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ADVANCED OXIDATIVE PROCESSES FOR DEGRADATION OF CARBAMAZEPINE IN WASTEWATER EFFLUENTS

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ABSTRACT

This paper presents a comprehensive evaluation of advanced oxidation based treatment processes for degradation of carbamazepine (CBZ) in wastewater effluents. CBZ is a prescribed antiepileptic drug and is one of the most frequently detected pharmaceutical in water bodies. Wastewater treatment plants (WWTPs) are considered to be the gate ways of CBZ into the environment as CBZ is resistant to biodegradation and mostly remains unaltered during the conventional treatment processes. Advanced Oxidation Processes such as ozonation, H₂O₂/UV and TiO₂/UV individually or in combinations have indicated possibility for degrading CBZ. In this study, various AOPs including UVC/H₂O₂, UVA/H₂O₂, Ozonation (O₃), and photocatalysis (TiO₂/UV) were evaluated for ability to degrade CBZ. Experiments were conducted in spiked pure water and postsecondary treated wastewater by varying doses of H₂O₂, TiO₂ and O₃. Among all the tested methods, fastest degradation of CBZ was observed in both, O₃ (14.4 mg/h) and UV/H₂O₂ (100 mg/L), with a half-life period of 35 sec. Rate of degradation of CBZ in wastewater followed zero-order and first-order for O₃ and UV/H₂O₂ with rate constants of 4.3 mgL⁻¹min⁻¹ and 1.2 min⁻¹ respectively. UV/H₂O₂ was deduced to be most suitable method for degradation of CBZ as highest degree of mineralization with a total organic carbon reduction of 87% was observed after a reaction time of 8 hours while O₃ resulted with less than 10% for the same reaction time. These results indicate that degradation of CBZ in existing WWTPs could be enhanced by adding small amounts H₂O₂ to UV disinfection units.

Keywords: - carbamazepine; advanced oxidation processes; UV/H₂O₂; emerging substances of concern; wastewater treatment

1. INTRODUCTION

Carbamazepine (CBZ) is one of the most persistent pharmaceutical frequently detected in aquatic environments including surface water, groundwater, sewage and drinking water. It is prescribed for treating epileptic seizures, severe nerve pain (trigeminal neuralgia) and bipolar disorder. Presence of CBZ in environment is primarily attributed to human/animal excretion via urine/feces or from the disposal into sewers. Wastewater treatment plants (WWTP) are considered as the major gateways of CBZ into the environment as it is highly resistant to biological degradation and very low removal efficiencies (below 10%) are achieved in conventional wastewater treatment plants. CBZ is considered as an indicator of pharmaceutical pollution due to its resistance to its ubiquitous presence in wastewater effluent-impacted surface water and groundwater worldwide and its resistance to environmental degradation. Apart from being stable in the environment, CBZ bio-accumulates through food contamination in the aquatic environment and is possibly harmful for aquatic life since literature shows it to be toxic even at concentrations below 100 mg/L (Jelic et al., 2013). According to Zhan et al., 2008, potentially chronic

toxicity rather than acute toxicity for aquatic organisms including bacteria, algae and fish such as feminizing effect on fish. Effects on human health is yet to be defined but precaution warrants developing efficient treatment methodologies (Cunningham et al., 2010, Kumar et al., 2010, Zhan et al., 2008, Jelic et al., 2013, Chen et al., 2006).

Advanced oxidation processes (AOP) have attracted considerable interest for treatment of pharmaceuticals in wastewater treatment as they generate hydroxyl radicals that can nonselectively degrade a wide range of pharmaceuticals including carbamazepine. Though many studies have investigated application of AOPs for degradation of CBZ, solid recommendations implementation of AOP based technology in existing WWTPs is still lacking. This study was focused on evaluation of AOPs, TiO₂/UV, UVC/ H₂O₂, UVA/ H₂O₂, and ozonation (O₃) from the view point of their suitability in implementing them in existing WWTPs with minimal modifications infrastructure. Initially, degradation of CBZ was studied through experiments conducted with pure water spiked with CBZ by varying doses of the oxidants/catalyst. Based on the performance of AOPs in pure water, selected AOPs with promising results were further evaluated in experiments conducted with wastewater spiked with CBZ.

2. MATERIALS AND METHODS

2.1 Chemicals

99.0% purity analytical grade CBZ was purchased from Sigma-Aldrich Co. (Canada). Degussa P25 TiO₂ powder (P25 D-60287 PI 52342) was purchased from Degussa AG (Frankfurt). Degussa P25 consists of 25:75 rutile : anatase crystal form, with a purity of 99.9%. Post- secondary treated wastewater was collected from a WWTP in Calgary, Canada. High performance liquid chromatography (HPLC) grade methanol and water was purchased from VWR (Canada).

2.2 Method

Batch experiments were conducted in LZC-ORG photoreactor supplied by Luzchem Research Inc, Canada. The reaction vessel was a cylindrical quartz beaker (D = 7 cm, H = 13 cm) with a working volume of 200 mL. Initial concentration of CBZ in all experiments was maintained as 5 mg/L by spiking 10 mL of CBZ from a stock solution (100 mg/L) prepared by ultra-sonication for 8 hours. The rest of the reaction solution consisted of either pure water or secondary treated wastewater along with doses of TiO₂ or H₂O₂ or Ozone. Experimental conditions evaluated for each AOP method are outlined in Table 1. UV dose from UVA and UVC light source of 10 bulbs was estimated to be 1.321E¹⁸ and 8.95E¹⁷ photons/sec by using ferrioxalate actinometry. The reactor was equipped with five lamps on each side of the reaction vessel. UVA and UVC irradiations used light sources from Hitachi FL8BL-B (352 nm, 8W) fluorescent lamps and Sankyo Denki G8T5 (254 nm, 8W) low pressure mercury lamps respectively. In all experiments, a magnetic stirrer was used to homogenise the solution and 2ml samples were collected at specified time intervals. All experiments were conducted in duplicates, and the average values are reported. CBZ concentrations were quantified using Varian Prostar 210 HPLC instrument equipped with a UV detector. Errors in quantification of CBZ in most of the data points are estimated to be less than SD ±1%. CBZ concentrations were quantified using Varian Prostar 210 HPLC instrument equipped with a UV detector. Errors in quantification of CBZ in most of the data points are estimated to be less than SD ±1%.

3. RESULTS AND DISCUSSION

3.1 Degradation of CBZ in pure water

Degradation of CBZ by various AOPs in pure water are shown in Figure 1. More than 99% of 4.5 mg/L of initial CBZ was degraded by O₃ (14.4 mg/h), UVC/H₂O₂ (50 mg/L) and UVA/TiO₂ (0.5 g/L) in 0.5, 2 and 10 min respectively under optimal doses in pure water. Rate of degradation was the slowest under UVA/H₂O₂(500 mg/L) among all the AOPs.

Degradation of CBZ by photocatalysis was tested in the presence of various loadings of TiO₂ (P25 Degussa) under both UVA and UVC irradiations. Adsorption of CBZ on TiO₂ in the dark over a period of 30 min was less than 4% even for TiO₂ loading of 2 g/L. Though there was no considerable difference in the rate of CBZ degradation under

various TiO₂ loadings, rate of degradation was faster under UVA irradiation. First order degradation rate coefficient for in case of UVC irradiation (K : 0.35 min⁻¹) for TiO₂ dose of 0.5 g/L was lower by 41.6% compared to UVA irradiation for the same dose (K : 0.6 min⁻¹). Strong absorption of TiO₂ in the near UV wavelength (λ : 385 nm) is the reason for faster degradation of CBZ observed in case of UVA/TiO₂.

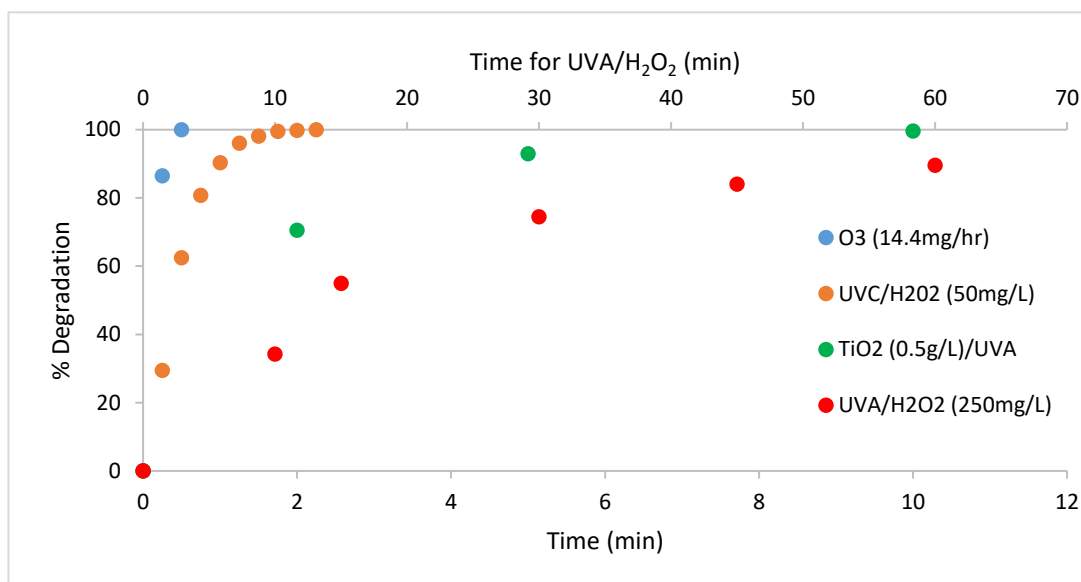


Figure 1: Degradation of CBZ by various AOPs in pure water

Table 1: Doses evaluated for each AOP method

Treatment method	Doses	Water/wastewater
TiO ₂ /UVA	0.5, 1, 1.5, 2 g/L	Water
UVA/H ₂ O ₂	100, 250 & 500 mg/L	Water
UVA/H ₂ O ₂	250, 500, 750 & 1000 mg/L	Wastewater
UVC/H ₂ O ₂	10, 25, 50, 100 mg/L	Water
UVC/H ₂ O ₂	10, 25, 50, 100 & 250 mg/L	Wastewater
Ozonation	4.8, 9.6 & 14.4 mg/L	Water and wastewater

The effect of H₂O₂ on CBZ degradation under both UVA and UVC irradiation was studied in the presence of by various doses of H₂O₂. Optimum dose of H₂O₂ for UVC/H₂O₂ and UVA/H₂O₂ treatment were estimated as 50 mg/L and 250 mg/L. Rate of degradation increased with increase in concentration of H₂O₂ dose under both UVA and UVC. However, significant improvement in rate of degradation is not observed above 50 and 250 mg/L of H₂O₂ under both UVA and UVC irradiations. Rate of CBZ degradation by UVA/H₂O₂ was slower and also required higher dose of H₂O₂ for optimal degradation compared to UVC irradiation. CBZ was highly recalcitrant to UVA photolysis as only 7.5 % of CBZ was degraded over period of 120 min while 31.7% was degraded under UVC photolysis. CBZ also exhibits strong absorption of UVC irradiation which peaks at 285 nm. Strong absorption of UVC by CBZ is assumed to sensitise the compound for faster degradation under UVC/H₂O₂ method.

Among all the tested AOPs, O₃ demonstrated the fastest rate of degradation of CBZ. More than 99.8% of CBZ was degraded within 2 min for the lowest dose of 4.8 mg/h of ozone tested in this study. For higher ozone doses of 9.6 and 14.4 mg/h, CBZ was degraded to below detection limits (>99.9%) by 0.75 and 0.5 min. Rate of CBZ degradation by ozone followed zero-order kinetics in contrast with other AOPs which followed first order kinetics. Zero-order kinetics during ozonation indicate that degradation of CBZ is not limited by the concentration of available ozone in the aqueous solution. High reactivity of CBZ with ozone at low ozone doses has been reported by Huber et al. (2003), however, in their studies they have used single spike of ozone dose in contrast to this present work in which ozone was continuously bubbled.

The half lives estimated for the optimal doses for degradation of CBZ in pure water by various AOPs are tabulated in Figure 2. According to the rate of degradation of CBZ the AOPs arranged in the order of O₃>UVC/H₂O₂>TiO₂/UVA>TiO₂/UVC>UVA/H₂O₂. O₃ and UVC/H₂O₂ show promise for easy implementation of these treatment methods as no major infrastructural units are required to remove residual H₂O₂ and O₃. Though TiO₂/UV also demonstrated faster degradation, removal of TiO₂ slurry from water requires energy and equipment and hence is not a viable option for implementing in existing WWTPs.

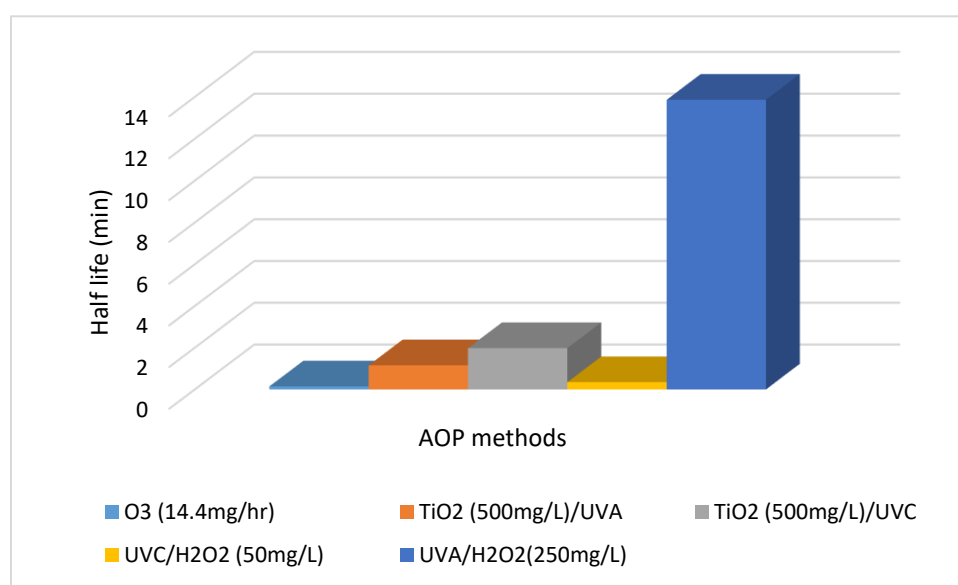


Figure 2: Half-life of CBZ for various AOPs in pure water

3.2 Degradation of CBZ in wastewater

Degradation of CBZ spiked in wastewater by AOPs O₃, UVA/ H₂O₂ and UVC/ H₂O₂ are shown in Figure 3. Rate of degradation of CBZ decreased in WW and also required higher doses of H₂O₂ under UVA and UVC irradiations. More than 99% of CBZ was degraded in the presence of 500 mg/L only after 240 min which is about 1.3 times higher than the time period observed in pure water experiments for achieving the same level of degradation with 250 mg/L of H₂O₂ in 180 min. In case of UVC/H₂O₂, the optimum concentration of H₂O₂ was estimated as 100 mg/L as rate of degradation increased only by 36.8% for a 60% increase in dose from 100 to 250 mg/L. Similar to UVA/H₂O₂ experiments higher doses of H₂O₂ were required to achieve optimal degradation rates in the presence of wastewater. Dissolved organic matter in secondary treated waste water can cause light shielding effect which reduce the rate of degradation. Also, the inorganic ions such as chloride, sulfate, nitrate and phosphate in the secondary treated water could compete for hydroxyl radicals as quenchers resulting in lower rates of degradation of carbamazepine.

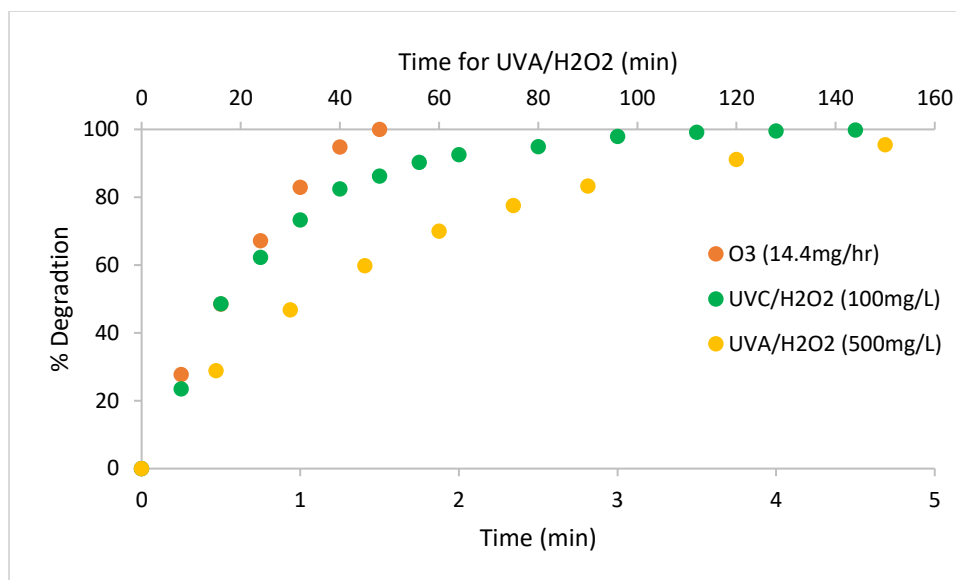


Figure 3: Percentage removal of CBZ by various AOPs in wastewater

Degradation of CBZ in wastewater by ozonation also followed zero order kinetics similar to experiments in pure water. However, in secondary treated wastewater, the rates of reaction were slower compared pure water spikes due to the presence of organic and inorganic matter that compete for ozone. For ozone dose of 14.4 mg/L, CBZ was degraded below detectable limits after a reaction time of 1.5 min which was 3 folds higher than reaction time observed in the presence of pure water.

Order of reaction and half-life of CBZ spiked in wastewater evaluated for various AOPs are tabulated in Table 2. The optimum dose of H₂O₂ required for UVC/H₂O₂ and UVA/H₂O₂ increased by 2 folds in the presence of WW as compared to pure water. However, experiments conducted in waste water show that O₃ and UVC/H₂O₂ are promising techniques for implementation in existing WWTPs as CBZ was rapidly degraded within 2 and 3 min respectively.

Table 2: Optimal doses and respective reaction rates in wastewater

Treatment method	Dose	Order of Reaction	Half life
Ozone	14.4 mg/h	Zero	0.58 min
UVA/H ₂ O ₂	500 mg/L	First	34.65 min
UVC/H ₂ O ₂	100 mg/L	First	0.58 min

4. CONCLUSIONS

This study investigated the application of advanced oxidation processes such as TiO₂/UVA, H₂O₂/UV and O₃ for the degradation of CBZ with perspective of implementing these technologies as tertiary treatment units in existing WWTPs. The study evaluated optimal conditions required for degradation of CBZ under each treatment method by conducting experiments in pure water and secondary treated wastewater. Ozonation yielded fastest rate of degradation of CBZ among all AOPs as 4.5mg/L of CBZ in wastewater was completely degraded within a period of 1.5 min (K: 4.3 mgL⁻¹min⁻¹). CBZ was also degraded by UVC/H₂O₂ photodegradation with a H₂O₂ dose of 100 mg/L within a period of 2.5 min (K:1.2 min⁻¹). Findings from this study indicate that augmentation of H₂O₂ in UV

disinfection units of existing WWTPs could aid degradation of CBZ and other recalcitrant organics in municipal wastewater.

5. REFERENCES

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