Evaluation of Multiple Advanced Oxidation Processes (AOPs) to Degrade Venlafaxine

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Background

Venlafaxine is an antidepressant sold under the trade name Effexor®. It has been measured in municipal wastewater effluent (post treatment) at a concentration of up to 2.9 µg/L. Biological study has measured neuroendocrine disrupting effects at as low as 1 µg/L. Study showed removal rates of about 50% in commonly used wastewater treatment processes of primary clarification, biological treatment, phosphate removal and sedimentation.

The regulation of discharge of pharmaceuticals has become an area of focus in wastewater regulation in recent years. In Canada, the CCME Canada-wide Strategy for the Management of Municipal Wastewater Effluent has specifically stated the need for increased research in the area of pharmaceuticals. To begin to address the issue, Alberta and British Columbia have released the first discharge guidelines for a pharmaceutical in Canada, for 17a-ethinylestradiol at a concentration of 0.5 ng/L. Policy makers in the European Union have been more aggressive in moving towards regulation of pharmaceuticals, with Directive 2013/39/EU outlining a number of compounds that will require regulation in the future, with the list being expanded periodically.

Advanced Oxidation Processes (AOPs) are processes that have potential to be used to degrade pharmaceuticals in wastewater. AOPs are chemical or photochemical processes that form highly reactive species (notably HO•) to degrade organic contaminants. HO• has more than double the oxidative potential of chlorine, and is capable of degrading recalcitrant compounds. A primary challenge in working with AOPs is that HO• reacts very quickly in solution, only lasting between pico and nano seconds.

Research Objectives

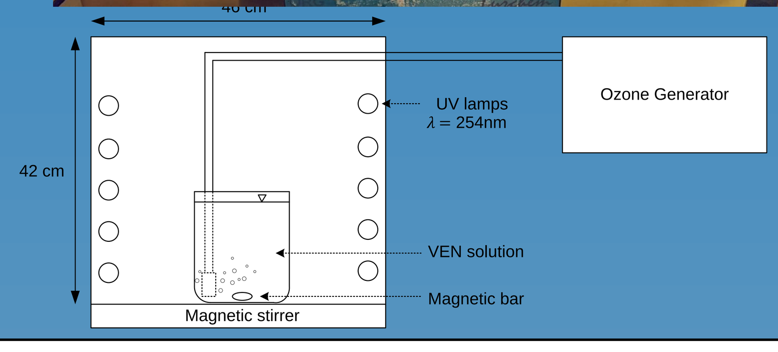
The main research objective is to determine the effectiveness of multiple AOPs to degrade venlafaxine.

Perform parametric study using four different methods:

- UV Photolysis
- Ozonation
- UV/O_3
- UV/H_2O_2

Tests on real secondary effluent obtained from Pine Creek will be preformed on the processes listed above.

Provide a preliminary comparative analysis on cost for each of the methods tested.



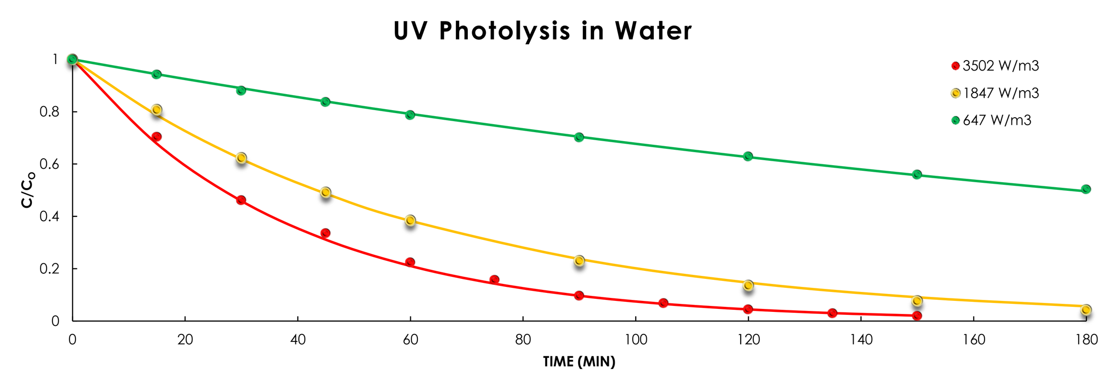
Methodology

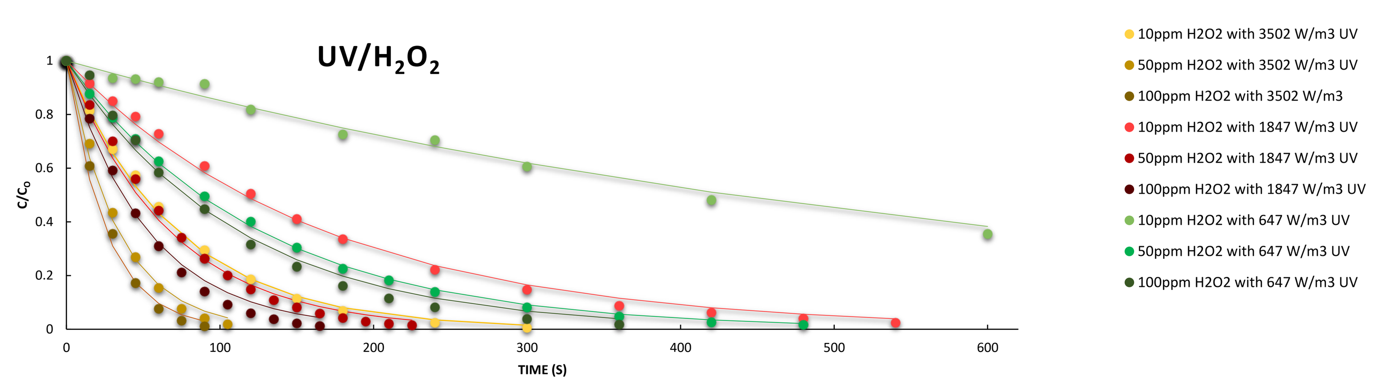
Initial VEN concentration in all experiments was 10 mg/L. Experiments were performed in a Luzchem batch reactor, with light radiation at a wavelength of 254 nm (UVC). The intensity of UV light was varied by adding or removing bulbs. Total photons to solution was measured using ferrioxalate actinometry.

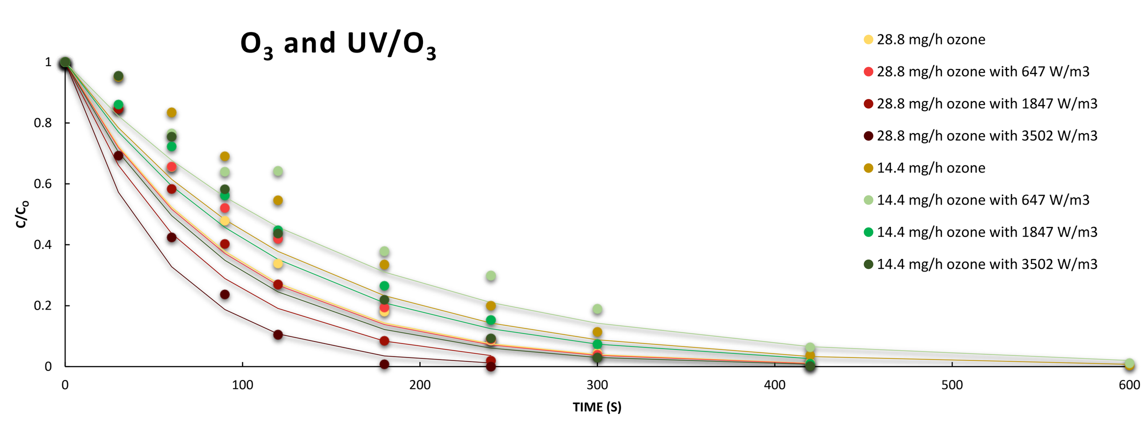
Ozone was produced using a corona discharge ozone generator (aa A2Z Ozone Inc. model 3GLAB) using oxygen as a feed gas. Ozone was sparged into solution using a coarse diffuser. Aqueous ozone concentration was measured using an indigo trisulfonate method.

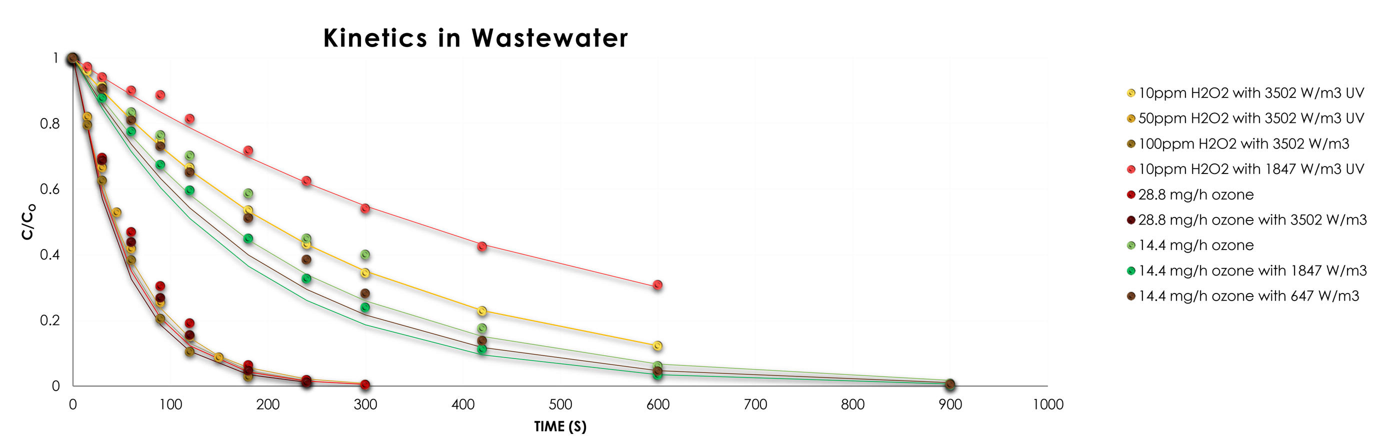
H_2O_2 was added at the beginning of each experiment to the desired concentration.

Results









Half-life of VEN in pure water by different treatment methods (seconds)

Process type	Chemical Dosage	No UV	647 W/m³ UV	1847 W/m³ UV	3502 W/m³ UV
Ozone	14.4 mg/h	86	107	80	59
Ozone	28.8 mg/h	64	63	50	37
UV photolysis	NA	NA	9039	2599	1599
H_2O_2	10 mg/L	NA	433	116	50
H_2O_2	50 mg/L	NA	87	46	23
H_2O_2	100 mg/L	NA	77	36	19

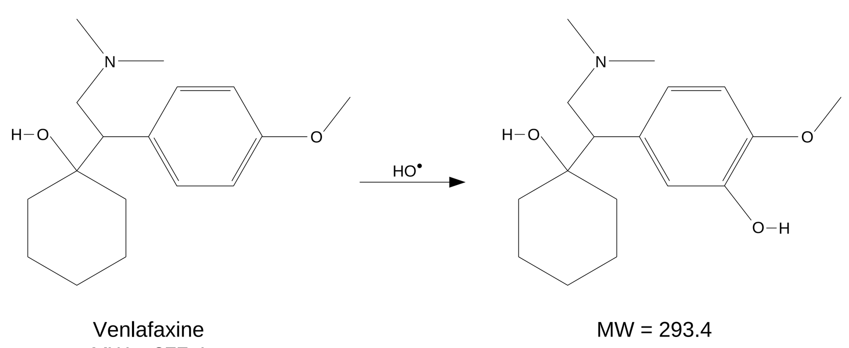
Estimated operating costs to remove 65% VEN from 1.0 m³ of water

Process type	Chemical Dosage	No UV	647 W/m³ UV	1847 W/m³ UV	3502 W/m³ UV
Ozone	14.4 mg/h	$0.0062	$0.011	$0.013	$0.015
Ozone	28.8 mg/h	$0.0093	$0.011	$0.012	$0.012
UV photolysis	NA	NA	$0.30	$0.25	$0.28
H_2O_2	10 mg/L	NA	$0.017	$0.014	$0.012
H_2O_2	50 mg/L	NA	$0.018	$0.017	$0.016
H_2O_2	100 mg/L	NA	$0.034	$0.035	$0.034

Cost estimates based on: 1.0 m³ of wastewater, energy cost of $0.12/kWh, H_2O_2 price of 0.345/lb at 50% purity, O_3 priced by energy requirement of air compressor to O_3, UV based on low pressure mercury bulbs converting 40% energy to 254nm.

Breakdown pathway

Only one breakdown product was detected in a measurable quantity. The product suggests that breakdown of venlafaxine occurs by sequential hydroxylation of the aromatic ring.



Future research plans

- Bring experimental concentration down to levels measured in wastewater (ng/L - µg/L).
- Test a cocktail of main pharmaceuticals in a flow-through reactor.
- Perform experiments at pilot scale using ACWA facility at Pine Creek.

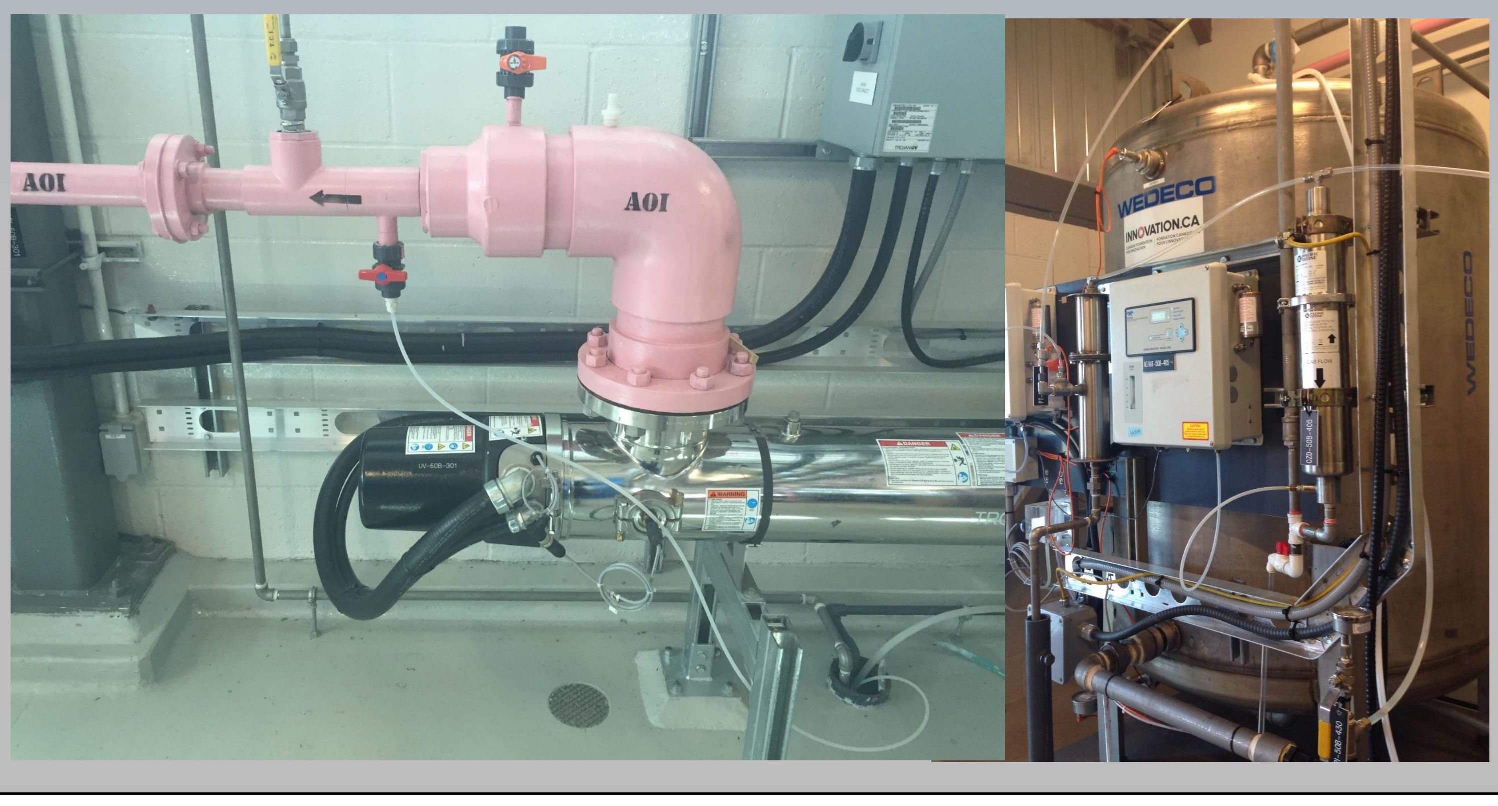
Comparison with wastewater

Repeating of experiments in wastewater showed a decrease in degradation rate, due to the turbidity of wastewater and the presence of scavenging constituents in the water.

- UV Photolysis was shown to degrade between 7-31% slower with high intensity light being more effective.
- Ozonation was shown to degrade VEN roughly 45% slower.
- UV/O_3 was shown to degrade 21-36% slower.
- UV/H_2O_2 was shown to degrade 46-75% slower.

Some of the scavenging species that were present in the secondary effluent used were:

- Bicarbonate of 189 mg/L.
- Sulphate of 178 mg/L.
- Chloride of 139 mg/L.
- Total organic carbon of 11.4 mg/L.
- Turbidity was measured at 3.3 NTU.



Conclusions

- All tested AOPs can degrade VEN, with pseudo-first order kinetics in all cases.
- UV Photolysis had a half-life of between 27 min and 150 min depending on intensity.
- UV Photolysis is primarily dependant upon total UV dose, not intensity.
- Ozonation degraded VEN with a half-life of 64-86 sec.
- Combining UV with ozonation provided little degradation rate benefit (or worse) compared to ozone alone, but improvement is seen with higher UV dosages.
- Adding H_2O_2 with UV provided substantial benefit, with degradation rate positively correlated with H_2O_2 dose. Diminishing returns on degradation rate were observed as H_2O_2 dose increases.
- Increasing UV dosage with H_2O_2 provided substantial benefit, with a half-life of 19 sec achieved with 100 mg/L of H_2O_2 and 3502 W/m³ of UV.
- Preliminary cost analysis showed that UV photolysis is notably more expensive to degrade VEN, due to the high UV dosage required.

Acknowledgements

THE CITY OF CALGARY

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