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**To cite this article:** Purnima Somathilake, John Albino Dominic, Gopal Achari, Cooper H. Langford & Joo-Hwa Tay (2019) Influence of UV dose on the UV/H<sub>2</sub>O<sub>2</sub> process for the degradation of carbamazepine in wastewater, *Environmental Technology*, 40:23, 3031-3039, DOI: [10.1080/09593330.2018.1464065](https://doi.org/10.1080/09593330.2018.1464065)

**To link to this article:** <https://doi.org/10.1080/09593330.2018.1464065>



Published online: 02 May 2018.



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## Influence of UV dose on the UV/H<sub>2</sub>O<sub>2</sub> process for the degradation of carbamazepine in wastewater

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### ABSTRACT

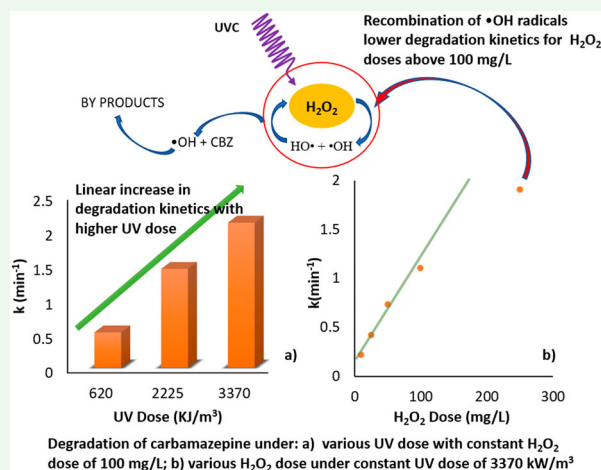
This study evaluates the influence of UV dose on degradation of carbamazepine (CBZ) in wastewater under UV-C ( $\lambda = 254$  nm) photolysis with and without H<sub>2</sub>O<sub>2</sub>. The rate of degradation of CBZ exhibited a direct dependence on the intensity of incident UV irradiation as the rate of degradation was observed to increase linearly ( $R^2 = 0.98$ ) with UV intensity between  $1.67$  and  $8.95 \times 10^{17}$  photons/s. More than 95% of the CBZ that spiked in wastewater rapidly degraded within 4 min with a first-order rate constant of  $1.2 \text{ min}^{-1}$  for an optimum H<sub>2</sub>O<sub>2</sub> dose of 100 mg/L. Bench-scale continuous flow reactor experiments also showed that CBZ degraded with first-order kinetics at a rate constant of  $1.02 \text{ min}^{-1}$ . The kinetic parameters obtained for a continuous bench-scale reactor were in good agreement with the relationships developed through batch experiments with only a marginal deviation of  $\pm 6.5\%$ . The relationship between UV intensity and CBZ degradation rate obtained in this study was extrapolated to the UV disinfection unit of a wastewater treatment plant to predict possible degradation of CBZ during UV disinfection. The addition of 100 mg/L of H<sub>2</sub>O<sub>2</sub> to the secondary-treated effluent entering the UV disinfection unit is predicted to achieve over 60% degradation of CBZ.

### ARTICLE HISTORY

Received 11 August 2017  
Accepted 30 March 2018

### KEYWORDS

Carbamazepine; UV/H<sub>2</sub>O<sub>2</sub>; advanced oxidation processes (AOPs); UV disinfection



**Abbreviations:** CBZ carbamazepine; AOPs advanced oxidation processes; UV ultraviolet radiation; UV-C ultraviolet C ( $\lambda = 254$  nm) radiation; NZVI non-zerovalent iron; WWTP wastewater treatment plant; HPLC high-performance liquid chromatography

## Introduction

Carbamazepine (CBZ) is one of the most persistent pharmaceutical frequently detected in aquatic environments including surface water [1,2], groundwater [3,4], sewage [5,6] and drinking water [7–9]. It is prescribed for treating epileptic seizures, severe nerve pain (trigeminal neuralgia) and bipolar disorder [10]. The presence of CBZ in the environment is primarily attributed to human

excretion via urine/feces or from disposal of expired/unused drug into sewers. Wastewater treatment plants (WWTPs) are considered as the major gateways for CBZ entry into the environment as it is highly resistant to biological degradation and removal efficiencies lesser than 10% are achieved in conventional WWTPs [6]. CBZ is considered as an indicator of pharmaceutical pollution due to its ubiquitous presence in wastewater effluent-

impacted surface water and groundwater worldwide and its resistance to environmental degradation [11]. Apart from being stable in the environment, CBZ bio-accumulates in the aquatic environment and it is possibly harmful to aquatic life [12]. Ecotoxicological studies have shown sensitivity in *Daphnia magna* at a concentration of 10 mg/L [13]. Though CBZ is not lethal to freshwater organisms at environmentally relevant concentrations (LD50 >4 mg/L), chronic effects including altered behaviour, reduced immune response, and changes in growth and fecundity have been reported in invertebrates of freshwater ecosystems [14]. While effects on human health are yet to be defined, the proactive precautionary approach requires the development of treatment methodologies for CBZ [15].

Advanced oxidation processes (AOP) have attracted considerable interest for the treatment of pharmaceuticals in wastewater as they use hydroxyl radicals ( $\cdot\text{OH}$ ) or similar potent oxidants [16]. Various treatment techniques based on the AOP have been suggested for the degradation of CBZ such as  $\text{TiO}_2/\text{UV}$  [17], Fenton [18], UV/Nano zerovalent iron (NZVI) [19],  $\text{O}_3$  [20],  $\text{O}_3/\text{UV}$  [21],  $\text{H}_2\text{O}_2/\text{UV}$  [15,22], thermally activated persulphate [23] and ultrasound [24]. An ideal treatment technology would be one that does not require major changes in infrastructure to an existing WWTP and that can be operated economically. From this perspective,  $\text{TiO}_2/\text{UV}$ , Fenton and NZVI/UV processes are not considered viable, as removal of  $\text{TiO}_2$  slurry and iron from wastewater requires energy-intensive treatment units. While use of  $\text{O}_3$  and  $\text{O}_3/\text{UV}$  is possible, the production of  $\text{O}_3$  may pose an energy constraint. Many of the modern WWTPs use UV disinfection as the final treatment process before the effluent is released to the environment. UV photolysis can degrade many pharmaceuticals including CBZ [25]. However, the rate of degradation by UV photolysis is as low as  $2.2 \times 10^{-3}$  and  $1.3 \times 10^{-3} \text{ min}^{-1}$  in surface water and laboratory water [26].

The addition of  $\text{H}_2\text{O}_2$  in the presence of UV has shown to increase the rate of degradation of CBZ by approximately 100 times in laboratory grade water and surface water [27]. This indicates that the addition of  $\cdot\text{OH}$  producing agents to disinfection units is a promising strategy that could enhance the degradation of CBZ in WWTPs.  $\text{H}_2\text{O}_2$  is also considered as an ideal hydroxyl radical producing agent among others due to its lesser environmental impact and greater operational control over the process [28]. While there are also other reports on degradation of CBZ by using UV/ $\text{H}_2\text{O}_2$ , these studies are of a parametric nature only and focus on degradation of CBZ in spiked pure water and/or elucidation of degradation pathways

[15,21,29]. Recently, a pilot-scale UV/ $\text{H}_2\text{O}_2$  system for degrading various endocrine disrupting compounds, pharmaceuticals, taste and odour and perfluorinated compounds have been reported [30]. However, the pilot study does not include CBZ as a target compound. The effectiveness of the UV/ $\text{H}_2\text{O}_2$  treatment method and the influence of operational parameters for the degradation of CBZ in actual wastewater has still not been studied and reported.

In this study, the correlation between UV intensity and  $\text{H}_2\text{O}_2$  dose on degradation of CBZ is evaluated. Initially, the relationship between the UV intensity and concentration of  $\text{H}_2\text{O}_2$  in batch experiments was conducted in CBZ spiked secondary effluent with various doses of  $\text{H}_2\text{O}_2$  under UV-C ( $\lambda = 254 \text{ nm}$ ) irradiation with varying intensities. Based on reaction rates obtained, correlations between  $\text{H}_2\text{O}_2$  dose, UV light intensity and rate of degradation were established. Furthermore, bench-scale continuous flow reactor experiments were conducted in the presence and absence of  $\text{H}_2\text{O}_2$  under UV irradiation. Kinetic parameters estimated from continuous reactor experiments were used to validate the relationships established using batch experiment results. The correlations developed were then applied to predict probable degradation of CBZ in the UV disinfection unit of a conventional WWTP.

## Materials and methods

### Chemicals

Analytical grade CBZ (99% purity) and high-performance liquid chromatography (HPLC) grade methanol were purchased from Sigma-Aldrich Co. (Canada). Hydrogen peroxide (30% w/w solution) was obtained from Fluka Analytical. Sodium sulphite used as quencher was purchased from J. T. Baker Chemicals. Secondary-treated effluent was collected from a WWTP in Nalgene HDPE storage containers and stored at  $4^\circ\text{C}$ .

### Photoreactor

Photodegradation experiments were conducted in LZC-ORG photoreactor supplied by Luzchem Research Inc, Canada. The reactor was equipped with five lamps on each side of the reaction chamber. Sankyo Denki G8T5 (254 nm, 8 W) low-pressure mercury lamps were used as the source of UV-C irradiation. The lamps were allowed to warm up for a period of 20 min before commencement of each experiment in order to obtain uniform irradiation in each experiment. Experiments conducted for evaluation of optimal dose of  $\text{H}_2\text{O}_2$  used 10 lamps. The effect of UV-C intensity was investigated by varying the number of lamps (10, 6 and 2). Ferrioxalate

**Table 1.** Light intensities for various lamp configurations.

Number of lamps	Light intensity (photon/s)	Energy (Joules)
10	$8.95 \times 10^{17}$	0.7
6	$5.91 \times 10^{17}$	0.4
2	$1.67 \times 10^{17}$	0.1

actinometry was used to determine the intensity of radiation for various number of lamps. The light intensity for various configurations of lamps is given in Table 1.

### Batch experiments

All experiments were conducted in a cylindrical quartz beaker ( $D = 7$  cm,  $H = 13$  cm) with a working volume of 200 mL at room temperature. Sample matrices for experiments were prepared by spiking 10 mL of the CBZ stock solution of strength 100 mg/L in 190 mL secondary-treated effluent with a resultant concentration of 5 mg/L. The CBZ stock solution was prepared by dissolving 100 mg of CBZ in one liter of milli-Q water by ultrasonication for 8 h and stored at 4°C. Concentration of CBZ in the stock solution was standardized against the standard calibration curve. Initially, the optimal  $H_2O_2$  dose for degradation of CBZ was evaluated by varying the  $H_2O_2$  dose at 10, 25, 50, 100 and 250 mg/L while keeping the UV intensity constant at  $8.95 \times 10^{17}$  photon/s. The effect of UV intensity was evaluated by varying the number of lamps while having a constant  $H_2O_2$  dose of 100 mg/L. Varying light intensities with 10, 6 and 2 bulbs were used to evaluate the effect of light intensity. The intensity of light corresponding to the number of light bulbs is given in Table 1. In all the experiments, a magnetic stirrer was used to homogenize the solution and 1 mL of the samples was collected at specified time intervals. Reproducibility of the experimental results was determined by conducting all experiments in duplicates and the average values are reported. The variation between the duplicate samples did not exceed 2%.

### Bench-scale continuous reactor experiments

Continuous reactor experiments were conducted in an Aquafine CSL-4R horizontal flow reactor procured from AQUAFINE Valencia, CA, USA. The volume of the reactor is 12 L and consists of four low-pressure mercury lamps (UV-C 254 nm) mounted with their longitudinal axis parallel to the flow. The reactor was fed from a reservoir of 30 L capacity which was completely mixed at a constant stirring of 100 rpm to homogenize the influent. Secondary-treated wastewater spiked with 5 mg/L of CBZ was used as the influent in both UV photolysis and UV/ $H_2O_2$ . In case of UV/ $H_2O_2$  experiments,

$H_2O_2$  was spiked in the influent water to a dose of 100 mg/L. The reactor was operated at a hydraulic retention time (HRT) of 2 min corresponding to a flow of 5.2 L/min. UV photolysis experiments were conducted by completely recirculating 30 L of reactor feed, while UV/ $H_2O_2$  experiments were conducted in a single pass mode. Initially, before commencement of each experiment, the reactor feed was pumped from the reservoir and recirculated for 15 min to equilibrate the system with feed water. Degradation of CBZ was observed by measuring the concentration of CBZ at the outlet of the reactor and at the reservoir for UV/ $H_2O_2$  and UV photolysis experiments, respectively. The UV dose of the system was evaluated using ferrioxalate actinometry. For UV photolysis experiments, kinetic constants were evaluated by considering the system as a batch reactor and by fitting the CBZ concentration profiles to the first-order batch kinetic equation after CBZ concentration profiles were plotted against effective UV exposure time. Kinetic constants for UV/ $H_2O_2$  experiments were estimated by fitting the experimental data to a first-order plug-flow model.

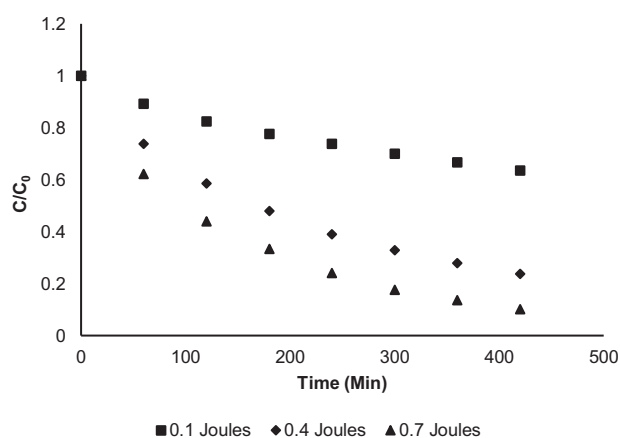
### Analytical methods

CBZ was quantified using HPLC in a Varian Prostar 210 HPLC instrument equipped with UV-visible detector. A Pinnacle DB C-18 ( $4.6 \times 150$  mm, 5  $\mu$ m) column was used to separate the target CBZ from its by-products. An isocratic elution with a 1 mL/min flow rate was used in the analysis; the eluent comprised 30% water and 60% methanol mixture with 10 mM phosphoric acid as the buffer. The UV-visible detector wavelength was set at 286 nm, and the temperature was kept constant at 25°C. The total runtime was 6 min and CBZ was eluted at 4.5 min. A calibration curve was prepared by using six different concentrations of standard solutions ranging from 0.25 to 5 mg/L. The concentration of CBZ in samples was determined by linear quadratic regression of the peak area obtained for samples against a calibration curve.

Analysis of total organic carbon (TOC) content in samples was performed on a Shimadzu TOC-L Total Organic Carbon Analyzer fitted with an ASI-L autosampler.

### Results and discussion

Degradation of CBZ under UV-C irradiation with and without  $H_2O_2$  was investigated in post-secondary-treated wastewater. The interdependence of  $H_2O_2$  and UV doses on the degradation process was evaluated by conducting experiments with various doses of  $H_2O_2$  and UV-C intensities.



**Figure 1.** Effect of UV dose on the degradation of CBZ spiked in wastewater.

### UV-C photolysis

The susceptibility of a compound to photodegradation depends on the molar extinction coefficient ( $\epsilon$ ) corresponding to the particular wavelength ( $\lambda$ ) of the incident irradiation [26]. The molar extinction coefficient of CBZ ( $\epsilon_{\text{CBZ}}$ ) was estimated by measuring the absorbance ( $A$ ) at  $\lambda_{254}$  in the solutions ranging from 0.4 to 20  $\mu\text{M}$  concentrations. The  $\epsilon_{\text{CBZ}}$  at  $\lambda_{254}$  was estimated as  $6140 \text{ M}^{-1}/\text{cm}$  which indicates that CBZ is susceptible to degradation under UV-C irradiation ( $\lambda_{254}$ ). This value was in good agreement with previously reported values of ( $6070 \text{ M}^{-1}/\text{cm}$ ) [26] and ( $6025 \text{ M}^{-1}/\text{cm}$ ) [15].

Degradation of CBZ spiked in secondary-treated effluent under various intensities of UV-C (254 nm) radiations are shown in Figure 1. Rate of degradation of CBZ increased with the intensity of the incident radiation. The kinetics of degradation under direct UV photolysis was observed to follow pseudo-first-order kinetics

**Table 2.** CBZ degradation rate constants under various experimental conditions.

UV photolysis/ UV/H <sub>2</sub> O <sub>2</sub>	UV intensity (photons/s)	UV dose (W/m <sup>3</sup> )	H <sub>2</sub> O <sub>2</sub> dose (mg/L)	Reaction rate coefficient (min <sup>-1</sup> )
UV photolysis (B)	$1.65 \times 10^{17}$	620	–	0.0012
UV photolysis (B)	$5.9 \times 10^{17}$	2220	–	0.004
UV photolysis (B)	$8.95 \times 10^{17}$	3370	–	0.006
UV photolysis (C)	$5.1 \times 10^{19}$	3160	–	0.0125
UV/H <sub>2</sub> O <sub>2</sub> (B)	$8.95 \times 10^{17}$	3370	10	0.22
UV/H <sub>2</sub> O <sub>2</sub> (B)	$8.95 \times 10^{17}$	3370	25	0.42
UV/H <sub>2</sub> O <sub>2</sub> (B)	$8.95 \times 10^{17}$	3370	50	0.75
UV/H <sub>2</sub> O <sub>2</sub> (B)	$8.95 \times 10^{17}$	3370	100	1.2
UV/H <sub>2</sub> O <sub>2</sub> (B)	$8.95 \times 10^{17}$	3370	250	1.9
UV/H <sub>2</sub> O <sub>2</sub> (B)	$1.65 \times 10^{17}$	620	100	0.2
UV/H <sub>2</sub> O <sub>2</sub> (B)	$5.9 \times 10^{17}$	2220	100	0.68
UV/H <sub>2</sub> O <sub>2</sub> (C)	$9.6 \times 10^{19}$	5930	100	1.02

Note: B: batch; C: continuous flow.

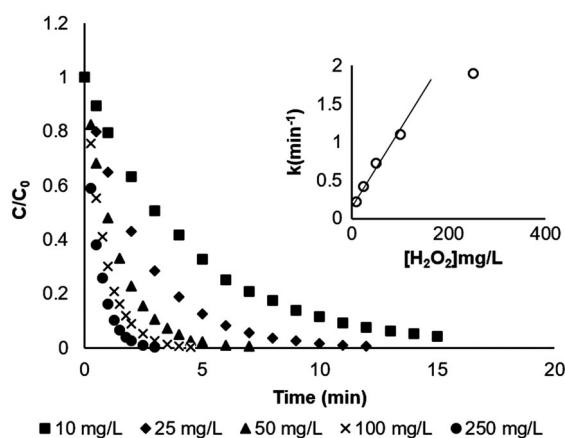
limited by the intensity of radiation and concentration of CBZ. Kinetic rate coefficients were estimated by fitting the experimental data with the pseudo-first-order equation. The estimated kinetic coefficients for various UV intensities are summarized in Table 2. Rate of degradation of CBZ increased linearly ( $R^2 = 0.996$ ) with the applied intensity.

The presence of organic matter in the reaction matrix enhanced the degradation of CBZ. The rate of degradation of CBZ in wastewater was faster than in pure water as half-life in wastewater and pure water are 115 and 178 min. Half-life is used as a parameter to compare the rate of degradation of CBZ in wastewater and pure water as rate of degradation was observed to fit pseudo-first order in the former and zero-order in the latter. Photosensitization by natural organic matter present in water has been reported to enhance degradation of organic contaminants including CBZ during UV photolysis [15,26,27,31,32]. The half-life of CBZ in river water with high organic content was two to four times lower than pure water. UV only photolysis of CBZ was faster in surface water by 1.6 times when compared with pure water [26]. Indirect photodegradation by reactive species  $^1\text{O}_2$  and  $^{\bullet}\text{OH}$  arising from sensitization by organic matter explains the enhancement of CBZ degradation in wastewater [31]. The secondary-treated effluent used in this present study strongly absorbed low wavelength UV which peaked at 221 nm indicating the presence of organic matter could be excited by UV-C irradiation.

### UV/H<sub>2</sub>O<sub>2</sub>

In UV/H<sub>2</sub>O<sub>2</sub> systems  $^{\bullet}\text{OH}$  radicals are generated by primary photolysis of H<sub>2</sub>O<sub>2</sub>.  $^{\bullet}\text{OH}$  radicals react rapidly and without selectivity in oxidation of organic contaminants. Effective degradation of target contaminants while using a UV/H<sub>2</sub>O<sub>2</sub> system is achieved by maintaining optimum concentration of H<sub>2</sub>O<sub>2</sub> which favours photosplitting of H<sub>2</sub>O<sub>2</sub> molecules and limits recombination of  $^{\bullet}\text{OH}$  radicals to form H<sub>2</sub>O<sub>2</sub> [31–34]. An increase in the concentration of H<sub>2</sub>O<sub>2</sub> above the optimum concentration can result in a decline of reaction rates. For this reason, the optimum H<sub>2</sub>O<sub>2</sub> concentration required for efficient degradation of CBZ was evaluated by varying the H<sub>2</sub>O<sub>2</sub> dose between 10 and 250 mg/L under constant UV irradiation of  $8.96 \times 10^{17}$  photon/s (Figure 2). The addition of H<sub>2</sub>O<sub>2</sub> highly enhanced degradation of CBZ under UV-C irradiation as more than 99% of CBZ spiked in pure water was degraded in 11, 6, 4 and 2.5 min for doses of 25, 50, 100 and 250 mg/L. The rate of degradation of CBZ by UV/H<sub>2</sub>O<sub>2</sub> also followed first-order kinetics as observed in direct UV photolysis. The rate constants increased linearly with increments in





**Figure 2.** Degradation of CBZ spiked in wastewater with various doses of  $H_2O_2$  under UV-C irradiation.

$H_2O_2$  dose from 10 to 100 mg/L after which it became curvilinear for 250 mg/L as expected from the second-order recombination (Table 2). A suitable concentration of  $H_2O_2$  was estimated as 100 mg/L as the rate of degradation increased by only 36.8% for a 150% increase in dose from 100 to 250 mg/L.

The presence of organic matter decreased the efficacy of the UV/ $H_2O_2$  process to degrade CBZ. The wastewater required a higher concentration of  $H_2O_2$  and longer reaction times to achieve the same level of degradation efficiency as compared to pure water. The time required for more than 99% of degradation of CBZ in wastewater with 100 mg/L of  $H_2O_2$  was 2.3 times higher than that obtained in pure water. The concentration of  $H_2O_2$  required for wastewater was twice as that required for pure water (50 mg/L) for the same level of treatment. Water quality analysis of wastewater showed the presence of bicarbonates, sulphates and TOC at concentrations of 189, 178 and 11 mg/L respectively. These components effectively scavenge the  $\cdot OH$  as they are present in wastewater at concentrations substantially higher than CBZ. Deng et al. [22] have shown the decrease in degradation efficiency in the presence of chloride ions, whereas the presence of carbonates increased degradation efficiency at concentrations below 1 mM [22]. Vogna et al. [15] have demonstrated that the presence of natural organic matter such as humic acids in high concentration could reduce the rate of degradation of CBZ by scavenging  $\cdot OH$  radicals. While the presence of humic acids below a threshold concentration of 4 mg/L aided photolysis of CBZ, higher concentrations of humic acids decreased the rate of degradation. Kinetic coefficients estimated for CBZ degradation spiked in surface water was 6 times lower than pure water experiments conducted with UV/ $H_2O_2$  photodegradation [26].

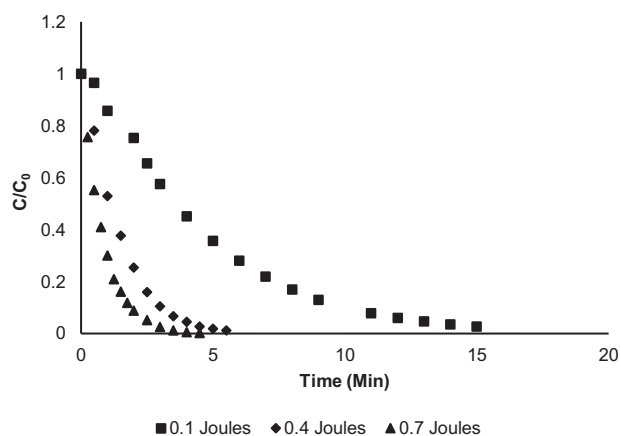
### Pathway of degradation and extent of mineralization

The extent of mineralization of CBZ was evaluated by measuring the residual TOC after the completion of each experiment. The extent of mineralization in case of UV photolysis was insignificant as more than 90% of TOC remained in solution after UV irradiation (0.7 J) of 8 h. UV photolysis is reported to result in the formation of acridine and acridone, which are significantly more recalcitrant than CBZ [15]. The degradation pathway of CBZ during UV photolysis present in natural waters and during water treatment has been reported in the literature [15,35,36]. Initially, hydroxylation of CBZ at the 10 position forms a radical intermediate resulting in 10,11-epoxycarbamazepine. Further, breaking of epoxide ring forms an unstable intermediate which suffers facile ring contraction to form 9-acridine-9-carboxaldehyde further decomposing into acridine [37]. Acridine is noted as an air and water pollutant with mutagenic and carcinogenic activities [38]. The formation of recalcitrant by-products of higher toxicity suggests that direct UV photolysis is not a suitable method for the treatment of CBZ.

In case of the UV/ $H_2O_2$  process, 87.5% of TOC degraded with only 12.5% left in solution for experiments conducted with an initial CBZ concentration of 25 mg/L. Further, in contrast to the degradation pathway of CBZ under direct UV photolysis, UV/ $H_2O_2$  treatment is reported to yield higher mineralization and by-products with less environmental significance [29]. Initial attack on the aromatic ring moieties of CBZ by  $\cdot OH$  radicals leads to hydroxylated derivatives which further form anthranilic acid, salicylic acid, catechol and other intermediates [15]. The present study indicates promise of complete mineralization of CBZ using UV/ $H_2O_2$  as removal of TOC is noted with an increase in the irradiation period. Significant reduction in TOC and the harmless by-products formed during UV/ $H_2O_2$  indicates promise for potential application for degradation of CBZ in domestic wastewater.

### Effect of UV intensity at constant $H_2O_2$

Degradation of CBZ under various intensities of UV irradiation at constant  $H_2O_2$  dose was studied to establish a relationship between UV intensity and rate of degradation of CBZ for an optimum dose of  $H_2O_2$ . The effect of intensity of UV-C irradiation on degradation of CBZ spiked in wastewater in the presence of 100 mg/L  $H_2O_2$  is presented in Figure 3. Increase in light intensity resulted in an increased rate of CBZ degradation. First-order rate coefficients for varying light intensities of  $1.65 \times 10^{17}$ ,  $5.9 \times 10^{17}$  and  $8.95 \times 10^{17}$  photon/s



**Figure 3** Effect of light intensity on the UV/H<sub>2</sub>O<sub>2</sub> system for degradation of CBZ spiked in wastewater.

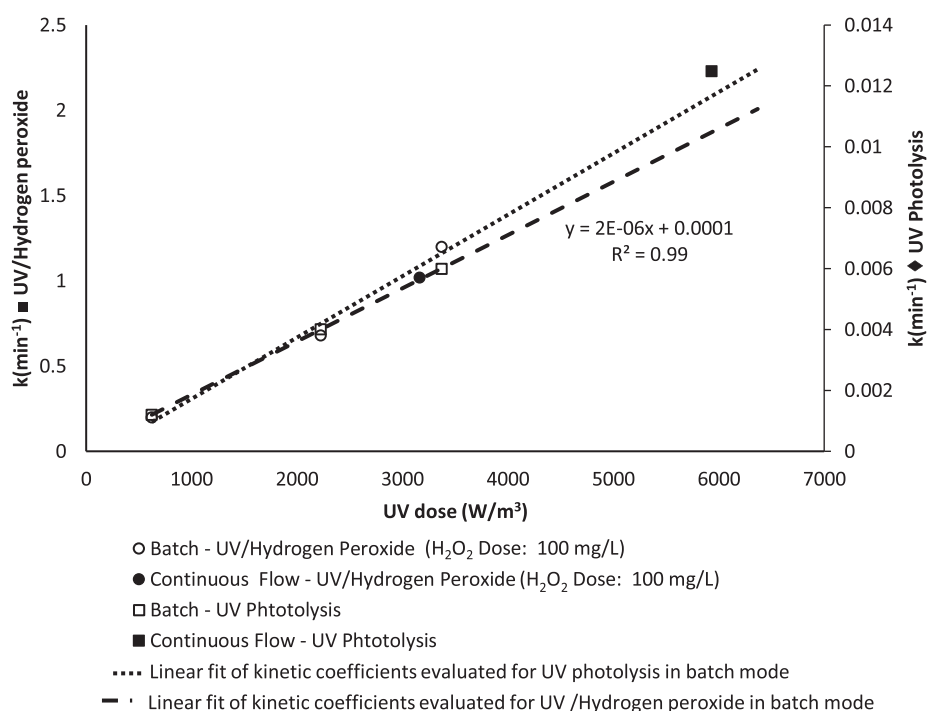
were estimated as 0.2, 0.68 and 1.2 min<sup>-1</sup> respectively. The rate constants and the intensity of UV-C irradiation followed a linear relationship ( $R^2 = 0.98$ ), as shown in Figure 4. The linear relationship observed between UV intensity and the rate of degradation of CBZ signifies that the intensity of the UV irradiation is limiting all tested cases and has not reached a point of saturation.

### Bench-scale continuous reactor studies

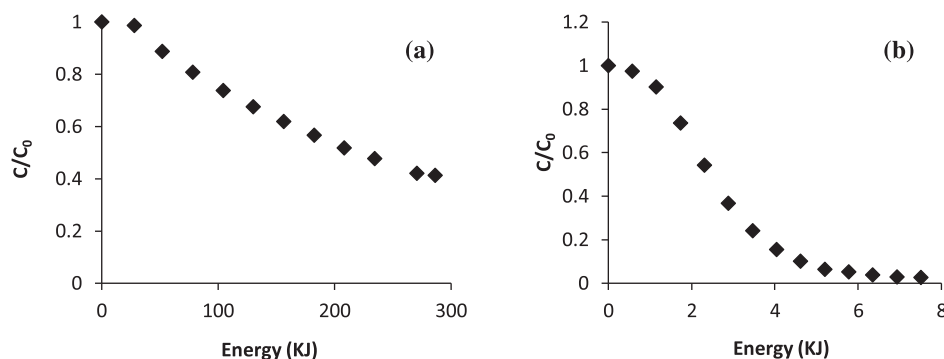
Continuous flow experiments were conducted to study degradation of CBZ in a system that resembles reactor

configuration that are used for practical applications and also to validate the kinetic values obtained from batch experiments. The normalized concentration profiles of CBZ observed in effluent for UV photolysis and UV/H<sub>2</sub>O<sub>2</sub> experiments are shown in Figure 5. The energy of UV intensity in UV photolysis and UV/H<sub>2</sub>O<sub>2</sub> experiments were estimated as 38.5 and 72.3 J which corresponds to UV doses of 3160 and 5930 W/m<sup>3</sup>, respectively. The difference in UV intensity is observed due to the difference in operational times used for both UV photolysis and UV/H<sub>2</sub>O<sub>2</sub>. Degradation of CBZ in the flow-through reactor also followed first-order reaction kinetics with estimated values of 0.0125 and 1.02 min<sup>-1</sup> for UV photo degradation in the absence and presence of H<sub>2</sub>O<sub>2</sub>. From these experimental data, degradation of CBZ through UV photolysis is expected to consume 8 kJ/L of energy to achieve 50% reduction in CBZ concentration, while UV/H<sub>2</sub>O<sub>2</sub> requires only 2.2 kJ/L for the same level of reduction.

Figure 5 compares the kinetic constant obtained from flow-through experiments with the linear relationship established for kinetic constants from batch experiments. In case of direct UV photolysis, the kinetic constant estimated for continuous reactor experiments was found to deviate by only 6%. Similarly, the kinetic constant for UV/H<sub>2</sub>O<sub>2</sub> experiments deviated only by 6.3%. These estimates signify high correlation between the UV intensity and the rate of degradation of CBZ irrespective of the mode of operation. These observations indicate that



**Figure 4.** Effect of UV dose on the rate of degradation of CBZ using (a) UV-C photolysis and (b) UV/H<sub>2</sub>O<sub>2</sub>.



**Figure 5.** Degradation of CBZ in a bench-scale continuous flow reactor (flow: 5.2 L/min; Initial CBZ concentration: 5 mg/L): (a) UV only photolysis in completely recycled mode and (b) UV/H<sub>2</sub>O<sub>2</sub> in a flow-through reactor in single pass mode.

these expressions could be used for the prediction of probable degradation of CBZ in disinfection units that use low-pressure mercury lamps with high validity.

#### Degradation of CBZ predicted in a disinfection unit of WWTP

The relationship between the UV and H<sub>2</sub>O<sub>2</sub> doses established in this study was applied to the disinfection system of a WWTP to estimate the reduction in CBZ that could be achieved by the addition of H<sub>2</sub>O<sub>2</sub>. The disinfection unit consists of 10 parallel channels, each with 3 UV lamp banks. Each lamp bank contains 384 low-pressure mercury lamps (254 nm, Philips UV, 65 W) of 1.6 m length functioning at an efficiency of 32%. The UV dose of the disinfection system was estimated to be 4140.6 W/m<sup>3</sup> based on these specifications [39]. The rate of CBZ degradation occurring in the disinfection unit is determined to be  $6.9 \times 10^{-2} \text{ min}^{-1}$  ( $1.13 \times 10^{-3} \text{ s}^{-1}$ ) from the linear relationship between UV dose and the degradation rate constant presented in Figure 4. The efficiency of degradation of CBZ based on this kinetic rate coefficient is estimated to be ~0.62% considering a retention time of 5 s.

Enhancement in efficiency of degradation of CBZ expected upon the addition of H<sub>2</sub>O<sub>2</sub> to the existing disinfection system is estimated from the relationship between UV dose and kinetic degradation constants in a UV/H<sub>2</sub>O<sub>2</sub> system (Figure 4). The degradation rate constant for the disinfection system at the WWTP was linearly extrapolated as  $14.8 \text{ min}^{-1}$  ( $0.25 \text{ s}^{-1}$ ) from the relationship presented in Figure 4 for a H<sub>2</sub>O<sub>2</sub> dose of 100 mg/L. CBZ degradation of ~64% is predicted with the addition of 100 mg/L of H<sub>2</sub>O<sub>2</sub> to the current disinfection unit at the WWTP. This highlights that the addition of H<sub>2</sub>O<sub>2</sub> to currently available UV disinfection units in WWTPs could also lower levels of other pharmaceuticals.

However, the economics and cost benefit analysis of addition of adding H<sub>2</sub>O<sub>2</sub> deserve a detailed study.

#### Conclusions

This study investigated the influence of UV and H<sub>2</sub>O<sub>2</sub> doses for UV photolysis and UV/H<sub>2</sub>O<sub>2</sub> systems with the perspective of implementing these technologies as tertiary treatment units in existing WWTPs for the degradation of CBZ. The following conclusions are drawn from this study after evaluation of optimal conditions for each treatment method by conducting batch and continuous reactor experiments with secondary-treated wastewater.

- Degradation of CBZ in wastewater followed first-order reaction kinetics with strong linear dependence on the UV intensity under UV-C irradiation.
- Indirect photodegradation by photosensitization of organic compounds in wastewater enhanced degradation of CBZ as half-life of CBZ in wastewater was 35.3% lesser than pure water under UV-C irradiation.
- Combination of H<sub>2</sub>O<sub>2</sub> and UV-C resulted in fast degradation of CBZ in treated wastewater for an optimal concentration of 100 mg/L of H<sub>2</sub>O<sub>2</sub> with first-order reaction rate constant of  $1.2 \text{ min}^{-1}$ .
- Rate of degradation of CBZ in wastewater was observed to have a linear relationship with tested UV intensities in the presence of H<sub>2</sub>O<sub>2</sub>.
- Kinetic rate constants estimated for the continuous reactor were in good agreement with relationships developed in the batch reactor with a marginal deviation of  $\pm 6.5\%$ .
- Under optimum H<sub>2</sub>O<sub>2</sub> dose of 100 mg/L maximum TOC removal of 87.5% was observed under UV-C after 8 h of irradiation.
- Addition of 100 mg/L of H<sub>2</sub>O<sub>2</sub> to secondary-treated effluent entering the disinfection unit in the WWTP



is expected to increase the degradation of CBZ from 0.62% to 64.4%.

## Disclosure statement

No potential conflict of interest was reported by the authors.

## Funding

This research was jointly funded by the Natural Sciences and Engineering Research Council of Canada and the City of Calgary through the NSERC-IRC research grant.

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## References

- [1] Yargeau V, Lopata A, Metcalfe C. Pharmaceuticals in the Yamaska River, Quebec, Canada. *Water Qual Res J Can.* 2007;42(4):231–239.
- [2] Zhou JL, Zhang ZL, Banks E, et al. Pharmaceutical residues in wastewater treatment works effluents and their impact on receiving river water. *J Hazard Mater.* 2009;166(2–3):655–661.
- [3] Fram MS, Belitz K. Occurrence and concentrations of pharmaceutical compounds in groundwater used for public drinking-water supply in California. *Sci Total Environ.* 2011;409(18):3409–3417.
- [4] López-Serna R, Jurado A, Vázquez-Suñé E, et al. Occurrence of 95 pharmaceuticals and transformation products in urban groundwaters underlying the metropolis of Barcelona, Spain. *Environ Pollut.* 2013;174:305–315.
- [5] Chen C, Bai H, Chang S, et al. Preparation of N-doped TiO<sub>2</sub> photocatalyst by atmospheric pressure plasma process for VOCs decomposition under UV and visible light sources. *J Nanoparticle Res.* 2007;9(3):365–375.
- [6] Miao X-S, Yang J-J, Metcalfe CD. Carbamazepine and its metabolites in wastewater and in biosolids in a municipal wastewater treatment plant. *Environ Sci Technol.* 2005;39(19):7469–7475.
- [7] Benotti MJ, Trenholm RA, Vanderford BJ, et al. Pharmaceuticals and endocrine disrupting compounds in U.S. drinking water. *Environ Sci Technol.* 2009;43(3):597–603.
- [8] Stackelberg PE, Furlong ET, Meyer MT, et al. Persistence of pharmaceutical compounds and other organic wastewater contaminants in a conventional drinking-water-treatment plant. *Sci Total Environ.* 2004;329(1–3):99–113.
- [9] Ternes T. Pharmaceuticals and metabolites as contaminants of the aquatic environment. In Daughton CG, Jones-Lepp TL, Editors. *Pharmaceuticals and care products in the environment.* Washington (DC): American Chemical Society; 2001. p. 39–54.
- [10] Mohapatra DP, Brar SK, Tyagi RD, et al. Analysis and advanced oxidation treatment of a persistent pharmaceutical compound in wastewater and wastewater sludge-carbamazepine. *Sci Total Environ.* 2014;470–471:58–75.
- [11] Clara M, Strenn B, Kreuzinger N. Carbamazepine as a possible anthropogenic marker in the aquatic environment: investigations on the behaviour of Carbamazepine in wastewater treatment and during groundwater infiltration. *Water Res.* 2004;38(4):947–954.
- [12] Vernouillet G, Eullaffroy P, Lajeunesse A, et al. Toxic effects and bioaccumulation of carbamazepine evaluated by biomarkers measured in organisms of different trophic levels. *Chemosphere.* 2010;80(9):1062–1068.
- [13] Jelic A, Michael I, Achilleos A, et al. Transformation products and reaction pathways of carbamazepine during photocatalytic and sonophotocatalytic treatment. *J Hazard Mater.* 2013;263(Part 1):177–186.
- [14] Jarvis AL, Bernot MJ, Bernot RJ. The effects of the psychiatric drug carbamazepine on freshwater invertebrate communities and ecosystem dynamics. *Sci Total Environ.* 2014;496:461–470.
- [15] Vogna D, Marotta R, Andreozzi R, et al. Kinetic and chemical assessment of the UV/H<sub>2</sub>O<sub>2</sub> treatment of antiepileptic drug carbamazepine. *Chemosphere.* 2004;54(4):497–505.
- [16] Klavarioti M, Mantzavinos D, Kassinos D. Removal of residual pharmaceuticals from aqueous systems by advanced oxidation processes. *Environ Int.* 2009;35(2):402–417.
- [17] Achilleos A, Hapeshi E, Xekoukoulotakis NP, et al. UV-A and solar photodegradation of ibuprofen and carbamazepine catalyzed by TiO<sub>2</sub>. *Sep Sci Technol.* 2010;45(11):1564–1570.
- [18] Domínguez JR, González T, Palo P, et al. Fenton + Fenton-like integrated process for carbamazepine degradation: optimizing the system. *Ind Eng Chem Res.* 2012;51(6):2531–2538.
- [19] Shirazi E, Torabian A, Nabi-Bidhendi G. Carbamazepine removal from groundwater: effectiveness of the TiO<sub>2</sub>/UV, nanoparticulate zero-valent iron, and fenton (NZVI/H<sub>2</sub>O<sub>2</sub>) processes. *CLEAN Soil Air Water.* 2013;41(11):1062–1072.
- [20] McDowell DC, Huber MM, Wagner M, et al. Ozonation of carbamazepine in drinking water: identification and kinetic study of major oxidation products. *Environ Sci Technol.* 2005;39(20):8014–8022.
- [21] Im J-K, Cho I-H, Kim S-K, et al. Optimization of carbamazepine removal in O<sub>3</sub>/UV/H<sub>2</sub>O<sub>2</sub> system using a response surface methodology with central composite design. *Desalination.* 2012;285:306–314.
- [22] Deng J, Shao Y, Gao N, et al. Degradation of the antiepileptic drug carbamazepine upon different UV-based advanced oxidation processes in water. *Chem Eng J.* 2013;222:150–158.
- [23] Deng J, Shao Y, Gao N, et al. Thermally activated persulfate (TAP) oxidation of antiepileptic drug carbamazepine in water. *Chem Eng J.* 2013;228:765–771.
- [24] Naddeo V, Meriç S, Kassinos D, et al. Fate of pharmaceuticals in contaminated urban wastewater effluent under ultrasonic irradiation. *Water Res.* 2009;43(16):4019–4027.
- [25] Donner E, Kosjek T, Qualmann S, et al. Ecotoxicity of carbamazepine and its UV photolysis transformation products. *Sci Total Environ.* 2013;443:870–876.
- [26] Pereira VJ, Weinberg HS, Linden KG, et al. UV degradation kinetics and modeling of pharmaceutical compounds in

- laboratory grade and surface water via direct and indirect photolysis at 254 nm. *Environ Sci Technol.* **2007**;41(5):1682–1688.
- [27] Pereira VJ, Linden KG, Weinberg HS. Evaluation of UV irradiation for photolytic and oxidative degradation of pharmaceutical compounds in water. *Water Res.* **2007**;41(19):4413–4423.
- [28] Block SS. Disinfection, sterilization, and preservation. Philadelphia (PA): Lippincott Williams & Wilkins; **2001**.
- [29] Lekkerkerker-Teunissen K, Benotti MJ, Snyder SA, et al. Transformation of atrazine, carbamazepine, diclofenac and sulfamethoxazole by low and medium pressure UV and UV/H<sub>2</sub>O<sub>2</sub> treatment. *Sep Purif Technol.* **2012**;96:33–43.
- [30] Chu X, Xiao Y, Hu J, et al. Pilot-scale UV/H<sub>2</sub>O<sub>2</sub> study for emerging organic contaminants decomposition. *Rev Environ Health.* **2016**;31(1):71–74.
- [31] Matamoros V, Duhec A, Albaigés J, et al. Photodegradation of carbamazepine, ibuprofen, ketoprofen and 17 $\alpha$ -ethinylestradiol in fresh and seawater. *Water Air Soil Pollut.* **2009**;196(1–4):161–168.
- [32] Chamoli U. Disinfection and self-sensitized degradation of natural organic matter (NOM) by TiO<sub>2</sub> photocatalysis with visible light [thesis]. Calgary: University of Calgary; **2013**.
- [33] Wilson Jr, WE. A critical review of the gas-phase reaction kinetics of the hydroxyl radical. *J Phys Chem Ref Data.* **1972**;1(2):535–573.
- [34] Li C, Gao N, Li W. Photochemical degradation of typical herbicides simazine by UV/H<sub>2</sub>O<sub>2</sub> in aqueous solution. *Desalination Water Treat.* **2011**;36(1–3):197–202.
- [35] Kosjek T, Andersen HR, Kompere B, et al. Fate of carbamazepine during water treatment. *Environ Sci Technol.* **2009**;43(16):6256–6261.
- [36] De Laurentiis E, Chiron S, Kouras-Hadef S, et al. Photochemical fate of carbamazepine in surface freshwaters: laboratory measures and modeling. *Environ Sci Technol.* **2012**;46(15):8164–8173.
- [37] Furst SM, Uetrecht JP. Carbamazepine metabolism to a reactive intermediate by the myeloperoxidase system of activated neutrophils. *Biochem Pharmacol.* **1993**;45(6):1267–1275.
- [38] Chiron S, Minero C, Vione D. Photodegradation processes of the antiepileptic drug carbamazepine, relevant To estuarine waters. *Environ Sci Technol.* **2006**;40(19):5977–5983.
- [39] Mehrabani-Zeinabad M, Achari G, Langford CH. Advanced oxidative degradation of bisphenol A and bisphenol S. *Environ Eng Sci.* **2015**;10(4):92–102.