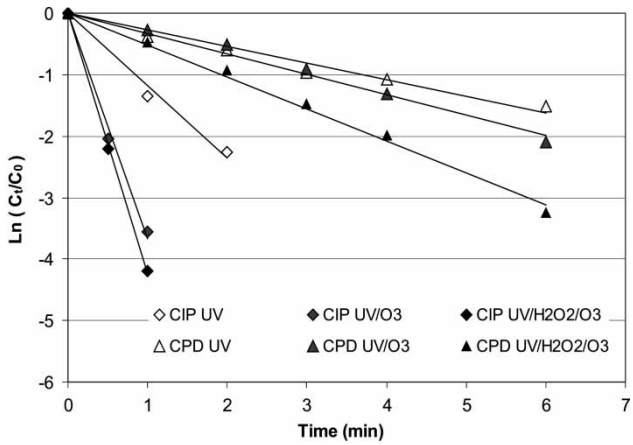


Figure 4 | Degradation of CPD and CIP with time by the UV, UV/O_3 and UV/H_2O_2/O_3 processes in PBS (2.5 mM, pH 7) ($[O_3]_0 = 0.5$ mg/L; $[H_2O_2]_0 = 2$ mg/L).

Wang *et al.* (2005) studied the impact of different AOPs on the degradation of three chlorophenols found in a Kraft-pulp bleach plant effluent. Their study showed that degradation efficacy of each AOP was compound dependent. For example the addition of H_2O_2 to an UV/O_3 system improved the degradation rate of 2, 3, 4, 5-tetrachlorophenol and had no effect on the degradation of 4, 5-dichloroguaiacol. Kusic *et al.* (2006) found that phenol decay was similar in the UV/O_3 and UV/H_2O_2/O_3 processes; however, UV/H_2O_2/O_3 achieved higher mineralization (i.e. TOC removal). Thus, the UV/H_2O_2/O_3 process may have an advantage over other AOPs in the degradation of specific (i.e. refractory) target compounds, as well as in their mineralization. Complete mineralization of the target pollutant is advantageous due to possible unwanted formation of active intermediate byproducts resulting from the degradation of the parent compound.

Electrical energy efficiency

The electrical-energy per order parameter (E_{EO}) was determined, as the studied degradation processes are electrical energy related processes. The E_{EO} parameter corresponds to the amount of electrical energy (kWh) required to reduce one order of magnitude (90% removal of contaminant) in a treated volume of contaminated water (Bolton *et al.* 2001).

$$E_{EO} = \frac{P}{26.1 \times V \times k_{app}} \quad (4)$$

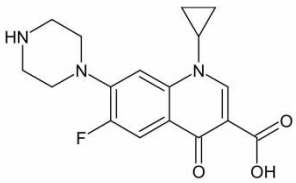
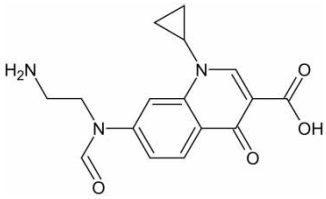
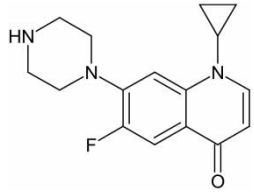
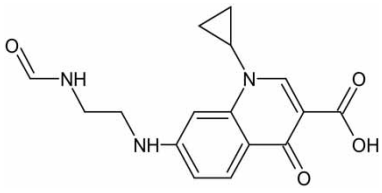
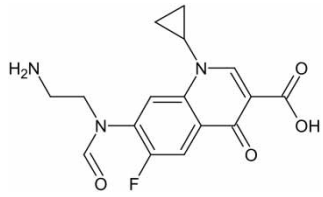
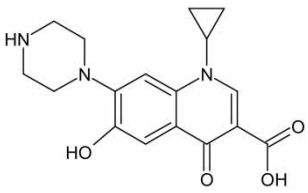
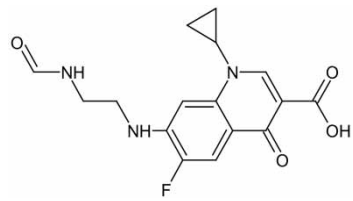
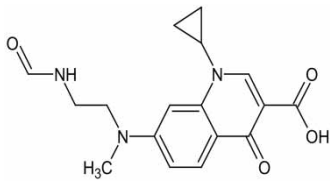
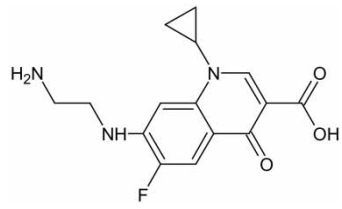
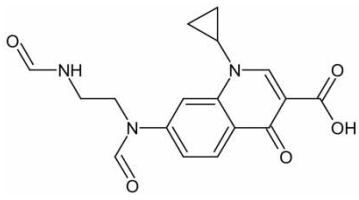
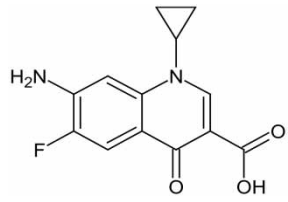
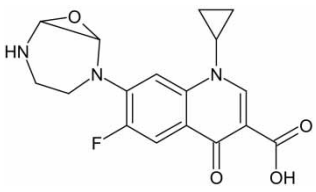
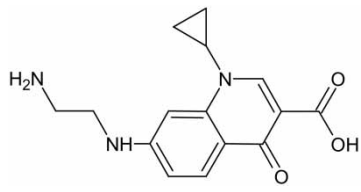
where, P is the rated power of the system (kW), V is the total volume of water treated (m^3) and k_{app} is the time-based degradation rate constant of the examined compound (1/min).

The rated power was calculated as the sum of the UV lamp power (0.45 kW), the O_3 production power and the energy cost of H_2O_2. Where, the O_3 production power

Table 3 | E_{EO} values (kWh/m^3/order) of CIP and CPD at different processes

	UV	UV/O_3	UV/H_2O_2/O_3	O_3	H_2O_2/O_3
CIP	16.3	5.2	5.1	3.2	2.2
CPD	70.7	59.1	37.8	19.7	7.2

Table 4 | HPLC/MS analysis of CIP direct UV degradation byproducts

N° (m/z)	Rt[a]	Proposed product structures	N° (m/z)	Rt[a]	Proposed product structures
CIP (332.1)	4.9				
1 (316.1)	2.9		7 (288.1)	7.0	
2 (316.1)	6.1		8 (334.1)	3.4	
3 (330.1)	2.8		9 (334.1)	6.8	
4 (330.1)	7		10 (306.1)	4.0	
5 (344.1)	5.5		11 (263.1)	7.5	
6 (346.1)	4.4		12 (288.1)	3.2	

[a]MS retention time (min).

was based on the product of the measured current and voltage of the ozone generator and the energy cost of H_2O_2 was calculated as the ratio between the local costs of H_2O_2 (US$/mg) and electricity (US$/kWh). It should be noted however that at the examined H_2O_2 range it had only minor contribution to the E_{EO} value. E_{EO} results for CIP and CPD in the 1 L batch reactor, for each of the examined process, are presented in Table 3. For the O_3-based process E_{EO} was calculated for initial O_3 concentration of 0.5 mg/L. For the H_2O_2/O_3 process E_{EO} was calculated for initial H_2O_2 concentration of 0.17 and 0.35 mg/L for CIP and CPD respectively.

From Table 3 it can be concluded that for the studied compounds and operating parameters, the O_3-based processes (i.e. O_3 and H_2O_2/O_3) consume less electrical energy than the processes where UV light was used. The electrical energy consumption for CPD was in the following order: UV > UV/O_3 > UV/H_2O_2/O_3 > O_3 > H_2O_2/O_3, while for CIP E_{EO} was similar for UV/O_3 and UV/H_2O_2/O_3, thus, the most energy-efficient process was the combination H_2O_2/O_3. Earlier studies have confirmed the advantage of O_3-based processes over UV-based processes in terms of energy efficiency (e.g. Muller & Jekel 2001).

Photo-degradation intermediates analysis

The formation of intermediate byproducts, following the degradation of an organic pollutant by UV- or O_3-based processes, is one of the most important issues in the field of pharmaceutical removal. Active degradation intermediates may occasionally be formed, in particular if the active part of the molecule remains unmodified. The importance of this topic is demonstrated in Table 4, where 12 byproducts, identified during direct UV photolysis of CIP, are presented. The moieties which are involved in the CIP photo-degradation are the piperazine residue, the carboxylic group and the fluorine atom. The quinolone skeleton however remains unchanged. The piperazine ring is either subjected to breakdown (intermediates 1–2, 4–5 and 8–12) or is epoxidized at positions 2, 3 (of the piperazine) (intermediate 6). Decarboxylation occurs at position 3 of the quinolone skeleton (intermediate 7). The fluorine at position 6 is either substituted by hydroxyl group (intermediate 3) or by hydrogen atom (intermediates 1, 2, 4, 5 and 12). Various researchers have already identified the formation different byproducts as a result of CIP photo-degradation (e.g. Vasconcelos *et al.* 2009b). In light of the fact that the characteristic quinolone is believed to be responsible for the CIP antimicrobial activity (Dodd *et al.* 2006), intermediates which merely involve modification of the piperazine residue may still potentially exhibit antibacterial potencies.

CONCLUSIONS

AOPs which combine UV photolysis, hydrogen peroxide and ozone may present an attractive treatment for the degradation of a wide range of pharmaceuticals in water. Out of the examined processes, O_3 had the highest degradation rate for TMP and H_2O_2/O_3 showed highest degradation rate for CIP and CPD. H_2O_2 concentration was found to be an important parameter in the UV/H_2O_2 and H_2O_2/O_3 sub-processes, acting as an $^{\bullet}OH$ initiator at low concentrations and as an $^{\bullet}OH$ radical scavenger at higher concentrations. The electrical energy consumption, as calculated using the E_{EO} parameter, showed that O_3-based processes were more efficient than UV-based processes, where O_3 was the most efficient process for the degradation of TMP, and H_2O_2/O_3 was the most efficient process for the degradation of CIP and CPD. Twelve degradation byproducts were identified following direct UV photolysis of CIP. Future research will investigate the formation of degradation byproducts for CIP, CPD and TMP under the different AOP conditions and evaluate their potential toxicity.

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