Removal of selected antibiotics and antiretroviral drugs during post-treatment of municipal wastewater with UV, UV/chlorine and UV/hydrogen peroxide

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Abstract

Active pharmaceutical ingredients (APIs) are only partially removed by conventional wastewater treatment plants. This study aimed at assessing the post-treatment degradation of selected antibiotics and antiretroviral drugs by direct UV photolysis and advanced oxidation processes (UV/H2O2 and UV/Cl2) using low-pressure mercury lamp. The rate of degradation largely followed pseudo first-order reaction kinetics. Amongst the six studied APIs, sulfamethoxazole, ciprofloxacin and zidovudine were readily degraded by more than 90% using direct UV photolysis. Addition of Cl2 and H2O2 to the UV process led to an increase in the rate of degradation for all the compounds. The effectiveness UV/Cl2 process was affected to a greater extent by the background effluent organic matter. This implies that higher electrical energy and oxidant would be required in the UV/Cl2 process relative to UV/H2O2 process. Generally, electrical energy required to remove 90% of the target compounds increased in the order UV/H2O2 < UV/Cl2 < UV processes.

Keywords
advanced oxidation process; antibiotics; antiretroviral drugs; chlorine; hydrogen peroxide; post-treatment; UV; wastewater.

Introduction

The presence of active pharmaceutical ingredients (APIs) in water resources is increasingly becoming an issue of great concern due to the potential harm that they pose to human health and the environment (Jjemba, 2006). APIs are unregulated environmental contaminants whose environmental fate and effects are not yet well understood (Daughton and Jones-Lepp, 2001; Ellis, 2006; Segura et al., 2015). APIs are discharged into the environment from various sources, such as wastewater treatment plants (WWTPs), industrial effluents, direct discharge of untreated domestic wastes and agricultural activities (Jjemba, 2006; Chen et al., 2016). WWTPs are by far the most significant route of entry of APIs into the environment largely because the conventional WWTPs are not designed to remove pharmaceuticals and other micropollutants resulting in poor removal efficiencies (Daughton and Ternes, 1999; Kümmerer, 2003; 2009; Zhang & Li, 2011; Celle-Jeanton et al., 2014; Kosma et al., 2014; Tang et al., 2015).

With increasing global water scarcity in many regions of the world, reuse of municipal wastewater is becoming increasingly inevitable to meet the current water demand. However, the presence of organic micropollutants such as pharmaceuticals is of a major concern (Yang et al., 2014). As a result, several advanced post-treatment technologies have been developed in an attempt to completely remove or degrade the APIs. Such technologies include the use of advanced oxidation processes (AOPs) in degrading recalcitrant organic compounds (O’Shea and Dionysiou, 2012). AOPs rely on the generation and utilisation of highly reactive nonselective radicals, the most important being the hydroxyl radical (•OH) which has a high oxidation potential (2.8 V) only lower than that of fluorine (3.03 V) (Parsons, 2004). The UV-based AOPs have several benefits that are making them more popular. Some of these benefits include: (i) AOPs do not transfer pollutants into another phase as in chemical and biological processes. (ii) The UV-based APOs are very good in disinfecting any pathogens that might be present in water and (iii) UV AOPs have rapid reaction rates. Several UV-based AOPs have been studied for the degradation of recalcitrant organic micropollutants in water (Wang and Xu, 2012). However, full-scale applications of most of these AOPs are hampered by the high costs largely associated with electrical energy consumption and chemical oxidants (Comninellis et al., 2008). Though UV/H2O2 has been applied in the full-scale wastewater treatment (Kruithof et al., 2007), the low molar absorption coefficient of H2O2 at 254 nm (about 20 M−1 cm−1) implies that only a small fraction of incident light is utilized for the radical formation and thus an excess H2O2 must

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Recently, the use of aqueous chlorine and UV as an AOP has been investigated and suggested to be effective in the degradation of recalcitrant organic micropollutants (Watts et al., 2007; Watts and Linden, 2007; Sichel et al., 2011; Watts et al., 2012; Boal et al., 2015). The UV/Cl₂ process has been suggested as a possible alternative to the UV/H₂O₂ in the removal of organic micropollutants for several reasons including: (i) the higher UV absorbance and the lower scavenging of HOCl as compared to H₂O₂ resulting in higher quantum yield (φ) during photolysis of aqueous chlorine (HOCl φ = 1.4 mol Es⁻¹ and H₂O₂ φ = 1.0 mol Es⁻¹ at 254 nm) (Watts and Linden, 2007; Jin et al., 2011; Rosenfeldt et al., 2013; Fang et al., 2014; Kishimoto and Nishimura, 2015). (ii) The UV/Cl₂ AOP produces

### Table 1: Names, structures and selected measured and literature properties

| Compound               | Chemical structure | Water solubility (mg/L)^a| pKa^a | Decadic molar absorption coefficient (ε,λ<sub>254</sub>(M⁻¹cm⁻¹)) |
|------------------------|--------------------|--------------------------|-------|---------------------------------------------------------------|
| Sulfamethoxazole (SMX) | ![Chemical structure](image) | 610                      | 5.6, 1.83 | 14 950                                                       |
| Ciprofloxacin (CIP)    | ![Chemical structure](image) | 13 500                   | 6.4, 8.2  | 13 470                                                       |
| Trimethoprim (TMP)     | ![Chemical structure](image) | 400                      | 7.2, 17.33 | 4300                                                         |
| Zidovudine (ZDV)       | ![Chemical structure](image) | 20 100                   | 9.7     | 7560                                                         |
| Lamivudine (3TC)       | ![Chemical structure](image) | 70 000                   | 4.3, 14.29 | 8970                                                         |
| Nevirapine (NVP)       | ![Chemical structure](image) | 0.7046                   | 2.8     | 7500                                                         |

ndf, no data found.

^aWishart et al. (2006), Babić et al. (2007), USEPA (2012).
^bKim and Tanaka (2009), Batchu et al. (2014), Gerrity et al. (2014), Carlson et al. (2015), Lian et al. (2015), Yang et al. (2016).
^cAvisar et al. (2010), Guo et al. (2013), Batchu et al. (2014).
^dGerrity et al. (2014), Carlson et al. (2015), Yang et al. (2016).
three reactive radicals including hydroxyl, chlorine and oxygen radicals (Feng et al., 2007; Jin et al., 2011).

In the present study, the removal of three antibiotics (sulfamethoxazole, ciprofloxacin and trimethoprim) and three antiretroviral drugs ( Nevirapine, zidovudine and lamivudine) from wastewater effluents by direct UV photolysis, UV/H_2O_2 and UV/Cl_2 was evaluated. Though the removal of antibiotics by various AOPs has been reported by several authors, less attention has been paid to the antiretroviral drugs. The selected APIs are frequently used for the treatment of bacterial and viral infections and they are particularly useful in the management of HIV/AIDS (World Health Organization, 2016). The target compounds have been detected in various aquatic environments including surface water, groundwater and wastewater effluents at concentrations ranging from ng/L to hundreds of µg/L (Watkinson et al., 2007; Watkinson et al., 2009; Valcárcel et al., 2011; K’oreje et al., 2016; Ngumba et al., 2016a). The compounds have a wide range of physico-chemical properties (Table 1) that directly affect their rate of degradation by various wastewater treatment processes. The bulk of the expense in the operation of a UV–based AOPs can be attributed to electrical energy consumption. In the present study, energy requirement was estimated by calculating the electrical energy per order of compound removal (E_{EO}) using Eq. (1) (which is the energy required to remove or degrade 90% of the target compound) (Parsons, 2004).

\[ E_{EO} = \frac{P (kW) \times t (min) \times 1000}{V (L) \times 60 \times \log C_0 / C_f} \]  \hspace{1cm} (1)

where \( P \) (kW) is the electrical power input into the reaction; \( C_0 \) and \( C_f \) are the initial and final API concentration, respectively; \( t \) (min) is the irradiation time in minutes; \( V \) is the volume of water in L.

Materials and methods

Chemicals and standards

Active chlorine and hydrogen peroxide solutions were prepared from sodium hypochlorite (EMPLURA® 6-14% active chlorine, Sigma-Aldrich) and hydrogen peroxide (30 wt. % Sigma-Aldrich), respectively. All the pharmaceutical standards (purity ≥ 95%) were a kind donation from Universal Corporation Ltd, Kenya. Internal standards \( [^{13}C_2H_2^{15}N_2] \)-lamivudine (Alsachim, Illkirch, France), while \( [^{2}H_4] \)-sulfamethoxazole, \( [^{13}C_2H_3] \)-zidovudine, \( [^{2}H_4] \)-nevirapine and \( [^{13}C_2H_2^{15}N_2] \)-lamivudine (Alsachim, Illkirch, France), while \( [^{1}H_4] \)-trimethoprim (Sigma-Aldrich, Steinheim, Germany), HPLC-grade methanol and acetonitrile (Merck, Darmstadt, Germany), formic acid 98% (Fluka, Darmstadt, Germany) were used in the preparation of chromatographic eluents. Ultrapure water was used throughout the study and was generated using Ultra Clear UV Plus and euRO 60 Reverse Osmosis unit (SG, Barsbuttel Germany). All other reagents used in this study were of analytical grade.

Irradiation experiments

UV irradiation experiments were performed using a 670 mm 40 W low-pressure mercury lamp (Aquada 2 UV system, Wedeco, Germany) emitting at \( \lambda_{\text{max}} = 254 \) nm. The UV output was determined as 13.7 W using hydrogen peroxide actinometry as described by Nicole et al. (1990) and had a UV intensity of 9.25 mW/cm² (details given in the Appendix A). The experiment was set-up as shown in Fig. 1. In brief, 3 L of water sample was added to the reservoir and reactor was run in a batch mode by recirculating the water at a flow rate of 0.5 L/min. Homogenisation of the sample was accomplished by the continuous recirculation of the water and use of magnetic stirrer.

To evaluate the degradation of individual APIs, the experiments were conducted based on the following experimental design: (i) Determination of target APIs degradation by direct UV photolysis, UV/H_2O_2 and UV/Cl_2 processes in spiked buffered ultrapure water and varying the sample pH, irradiation time and the initial oxidant concentrations; (ii) Determination of the target APIs degradation in biologically treated municipal wastewater effluent varying the initial oxidant concentrations and irradiation time. (iii) Oxidation of the target APIs degradation by Cl_2 and H_2O_2 in ultrapure water at pH 7.5 without UV irradiation (dark experiments). The irradiation experiments with wastewater were conducted without pH adjustment; however, the initial and final pHs of each batch were determined and overall the initial and final pHs for all the samples.
were between 7.6 and 8.1 which are well within the typical municipal wastewater effluents. The injected doses for chlorine (as Cl2) and hydrogen peroxide ranged between 8.52–85.2 and 4.1–41.2 mg/L, respectively, and were added at the beginning of the experiment. The initial concentration of the APIs was 20 µM. Before oxidant addition, the first sample (C0) was drawn directly from the reservoir. The oxidant was then injected and quickly homogenized with the magnetic stirrer after which the recirculation was started. Degradation samples (Ct) were periodically withdrawn from the sample valve/directly from the reservoir and residual oxidants quenched with sodium thiosulfate followed by the final APIs analysis.

Analytical methods

The SPE-LC-MS/MS procedures followed methods reported in previous studies with slight modifications (Ngumba et al., 2016a; 2016b). Briefly, water samples were filtered through 47 mm GF/D (2.7 µm) and GF/F (0.7 µm) glass microfibre filters (Whatman, Maidstone, England). Prior to SPE process corresponding isotopically labelled internal standards were added to 50 mL of filtered sample then loaded into Oasis HLB cartridges (3 cc, 60 mg Waters, Milford, USA) which had been conditioned with 3 mL of methanol (EMSURE, analytical grade) and 3 mL of distilled water, respectively. The cartridges were then dried in vacuum for 10 min and with 5 mL of ultrapure water followed by 5 mL of 2% methanol and then dried for further 10 min before elution with 4 mL of ACN/MeOH, (1:1 v/v). The solvent was then evaporated in a stream of nitrogen at 40°C, re-constituted to 1 mL with acetonitrile/water (20:80 v/v) and then filtered through a 0.2 µm cellulose acetate syringe filter before injection into an LC-MS/MS system as previously reported (Ngumba et al., 2016b).

The concentration of free chlorine was determined by diethyl-p-phenylenediamine (DPD) ferrous iodometric titration method (American Public Health Association (APHA), 1999). Hydrogen peroxide concentration was standardized by 1999 spectrophotometrically using a molar absorption coefficient of 43.6 M⁻¹ cm⁻¹ at 240 nm (Cohn et al., 2005). Dissolved organic carbon (DOC) was measured with total TOC analyser (TOC-LCPH; Shimadzu, Japan). The UV absorbance of the samples was measured using the Hitachi U-1500 spectrophotometer (Hitachi Instruments, Inc. USA).

Results and discussion

Molar extinction coefficients for the target APIs

The degradation of an organic compound by UV is strongly dependent on the compound’s ability to absorb UV radiation expressed as a molar extinction coefficient. The presence of conjugated π system as well as aromatic rings and heteroatoms is some of the indicators of good UV chromophores that readily undergo direct photolysis. In this study, the molar extinction coefficients at 254 nm were determined from the slope of the linear plot of the UV absorbance against the concentration of individual API (5–40 µM) dissolved in ultrapure water. The results are shown in Table 1. The molar extinction coefficients ranged from 4300 M⁻¹ cm⁻¹ to 14 950 M⁻¹ cm⁻¹ and increased in the order TMP < NVP < ZDV < 3TC < CIP < SMX. The molar extinction coefficients for TMP, CIP and SMX were within the range previously reported in the literature Table 1. However, no data were found for the antiretroviral drugs.

Determination of reaction rates

In order to compare the impact of selected UV-processes on the degradation of the target analytes, the reaction rates constants were determined in spiked wastewater effluents and ultrapure water. The rate of degradation of the APIs was evaluated by calculating the pseudo first-order rate constants as shown in Eq. (2)

\[
\frac{-d[C]}{dt} = k_{obs} [C]
\]

where \(k_{obs} \) (min⁻¹) is the time-based pseudo first-order rate constant for each compound with concentration C.

The direct UV photolysis, UV/H2O2 and UV/Cl2 treatment linear plots of ln [(Ct/C0)] against time for each compound in wastewater effluent are shown in Fig. 2. Table 2 compares the Pseudo first-order rate constants at different oxidant concentrations in wastewater effluent and ultrapure water together with their corresponding coefficients of determination \(R^2\). The degradation of the compounds in wastewater effluents by the three UV-based processes followed a pseudo first-order kinetic model in the studied experimental conditions and the \(R^2\) for UV/Cl2, UV/H2O2 and UV photolysis ranged from 0.89 to 0.99, 0.95 to 1.0 and 0.96 to 0.99, respectively. The UV/Cl2 showed some deviations from the curve as evidenced by the relatively lower \(R^2\) values. The deviation can be attributed to the multiple degradation processes in the UV/Cl2 such as UV photolysis, oxidation by free chlorine and radical attack. The degradation in ultrapure water similarly followed a pseudo first-order kinetic model under the experimental conditions with few exceptions. The \(R^2\) calculated from the experimental results for UV/Cl2, UV/ H2O2 and UV photolysis ranged from 0.87 to 0.98, 0.94 to 1.0 and 0.95 to 1.0, respectively. NVP and 3TC reacted instantaneously with chlorine and as a result, the rate
constants could not be approximated for the UV/Cl₂ process.

The application of UV/Cl₂ and UV/H₂O₂ AOPs resulted in increased degradation of the target APIs relative to direct photolysis both in the wastewater effluents and in ultrapure water. For instance, when 20.4 mg/L of hydrogen peroxide was added to wastewater effluent, the rate of degradation for TMP and NVP w was increased by a factor of 4.1 and 4.2, respectively.

Degradation of APIs with Cl₂ and H₂O₂ (dark experiments)

The degradation of the selected APIs by chlorination (dark experiments) is shown in Fig. 3. Based on the extent of degradation, the compounds could be put in three categories: (i) APIs that reacted instantly with chlorine: - NVP and 3TC, (ii) APIs that remained less than 50% after 10 min of reaction time: - SMX, TMP and CIP and (iii) ZDV which reacted less than 10% with chlorine. The relatively fast reaction of a majority APIs with chlorine can be attributed to the presence of electron-rich moieties (Lee and von Gunten, 2010; Oulton et al., 2010). Oxidation reactions, addition reactions to unsaturated bonds and electrophilic substitution reactions at nucleophilic sites are possible reaction pathways of APIs with aqueous chlorine (Deborde and Von Gunten, 2007). This implies that the APIs may not be substantially oxidized but instead may be transformed into chlorinated addition and substitution products.

None of the APIs degraded in the dark experiments in presence of 8.2 mg/L of H₂O₂. Direct reactions of hydrogen...
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peroxide with most organic compounds are generally too slow and are not usually viewed as a significant pathway for the degradation of organic micropollutants (Watts and Teel, 2005; Petri et al., 2011). The use of hydrogen peroxide in the presence of a catalyst or an activator resulting to the generation of highly reactive and non-selective hydroxyl radicals is the most significant application (Oppenländer, 2002; Boczkaj and Fernandes, 2017).

The effect of pH on the direct UV photolysis, UV/H₂O₂ and UV/Cl₂ processes in ultrapure water

The effect of pH on degradation of the target compounds by the three treatment methods was evaluated at three pH levels in phosphate-buffered ultrapure water spiked with the analytes. An initial concentration of 8.2 and 17.0 mg/L for H₂O₂ and Cl₂, respectively, and an electrical energy dose of 2.2 kWh/10³ L was used. The obtained results are shown in Fig. 4.

Table 2  Direct UV photolysis, UV/H₂O₂ and UV/Cl₂ pseudo first-order rate constants for 20 µM of the selected antibiotics and antiretroviral drugs in wastewater effluent and ultrapure water

| Initial oxidant concentration | Wastewater effluent | Ultrapure water |
|------------------------------|---------------------|-----------------|
|                              | Kₘₐₓ (s⁻¹) | R²       | Kₘₐₓ (s⁻¹) | R²       |
| TMP 0                       | 1.33E-04 | 0.971    | 1.67E-04 | 0.948    |
| 20.4 mg/L H₂O₂             | 5.50E-04 | 0.98     | 1.47E-03 | 0.952    |
| 40.8 mg/L H₂O₂             | 8.33E-04 | 0.997    | nd       | nd       |
| 42.6 mg/L Cl₂              | 1.83E-04 | 0.955    | 2.43E-03 | 0.944    |
| 85.2 mg/L Cl₂              | 3.00E-04 | 0.985    | nd       | nd       |
| 3 TC 0                     | 3.33E-04 | 0.958    | 2.50E-04 | 0.976    |
| 20.4 mg/L H₂O₂             | 7.00E-04 | 0.994    | 1.90E-03 | 0.98     |
| 40.8 mg/L H₂O₂             | 1.08E-03 | 0.987    | nd       | nd       |
| 42.6 mg/L Cl₂              | 7.00E-04 | 0.967    | *        | *        |
| 85.2 mg/L Cl₂              | 1.08E-03 | 0.985    | nd       | nd       |
| ZDV 0                      | 1.37E-03 | 0.991    | 1.55E-03 | 0.995    |
| 20.4 mg/L H₂O₂             | 1.68E-03 | 0.952    | 2.08E-03 | 0.984    |
| 40.8 mg/L H₂O₂             | 2.07E-03 | 0.994    | nd       | nd       |
| 42.6 mg/L Cl₂              | 1.13E-03 | 0.996    | 3.20E-03 | 0.975    |
| 85.2 mg/L Cl₂              | 1.05E-03 | 0.968    | nd       | nd       |
| CIP 0                      | 1.52E-03 | 0.992    | 1.80E-03 | 0.996    |
| 20.4 mg/L H₂O₂             | 2.07E-03 | 1        | 3.27E-03 | 0.955    |
| 40.8 mg/L H₂O₂             | 2.18E-03 | 0.997    | nd       | nd       |
| 42.6 mg/L Cl₂              | 2.23E-03 | 0.989    | 4.30E-03 | 0.97     |
| 85.2 mg/L Cl₂              | 2.77E-03 | 0.914    | nd       | nd       |
| NVP 0                      | 1.00E-04 | 0.993    | 8.33E-05 | 0.961    |
| 20.4 mg/L H₂O₂             | 4.17E-04 | 0.987    | 1.32E-03 | 0.94     |
| 40.8 mg/L H₂O₂             | 7.00E-04 | 0.997    | nd       | nd       |
| 42.6 mg/L Cl₂              | 1.17E-04 | 0.89     | *        | *        |
| 85.2 mg/L Cl₂              | 1.67E-04 | 0.989    | nd       | nd       |
| SMX 0                      | 1.70E-03 | 0.977    | 2.25E-03 | 0.996    |
| 20.4 mg/L H₂O₂             | 2.28E-03 | 0.993    | 3.78E-03 | 0.997    |
| 40.8 mg/L H₂O₂             | 2.45E-03 | 0.995    | nd       | nd       |
| 42.6 mg/L Cl₂              | 2.78E-03 | 0.997    | 8.47E-03 | 0.87     |
| 85.2 mg/L Cl₂              | 2.92E-03 | 0.996    | nd       | nd       |

nd, not done.

*Instant reaction with chlorine.

Fig. 3. Degradation of the target APIs spiked in ultrapure water by 17 mg/L of Cl₂ after 10 min reaction in the dark. [Colour figure can be viewed at wileyonlinelibrary.com]

Fig. 4. Effect of the pH of the sample on the degradation of 20 µM target compounds by direct UV photolysis, UV/H₂O₂ and UV/Cl₂ spiked in an ultrapure water electrical energy dose of 2.2 kWh/10³ L and an initial oxidant concentration of 8.2 mg/L of H₂O₂ and 17.0 mg/L of Cl₂. [Colour figure can be viewed at wileyonlinelibrary.com]
For UV treatment, only SMX and CIP were significantly affected by the pH changes. Increasing the pH from 5 to 9 led to an increased rate of photolysis of CIP. A different trend was observed for SMX with a higher rate of photolysis at pH 5 (>95% removal) which decreased at near neutral pH 7.5 (~73% removal) and further increase to pH 9 resulted in an increase in the degradation rate (83% removal). The strong dependence on pH in the rates of photolysis for SMX and CIP can be largely attributed to their acid-base speciation properties in the aqueous solution that consequently affects the optical properties of the compounds (Avisar et al., 2010; Lian et al., 2015). The effect of pH on UV/H2O2 treatment was quite similar to direct UV photolysis where lower pH was favoured for SMX and higher pH for CIP, while no particular trend or significant influence of pH was observed in the other APIs. For UV/Cl2, TMP degradation was favoured at lower pH values, while NVP was degraded to a greater extent at higher pH values. Previous studies show that UV/Cl2 is less efficient at high pH due to the scavenging of •OH by OCl– (Wang et al., 2016). However, in this case, the higher NVP degradation can be largely attributed to the direct attack by the free chlorine rather than the radical pathway.

**Removal of APIs from wastewater by UV-based processes**

The removal of target antibiotics and antiretroviral drugs spiked wastewater effluent by the selected UV-based processes (direct UV photolysis, UV/H2O2, and UV/Cl2) is shown in Fig. 5. SMX, CIP and ZDV were inefficiently removed by more than 90% by direct UV photolysis over an irradiation period of 30 min. However, the removal efficiency for TMP, NVP and 3TC was 12.2, 13.4 and 48.1%, respectively, which was majorly attributed to the relatively low molar absorption coefficients for the compounds (Table 1). Generally, the removal of SMX, CIP and TMP by direct UV photolysis was consistent with what has been reported in the literature. Kim et al. (2009) reported a removal efficiency of >90 and 10% for the removal of SMX and TMP, respectively, by direct UV photolysis of wastewater effluent using a low-pressure mercury lamp (65 W) for 5 min. In another study, Yang et al. (2016) reported an approximately 50% reduction in CIP concentration in wastewater effluent when irradiated with a low-pressure mercury lamp (10 W) for 3 min. The removal efficiency by direct UV photolysis for ZDV was generally higher than for 3TC and NVP that have similar molar extinction coefficients. This can possibly be due to a higher quantum yield for ZDV which was not evaluated in this study.

The degradation of the compounds that were not readily removed by direct UV photolysis was significantly enhanced by UV/H2O2 and UV/Cl2 processes. In the UV/H2O2 process, the removal of TMP, 3TC and NVP was 62.9, 72.2 and 52.9%, respectively, due to the contribution of the radicals in the removal of the APIs. Several studies have reported efficient removal of SMP, TMP and CIP by UV/H2O2 AOP. De la Cruz et al. (2012) found that SMX, CIP and TMP were entirely degraded in wastewater effluents by low pressure 25W mercury lamp and 50 mg/L of H2O2 after 30 min irradiation. With the UV/Cl2 process, the degradation of TMP, 3TC and NVP was 35, 77.4 and 20.8%, respectively. The removal of TMP and NVP was much lower than for UV/H2O2 but higher than that of direct UV photolysis. Yang et al. (2016) found higher removal efficiency of TMP >90% by UV/Cl2 using low-pressure mercury lamp (10 W) for 3 min. The relatively lower removal efficiency in the present study can be largely attributed to the higher DOC content in the effluent waters which ranged between 11.1 and 15.5 mg/L as compared to effluents reported by Yang et al. (2016) of between 1.1 and 3.5 mg/L.
Though the UV/Cl₂ process has been touted by several authors (Sichel et al., 2011; Wang et al., 2015; Yang et al., 2016) as a possible alternative to UV/H₂O₂ AOP, several drawbacks arise when applied for post-treatment of wastewater effluents. First, the current study shows that large doses of chlorine are required for an effective removal of recalcitrant compounds in wastewater such as TMP and NVP. This is primarily because the electron-rich moieties in the effluent organic matter compete for chlorine with the APIs. In addition, the large quantities of chlorine will essentially lead to the need for the removal of residual chlorine after the treatment process before the wastewater is discharged into the environment. Second, there is a great potential of the formation of chlorinated electrophilic substitution products which can be more toxic or have similar antimicrobial activity as with the parent molecule (Aga, 2008).

The observations in the present study are in agreement with the findings by Jin et al. (2011) who compared the effectiveness of UV/Cl₂ and UV/H₂O₂ in the removal of cyclohexanoic acid in wastewater streams. In their study, the UV/Cl₂ was found to be less efficient than UV/H₂O₂ and thus not ideal for the degradation of cyclohexanoic acid in the studied wastewater stream.

**Removal of DOC during direct UV photolysis, UV/H₂O₂ and UV/Cl₂**

The removal of DOC by the selected UV-based treatment processes was evaluated for effluent wastewater and ultrapure water spiked with mixed APIs. The results are shown in Fig. 6. The removal in wastewater was 1.5, 4.9 and 12.1% by UV, UV/Cl₂ and UV/H₂O₂, respectively. The removal of DOC in ultrapure water was significantly higher at 3.2, 11.9 and 20.3% for UV, UV/Cl₂ and UV/H₂O₂, respectively. The removal of DOC by AOP processes showed a remarkable increase due to the synergetic effect of radical reactions, direct photolysis and oxidation by chlorine. Similar studies (Goslan et al., 2006; Kim et al., 2009) have shown minimal DOC removal in water by direct UV photolysis. Whereas UV-based AOPs show an enhanced removal and very high doses of UV would be required for effective removal of DOC. The significantly lower DOC removal by the UV/Cl₂ process is an indicator that the majority of the APIs have undergone a minimal transformation. This implies that further studies need to be undertaken to investigate the nature of the transformation products.

**Comparison of direct UV photolysis, UV/H₂O₂ and UV/Cl₂ energy consumption**

The energy consumption for the degradation of each compound was evaluated based on the electrical energy per order of compound removal (EEO, Eq. 1). Table 3 shows the EEO in kWh/order/10³L for effluent wastewater at an initial oxidant concentration of 20.4 mg/L of H₂O₂ and 42.6 mg/L of Cl₂. For the direct UV photolysis, the EEO ranged from 5.4 to 97.1 kWh/order/10³L. The EEO for the target compounds increased in the following order SMX < CIP < ZDV < 3TC < NVP < TMP. The lower EEO for SMX and CIP can be attributed to the relatively high molar extinction coefficients (10,000 M⁻¹ cm⁻¹ at 254 nm) and are hence readily degraded by direct UV photolysis. In contrast, TMP and NVP have relatively lower molar extinction coefficients and as a result, high electrical energy is required to achieve one order of compound degradation. UV/H₂O₂ treatment showed a significant reduction in the EEO in comparison to direct UV photolysis and ranged between 4.1 and 23.5 kWh (1.1–5.4 times more efficient). TMP and NVP showed marked reduction in EEO from 97.1 to 17.8 and 96.7 to 23.5 kWh which translates to 81.6 and 75.7% electrical energy reduction, respectively. In the case UV/Cl₂, the EEO ranged between 3.3 and 61.2 kWh. Apart from ZDV which did not show EEO reduction in the UV/Cl₂ process relative to direct UV photolysis, the rest of the compounds showed 1.5–3.5 times reduction in EEO. Comparing the EEO for UV/Cl₂ and UV/ H₂O₂, the UV/Cl₂ was 1.2–1.4 times more efficient in the

**Table 3** The electrical energy per order of compound removal (EEO, kWh/order/10³L) for direct UV photolysis, UV/H₂O₂ (20.4 mg/L) and UV/Cl₂ (42.6 mg/L) in treated wastewater

| Compound | UV   | UV/H₂O₂ | UV/Cl₂ |
|----------|------|---------|--------|
| SMX      | 5.4 (0.3) | 4.1 (0.4) | 3.3 (0.3) |
| CIP      | 6.2 (0.5) | 4.2 (0.1) | 3.5 (0.3) |
| TMP      | 97.1 (9.1) | 17.8 (2.4) | 35.8 (0.4) |
| ZDV      | 6.4 (0.5) | 5.8 (1.2) | 7.8 (0.4) |
| 3TC      | 30.5 (4.6) | 12.7 (0.9) | 8.9 (1.5) |
| NVP      | 96.7 (13.0) | 23.5 (2.8) | 58.1 (7.8) |

*Mean (±SD).*
degradation of SMX, CIP and 3TC. However, UV/H₂O₂ was 2.6, 2.0 and 1.3 times more efficient in degrading of NVP, TMP and ZDV, respectively.

Conclusion

This study compared the bench-scale wastewater post-treatment removal of three antibiotics and three antiretroviral drugs in by direct UV photolysis, UV/H₂O₂ and UV/Cl₂ processes using low-pressure mercury lamp (λmax = 254 nm). The removal of the antiretroviral drugs has not been previously reported for any of the studied UV processes. Based on the experimental results, the following conclusions can be drawn:

(1) The rate of degradation of the six compounds by direct UV photolysis, UV/H₂O₂ and UV/Cl₂ processes followed pseudo first-order reaction kinetics.

(2) SMX, CIP and ZDV were readily removed by direct UV photolysis.

(3) The pseudo first-order rate constants for the UV/H₂O₂ process in wastewater were significantly higher than the UV/Cl₂ process, especially for NVP and TMP. This implies that the treatment efficiency UV/Cl₂ process is inferior to that of UV/H₂O₂ and much more electrical energy would be required to achieve similar removal efficiencies. However, due to the relatively low chemical costs, the UV/Cl₂ AOP process can be an alternative to UV/H₂O₂ in water with low DOC and after thorough suitability evaluation of each target water stream.

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Data availability statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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APPENDIX A

Chemical actinometry

The determination of the intensity of the incident radiation $I_0$ was conducted using hydrogen peroxide as an actinometer as demonstrated by Nicole et al. (1990). In brief, the photochemical degradation of hydrogen peroxide from the absorption of monochromatic radiation at 254 nm follows the Beer-Lambert's law as expressed in the Eq. (A1)

$$- \frac{d [H_2O_2]}{dt} = \frac{\Phi_{H_2O_2} I_0}{V} (1 - \exp (-2.303 L \epsilon_{H_2O_2} [H_2O_2])) \quad (A1)$$

where $\Phi_{H_2O_2}$, $\epsilon_{H_2O_2}$, $[H_2O_2]$ and $V$ are the quantum yield, molar extinction coefficient, concentration and volume of hydrogen peroxide, respectively, while $L$ is the effective path of the radiation. When the exponential term $2.303 L \epsilon_{H_2O_2} [H_2O_2] > 2$, the equation is simplified to Eq. (A2)

$$- \frac{d [H_2O_2]}{dt} = \frac{\Phi_{H_2O_2} I_0}{V} \quad (A2)$$

At 254 nm, the molar absorption coefficient and quantum yield for hydrogen peroxide are 18.6 M⁻¹ cm⁻¹ and 1 mol/Einstein, respectively (Andreozzi, 1999).

Integrating Eq. (A2)

$$[H_2O_2]_t = \frac{\Phi_{H_2O_2} I_0}{V} t + [H_2O_2]_0 \quad (A3)$$

A plot of $[H_2O_2]_t$ against time gives $\frac{\Phi_{H_2O_2} I_0}{V}$ as the gradient enabling the computation of the $I_0$. In this study, photolysis of 3 L 0.1 M hydrogen peroxide in ultrapure water at pH 7.5 and samples were taken at various time intervals. A plot of the residual hydrogen peroxide after irradiation at UV 254 nm against time is shown in Figure A1. The concentration of hydrogen peroxide decreased linearly with an $R^2 > 0.99$ and gradient of 9.66 x 10⁻⁶ translating to a photon flux of 2.9 x 10⁻⁵ Einstein/s. Since the energy of a photon at 254 nm is 7.83 x 10⁻¹⁹ J and the total number of photons is 1.75 x 10¹⁹ photons/s results to total UV intensity of 13.6 W or 9.25 mW/cm².

Fig. A1. Linear plot showing the degradation of hydrogen peroxide with UV at 254 nm. [Colour figure can be viewed at wileyonlinelibrary.com]