

Guidance Document for Integrating UV-based Advanced Oxidation Processes (AOPs) Into Municipal Wastewater Treatment Plants

Ministry of the Environment and Climate Change

Showcasing Water Innovation Program (SWI)

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1.0 Introduction

This document summarizes results from a project called “The Removal of Micropollutants from Municipal Wastewater”, which was sponsored by the Ontario Ministry of the Environment and Climate Change, as part of their Showcasing Water Innovation Program for Ontario municipalities. The overall goal of the project was to demonstrate the ability of ultraviolet (UV)-based advanced oxidation technologies to destroy micropollutants during wastewater treatment, and to identify simple methods to reduce these treatment costs. In addressing the treatment of micropollutants, this document is intended to provide municipalities with information to assist in understanding the factors and limitations that should be taken into consideration from an operational and economic perspective when integrating UV-based advanced oxidation into a wastewater treatment plant.

2.0 Objectives/Scope of Document

The information provided in this guidance document is generally applicable to municipal wastewater treatment facilities where the influent is comprised primarily of sewage from residential areas. The objectives of the work were as follows:

1. Outline an approach that can be used to improve the economic and practical feasibility of using UV-based advanced oxidation processes (AOPs) for treating micropollutants in municipal wastewater.
2. Identify operational and design criteria that should be considered in a full-scale facility when implementing this technology.
3. Outline an approach that can be used to assess the cost and energy requirements for implementing advanced oxidation technology in a full-scale facility.

Evaluating the application of the approaches outlined in this study to any specific treatment facility must involve detailed consideration of plant-specific factors prior to implementing technologies. Some considerations for integrating advanced oxidation technologies are discussed further in section 5.

3.0 Background

3.1 Lake Simcoe Region

Emerging contaminants or micropollutants refer to trace organic compounds that are present in the environment in $\mu\text{g/L}$ (microgram per litre) and ng/L (nanogram per litre) concentrations such as pharmaceuticals, endocrine disruptors, personal care products and household cleaners. Detecting these compounds is possible because of improvements in analytical capabilities at very low concentrations, and the presence of these contaminants in the environment is a growing concern worldwide as the potential effects of these compounds are not well understood. Through human consumption and use these compounds become part of the influent to wastewater treatment plants. Current wastewater technologies are not

designed to remove these compounds and so the compounds are found in the environment due to the discharge from wastewater treatment plants, septic and farm runoff to surface water bodies. These water bodies are the final receiving points for the effluent, and also function as the source for water intakes to drinking water treatment facilities.

Whole lake studies conducted at the Experimental Lakes area in northwestern Ontario demonstrated that some micropollutants can potentially eliminate entire fish species by disrupting spawning patterns and reproductive activities and functions.¹⁻⁴ Hence, preventing the release of these compounds to the environment should help to improve the water quality of lakes and ensure the sustainability of our aquatic ecosystems.

Lake Simcoe was selected as the site for the project since it is the largest and one of the most intensively fished inland lakes in Ontario. At Lake Simcoe, fishing, particularly ice-fishing, is a primary industry³ such that recreational activities contribute \$200 million annually to the local economy.² The lake supports a population of approximately 350,000 persons and serves as the intake source for 7 water treatment facilities serving 6 municipalities, and the final discharge point for 14 water pollution control plants (WPCP).^{5,6}

3.2 Regulatory Outlook

It is anticipated that the presence of micropollutants in the environment may increase over time because of the higher human use of prescription and over-the-counter drugs, personal care products, as well as agricultural and veterinary medications. At present, the removal of these compounds during wastewater treatment is not regulated. However, organizations such as Environment Canada, the U.S. Environmental Protection Agency, and the World Health Organization (WHO) have focused their efforts in collecting comprehensive information on analytical methodologies, occurrence and environmental fate, and the response of these compounds to different treatment strategies.^{15,16} The U.S. EPA has established a strategy which aims to improve the scientific and public understanding of these micropollutants, and create partnerships with research groups and organisations through federal collaborations and working groups.¹⁶ In Canada, the *Wastewater Systems Effluent Regulations*, S.O.R./2012-139 made under the *Fisheries Act*, R.S.C., 1985, c.F-14 establishes federal effluent quality standards as well as requirements for monitoring water quality and environmental effects. Ongoing initiatives in Canada, the United States, and elsewhere aim to improve our understanding of the potential effects of these compounds in the environment and on human health.

3.3 Advanced Oxidation Processes (AOPs)

Studies have shown that activated carbon, membranes, and advanced oxidation are options that can be considered for treating micropollutants. Of these, numerous research studies have shown that advanced oxidation processes are very effective for the degradation of these compounds in waters of varying quality.⁷⁻¹⁰ Typical AOPs include ultraviolet light (UV)-based or ozone (O₃)-based AOPs such as using hydrogen peroxide with ultraviolet light

(UV/H₂O₂) or ozone (O₃/H₂O₂), ozone and UV(O₃/UV), chlorine and UV(HOCl/UV), as well as the Fenton's reagent (Fe²⁺/H₂O₂) and photocatalysis using titanium dioxide and UV (TiO₂/UV). AOPs are effective for the degradation of these target pollutants due to the generation of the highly reactive hydroxyl radical ([•]OH). The radical is non-selective in its reactions with other compounds so it can oxidise a wide range of compounds, thereby making it suitable for complex wastewater matrices.

In Ontario, UV is typically the preferred alternative for wastewater disinfection. This is due to strict regulations for residual chlorine in the treated effluent of less than or equal to 0.02 mg/L.¹⁷ Hence, UV-based AOPs would be a practical choice for integrating AOPs into wastewater treatment facilities. The purpose of disinfecting the final effluent in wastewater plants is to reduce the microbial content of the effluent before it is released to the environment, so using AOPs as the final step can achieve a dual purpose of disinfection of the final effluent and removal of trace organic contaminants which were not removed during upstream treatment. Therefore, with an UV-AOP system, a separate disinfection system would not be required. Using UV in an AOP mode (UV photolysis) would require substantially more power than UV solely for disinfection purposes, which would increase plant energy costs.

3.4 Pre-treatment Options for Organic Matter Removal

Elevated concentrations of dissolved organic matter in wastewater effluents exert an oxidant demand. In an AOP process, the dissolved organic matter reacts with the hydroxyl radicals, reducing the concentration of the radicals available for reacting with and destroying the target micropollutant compounds. Hence, larger AOP doses are required to account for the demand exerted by the dissolved organic matter and to ensure the desired level of removal of the micropollutants in the effluent. A consequence of these higher doses is an increase in energy and operating costs. Therefore, measures to reduce the concentration of dissolved organic matter in the water prior to applying AOP treatment can improve the effectiveness of the AOP process, and reduce associated cost and energy requirements. Coagulation and activated carbon adsorption are two proven and standard technologies typically used for removing organic matter during drinking water treatment, but are not widely used in the wastewater treatment industry for removing dissolved organic matter.

Traditionally, secondary clarifiers are used to separate solid particles from the secondary effluent prior to disinfection and subsequent release to the environment. This is the only point after secondary treatment and prior to discharge for which there is an opportunity for organic matter to be removed from the secondary effluent. However, a significant portion of organic matter remains dissolved and will not settle using this traditional approach. Enhanced coagulation focuses on removing dissolved organic matter instead of only particles during the clarification process. Therefore, using enhanced coagulation or activated carbon adsorption will improve the removal of dissolved organic matter in the effluent.

4.0 Description of Study

4.1 Purpose of the study

The purpose of the study was to demonstrate an innovative and feasible approach that can be used to integrate advanced oxidation processes into wastewater treatment plants to reduce the concentration of micropollutants released to the environment. In this approach, enhanced coagulation/activated carbon adsorption was combined with advanced oxidation to treat micropollutants in secondary municipal wastewater effluent. Two advanced oxidation processes were evaluated in the study: UV/hydrogen peroxide (UV/H₂O₂) and UV/titanium dioxide (UV/TiO₂). In comparison to UV/H₂O₂ treatment, UV/TiO₂ is a relatively new or emerging technology. It was included in the case study as a demonstration of its potential capabilities for micropollutant removal.

4.2 Description of Plant Process

The project was undertaken at the Keswick Water Pollution Control Plant which is owned and operated by the Regional Municipality of York. The Keswick plant uses an extended aeration treatment process, and has a peak capacity of 64,500 m³/day. Figure 1 shows a schematic of the plant.

4.3 Overview of Study

A grab sample of secondary effluent was collected after the secondary clarifier, but prior to any tertiary treatment or disinfection (Figure 1). This sampling point was selected to account for wastewater treatment plants that do not apply tertiary treatment to the secondary effluent, although AOP treatment would typically occur after tertiary treatment in order to maximize organic matter removal prior to the AOP. The effluent sample was characterized (Table 1) and initial bench-scale tests were performed to identify the optimum coagulant and powdered activated carbon dose for reducing the concentration of dissolved organic matter (DOM) in the effluent. These doses were determined using the Point-of-Diminishing>Returns analysis where the PODR is the dose for which a 10 mg/L incremental increase in the applied coagulant or activated carbon dose results in a change in DOM removal of less than 0.3 mg/L.¹¹ The optimum doses and percentage reductions in DOM concentration are shown in Table 2. The coagulants used included aluminium sulphate (alum), polyaluminum chloride (PACl), and ferric chloride. The powdered activated carbons included WPH-1000 and WPC products from Calgon Carbon Corporation. Details of the bench-scale tests are in Appendix A.

Table 1: Water quality characteristics of the secondary wastewater effluent

Parameter	Secondary Effluent
pH	7.1
Temperature (°C)	20
UVA ₂₅₄ (cm ⁻¹)	0.13
UVT (%/cm)	64
Conductivity (µS/cm)	1086
SUVA ₂₅₄ (L/mg-cm)	2.2
TOC (mg/L-C)	9.7
DOC (mg/L-C)	8.4
TIC (mg/L-C)	37.7
Carbonate (mg CO ₃ ²⁻ /L)	0.02
Bicarbonate (mg HCO ₃ ⁻ /L)	32.4
Total Alkalinity (mg CaCO ₃ ⁻ /L)	185
Nitrite (mg/L-N)	< 0.08*
Nitrate (mg/L-N)	25.1

*Method detection limit

Definition of Acronyms:

UVA₂₅₄ – UV absorbance at 254 nm

SUVA₂₅₄ – specific UV absorbance at 254 nm

TOC – total organic carbon

DOC – dissolved organic carbon

TIC – total inorganic carbon

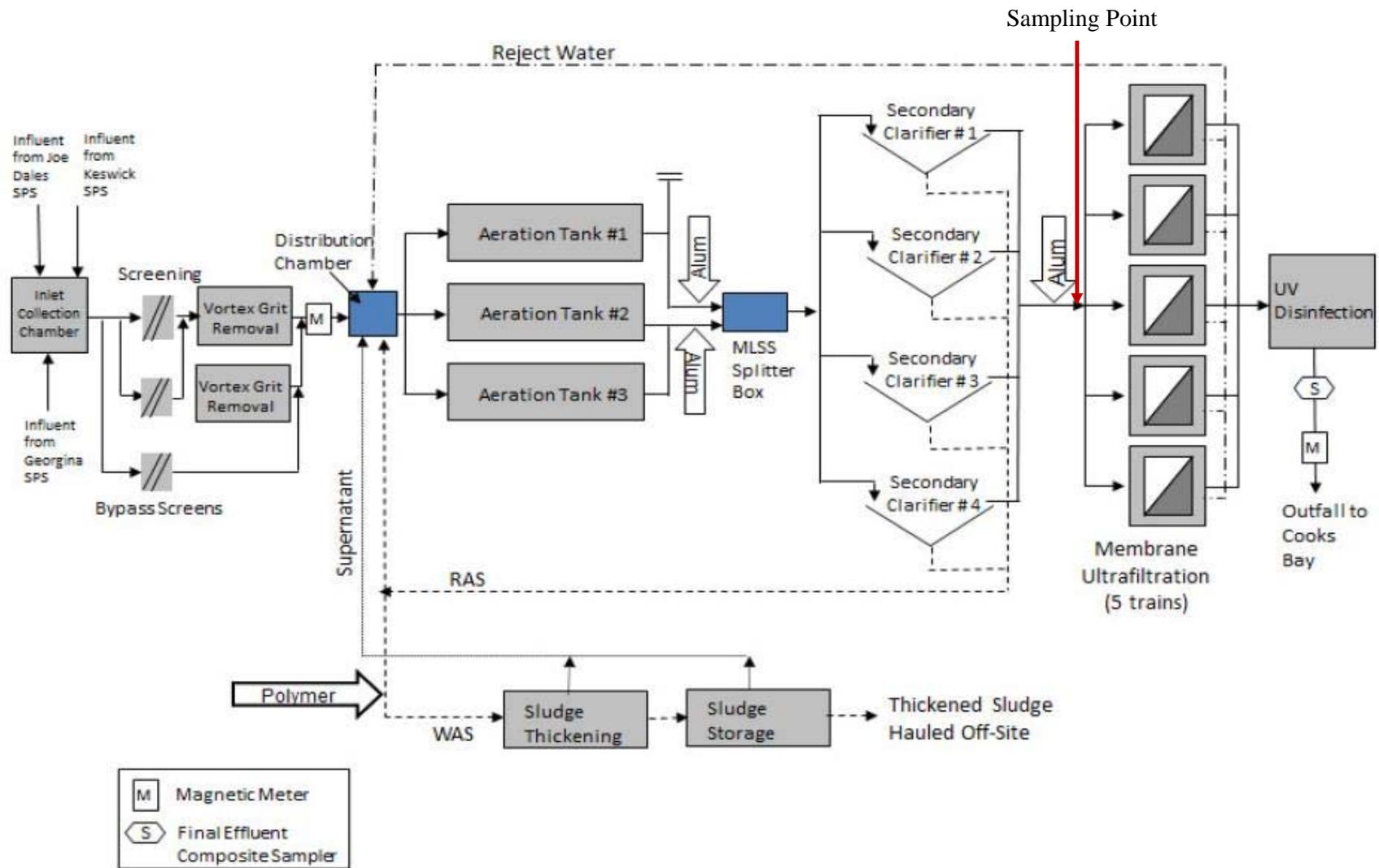


Figure 1 – Schematic of the Keswick Water Pollution Control Plant

Table 2: Optimum doses and percentage removals for the pretreatment options

Treatment	Optimum Dose	% Removal of Dissolved Organic Carbon (DOC)
Ferric chloride	60 mg/L as FeCl ₃	39
Aluminium sulphate	12 mg Al/L	41
Polyaluminium chloride	16 mg Al/L	34
WPH-1000 activated carbon	80 mg/L	61
WPC activated carbon	80 mg/L	31

The identified pretreatment optimum doses were used in the pilot study. The objective was to evaluate the influence of the combined treatment approach on the cost and energy requirements of treating micropollutants in the secondary effluent. The approach uses enhanced coagulation or activated carbon adsorption followed by AOP treatment using UV/H₂O₂ or UV/TiO₂. Enhanced coagulation and activated carbon adsorption were conducted in a 100L stainless steel tank. AOP treatment was performed using either a Calgon Carbon Rayox[®] Advanced Oxidation Batch Pilot Reactor for UV/H₂O₂ treatment (Figure 2), or a pilot-scale Purifics[®] UV/TiO₂ reactor (Figure 3). Additional details of the pilot study are outlined in Appendix B.



Figure 2: Calgon Carbon[®] Advanced Oxidation Batch Reactor



Figure 3: Pilot-scale Puriflcs[®] UV/TiO₂ Reactor

4.4 Findings

For UV/H₂O₂ testing, the secondary effluent was spiked with 50 µg/L of seven micropollutants (caffeine, carbamazepine (CBZ), naproxen, 17β-estradiol (E2), sulphamethoxazole (SMZ), diclofenac, clofibric acid) and treated at 0, 10 and 20 mg/L H₂O₂. For treatment with UV/TiO₂ using 1 g/L TiO₂, the secondary effluent was spiked with caffeine and carbamazepine only as these were found to be the most recalcitrant compounds. The 1 g/L TiO₂ dose was used based on the recommendation of the manufacturer of the pilot-unit. The micropollutant compounds in the study were selected to be representative of different classes of micropollutants, and on the basis of their common occurrence in wastewater effluents as reported in the literature.^{12,13} The spike concentration for the micropollutants exceeds the typical values found in wastewater effluents, but this high concentration was necessary to monitor the degradation of the compounds during treatment. Powdered activated carbon used as a pretreatment agent in this study is also capable of removing micropollutant compounds¹⁹. However, removal of the compounds by adsorption was not within the scope of this case study, therefore for waters pretreated with PAC, micropollutants were spiked into the effluent after the activated carbon was removed. The UV transmittance (UVT) of the effluent for these experiments was in the order of 74% per cm after pretreatment (UVT was 64% per cm prior to pretreatment). This is a comparatively low UVT since a 74% per cm UVT is a relatively typical average for secondary wastewater effluents from activated sludge treatment processes with no pretreatment of the effluent. Higher UVT values in the order of 85% per cm or more may be expected in some effluents. The UV dose requirements, and therefore costs, are dependent on UVT values. Higher UVT will result in lower costs and vice versa. The effluent used in the case study can be characterised as “challenging” (and therefore expensive) to treat when using UV-based disinfection or advanced oxidation processes, compared to many other wastewaters. This information should be kept in mind when interpreting the subsequent results.

Treatment with UV alone

Five compounds were easily degraded using UV photolysis alone, with removals exceeding 90%. Using the Rayox[®] AOP reactor, these removals were obtained with a maximum UV dose of 2400 mJ/cm² where dose relates to lamp intensity and exposure time. This dose is approximately 100 times the typical UV disinfection dose of 20–30 mJ/cm² required to achieve a disinfection of <200 faecal coliform/100 mL as a 30 day geometric mean in secondary treated effluent.¹⁸ A dose that is 100 times the typical dose for UV disinfection does not mean that the treatment cost will be 100 times higher, due to issues of scale. Our cost model suggests that the capital cost can increase by a factor of 2.6. Caffeine and carbamazepine were not easily removed by UV photolysis (37% reduction) and required advanced treatment (see Figure 4). Since these two compounds were the most difficult to treat, the removal of caffeine and carbamazepine was used as the performance standard for the rest of the study and analyses.

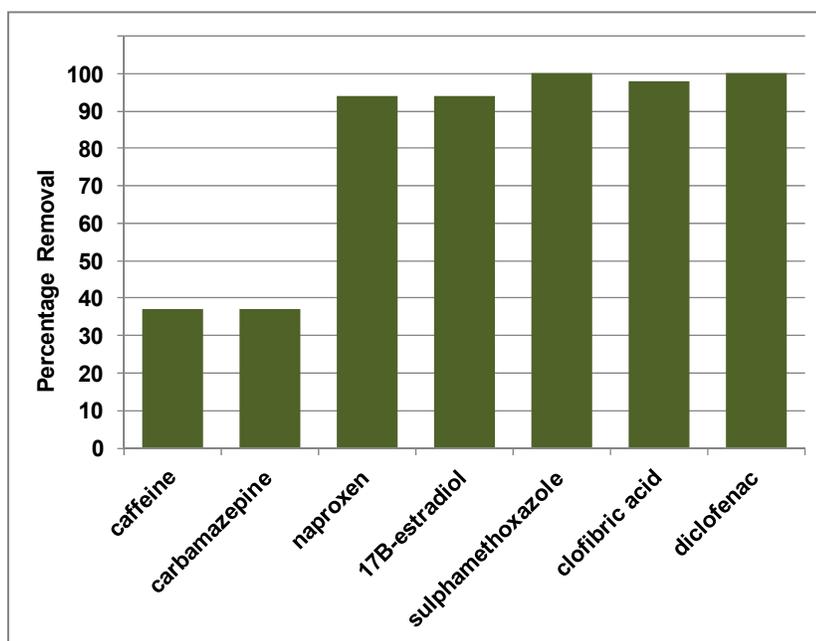


Figure 4: Percentage removal of the micropollutants with UV alone (maximum UV Dose = 2400 mJ/cm²)

Treatment with UV/H₂O₂

Caffeine and carbamazepine removals improved with AOP treatment at 10 mg/L H₂O₂ and 20 mg/L H₂O₂ as shown in Figure 5. As the hydrogen peroxide concentration was doubled, the percentage removals of both compounds increased. It is possible that H₂O₂ higher than 20 mg/L would have continued to improve treatment effectiveness, but higher doses were outside of the scope of this study. Specific wastewater treatment applications, especially industrial waste streams with low UVT, may employ H₂O₂ doses in the order of 100 mg/L to maximize efficiency.

Pretreating the effluent using enhanced coagulation or activated carbon to remove organic matter prior to UV/H₂O₂ had little impact on the five compounds that were easily removed with UV photolysis alone, so the same level of removal (> 90%) was obtained. For caffeine and carbamazepine, additional reductions in the order of 10% were observed due to pretreatment, compared to treatment with UV photolysis alone and UV/H₂O₂ alone (see Figure 5).

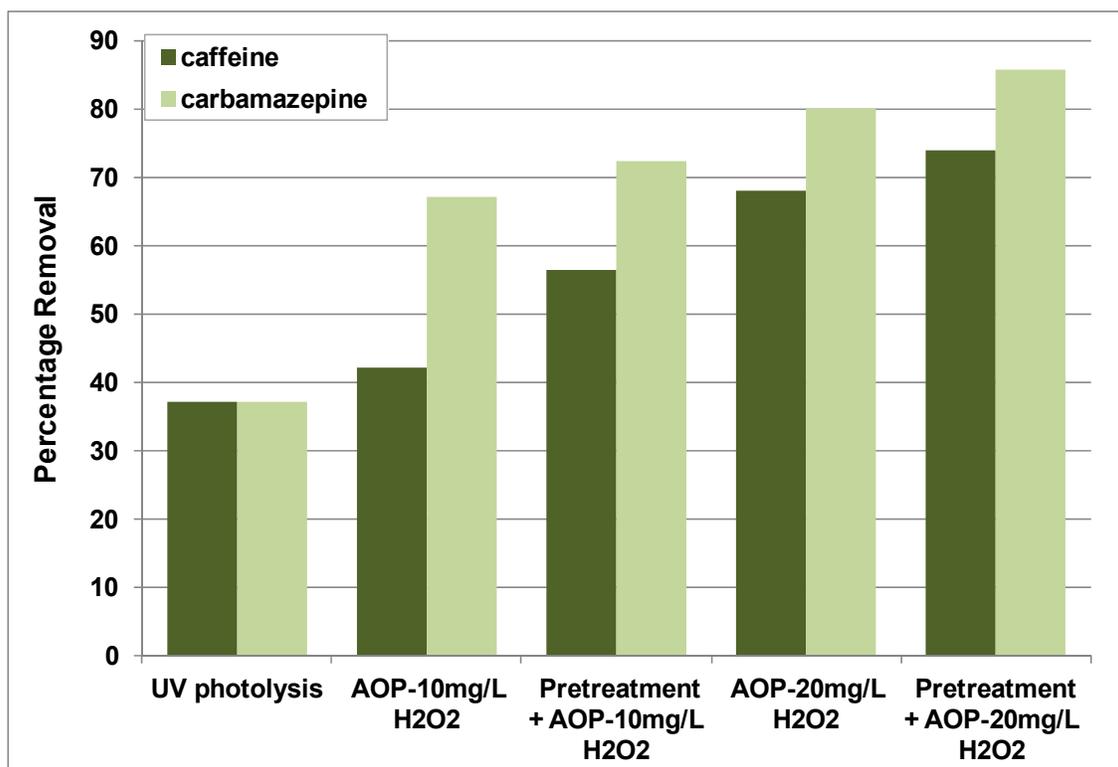


Figure 5: Removal of caffeine and carbamazepine with UV/H₂O₂ treatment (maximum UV Dose = 2400 mJ/cm²)

Treatment with UV/TiO₂

In UV/TiO₂ treatment of the secondary effluent, the removal of caffeine and carbamazepine improved with longer exposure such that 100% removal (i.e. removal to below the method detection limit) was obtained with a maximum UV dose of 3000 mJ/cm². Pretreatment of the effluent using enhanced coagulation before applying UV/TiO₂ had no additional benefit to the treatment process as similar removals (100%) for both compounds were obtained after the same exposure time (Figure 6 and 7).

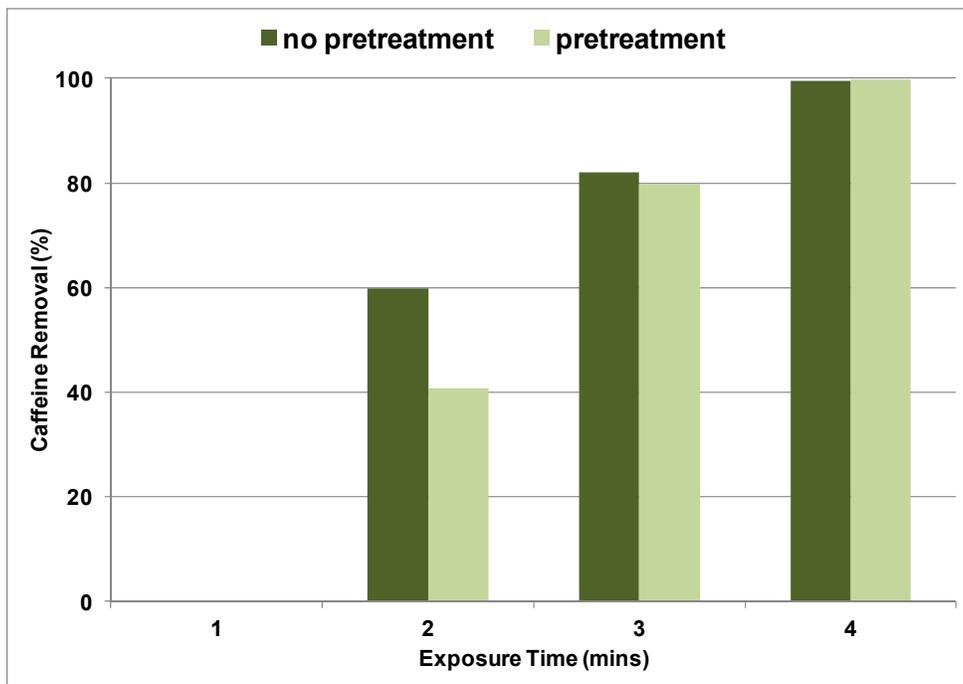


Figure 6: Caffeine removal with UV/TiO₂ treatment (refer to Appendix B for details)

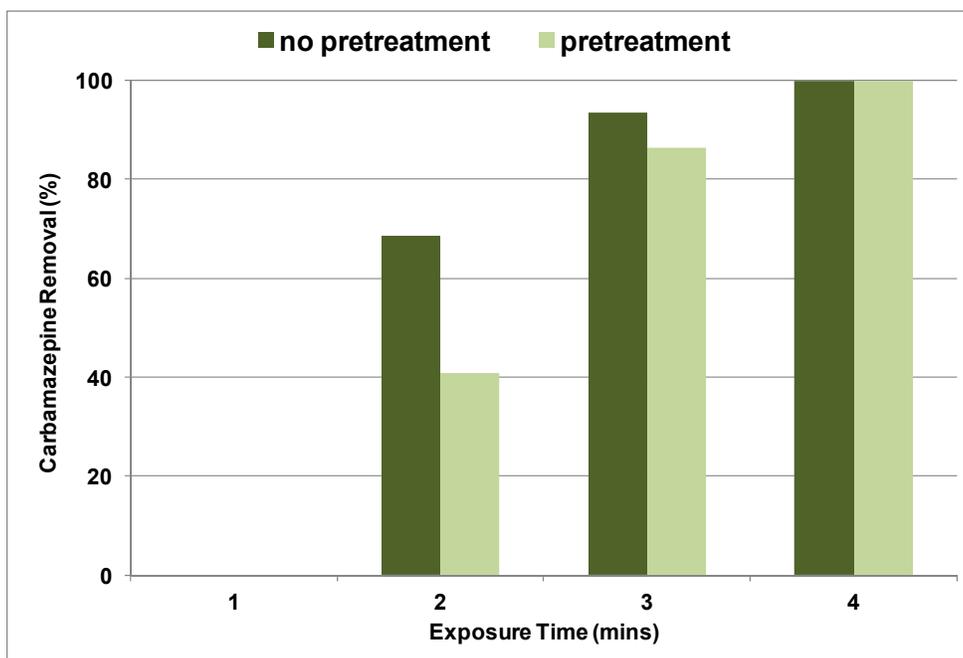


Figure 7: Carbamazepine removal with UV/TiO₂ treatment (refer to Appendix B for details)

Summary of Findings

The findings from this pilot study demonstrate that while some compounds are easily removed with UV photolysis alone, others will require advanced treatment such as AOPs.

While the UV/TiO₂ system provided higher overall destruction of the contaminants than the UV/H₂O₂ system, the two should not be compared in this way because they did not receive the same UV/chemical dose per unit volume of water. An objective comparison of the efficiencies of the two systems would require converting the data into a measure of the amount of contaminant destroyed per unit volume of water, and per dollar of treatment cost. While this type of analysis is performed in the next section for the UV/H₂O₂ system, an appropriate cost model was not available for the UV/TiO₂ system. The UV/TiO₂ pilot was included in the study solely for demonstrating an emerging technology.

For those compounds that require AOPs, the study showed that pretreatment can sometimes improve the amount of degradation, although only by a small amount (about 10%) under the conditions of this study. The question, however, is whether the additional costs associated with the enhanced coagulation or activated carbon pretreatment are offset by the reduced AOP cost to meet the same level of treatment. This is addressed in the next section.

4.5 Energy & Cost Analysis

4.5.1 Energy Requirements

The energy requirements of UV-based advanced oxidation processes are evaluated using electrical energy per order (EEO) values. An EEO value is the amount of electrical energy (kWh) that is required to reduce the concentration of a target pollutant by 90% in 1 m³ of water.¹⁴

For a batch system, such as used in this study, the EEO value for each compound is calculated using Equation 1:

$$\text{EEO (kWh/m}^3\text{/order)} = \frac{1000Pt}{V \log\left(\frac{C_i}{C_f}\right)} \quad (1)$$

where

P – rated power of the AOP system (kW)

V – volume of water being treated (L)

t – time taken to treat the volume of water (h)

[C]_i – influent or initial concentration of the target pollutant (M or mol L⁻¹)

[C]_f – effluent or final concentration of the target pollutant (M or mol L⁻¹)

Log – logarithm to base 10.

EEO values with UV photolysis alone and UV/H₂O₂ AOP treatment alone

With UV photolysis alone, naproxen, E2, SMZ, clofibric acid and diclofenac required less than 2.0 kWh/m³/order of electrical energy. In contrast, caffeine and CBZ required 18 kWh/m³/order and 12.7 kWh/m³/order of electrical energy respectively. When adding 10 mg/L H₂O₂ to turn the UV system into an AOP, the EEOs required to destroy caffeine and CBZ were reduced to 9.70 kWh/m³/order and 4.19 kWh/m³/order. With the H₂O₂ dose increased to 20 mg/L, the EEOs were lower still, at 3.88 kWh/m³/order and 3.11 kWh/m³/order. Please see Table 3.

EEO values with pretreatment followed by UV/H₂O₂ AOP treatment

It was anticipated that pretreatment would make UV photolysis and AOP treatments more effective, as measured by reduced EEOs. Pretreatment of the effluent reduced the AOP EEO requirements by 28% and 7%-19% for caffeine and carbamazepine respectively, although EEOs for caffeine increased by 16% at 20 mg/L hydrogen peroxide. Table 3 summarises the EEO values for all of the compounds.

Table 3: EEO values for the degradation of target micropollutants with UV/H₂O₂

Treatment	Caffeine	CBZ	Naproxen	Clofibric acid	17β-estradiol	SMZ	Diclofenac
UV photolysis	18	13	1.8	1.1	2.1	0.7	0.5
PT + UV	13.3	6.8	1.7	0.8	2.0	0.9	0.3
AOP (10)	9.7	4.2	1.7	1.2	1.3	0.9	0.5
PT + AOP(10)	7.0	3.9	1.3	0.7	1.3	0.8	0.3
AOP (20)	3.8	3.1	1.6	1.8	1.0	0.8	0.3
PT + AOP(20)	4.4	2.5	1.2	0.8	1.3	0.8	0.3

PT – pretreatment (coagulation or activated carbon adsorption)

AOP(10) – UV/H₂O₂ treatment with 10 mg/L H₂O₂

PT + AOP(10) – pretreatment followed by UV/H₂O₂ treatment with 10 mg/L H₂O₂

AOP(20) – UV/H₂O₂ treatment with 20 mg/L H₂O₂

PT + AOP(20) – pretreatment followed by UV/H₂O₂ treatment with 20 mg/L H₂O₂

CBZ – carbamazepine

SMZ – sulphamethoxazole

EEO values with UV/TiO₂ treatment

Caffeine and carbamazepine removals were similar with and without pretreatment of the effluent before UV/TiO₂ treatment of the effluent. On average, both compounds required 3.6 kWh/m³/order of energy to achieve 90% removal of the compounds.

4.5.2 Cost Analysis

The cost analysis was based on a new extended aeration plant operating with a peak flow of 64,500 m³/day, an average flow of 18,000 m³/day, and a secondary effluent with a 64% per cm UV transmittance (UVT) that will be treated using UV/H₂O₂. Given its resistance to degradation by UV alone, a 1-log (90%) removal of carbamazepine was used as the performance standard for the UV/H₂O₂ AOP system. The increase in UVT of the secondary effluent due to pretreatment to 74%/cm UVT and 84%/cm UVT at operating conditions was also considered. A Net Present Value (NPV) analysis was based on a plant life of 20 years and a 6% interest rate. This analysis was done for the current plant encompassing only primary and secondary treatment (excluding tertiary treatment), and for the UV/H₂O₂ AOP as a separate system that could be included for tertiary treatment. Therefore, all the costs for the UV/H₂O₂ system are based on the assumption that the infrastructure already exists for pretreatment upstream of the AOP system during secondary treatment. The CapDet Works Software from Hydromantis Environmental Software Solutions Inc. (Hamilton, Ontario, Canada) and collaboration with Calgon Carbon Corporation (Pittsburgh, PA, USA) were used for the cost estimations. Calgon Carbon Corporation internal models were used to predict carbamazepine degradation and EEO values at additional parameters of 84%/cm UVT and at higher hydrogen peroxide doses of 50 mg/L and 100 mg/L, which were also included in the cost analysis. The cost analysis for a UV/TiO₂ system is not included as UV/TiO₂ is an emerging technology and a cost model for a treatment plant of this scale is not available.

A breakdown of the NPV analysis for the new extended aeration wastewater treatment plant excluding tertiary treatment (i.e. UV and UV-AOP) is shown in Table 4. The cost breakdown specifically for a UV/H₂O₂ system for different treatment scenarios at an operating UVT of 64%, 74% and 84% per cm are shown in Table 5, Table 6, and Table 7 respectively, where 74% and 84% per cm are the operating UVT achieved with upstream pretreatment of the secondary effluent. When the UV/H₂O₂ AOP system is added to the plant as a tertiary treatment step, the NPV analyses for the overall plant for different treatment scenarios at 74%/cm UVT and 84%/cm UVT are shown in Table 8 and Table 9 respectively.

Greenhouse Gas (GHG) emissions as related to energy production and consumption were not part of the scope of this study. However, the environmental value of GHGs associated with AOP energy requirements above plant base operating levels are another metric that could be considered under a cost analysis.

Table 4: Cost breakdown for primary and secondary treatment of a new extended aeration wastewater plant (excludes UV and UV-AOP)

Treatment	Total Present Worth	Capital Costs (CAD\$)	Annual Operating Costs (CAD\$)					Total Annual Operating Costs
			Labour	Chemical	Energy	Maintenance	Material	
Primary and secondary treatment only	443,000,000	49,900,000	1,400,000	52,400	28,000,000	872,000	3,460,000	33,784,400

Table 5: Cost breakdown for UV/H₂O₂ system for 90% carbamazepine removal for secondary effluent at 64%/cm UVT (no pretreatment)

Treatment	No. of UV Reactors	Total Present Worth	Capital Cost	Annual Operating Costs (CAD\$)			Total Operating Costs (CAD\$)
				Chemical	Energy	Maintenance	
UV photolysis	156	213,797,222	72,399,505	-	9,159,656	2,812,368	11,972,024
AOP – 10 mg/L H ₂ O ₂	48	72,296,085	22,356,916	132,985	3,168,982	926,340	4,228,307
AOP – 20 mg/L H ₂ O ₂	35	53,716,095	16,333,951	265,970	2,244,848	654,296	3,165,114
AOP - 50 mg/L H ₂ O ₂	24	39,592,199	11,236,978	664,924	1,272,546	463,342	2,400,812
AOP – 100 mg/L H ₂ O ₂	15	33,144,486	7,067,145	797,909	1,113,235	2,812,368	2,207,946

Table 6: Cost breakdown for UV/H₂O₂ system for 90% carbamazepine removal for secondary effluent at 74%/cm UVT with pretreatment

Treatment	No. of UV Reactors	Total Present Worth	Capital Cost	Annual Operating Costs (CAD\$)			Total Operating Costs (CAD\$)
				Chemical	Energy	Maintenance	
UV photolysis	90	118,379,376	41,817,668	-	4,872,447	1,609,968	6,482,415
AOP – 10 mg/L H ₂ O ₂	42	61,929,085	19,577,792	132,985	2,656,441	796,422	3,585,848
AOP – 20 mg/L H ₂ O ₂	30	45,398,504	14,017,249	265,970	1,797,794	593,260	2,657,024
AOP - 50 mg/L H ₂ O ₂	15	27,398,939	7,067,145	664,924	787,637	268,915	1,721,476
AOP – 100 mg/L H ₂ O ₂	8	23,145,869	3,823,303	664,924	787,637	183,464	1,636,025

Table 7: Cost breakdown for a UV/H₂O₂ system for 90% carbamazepine removal for secondary effluent at 84%/cm UVT with pretreatment

Treatment	No. of UV Reactors	Total Present Worth	Capital Cost	Annual Operating Costs (CAD\$)			Total Operating Costs (CAD\$)
				Chemical	Energy	Maintenance	
UV photolysis	48	63,239,792	22,356,916	-	2,591,853	869,665	3,461,518
AOP – 10 mg/L H ₂ O ₂	24	34,714,705	11,236,978	132,985	1,391,512	463,342	1,987,839
AOP – 20 mg/L H ₂ O ₂	15	23,677,145	7,067,145	265,970	871,470	268,915	1,406,355
AOP - 50 mg/L H ₂ O ₂	8	18,087,669	3,823,303	465,447	587,628	154,677	1,207,752
AOP – 100 mg/L H ₂ O ₂	6	16,872,178	2,896,164	465,447	587,628	130,262	1,183,337

Table 8: Cost breakdown for 90% removal of carbamazepine using primary & secondary treatment of the new plant + UV/H₂O₂ AOP (74%/cm UVT)

Treatment	No. of UV Reactors	Total Present Worth	Capital Cost (CAD\$)	Annual Operating Costs (CAD\$)					Total Operating Costs (CAD\$)
				Labour	Chemical	Energy	Maintenance	Material	
UV photolysis	90	562,879,376	91,717,668	1,420,000	137,500	32,872,447	2,481,968	3,460,000	40,371,915
AOP – 10 mg/L H ₂ O ₂	42	506,429,085	69,477,792	1,420,000	270,485	30,656,441	1,668,422	3,460,000	37,475,348
AOP – 20 mg/L H ₂ O ₂	30	489,898,504	63,917,249	1,420,000	403,470	29,797,794	1,465,260	3,460,000	36,546,524
AOP - 50 mg/L H ₂ O ₂	15	471,898,939	61,317,145	1,420,000	802,424	28,787,637	1,140,915	3,460,000	35,610,976
AOP – 100 mg/L H ₂ O ₂	8	467,645,869	53,723,303	1,420,000	802,424	28,787,637	1,055,464	3,460,000	35,525,525

Table 9: Cost breakdown for 90% removal of carbamazepine using primary & secondary treatment of the new plant + UV/H₂O₂ AOP (84%/cm UVT)

Treatment	No. of UV Reactors	Total Present Worth	Capital Cost (CAD\$)	Annual Operating Costs (CAD\$)					Total Operating Costs (CAD\$)
				Labour	Chemical	Energy	Maintenance	Material	
UV photolysis	48	507,739,792	72,256,916	1,420,000	137,500	30,591,853	1,741,665	3,460,000	37,351,018
AOP – 10 mg/L H ₂ O ₂	24	479,214,705	61,136,978	1,420,000	270,485	29,391,512	1,335,342	3,460,000	35,877,339
AOP – 20 mg/L H ₂ O ₂	15	468,177,145	56,967,145	1,420,000	403,470	28,871,470	1,140,915	3,460,000	35,295,855
AOP - 50 mg/L H ₂ O ₂	8	462,587,669	53,723,303	1,420,000	602,947	28,587,628	1,026,677	3,460,000	35,097,252
AOP – 100 mg/L H ₂ O ₂	6	461,372,178	52,796,164	1,420,000	602,947	28,587,628	1,002,262	3,460,000	35,072,837

Cost implications of micropollutant removal

In achieving a performance target of 90% degradation of carbamazepine in the final effluent by installing tertiary treatment using UV photolysis or UV/H₂O₂, it was found that the 20 year plant costs can increase by \$17 million to \$213 million (an increase of 4% to 48%) depending on the particular treatment approach (see Figure 8). It is important to recall, that as previously mentioned, the UVT of the effluent used in this case study is quite low (64%/cm), which can increase the treatment costs. Cost model results for the effluent with a higher UVT found that subject to the treatment strategy, the 20 year plant costs were reduced by \$7 million to \$94 million (a reduction of 2% to 14% of the overall plant costs) at 74%/cm UVT and \$15 million to \$149 million (3% to 23% reduction) at 84%/cm UVT. Since the effluent UVT can vary from one plant to another, the values in this document can be regarded as conservative estimates of the influence of these different treatment strategies on plant costs.

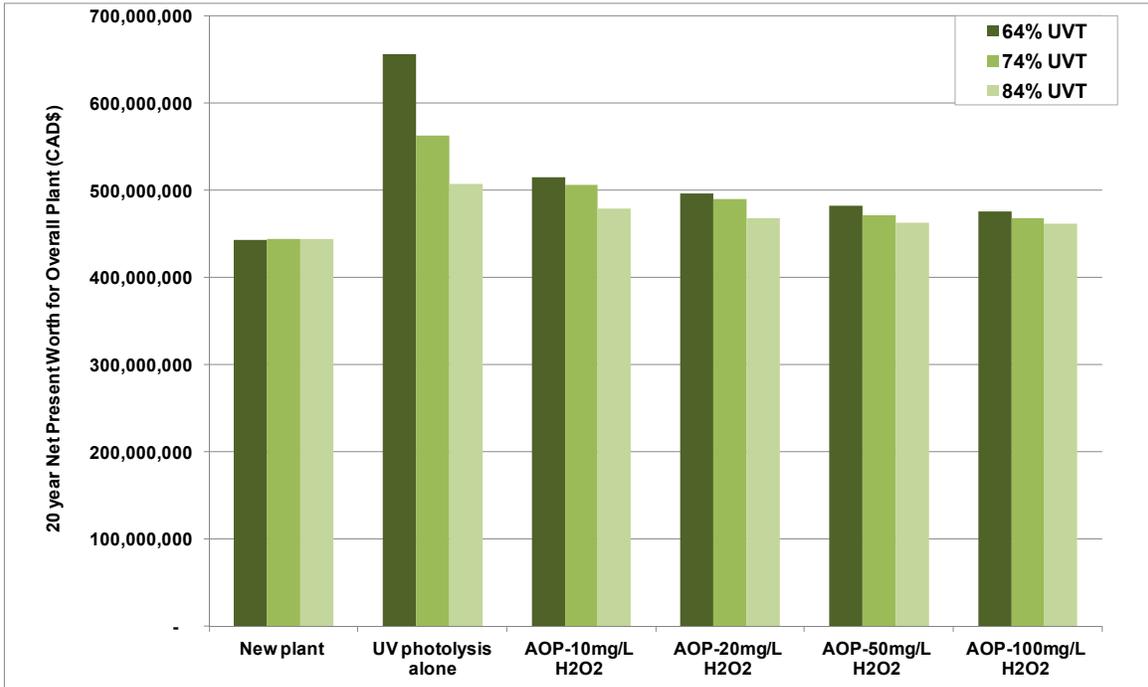


Figure 8: Comparing the NPV of the new extended aeration plant (baseline) against the baseline plus costs associated with different treatment approaches for micropollutant removal

Comparing UV photolysis and UV/H₂O₂ treatment

Compared to using UV photolysis alone, UV/H₂O₂ reduced the overall plant costs by 22% with 10 mg/L H₂O₂ and by 24% at 20 mg/L H₂O₂ (see Figure 9). These costs were reduced as the number of UV reactors and lamps needed for effective AOP treatment decreased as the hydrogen peroxide dose increased (see Table 6 and Table 7). As such, increasing the hydrogen concentration from 10 mg/L to 20 mg/L resulted in total cost savings of approximately \$19 million over 20 years. Using the model estimates, higher H₂O₂ doses at 50 mg/L and 100 mg/L provided an additional 3% and 4% reduction in cost respectively which corresponds to extra savings of \$14 million and \$21 million respectively over 20 years.

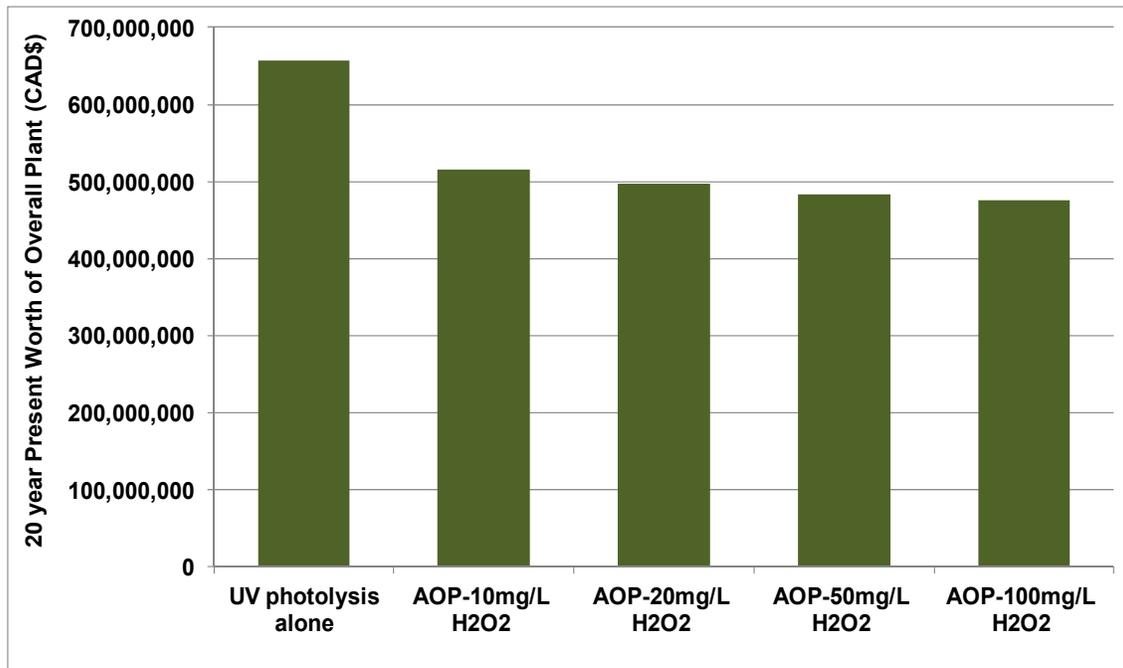


Figure 9: Comparison of the present worth of overall plant with UV/H₂O₂

Influence of pretreatment before UV/H₂O₂ treatment

Pretreatment (enhanced coagulation or activated carbon adsorption) of the secondary effluent had only a small impact on UV/H₂O₂ effectiveness under the conditions evaluated in this study (Figure 10). With an improvement in the UVT of the wastewater from 64%/cm to 74%/cm, pretreatment prior to UV/H₂O₂ reduced the total cost by 2% when using 10 mg/L of H₂O₂ and by 1% with 20 mg/L H₂O₂. However, if pretreatment could be applied to achieve a higher UVT such as 84%/cm, the model estimates for this condition shows that the total costs would be reduced by 7% with 10 mg/L H₂O₂, and by 6% with 20 mg/L H₂O₂. This demonstrates that costs are reduced as the hydrogen peroxide concentration is increased and pretreatment can provide marginal benefits to the overall plant costs depending on the degree to which the quality of the wastewater is improved.

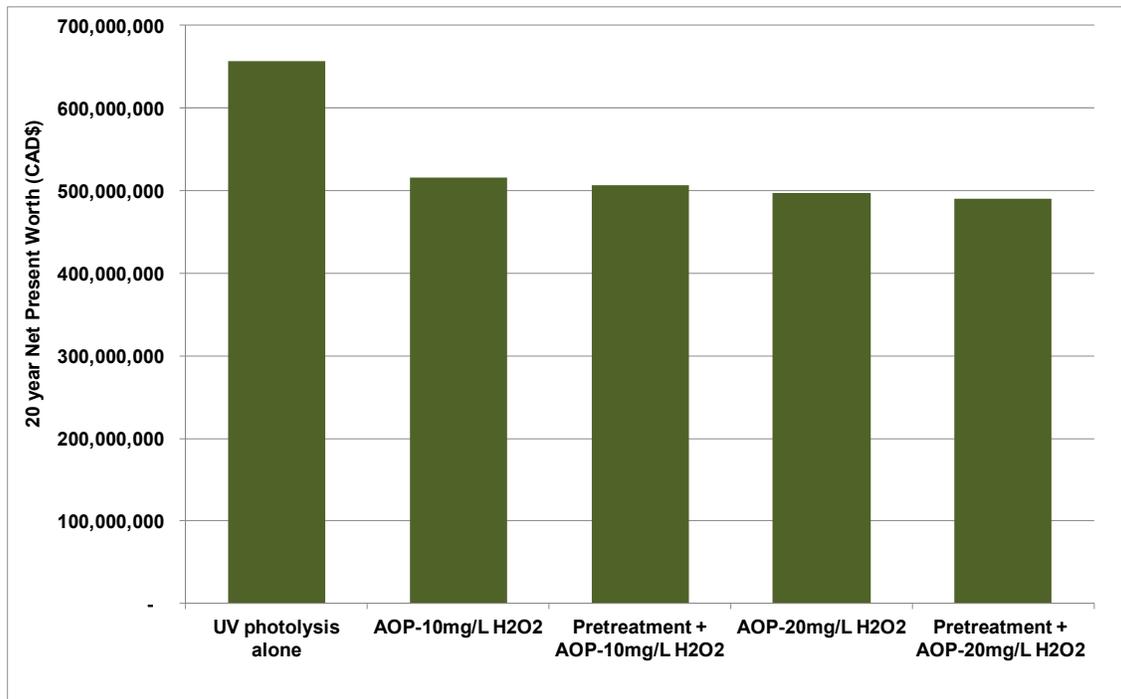


Figure 10: Comparison of overall costs for different treatment scenarios with UV/H₂O₂

4.6 Final Conclusions & Lessons Learned

Some micropollutants can be easily removed using UV light only (photolysis). However, a maximum UV dose of 2400 mJ/cm² would be required to achieve 1-log (90%) removal of the most UV-resistant compound examined in this study (E2, or 17β-estradiol), which is approximately 100 times the typical UV disinfection dose. For other compounds that are not readily removed with UV alone, advanced oxidation may be a suitable option. Implementing an AOP system, however, can significantly increase overall plant costs. This case study provides an illustration of the costs that might be involved for a wastewater with a UVT that is relatively low, and when using H₂O₂ doses in the order of 10-20 mg/L. Modelling was further used to estimate costs at higher doses of 50 mg/L and 100 mg/L H₂O₂, and the costs for wastewaters of higher UVTs of 74%/cm and 84%/cm with doses of 10-100 mg/L H₂O₂.

Treatment of other wastewaters with higher UVTs for micropollutant removal would result in a less expensive AOP treatment system and model estimates indicated that higher H₂O₂ doses could lead to lower overall costs.

For the effluent used in this case study and based on our model estimates, the highest cost savings were obtained at a high H₂O₂ concentration (100 mg/L) when coupled with pretreatment of the secondary effluent. While pretreatment reduced the concentration of organic matter, the improvements in the overall plant costs due to pretreatment were marginal when compared to no pretreatment of the wastewater. Hence, in treating secondary wastewater effluents to reduce the concentration of micropollutants that are not easily

removed with UV alone, depending on the specific conditions of a given plant, increasing the hydrogen peroxide dose should be considered.

If pretreatment is considered a viable option for a given plant, effluent organic matter can be very effectively removed using enhanced coagulation or activated carbon adsorption. As noted in Section 4.4, activated carbon adsorption is expected to have an added benefit of also removing some micropollutant compounds, but this was not within the scope of this study.

5.0 Full-Scale Facilities - Integrating AOPs

When implementing UV-based advanced oxidation, the characteristics of the effluent to be treated must be evaluated. The important water quality parameters are pH, alkalinity, UV transmittance (UVT), nitrite, nitrate, and total and dissolved organic (TOC and DOC) concentrations.

Nitrate and nitrite concentrations in secondary effluents can negatively influence the effectiveness of AOP systems depending on the type of UV lamp being used. UV lamps for AOP treatment are usually low-pressure (LP) or medium-pressure (MP) lamps. While LP lamps emit UV light at 254 nm, the MP lamps emit light ranging from 200 – 800 nm. Due to the lower range of wavelengths when using MP lamps, nitrate can undergo photolysis to form nitrite, which dramatically increases the $\bullet\text{OH}$ scavenging potential of the effluent, thereby reducing the concentration of $\bullet\text{OH}$ radicals available for reacting with the target micropollutant compounds. This attribute is not observed with LP lamps, or with MP lamps that are specially designed to prevent this phenomenon from occurring (the quartz sleeves housing the UV lamps can be doped with a material that blocks transmission of the lower wavelength UV light).

5.1 Reducing Effluent Organic Matter Concentration

Ferric chloride and aluminium sulphate are commonly used by wastewater treatment plants for phosphorous control. This is achieved by addition at different points in the treatment train depending on the treatment process. However, higher doses may be required to achieve optimum DOC removal for subsequent AOP treatment. Bench-scale jar tests, as described in the case study, should be performed to identify the optimum coagulant dose and pH for DOC removal.

For implementation, one option is to apply the coagulant dose to the water entering the secondary clarifier to allow removal of the flocs with the settled sludge. However, some coagulants may not be compatible with filters, and/or can change sludge characteristics, which was not investigated in the scope of this pilot work.

5.2 Other Considerations

In addition to the aspects outlined in the previous sections, some other factors that should be evaluated are as follows:

1. A rational selection of the treatment goal, given that regulatory targets do not exist at present.
2. Available space since the footprint for an AOP system can be quite large.
3. The AOP system must be housed indoors. Hence, a separate building may be required.
4. Electrical requirements for the AOP system. The current power capacity of the plant should be reviewed including the standby power requirements to ensure that it will meet the requirements for an AOP unit.
5. Delivery and storage of the hydrogen peroxide. Adequate storage volume and space with secondary containment must be provided. In the event that the hydrogen peroxide storage cannot be located in close proximity at the plant, a day tank will be required with the necessary piping and pumps to facilitate transfer of the hydrogen peroxide when required. Hydrogen peroxide can be a difficult chemical to handle, requiring special pipe material and pump considerations. In particular, H₂O₂ can be incompatible with the solvents used to bind PVC connections. Thoroughly-pacified stainless steel is typically preferred. As well, the piping configuration must take into consideration the tendency for H₂O₂ solutions to off-gas and to cause vapour lock.

5.3 Approach for Assessing Energy Requirements

In assessing the energy requirements for a UV-based AOP, the electrical energy per order values for the target pollutant must be determined. In this case study, the UV-resistant compound, carbamazepine, was selected with a performance target of 90% reduction. The electrical energy per order EEO values should be determined from experimentation using a sample of the same water to be subsequently treated, since EEO values are water-specific. The EEO values can then be used to scale-up for a full scale facility.

The energy requirement of an UV-based AOP is assessed using the electrical energy per order values as described in Section 4.5.1. For a full-scale facility, the equation for a flow-through operation should be used as shown in Equation 2.

$$\text{EEO (kWh/m}^3\text{/order)} = \frac{P}{F \log\left(\frac{C_i}{C_f}\right)} \quad (2)$$

where

P – rated power of the AOP system (kW)

F – flow rate of water being treated (m³/h)

[C]_i – influent or initial concentration of the target pollutant (M or mol L⁻¹)

[C]_f – effluent or final concentration of the target pollutant (M or mol L⁻¹)

log – logarithm to base 10

Equation 2 can be rearranged to determine the power required, flowrate or final effluent concentration for a given concentration of a target pollutant with the known EEO value.

5.4 Approach for Assessing Cost Implications

Capital and operating costs must be considered. Important factors that should be taken into account in assessing the operating costs are as follows:

1. Electrical costs (from the UV lamps, pumps, standby power and other equipment).
2. Chemical costs (coagulant, hydrogen peroxide, sodium hypochlorite).
3. Capital costs for installation of a new system (site preparation (including land acquisition if required, mechanical electrical and instrumentation contractors, engineering, etc.).
4. Sludge handling costs associated with coagulant or powder activated carbon.
5. Labour costs for operating and maintaining the system.
6. Maintenance costs.

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APPENDIX A

Bench-scale tests for identifying the optimum coagulant and activated carbon doses

Three coagulants (aluminium sulphate, ferric chloride, and polyaluminium chloride) and two powdered activated carbons (WPC and WPH-1000) were used. Both activated carbons are proprietary to Calgon Carbon Corporation where the WPH-1000[®] is a virgin high-performance agglomerated coal-based powdered activated carbon with an iodine number of 1000 mg/g and the WPC[®] is a direct-activated coconut shell based powdered activated with an iodine number of 800 mg/g.

Coagulation was performed with an initial broad dose range of 0 – 50 mg Al/L for alum, 0 – 100 mg/L for FeCl₃ and 0 -100 mg Al/L for PACl. Broad ranges doses of 0 – 100 mg/L were used for both powdered activated carbons (WPH-1000 and WPC). Depending on the level of DOC removal achieved, a narrower range of coagulant doses was selected for testing. Alum coagulation was optimised at pH 6.0 and FeCl₃ coagulation was optimised at pH 7.0 using sulphuric acid (H₂SO₄) or sodium hydroxide (NaOH) for pH adjustment. Jar testing was done using a rapid mix of 200 rpm for 1 minute to ensure proper mixing of the coagulant, a slow mix at 30 rpm for 30 minutes to promote flocculation, and settling for a period of 30 minutes with the paddles removed.

Bench-scale adsorption experiments using the WPH-1000 and WPC carbons were conducted using 1 L glass amber bottles which were filled with 800 ml of the secondary effluent. A dose range of 0 – 100 mg/L was used and the samples were shaken at 200 rpm for a contact time of 1h and 6h. Two contact times were evaluated to determine the extent to which the contact time would impact DOC removal. After the required contact time, the samples were filtered using a 1.2 µm filter to ensure removal of the carbon fines followed by a 0.45 µm glass microfiber filter.

APPENDIX B

Details of pilot study using the combined approach of enhanced coagulation/activated carbon adsorption and AOP treatment using UV/H₂O₂ and UV/TiO₂

A 100L stainless steel tank was used for pretreatment of the secondary effluent using the pre-determined optimum coagulant or activated carbon doses from the bench-scale tests. Coagulation was performed using the same procedure for the bench-scale jar tests with a rapid mix of 200 rpm for 1 minute, a slow mix at 30 rpm for 30 minutes followed by settling for 30 minutes.

A 42L Calgon Carbon Rayox[®] Advanced Oxidation Batch Pilot Reactor was used for UV/H₂O₂ treatment of the pre-treated effluent. A volume of 40 L of the pre-treated effluent was spiked with 50 µg/L of each target pharmaceutical compound before UV/H₂O₂ treatment. Experiments were performed in two phases. In Phase 1, the effluent was spiked with only three compounds (caffeine, naproxen, 17β-estradiol) and subjected to UV/H₂O₂ treatment with H₂O₂ doses of 0, 10, 15 and 20 mg/L. In Phase 2, the effluent was spiked with seven micropollutants (caffeine, carbamazepine (CBZ), naproxen, 17β-estradiol (E2), sulphamethoxazole (SMZ), diclofenac, clofibric acid) and treated with UV/H₂O₂ treatment at 0, 10 and 20 mg/L. For both phases, 500 mL of effluent were collected every minute for a maximum exposure time of 5 minutes. Sodium thiosulphate was used to quench any residual hydrogen peroxide and pharmaceutical concentration of the samples was subsequently determined using LC-MS/MS analysis.

A 20L lab-scale photocatalytic pilot reactor was used for UV/TiO₂ treatment of the pre-treated effluent. The reactor is equipped with eight UV lamps enclosed in photocatalytic cells. A volume of 20L of the pretreated effluent was spiked with 50 µg/L of caffeine and carbamazepine. The titanium dioxide catalyst was also added to the effluent at a dose 1g/L. For a maximum exposure time of 10 minutes, 500 ml of sample was collected at intervals of 0, 1 2, 4, 6, 8 and 10 minutes. The concentrations of the spiked compounds were determined using LC-MS/MS analysis.