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# 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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## Keywords

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

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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/H<sub>2</sub>O<sub>2</sub> and UV/Cl<sub>2</sub>) 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 Cl<sub>2</sub> and H<sub>2</sub>O<sub>2</sub> to the UV process led to an increase in the rate of degradation for all the compounds. The effectiveness UV/Cl<sub>2</sub> 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/Cl<sub>2</sub> process relative to UV/H<sub>2</sub>O<sub>2</sub> process. Generally, electrical energy required to remove 90% of the target compounds increased in the order UV/H<sub>2</sub>O<sub>2</sub> < UV/Cl<sub>2</sub> < UV processes.

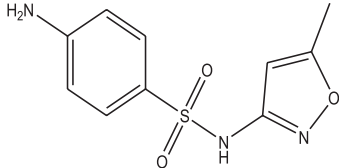
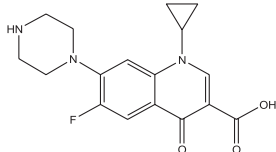
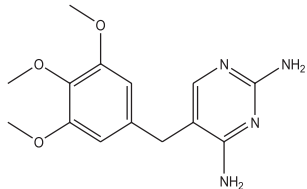
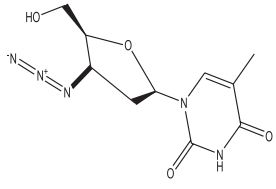
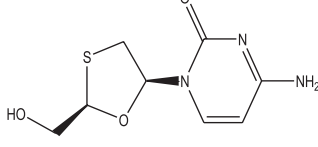
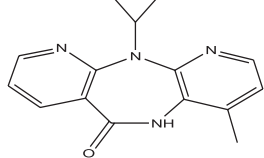
## Introduction

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 AOPs 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/H<sub>2</sub>O<sub>2</sub> has been applied in the full-scale wastewater treatment (Kruithof *et al.*, 2007), the low molar absorption coefficient of H<sub>2</sub>O<sub>2</sub> at 254 nm (about 20 M<sup>-1</sup> cm<sup>-1</sup>) implies that only a small fraction of incident light is utilized for the radical formation and thus an excess H<sub>2</sub>O<sub>2</sub> must

**Table 1** Names, structures and selected measured and literature properties

Compound	Chemical structure	Water solubility (mg/L) <sup>a</sup>	pKa <sup>a</sup>	Decadic molar absorption coefficient ( $\epsilon$ , $\lambda_{254\text{ nm}}$ , (M <sup>-1</sup> cm <sup>-1</sup> ))	
				This study	Literature
Sulfamethoxazole (SMX)		610	5.6, 1.83	14 950	7345–24 018 <sup>b</sup>
Ciprofloxacin (CIP)		13 500	6.4, 8.2	13 470	12 899–14 911 <sup>c</sup>
Trimethoprim (TMP)		400	7.2, 17.33	4300	3053–8430 <sup>d</sup>
Zidovudine (ZDV)		20 100	9.7	7560	ndf
Lamivudine (3TC)		70 000	4.3, 14.29	8970	ndf
Nevirapine (NVP)		0.7046	2.8	7500	ndf

ndf, no data found.

<sup>a</sup>Wishart *et al.* (2006), Babić *et al.* (2007), USEPA (2012).

<sup>b</sup>Kim and Tanaka (2009), Batchu *et al.* (2014), Gerrity *et al.* (2014), Carlson *et al.* (2015), Lian *et al.* (2015), Yang *et al.* (2016).

<sup>c</sup>Avisar *et al.* (2010), Guo *et al.* (2013), Batchu *et al.* (2014).

<sup>d</sup>Gerrity *et al.* (2014), Carlson *et al.* (2015), Yang *et al.* (2016).

be added for sufficient •OH radical formation (Muruganandham *et al.*, 2014; Boal *et al.*, 2015).

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/Cl<sub>2</sub> process has been suggested as a possible alternative to

the UV/H<sub>2</sub>O<sub>2</sub> in the removal of organic micropollutants for several reasons including; (i) the higher UV absorbance and the lower scavenging of HOCl as compared to H<sub>2</sub>O<sub>2</sub> resulting in higher quantum yield ( $\phi$ ) during photolysis of aqueous chlorine (HOCl  $\phi = 1.4 \text{ mol Es}^{-1}$  and H<sub>2</sub>O<sub>2</sub>  $\phi = 1.0 \text{ mol Es}^{-1}$  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/Cl<sub>2</sub> AOP produces

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<sub>2</sub>O<sub>2</sub> and UV/Cl<sub>2</sub> 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).

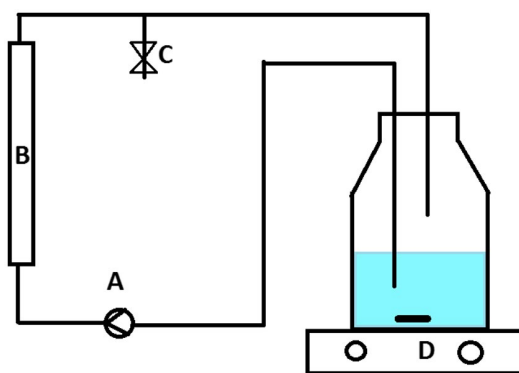
$$E_{EO} \text{ (kWh/order/10}^3\text{L)} = \frac{P \text{ (kW)} \times t \text{ (min)} \times 1000}{V \text{ (L)} \times 60 \times \log C_0/C_f} \quad (1)$$

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 [<sup>2</sup>H<sub>8</sub>]-ciprofloxacin, [<sup>2</sup>H<sub>4</sub>]-sulfamethoxazole, [<sup>13</sup>C<sup>2</sup>H<sub>3</sub>]-zidovudine, [<sup>2</sup>H<sub>4</sub>]-nevirapine and [<sup>13</sup>C <sup>2</sup>H<sub>2</sub> <sup>15</sup>N<sub>2</sub>]-lamivudine (Alsachim, Illkirch, France), while [<sup>2</sup>H<sub>9</sub>]-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



**Fig. 1.** Scheme of AOP experimental set-up. (a) Recirculation pump, (b) UV reactor, (c) Sample valve and (d) Magnetic stirrer.

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.

Composite 24 hours effluent samples were collected from the Jyväskylä wastewater treatment plant. The pH and dissolved organic carbon (DOC) for the wastewater effluent ranged from 7.7–8.1 to 11.1–15.5 mg/L, respectively.

### 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  $\lambda_{\max} = 254$  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/cm<sup>2</sup> (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<sub>2</sub>O<sub>2</sub> and UV/Cl<sub>2</sub> 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) Determination of the target APIs degradation by Cl<sub>2</sub> and H<sub>2</sub>O<sub>2</sub> 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  $\text{Cl}_2$ ) 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  $\mu\text{M}$ . Before oxidant addition, the first sample ( $C_0$ ) 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 ( $C_t$ ) were periodically withdrawn from the sample valve/directly from the reservoir and residual oxidants quenched with sodium thiosulphate 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  $\mu\text{m}$ ) and GF/F (0.7  $\mu\text{m}$ ) 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 washed 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  $\mu\text{m}$  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 spectrophotometrically using a molar absorption coefficient of 43.6  $\text{M}^{-1} \text{cm}^{-1}$  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  $\pi$  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  $\mu\text{M}$ ) dissolved in ultrapure water. The results are shown in Table 1. The molar extinction coefficients ranged from 4300  $\text{M}^{-1}\text{cm}^{-1}$  to 14 950  $\text{M}^{-1}\text{cm}^{-1}$  and increased in the order  $\text{TMP} < \text{NVP} < \text{ZDV} < \text{3TC} < \text{CIP} < \text{SMX}$ . 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)

$$\frac{-d[C]}{dt} = k_{\text{obs}} [C] \quad (2)$$

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

The direct UV photolysis, UV/ $\text{H}_2\text{O}_2$  and UV/ $\text{Cl}_2$  treatment linear plots of  $\ln([C_0]/[C])$  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/ $\text{Cl}_2$ , UV/ $\text{H}_2\text{O}_2$  and UV photolysis ranged from 0.89 to 0.99, 0.95 to 1.0 and 0.96 to 0.99, respectively. The UV/ $\text{Cl}_2$  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/ $\text{Cl}_2$  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/ $\text{Cl}_2$ , UV/ $\text{H}_2\text{O}_2$  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

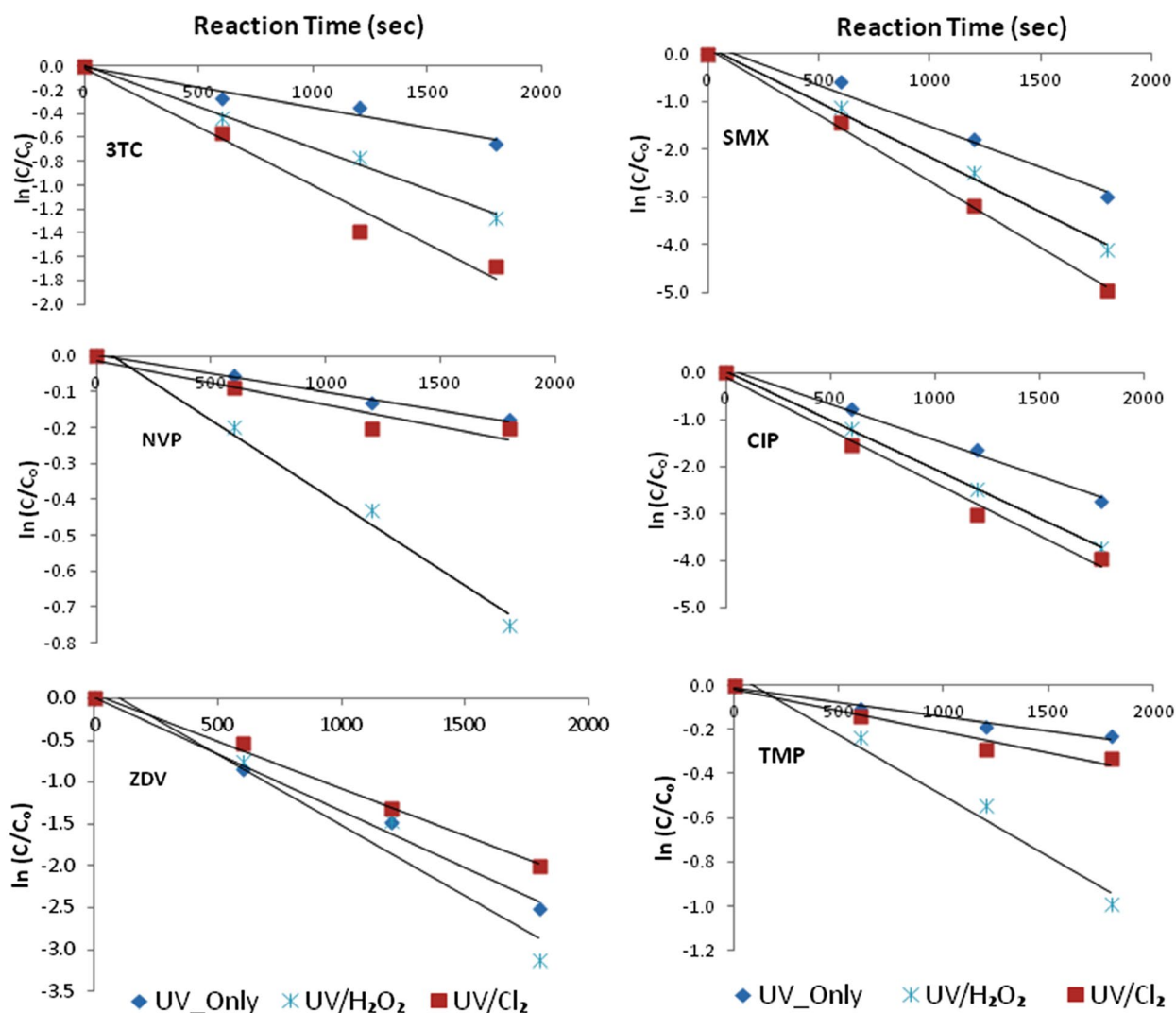


Fig. 2. UV photolysis, UV/H<sub>2</sub>O<sub>2</sub> and UV/Cl<sub>2</sub> treatment linear plots of  $\ln(C_0/C)$  against time for 20  $\mu\text{M}$  each compound in wastewater.

constants could not be approximated for the UV/Cl<sub>2</sub> process.

The application of UV/Cl<sub>2</sub> and UV/H<sub>2</sub>O<sub>2</sub> 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 was increased by a factor of 4.1 and 4.2, respectively.

### Degradation of APIs with Cl<sub>2</sub> and H<sub>2</sub>O<sub>2</sub> (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 H<sub>2</sub>O<sub>2</sub>. Direct reactions of hydrogen

**Table 2** Direct UV photolysis, UV/H<sub>2</sub>O<sub>2</sub> and UV/Cl<sub>2</sub> 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	
		$K_{obs}$ (s <sup>-1</sup> )	$R^2$	$K_{obs}$ (s <sup>-1</sup> )	$R^2$
TMP	0	1.33E-04	0.971	1.67E-04	0.948
	20.4 mg/L_H <sub>2</sub> O <sub>2</sub>	5.50E-04	0.98	1.47E-03	0.952
	40.8 mg/L_H <sub>2</sub> O <sub>2</sub>	8.33E-04	0.997	nd	nd
	42.6 mg/L_Cl <sub>2</sub>	1.83E-04	0.955	2.43E-03	0.944
	85.2 mg/L_Cl <sub>2</sub>	3.00E-04	0.985	nd	nd
3 TC	0	3.33E-04	0.958	2.50E-04	0.976
	20.4 mg/L_H <sub>2</sub> O <sub>2</sub>	7.00E-04	0.994	1.90E-03	0.98
	40.8 mg/L_H <sub>2</sub> O <sub>2</sub>	1.08E-03	0.987	nd	nd
	42.6 mg/L_Cl <sub>2</sub>	7.00E-04	0.967	<sup>a</sup>	<sup>a</sup>
	85.2 mg/L_Cl <sub>2</sub>	1.08E-03	0.985	nd	nd
ZDV	0	1.37E-03	0.991	1.55E-03	0.995
	20.4 mg/L_H <sub>2</sub> O <sub>2</sub>	1.68E-03	0.952	2.08E-03	0.984
	40.8 mg/L_H <sub>2</sub> O <sub>2</sub>	2.07E-03	0.994	nd	nd
	42.6 mg/L_Cl <sub>2</sub>	1.13E-03	0.996	3.20E-03	0.975
	85.2 mg/L_Cl <sub>2</sub>	1.05E-03	0.968	nd	nd
CIP	0	1.52E-03	0.992	1.80E-03	0.996
	20.4 mg/L_H <sub>2</sub> O <sub>2</sub>	2.07E-03	1	3.27E-03	0.955
	40.8 mg/L_H <sub>2</sub> O <sub>2</sub>	2.18E-03	0.997	nd	nd
	42.6 mg/L_Cl <sub>2</sub>	2.23E-03	0.989	4.30E-03	0.97
	85.2 mg/L_Cl <sub>2</sub>	2.77E-03	0.914	nd	nd
NVP	0	1.00E-04	0.993	8.33E-05	0.961
	20.4 mg/L_H <sub>2</sub> O <sub>2</sub>	4.17E-04	0.987	1.32E-03	0.94
	40.8 mg/L_H <sub>2</sub> O <sub>2</sub>	7.00E-04	0.997	nd	nd
	42.6 mg/L_Cl <sub>2</sub>	1.17E-04	0.89	<sup>a</sup>	<sup>a</sup>
	85.2 mg/L_Cl <sub>2</sub>	1.67E-04	0.989	nd	nd
SMX	0	1.70E-03	0.977	2.25E-03	0.996
	20.4 mg/L_H <sub>2</sub> O <sub>2</sub>	2.28E-03	0.993	3.78E-03	0.997
	40.8 mg/L_H <sub>2</sub> O <sub>2</sub>	2.45E-03	0.995	nd	nd
	42.6 mg/L_Cl <sub>2</sub>	2.78E-03	0.997	8.47E-03	0.87
	85.2 mg/L_Cl <sub>2</sub>	2.92E-03	0.996	nd	nd

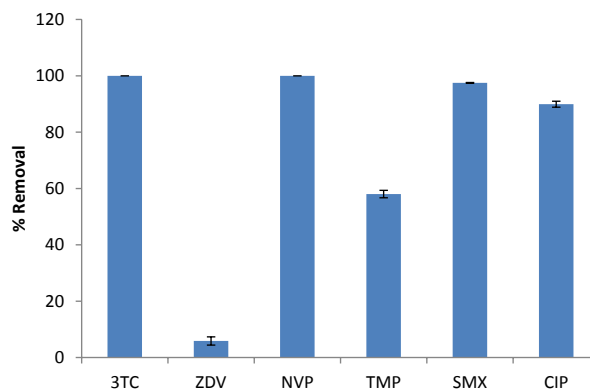
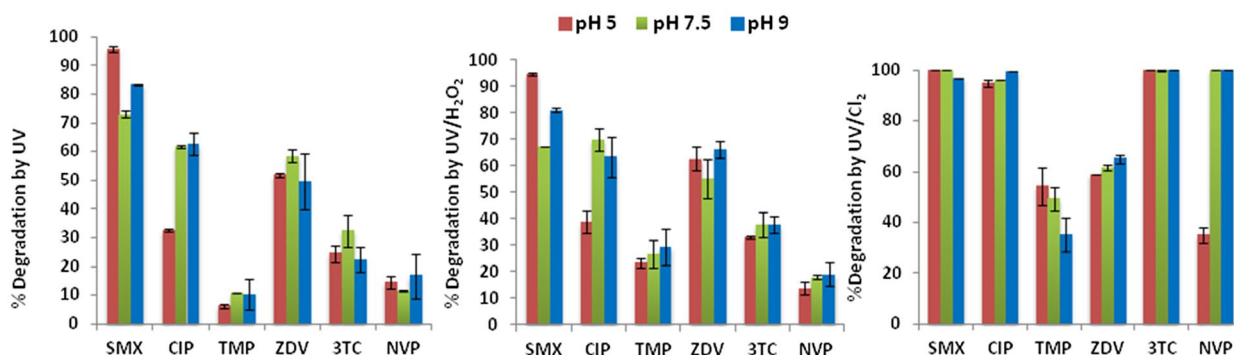
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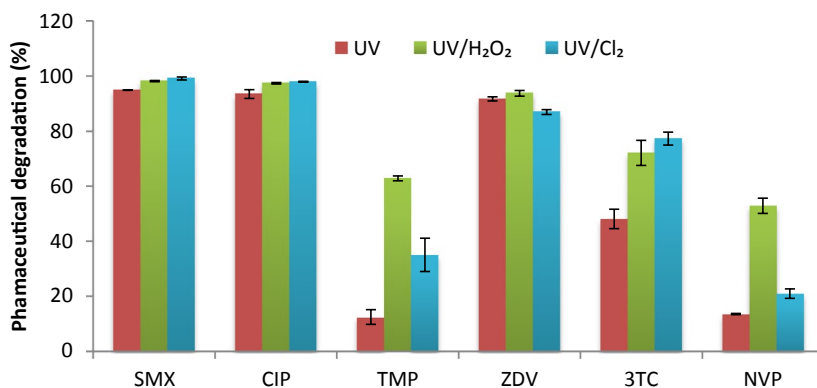
<sup>a</sup>Instant reaction with chlorine.

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/H<sub>2</sub>O<sub>2</sub> and UV/Cl<sub>2</sub> 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 H<sub>2</sub>O<sub>2</sub> and Cl<sub>2</sub>, respectively, and an electrical energy dose of 2.2 kWh/10<sup>3</sup>L was used. The obtained results are shown in Fig. 4.

**Fig. 3.** Degradation of the target APIs spiked in ultrapure water by 17 mg/L of Cl<sub>2</sub> after 10 min reaction in the dark.**Fig. 4.** Effect of the pH of the sample on the degradation of 20 µM target compounds by direct UV photolysis, UV/H<sub>2</sub>O<sub>2</sub> and UV/Cl<sub>2</sub> spiked in an ultrapure water electrical energy dose of 2.2 kWh/10<sup>3</sup>L and an initial oxidant concentration of 8.2 mg/L of H<sub>2</sub>O<sub>2</sub> and 17.0 mg/L of Cl<sub>2</sub>.



**Fig. 5.** The removal of 20  $\mu\text{M}$  target antibiotics and antiretroviral drugs in wastewater by direct UV photolysis, UV/H<sub>2</sub>O<sub>2</sub> and UV/Cl<sub>2</sub> at an electrical energy dose of 6.67 kWh/10<sup>3</sup>L and 20.4 mg/L of H<sub>2</sub>O<sub>2</sub> and 42.6 mg/L of Cl<sub>2</sub>. The error bars present the standard deviation ( $n = 3$ ).

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 pH 5 (>95% removal) which decreased at near neutral pH 7.5 ( $\approx$ 73% removal) and further increase to pH 9 resulted to 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/H<sub>2</sub>O<sub>2</sub> 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/Cl<sub>2</sub>, 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/Cl<sub>2</sub> is less efficient at high pH due to the scavenging of  $\cdot\text{OH}$  by  $\text{OCl}^-$  (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/H<sub>2</sub>O<sub>2</sub> and UV/Cl<sub>2</sub>) is shown in Fig. 5. SMX, CIP and ZDV were efficiently 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/H<sub>2</sub>O<sub>2</sub> and UV/Cl<sub>2</sub> processes. In the UV/H<sub>2</sub>O<sub>2</sub> 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/H<sub>2</sub>O<sub>2</sub> 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 H<sub>2</sub>O<sub>2</sub> after 30 min irradiation. With the UV/Cl<sub>2</sub> 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/H<sub>2</sub>O<sub>2</sub> but higher than that of direct UV photolysis. Yang *et al.* (2016) found higher removal efficiency of TMP >90% by UV/Cl<sub>2</sub> 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.

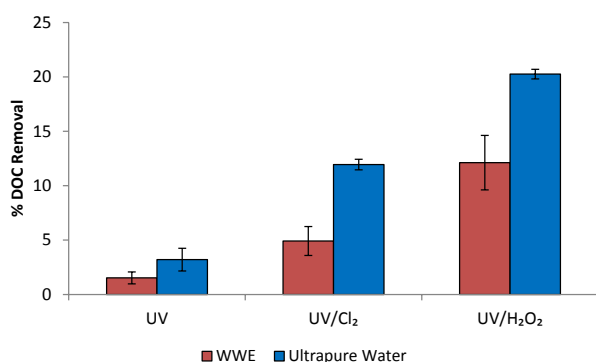


Though the UV/Cl<sub>2</sub> process has been touted by several authors (Sichel *et al.*, 2011; Wang *et al.*, 2015; Yang *et al.*, 2016) as a possible alternative to UV/H<sub>2</sub>O<sub>2</sub> AOP, several drawbacks arise when applied for post-treatment of wastewater effluents. First, the current 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/Cl<sub>2</sub> and UV/H<sub>2</sub>O<sub>2</sub> in the removal of cyclohexanoic acid in wastewater streams. In their study, the UV/Cl<sub>2</sub> was found to be less efficient than UV/H<sub>2</sub>O<sub>2</sub> and thus not ideal for the degradation of cyclohexanoic acid in the studied wastewater stream.

### Removal of DOC during direct UV photolysis, UV/H<sub>2</sub>O<sub>2</sub> and UV/Cl<sub>2</sub>

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/Cl<sub>2</sub> and UV/H<sub>2</sub>O<sub>2</sub>, respectively. The removal of DOC in ultrapure water was significantly higher at 3.2, 11.9 and 20.3% for UV, UV/Cl<sub>2</sub> and UV/H<sub>2</sub>O<sub>2</sub>, respectively. The removal of DOC by AOP processes showed a remarkable increase due to the synergetic effect of radical



**Fig. 6.** Comparison of the removal of DOC in wastewater and ultrapure water by direct UV photolysis, UV/H<sub>2</sub>O<sub>2</sub> and UV/Cl<sub>2</sub>.

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/Cl<sub>2</sub> 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/H<sub>2</sub>O<sub>2</sub> and UV/Cl<sub>2</sub> energy consumption

The energy consumption for the degradation of each compound was evaluated based on the electrical energy per order of compound removal ( $E_{EO}$ , Eq. 1). Table 3 shows the  $E_{EO}$  in kWh/order/10<sup>3</sup>L for effluent wastewater at an initial oxidant concentration of 20.4 mg/L of H<sub>2</sub>O<sub>2</sub> and 42.6 mg/L of Cl<sub>2</sub>. For the direct UV photolysis, the  $E_{EO}$  ranged from 5.4 to 97.1 kWh/order/10<sup>3</sup>L. The  $E_{EO}$  for the target compounds increased in the following order SMX < CIP < ZDV << 3TC << NVP < TMP. The lower  $E_{EO}$  for SMX and CIP can be attributed to the relatively high molar extinction coefficients >10 000 M<sup>-1</sup>cm<sup>-1</sup> 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/H<sub>2</sub>O<sub>2</sub> treatment showed a significant reduction in the  $E_{EO}$  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  $E_{EO}$  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/Cl<sub>2</sub>, the  $E_{EO}$  ranged between 3.3 and 61.2 kWh. Apart from ZDV which did not show EEO reduction in the UV/Cl<sub>2</sub> 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/Cl<sub>2</sub> and UV/H<sub>2</sub>O<sub>2</sub>, the UV/Cl<sub>2</sub> was 1.2–1.4 times more efficient in the

**Table 3** The electrical energy per order of compound removal (EEO, kWh/order/10<sup>3</sup>L) for direct UV photolysis, UV/H<sub>2</sub>O<sub>2</sub> (20.4 mg/L) and UV/Cl<sub>2</sub> (42.6 mg/L) in treated wastewater

Compound	UV	UV/H <sub>2</sub> O <sub>2</sub>	UV/Cl <sub>2</sub>
SMX	5.4 (0.3) <sup>a</sup>	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)

<sup>a</sup>Mean (±SD).

degradation of SMX, CIP and 3TC. However, UV/H<sub>2</sub>O<sub>2</sub> 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/H<sub>2</sub>O<sub>2</sub> and UV/Cl<sub>2</sub> processes using low-pressure mercury lamp ( $\lambda_{\text{max}} = 254 \text{ nm}$ ). 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/H<sub>2</sub>O<sub>2</sub> and UV/Cl<sub>2</sub> 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/H<sub>2</sub>O<sub>2</sub> process in wastewater were significantly higher than the UV/Cl<sub>2</sub> process, especially for NVP and TMP. This implies that the treatment efficiency UV/Cl<sub>2</sub> process is inferior to that of UV/H<sub>2</sub>O<sub>2</sub> and much more electrical energy would be required to achieve similar removal efficiencies. However, due to the relatively low chemical costs, the UV/Cl<sub>2</sub> AOP process can be an alternative to UV/H<sub>2</sub>O<sub>2</sub> 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)

$$-\frac{d[\text{H}_2\text{O}_2]}{dt} = \frac{\Phi_{\text{H}_2\text{O}_2} I_0}{V} (1 - \exp(-2.303L\epsilon_{\text{H}_2\text{O}_2} [\text{H}_2\text{O}_2])) \quad (\text{A1})$$

where  $\Phi_{\text{H}_2\text{O}_2}$ ,  $\epsilon_{\text{H}_2\text{O}_2}$ ,  $[\text{H}_2\text{O}_2]$  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  $2.303L\epsilon_{\text{H}_2\text{O}_2} [\text{H}_2\text{O}_2] > 2$ , the equation is simplified to Eq. (A2)

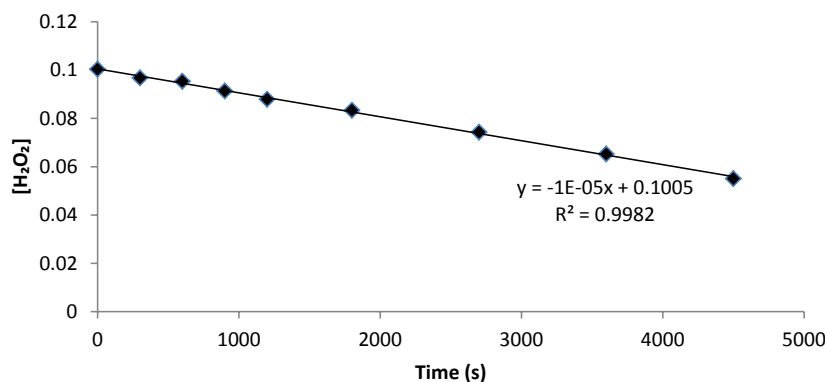
$$-\frac{d[\text{H}_2\text{O}_2]}{dt} = \frac{\Phi_{\text{H}_2\text{O}_2} I_0}{V} \quad (\text{A2})$$

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

Integrating Eq. (A2)

$$[\text{H}_2\text{O}_2]_t = \frac{\Phi_{\text{H}_2\text{O}_2} I_0}{V} t + [\text{H}_2\text{O}_2]_0 \quad (\text{A3})$$

A plot of  $[\text{H}_2\text{O}_2]_t$  against time gives  $\frac{\Phi_{\text{H}_2\text{O}_2} I_0}{V}$  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  $9.66 \times 10^{-6}$  translating to a photon flux of  $2.9 \times 10^{-5}$  Einstein/s. Since the energy of a photon at 254 nm is  $7.83 \times 10^{-19}$  J and the total number of photons are  $1.75 \times 10^{19}$  photons/s results to total UV intensity of 13.6 W or 9.25 mW/cm<sup>2</sup>.



**Fig. A1.** Linear plot showing the degradation of hydrogen peroxide with UV at 254 nm.