Vancouver, Canada

May 31 - June 3, 2017/ Mai 31 - Juin 3, 2017



COST FOCUSED EVALUATION OF ADVANCED OXIDATION PROCESSES TO REMOVE VENLAFAXINE IN WASTEWATER

Jordan Hollman ^{1, 6}, John Albino Dominic ², Gopal Achari ³, Cooper H. Langford ⁴ and Joo-Hwa Tay ⁵

1, 2, 3, 4, 5 University of Calgary, Canada

ABSTRACT

Concern over the negative effects of discharging residual pharmaceuticals into public waters through wastewater effluent has led to new technologies to remove these contaminants. Advanced oxidation processes (AOPs) have been proposed as a strong option to remove pharmaceuticals, as they have been shown to effectively degrade a variety of recalcitrant contaminants and have the advantage of creating no additional waste stream. However, with many different chemical processes such as O₃, UV/O₃, UV/H₂O₂, Fenton reagent and photocatalysis, there are clearly a large variety of possible options for AOP treatment. This paper presents a laboratory study on the degradation of venlafaxine (VEN) using a variety of different AOPs. VEN is an antidepressant of high concern in wastewater discharge, chosen as a candidate compound to compare AOPs. To focus future research on the best possible AOPs, a cost analysis study was performed for the removal of VEN. The analysis looked at costs in terms of operating cost, capital cost, and required basin volume. Results indicated that UV/H₂O₂, UV/O₃ and O₃ are all cost competitive processes, while UV alone is not viable. Parametric analysis found that increasing O₃ dosage decreased both operating costs and basin volume. Increasing H₂O₂ dosage increases operating cost while decreasing required basin volume considerably. Increasing UV dose decreased basin volume in all cases, while increasing operating costs for UV treatment, and keeping operating costs stable in H₂O₂ based treatment.

Keywords: - Advanced oxidation process, ozone, hydrogen peroxide, UV, venlafaxine

1. BACKGROUND

Concerns over potential negative consequences of pharmaceuticals being discharged from municipal wastewater in recent years has become a topic of high concern in the advancement of wastewater treatment technologies. Biological studies on the negative impacts that low concentrations of pharmaceuticals can have on aquatic life are of primary concern. There are many potential negative effects, with endocrine disruption being of particular concern. Male fish have shown the development of female sex characteristics, with reproductive failure in fish populations as a potential outcome (Hamilton et al. 2016). While some compounds are partially removed by existing wastewater treatment processes, they are not currently brining concentrations below levels of environmental concern.

Venlafaxine (VEN) was selected as a candidate compound for this study to test the effectiveness of various advanced oxidation processes (AOPs). VEN is among the most highly prescribed antidepressants under the trade name Effexor®. In a study measuring the discharge concentration of antidepressants being discharged for WWTPs across Canada, VEN was found to be the most prevalent with discharge

⁶ jordan.hollman@ucalgary.ca

concentrations of up to 2.9 μ g/L (Lajeunesse et al. 2012). VEN has been shown to have neuroendocrine disrupting properties at concentrations as low as 1 μ g/L(Melnyk-Lamont et al. 2014). Based on high prevalence and low effect level, VEN is an antidepressant of high concern in municipal wastewater effluents. Based on the concentrations of discharge and of environmental effect levels found in literature, removal of about 65% would be required to bring discharge below levels of environmental effect. For this reason, a removal rate of 65% was targeted in this study as the level of treatment required in evaluation of various AOPs.

AOPs are a process with high potential to be used in municipal WWTPs to provide removal of pharmaceuticals from wastewater. AOPs function by creating highly reactive species such as hydroxyl radicals (HO•) that are able to chemically degrade recalcitrant contaminants. Typical AOPs consist of chemical reagents combined with UV light to create HO•, although processes utilizing photolytic materials may also be considered. One significant advantage that AOPs have over other treatment processes is that they do not create any additional waste streams, which are a major drawback of filtration or reverse osmosis (Subramani and Jacangelo 2014). An additional advantage of AOPs is that many existing WWTPs utilize UV for disinfection prior to discharge, allowing for considerable cost saving by simply modifying an existing process rather than installing a completely new treatment module.

Some literature exists showing that VEN can be successfully degraded by HO•, as presented by García-Galán et al. (García-Galán et al. 2016). However, a comprehensive study on the effectiveness of various AOPs to degrade VEN is lacking in literature. Various other studies have been published on the potential effectiveness of AOPs to degrade other pharmaceuticals in wastewater, demonstrating that AOPs have the potential to be a robust treatment technique to remove pharmaceuticals from wastewater (Ribeiro et al. 2015).

Evaluating the economic applicability of different AOPs can be a challenge, as studies typically provide results of a given method based on laboratory results measuring chemical and light dosages in the evaluation of different treatment methods, without translating those results to cost. In this paper, laboratory data is presented on a variety of AOP treatment options, with lab results being applied to estimate expected level of cost for each process. Laboratory data presented is based upon batch experiments on milli-Q water. It is noteworthy that significant uncertainty exists when scaling these experiments to full scale treatment. Some of the factors causing uncertainty are: experiments were conducted in milli-Q water rather than wastewater, concentrations tested were significantly higher than actual wastewater concentrations, and that tests were conducted in batch rather than flow through. The primary focus of the economic analysis is in this paper is for comparative purpose between different AOPs, with specific dollar amounts presenting high uncertainty. The level off accuracy in the values presented are acceptable for comparative purposes, providing a basis for which processes are worth further development.

When choosing a potential process, a holistic approach should be taken, with operating costs, capital costs, required basin volume, potential safety hazards, process adjustability and amount of maintenance required being some of the areas that should be considered when choosing the ideal process. For this paper, only areas that directly affect the costs of implementing each process are considered. By breaking down different potential treatment options directly into cost terms, choosing the ideal process for any given treatment facility becomes considerably easier.

2. MATERIALS AND METHODS

2.1 Chemicals

VEN was supplied by BOC Sciences at high purity (>98%). Methanol for High performance liquid chromatography (HPLC) analysis was provided by Sigma-Aldrich (>99% purity). Phosphoric acid for eluent acidification was provided by ACROS Organics (>85% purity). Hydrogen peroxide at 30% purity was provided by Fluka Analytical. Oxygen feed for ozone generator was provided by Praxair (99.99% purity).

Quenching solution was prepared using Na₂SO₃ at a concentration of 100 g/L in water.

2.2 Ozone Production

Ozone was produced using aa A2Z Ozone Inc. ozone generator (model 3GLAB) with ozone production by corona discharge tube. Feed gas was oxygen at 99.99% purity. Ozone was sparged into solution through a course gas diffuser.

Measurement of aqueous concentration of ozone was done using an indigo trisulfonate method (Bader and Hoigné 1981). Fine calibration of ozone dosage was performed before each set of experiments to provide consistency in ozone dosage.

2.3 Photoreactor

UV irradiation for all experiments was done in a Luzchem batch reactor (LZC-ORG, Luzchem Research Inc.). Low pressure mercury bulbs irradiating at a wavelength of 254nm. UV intensity was measured using ferrioxalate actinometry (Calvert and Pitts 1966), with light intensity adjusted by varying the number of active UV bulbs.

Experiments were conducted in a quartz beaker placed at the center of reactor containing 200mL of sample in all cases. Vessel was continuously mixed throughout all experiments.

3.4 Sample Analysis

Quantification of VEN in all samples was done by isocratic elution on HPLC with a UV-visible detector. All injections were performed in duplicate, with less than 1% variance noted between duplicate injections. The instrument used was a Varian Prostar 210 equipped with a Pinnacle DB C18 5µm column with dimensions of 150 x 4.6mm. A flow rate of 0.5mL/min was used with an eluent ratio of 30% water to 70% methanol. All eluents were acidified by phosphoric acid to a pH of 2.6. Calibration was performed using known standards, with a lower detection limit of 0.25 mg/L.

3.5 Experimental Procedure

Starting concentration for all experiments was selected at 10 mg/L of VEN in Milli-Q water, to accurately measure >95% degradation.

Prior to the beginning of experiments UV lamps and ozone generator were run for 10 minutes for warm up. VEN solutions equilibrated to room temperature prior to starting experiments. Before ozone experiments, calibration of ozone dosage was performed.

200 mL of VEN solution was placed into a quartz beaker. Sample volumes were 2 mL, with initial sample taken prior to starting experiments. UV irradiation, O_3 and/or H_2O_2 were added concurrently at the start of experiment. A small volume of quencher (<10 μ L) was added to each sample vial, with exact amount determined by the concentration of O_3 or H_2O_2 in any given experiment. All samples were filtered using 0.45 μ m polytetrafluoroethylene filters prior to analysis.

3. RESULTS AND DISCUSSION

3.1 Experimental Results

3.1.1 Degradation Kinetics

For comparative analysis of AOPs to degrade VEN in water, a variety of methods were tested. Results presented in this paper are degradation under UV, O_3 , UV/ O_3 and UV/ H_2O_2 . A sample of kinetics by different process are presented in Figure 1 for comparison. When reading the figure, it should be noted that the result for UV only follows a scale of minutes on the x-axis, while all other results are on a scale of seconds. Experiments on H_2O_2 alone, H_2O_2/O_3 , as well as $UV/H_2O_2/O_3$ were also conducted, but are not presented here. Degradation by H_2O_2 alone was extremely slow to the point of being not competitive with other processes. H_2O_2/O_3 and $UV/H_2O_2/O_3$ experiments showed no note worthy improvement over AOPs with O_3 and UV/O_3 , and were therefore not considered for analysis.

In processes using O_3 , an ozone concentration of 14.4 mg/h and 28.8 mg/h were used, while H_2O_2 concentrations of 50 and 100 mg/L were used. For UV irradiation, light intensity ranging from 647 to 3502 W/M³ were utilized for the comparison. Only one reagent dosage for different AOPs were presented in the figure for comparative purposes.

The different AOPs reported here were able to degrade VEN to the lower detection limit of detection by HPLC, over 95% degradation. However, degradation rates varied considerably between processes, with O_3 , O_3 /UV and H_2O_2 /UV being the most rapid, degrading with a half life of 64s 63s and 77s for the parameters considered in Figure 1, respectively. Although UV alone could completely degrade VEN, it had a considerably higher half life of 43.4 min.

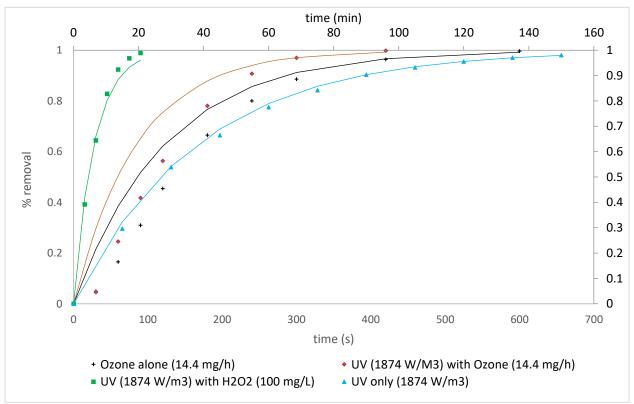


Figure 1: Removal kinetics for various AOPs Note that UV alone follows a minute time scale

3.2.1 Parametric Analysis

Parametric analysis on the effect of UV, O₃, or H₂O₂ dosages have been discussed in other works currently seeking publication. In experiments using only UV, first order degradation rate constant was found to have a positive linear correlation with light intensity, with first order rate increasing by 0.1 s⁻¹ for every additional 1 MW/m³ of additional light intensity. In experiments with UV/H₂O₂ and UV/O₃, first order degradation rate constant was again positively correlated with light intensity, with increases of approximately 7.0 s⁻¹ and 2.0 s⁻¹ for every 1 MW/m³ increase in light intensity, respectively. When chemical dosages of O₃ or H₂O₂ were increased, an increase in degradation rate was seen, although rate increase was dependant on UV dosage and did not follow a linear trend.

The significant effect of light dosage on degradation of using UV/H₂O₂ compared to UV/O₃ indicates differences in breakdown mechanism between the two AOPs. In both UV/H₂O₂ and UV/O₃ processes, there is an expectation that in the presence of UV irradiation that HO• production will be of primary importance to the degradation of recalcitrant contaminants such as VEN. For UV/H₂O₂ processes, experiments utilizing H₂O₂ in dark conditions yielded extremely low degradation, indicating that when irradiated with UV the primary degradation mechanism is the formation of HO• that subsequently oxidizes VEN. Alternately, processes utilizing O₃ in dark conditions showed considerable degradation of VEN, with marginal improvement in degradation rate as UV intensity was increased. This demonstrates that O₃ is capable of degrading VEN alone, and that there is only partial HO conversion as UV intensity is increased. Experiments to isolate the formation of HO[•] in solution have not been conducted for the purpose of this paper, leaving a gap in knowledge regarding how much degradation under UV/O₃ can be attributed to HO• formation as opposed to UV simply exciting VEN molecules making them more reactive to the O₃ present in solution. However, the practical implications of the experimental findings presented in this paper are clear regarding controlling design parameters in the development of AOP processes for large scale application; that increases in UV dosage provide much greater value in H₂O₂ AOPs compared to marginal improvement to O₃ processes.

3.2 Cost Analysis

When measuring the current discharge levels of VEN from WWTPs along with the lowest adverse effect levels seen in literature, it can be estimated that removal of roughly 65% of VEN must be accomplished during additional tertiary treatment if discharge levels are to be brought below levels of environmental concern.

Understanding the operational costs for each treatment process is of high importance in the determination of which process is likely to be applied on a large scale. Further, capital costs in the setup of a process are a major consideration. Basin volume requirements are directly related to the minimum retention time of each process and can indicate the amount of land space required for the process. As land costs can vary based on location, basic volume was taken as an economic consideration apart from capital costs. The relative cost increase to increase basin volume can vary dependant on WWTP location. It should be noted, that although plant size is an important factor in determining both operating and capital costs, it has been excluded from this analysis for simplicity.

To provide a general overview of how the different AOPs presented relate in terms of applicability, they were each ranked from 1-4 in each of the above categories for quick comparison.

3.2.1 Operating Cost

Calculation of estimated operating cost was performed considering parameters that would be required to achieve 65% removal of VEN, based on lab studies. As all AOPs considered followed pseudo first order degradation kinetics, removing the desired percentage of VEN should be comparable.

Pricing should be considered rough values, as costs for energy and chemicals can vary considerably between regions. Dollar values are presented in American dollars, as pricing information for more readily available. Data on chemical costs and process efficiencies were sourced from specifications and prices publicly listed by manufacturers and suppliers.

Some of the input data used for cost analysis is as follows:

- Energy costs were estimated at \$0.12/kWh as an average value in the United States.
- H₂O₂ pricing estimated at \$0.345/lb at 50% purity (\$0.157/kg). With 100 mg/L of H₂O₂ being considered, pricing is approximately \$0.03/m³ of water treated. Pricing assumes large quantity of H₂O₂ and does not include freight costs USP Technologies, 2017).
- O₃ production was assumed to be performed using a compressed air to O₃ setup. Estimated energy costs are based on power requirements of 50 kW for feed gas compressor and 150 kW for ozone generator. Generator considered produces 10 kg of O₃ per hour (Baratharaj, n.d.).
- Energy efficiency of low pressure mercury UV bulbs is 40% conversion to light at the required 254nm (Haraeus, 2017).

Table 1: Estimated operating costs to remove 65% venlafaxine from 1.0 m³ of water

| Process | Chemical | No UV | 647 W/m ³ | 1847 W/m ³ UV | 3502 W/m ³ UV |
|----------|-----------|----------|----------------------|--------------------------|--------------------------|
| type | Dosage | | UV | | |
| Ozone | 14.4 mg/h | \$0.0062 | \$0.0112 | \$0.0133 | \$0.0148 |
| Ozone | 28.8 mg/h | \$0.0093 | \$0.0112 | \$0.0121 | \$0.0120 |
| UV alone | NA | NA | \$0.2954 | \$0.2459 | \$0.2828 |
| H_2O_2 | 100 mg/L | NA | \$0.0335 | \$0.0345 | \$0.0344 |
| H_2O_2 | 50 mg/L | NA | \$0.0183 | \$0.0171 | \$0.0163 |

When considering the operating costs of the different processes analysed, it is apparent that the two processes which provide the strongest value for treatment are O₃ and H₂O₂ processes. Operating cost of UV alone becomes very high due to the long retention times needed.

When considering the operating costs for O_3 AOPs, operating cost increases as UV intensity is increased. With only marginal improvements in degradation rate by adding UV to these processes, the faster degradation obtainable with UV is not enough to offset the additional energy costs required to power the UV bulbs. When O_3 dosage is increased for O_3 alone, operating cost increases to obtain the same level of treatment. However, processes with UV/ O_3 show lower operating cost as O_3 dosage is increased.

In general, when considering O₃ AOPs, there is clearly some trade off that must be made between cost efficiency and degradation rate.

In H_2O_2 AOPs, there is little impact on operating cost as UV dose is adjusted. Degradation rates under high intensity increase enough to offset the additional energy cost of using a higher UV intensity. Therefore, designing a process with very high UV intensity can provide significantly faster degradation for the same operational cost. However, increasing H_2O_2 dosage considerably increases operational costs, with doubling the H_2O_2 dosage from 50 mg/L to 100 mg/L roughly doubling costs at all UV intensities tested. With the significant impact that H_2O_2 dosage has on operating costs, care should be taken in selecting the minimal dosage required for the required task, with higher dosages useful for applications that require short retention time.

Ranking based on operating costs:

- 1. O₃ alone
- 2. UV/O₃
- 3. UV/H₂O₂
- 4. UV alone

3.2.2 Capital Cost

There can be significant capital costs when setting up an AOP process on large scale for wastewater treatment. These costs can vary significantly depending on what processes are currently in place. For instance, adding an UV/H_2O_2 process to a facility that already utilizes UV disinfection can be done at considerably lower cost than a completely new system. For this analysis, it will be assumed that there is no existing infrastructure in place, to provide a fair comparison of the technologies for new facilities. Analysis presented is of a basic nature, and consists primarily of major costs obtained from literature only, to allow for a general comparison.

Considerable literature has been published on the costs of implementation of various treatment processes, with costs can varying considerably based on many factors. Influent quality, desired effluent quality, site specifics, required capacity and variability in manufacturer quotes are only a few of the factors that can impact capital costs. Due to the complexity of the issue, a review of literature was performed to provide a general estimate of how costs compare between different treatment processes.

Plumlee et al. (2014) provided the most comprehensive available cost data on the processes considered, and was therefore used as the primary resource in ranking capital costs of treatment equipment (Plumlee et al. 2014). For UV/H_2O_2 based systems, total capital costs for various system capacities were determined, with average total unit cost estimated in terms of million dollars spent per mega gallon per day (MGD) of treatment capacity. For this analysis, an average plant capacity of 50 MGD was chosen, unit total unit cost was estimated to be 0.21 \$M/MGD. It should be noted that H_2O_2 dosage considered for the estimate was considerably lower than that considered for this paper, but change in H_2O_2 dosage will have only a small impact on total capital cost.

Ozone based systems, estimated by Plumlee et al. (2014) showed that at roughly 50 MGD, that the total capital costs are estimated at 0.29 M/MGD. It should be noted that estimates for capital costs of ozone based systems show considerably more variance that H_2O_2 based systems, with costs per treatment decreasing considerably as plant capacity increases.

A paper by Cotton et al. provided a detailed breakdown of costs associated with implementing UV treatment systems (Cotton et al. 2001). Based on their estimation, at a design for of roughly 50 MGD, a capital cost of roughly \$72 000 per MGD were expected. These costs can vary considerably based on required UV intensity, with the upper range of UV intensity of this study being roughly 5 times higher than in standard practice for disinfection. Further, the very high contact times for UV treatment alone would necessitate a drastically larger number of lamps, ranging from 20 to as high as 100 times the amount of UV lamps required compared to other systems considered based on retention time requirements. An estimate for the amount of UV scale-up required was taken to be on the low end at 20 times traditional UV disinfection treatment, considerably increasing the capital costs to 1.4 \$M/MGD.

A combination of the above costs was considered for estimating the capital costs of a UV/O_3 treatment system. A combination of the estimated capital costs for an O_3 system along with a standard UV disinfection system yielded an estimated total capital cost of 0.36 \$M/MGD.

Ranking based on capital cost:

- 1. UV/H₂O₂
- 2. O₃ alone
- 3. UV/O₃

4. UV alone

3.2.3 Basin volume requirements

When considering any potential new process, retention times are of high importance. With the large water volumes being treated daily at municipal wastewater treatment plants, even small increases in retention time can lead to very large increases in required basin volume. The significance of these requirements will vary depending on the location of a given facility. Therefore, estimated volume requirements for each process will be determined by tank volume needed per 1000 m³/d of flow input to the facility.

Table 2: Estimated basin volume needed to remove 65% venlafaxine from a 1000 m³/d influent

| Process | Chemical | No UV | 647 W/m ³ | 1847 W/m ³ UV | 3502 W/m ³ UV |
|----------|-----------|---------------------|----------------------|--------------------------|--------------------------|
| type | Dosage | | UV | | |
| Ozone | 14.4 mg/h | 1.50 m ³ | 1.87 m ³ | 1.40 m ³ | 1.04 m ³ |
| Ozone | 28.8 mg/h | 1.13 m ³ | 1.10 m ³ | $0.88 \; \text{m}^3$ | 0.65 m^3 |
| UV alone | NA | NA | 158.5 m ³ | 45.6 m ³ | 28.0 m ³ |
| H_2O_2 | 100 mg/L | NA | 1.35 m ³ | 0.64 m^3 | 0.34 m^3 |
| H_2O_2 | 50 mg/L | NA | 1.51 m ³ | $0.87 \; m^3$ | 0.42 m^3 |

 UV/H_2O_2 processes provide a significant advantage over all other processes when considering required basin volume. Ozone based processes are competitive with H_2O_2 based processes, particularly when UV irradiation is utilized. In general, the addition of UV provides the ability to significantly reduce the volume required in any of the AOPs discussed.

Considering treatment with UV alone, the volume requirement to treat VEN are high enough to make it non-viable.

Ranking based on required basin volume:

- 1. UV/H₂O₂
- 2. UV/O₃
- 3. O₃ alone
- 4. UV alone

3.2.4 AOP Comparison

When selecting an AOP for a given process, there are multiple factors to consider, the most significant of which is cost. In comparing the potential costs of AOPs to degrade VEN, cost considerations were broken down into three categories: operating cost, capital cost, and required basin volume. As research on new technologies for the removal of pharmaceuticals from water emerge, it is essential that engineers keep a perspective on which processes are the most viable financially, to ensure that research is focused on areas with the highest potential.

As detailed above, operating costs and basin volumes were based on extrapolation of data obtained in lab scale experiments to degrade VEN. Capital costs were based on a review of literature on existing processes that are similar to the proposed AOPs. Trying to estimate costs for a process to remove VEN or other pharmaceuticals at this early point of technology refinement does not allow for high accuracy in cost analysis. However, data was sufficient to do a ranking based comparison, with differences in cost between different process being large enough to do so confidently.

It is immediately clear that attempting to degrade VEN by UV alone would not be a cost-effective method of treatment. Existing WWTPs that utilize UV disinfection are typically orders of magnitude below the UV dosage that would be required to sufficiently remove VEN from wastewater effluents. The massive volume

requirements to obtain sufficient removal, along with the energy requirements to reach sufficient UV dosage makes UV alone a process that is not viable for removing VEN in wastewater.

When considering O₃ and UV/O₃ processes, both processes are competitive in terms of pricing analysis. On site ozone generation, along with contact tanks and ozone diffusers come with an increase in capital costs, these costs can be offset by reducing the required basin volume. When choosing to add UV along with an ozone based process, the primary trade-off is a reduction in required contact time versus the additional operational cost required to power the UV system. If ozone based AOPs are ultimately found to be the most prominent technology finding implementation in coming years, there will likely always be a balance between the design levels of UV intensity and cost. Urban environments where space is at a premium may find that using a high UV intensity allows them to use considerably smaller contact tanks, while small rural WWTPs may choose to utilize UV alone.

AOPs using UV/H_2O_2 present an interesting case, because they allow for a very high amount of control over degradation parameters. When applied with H_2O_2 , UV irradiation showed a very large impact on degradation rates of VEN, with the affect being particularly pronounced at higher concentrations of H_2O_2 . In terms of operating costs, H_2O_2 based AOPs showed a trend that as UV dosage was increased, operating costs either remained constant or decreased. Although still behind O_3 processes for operating costs, this trend presents an interesting opportunity in the cost optimization of H_2O_2 processes, where increasing UV intensity allows for a decrease in not only retention times, but also in operating costs. It is possible that with a high level of optimization, H_2O_2 processes may prove to be ideal for many applications. The relative simplicity of applying H_2O_2 AOPs allows for lower capital costs, with further a further advantage being that existing WWTPs with UV disinfection systems could be easily retrofitted to utilize H_2O_2 . When optimizing H_2O_2 AOPs, there appears to be opportunity to create a process that is highly efficient in terms of all the cost categories considered if UV intensities can be increased by a factor of 5 or more.

4. CONCLUSIONS

A laboratory study was conducted to determine the effectiveness of various AOPs to remove the pharmaceutical VEN. The methods compared in this study were: UV alone, UV/H_2O_2 , UV/O_3 , and O_3 alone. All methods can achieve greater that 95% degradation of VEN. A cost analysis was then performed based upon energy consumption and chemical requirements for each process.

The major conclusions of this study are:

- UV/H₂O₂, UV/O₃ and O₃ are all potentially cost competitive options for the removal of VEN. Large retention time and energy requirements makes UV an non-viable choice for the treatment of VEN.
- O₃ proved to be the best option in terms of operating cost. The addition of UV to O₃ treatment showed
 a decrease in required retention time, but the increased energy requirement makes the process less
 cost efficient.
- UV/H₂O₂ was found to be more expensive in terms of operating costs. However, increasing UV intensity allows for decreased retention times, while remaining neutral in terms of operating costs.
- In terms of basin volume, UV/H₂O₂ was the best, with UV/O₃ second. Required basin volume can be significantly reduced by increasing UV dosage in H₂O₂ processes, and marginally improved by increasing UV dosage in O₃ processes.
- UV/H₂O₂ was determined to have the lowest capital costs, followed by O₃ then UV/O₃.

Based on this study, all the considered processes except for UV have potential to be effective to remove VEN. Determining the most effective process may come down to a case by case basis. It is significant however that higher UV dosages can provide substantial improvements to AOP processes. Particularly for H_2O_2 based processes, drastic reduction in the required basin volume along with no increase in operational costs makes finding methods to increase UV intensity a strong consideration.

5. REFERENCES

- Bader, H., and J. Hoigné. 1981. "Determination of Ozone in Water by the Indigo Method." *Water Research* 15 (4): 449–56. doi:10.1016/0043-1354(81)90054-3.
- Baratharaj, V. n.d. "How to Evaluate and Select an Ozone Generator.". Ozone Technologies & Systems (India) Pvt. Ltd. Accessed February 7, 2017. http://www.otsil.net/articles/HOW%20TO%20EVALUATE%20AND%20SELECT%20AN%20OZONE %20GENERATOR.pdf
- Calvert, JG, and JN Pitts. 1966. "Photochemistry." http://www.bcin.ca/Interface/openbcin.cgi?submit=submit&Chinkey=136979.
- Cotton, C. A., Douglas M Owen, G. C. Ćline, and Timothy P Brodeur. 2001. "UV Disinfection Costs for Inactivating Cryptosporidium." *Journal / American Water Works Association* 93 (6): 82–94.
- García-Galán, Jesús J., Alba Anfruns, Rafael Gonzalez-Olmos, Sara Rodríguez-Mozaz, and Joaquim Comas. 2016. "UV/H2O2degradation of the Antidepressants Venlafaxine and O-Desmethylvenlafaxine: Elucidation of Their Transformation Pathway and Environmental Fate." *Journal of Hazardous Materials* 311. Elsevier B.V.: 70–80. doi:10.1016/j.jhazmat.2016.02.070.
- Heraeus "UV Low-Pressure Lamps.". Accessed February 7, 2017. https://www.heraeus.com/en/hng/products_and_solutions/uv_lamps_and_systems/uv_low_pressure _lamps.aspx.
- Hamilton, Patrick B, Ian G Cowx, Marjorie F Oleksiak, Andrew M Griffiths, Mats Grahn, Jamie R Stevens, Gary R Carvalho, Elizabeth Nicol, and Charles R Tyler. 2016. "Population-Level Consequences for Wild Fish Exposed to Sublethal Concentrations of Chemicals a Critical Review." Fish and Fisheries 17 (3): 545–66. doi:10.1111/faf.12125.
- Lajeunesse, A., S. A. Smyth, K. Barclay, S. Sauvé, and C. Gagnon. 2012. "Distribution of Antidepressant Residues in Wastewater and Biosolids Following Different Treatment Processes by Municipal Wastewater Treatment Plants in Canada." *Water Research* 46 (17): 5600–5612. doi:10.1016/j.watres.2012.07.042.
- Melnyk-Lamont, Nataliya, Carol Best, Manuel Gesto, and Mathilakath M. Vijayan. 2014. "The Antidepressant Venlafaxine Disrupts Brain Monoamine Levels and Neuroendocrine Responses to Stress in Rainbow Trout." *Environmental Science and Technology* 48 (22): 13434–42. doi:10.1021/es504331n.
- Plumlee, Megan H., Benjamin D. Stanford, Jean-François Debroux, D. Cory Hopkins, and Shane A. Snyder. 2014. "Costs of Advanced Treatment in Water Reclamation." *Ozone: Science & Engineering* 36 (5). Taylor & Francis: 485–95. doi:10.1080/01919512.2014.921565.
- Ribeiro, Ana R., Olga C. Nunes, Manuel F R Pereira, and Adrián M T Silva. 2015. "An Overview on the Advanced Oxidation Processes Applied for the Treatment of Water Pollutants Defined in the Recently Launched Directive 2013/39/EU." *Environment International* 75. Elsevier Ltd: 33–51. doi:10.1016/j.envint.2014.10.027.
- Subramani, Arun, and Joseph G. Jacangelo. 2014. "Treatment Technologies for Reverse Osmosis Concentrate Volume Minimization: A Review." *Separation and Purification Technology* 122. Elsevier B.V.: 472–89. doi:10.1016/j.seppur.2013.12.004.
- USP Technologies "How Much Does H2O2 Cost?." . Accessed February 7, 2017. http://www.h2o2.com/fags/FagDetail.aspx?fld=25.