UV Photolysis, AOPs and/or Biofiltration for Micropollutants in Water Reuse

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Introduction
As global water professionals look deeper into approaches for Integrated Water Supply Management driven by worldwide climate change and its record-breaking water shortages, as well as stakeholder desires for sustainable water and energy options that minimize environmental impacts, the importance of innovative treatment technologies for water reuse grow. Numerous researchers since 2009 have focused on the challenges posed by pharmaceuticals and personal care products in wastewater, natural waters receiving wastewater and water reuse production. These compounds can be detected at extremely low levels (nanograms per liter) and exert risk to environmental (aquatic ecosystem) and human health at those levels. In research reports these compounds have been given several names from endocrine-disrupting compounds to PPCPs. This paper will adopt the terminology “micropollutants” to refer to all these compounds.

Researchers have examined a wide variety of technologies to address micropollutants from conventional wastewater and drinking water technologies to membrane filtration including reverse osmosis, granular activated carbon (GAC) filtration and advanced oxidation processes. Several researchers also have reported increases in toxicity as measured by aggregate measures and techniques following advanced oxidation processes in certain water qualities that can be controlled by GAC. The purpose of this paper is to compare the effects of conventional treatment wastewater and drinking water treatments, AOPs and biofiltration on the overall removal of target micropollutants.

Figure 1. Chemical formulas for organic micropollutants tested
Organic micropollutants studied

Compound selection was based upon three criteria: prevalence in wastewater and drinking water; susceptibility to direct photolysis, radical oxidation, and/or biodegradation; and emerging contaminant that lacks information. Using this basis, three compounds were selected for study (Figure 1): Norfloxacin, a common synthetic antibacterial agent that belongs to the class of fluoroquinolone antibiotics; 17β-estradiol, a common synthetic estrogen used for hormone replacement therapy; and sucralose, a chlorinated organic compound commonly used as an artificial sweetener and sugar substitute in many foods or directly in packets of Splenda™. In the European Union, sucralose is also known under the E number E955. Each of the compounds were purchased as reagent grade from Sigma-Aldrich and spiked into the test waters at levels of 100 µg/L to ensure similar levels reported in the literature and allow for detection of up to two log removals.

The relative vulnerability of each of these compounds to direct photolysis are shown in Figure 2. Norfloxacin exhibits a strong absorbance in the 200 nm to 350 nm UV wavelengths. 17β-estadiol has strong absorbance in the 200 nm to 240 nm range with significantly lower absorbance in the 250 nm to 300 nm range. Sucralose does not exhibit any significant absorbance in the 200 nm to 500 nm range. These results suggest a good range of potentials to evaluate impacts of direct UV photolysis on compound removal in this study. Analysis of organic micropollutants was conducted by sending split samples to two commercial laboratories that were selected based upon demonstrating practical quantification limits of 2 µg/L or lower.

Water sources examined

Initial studies were performed using all three compounds in high-quality laboratory water (Type I) to provide a baseline for comparison (UV-T = 100%). Those studies were followed with studies performed in treated drinking water samples taken prior to disinfection from a drinking water treatment facility which uses conventional coagulation, intermediate ozonation, GAC filtration and chloramination (UV-T = 95%).

The final set of studies used samples taken from a conventional wastewater (activated sludge) treatment facility to explore challenging water quality conditions (UV-T = 55%). Samples of activated sludge and settled effluent were used in these studies. Background studies were performed by spiking activated sludge with the micropollutants, mixing with aeration for a six-hour reaction period followed by a two-hour settling period prior to analysis. This experiment was also repeated with the addition of H₂O₂ to ensure any background effects or removals could be quantified. Settled effluent samples from the facility were also spiked with the micropollutants to be used in UV alone, UV-H₂O₂, ozone alone and ozone-H₂O₂ studies.

Advanced oxidation conditions

An Infilco-Degremont (IDI) LPHO UV collimated beam device (Figure 3) was used to deliver UV doses at 254 nm to batch samples in 250 mL aliquots adding up to five liters of volume composited. Doses of zero, 600 and 1,200 mJ/
cm² were delivered using the latest generation of UV dose determination spreadsheets prepared by Bolton and Linden and made available through IUVA. Fisher Chemical certified ACS reagent grade 30% (w/w) $\text{H}_2\text{O}_2$ was used to develop day stocks that provided 0, 6 and 12 mg/L $\text{H}_2\text{O}_2$ to the test samples prior to mixing and further testing.

All studies were performed at a pH of 7.0 and the dissolved inorganic carbon (DIC) was 60 mg/L +/- 5 mg/L. The 12 mg/L results for the UV doses were the most promising studied and are reported in this paper. A preliminary study was also conducted with ozone and ozone-$\text{H}_2\text{O}_2$ on a wastewater effluent samples for comparative purposes to UV and UV-$\text{H}_2\text{O}_2$. In that study ozone was generated from ultra-high purity (UHP) oxygen using an Ozotech, Inc. bench scale unit. These experiments were performed in duplicate using 2 mg/L ozone alone and then adding 6 mg/L $\text{H}_2\text{O}_2$ followed by 2 mg/L ozone resulting in an $\text{H}_2\text{O}_2$/ozone ration of 3.0 to maximize micropollutant removals.

Biofiltration conditions
Core samples of biologically active GAC (Calgon-F300TM) were taken from the filters of the full-scale water treatment plant Waterworks, at Manchester, New Hampshire. These samples had been biologically active for several years, and the adsorption capacity of the GAC had long been exhausted by the natural organic matter being removed. Cores from this treatment facilities GAC have been studied extensively in other UNH research and the biological activity has been fully documented. These samples were placed in small scale columns (3.8 cm diameter by 23 cm deep) packed with 15.4 cm of glass beads and 7.6 cm of GAC to ensure flow distribution at the inlet and minimize risks of wall effects or any short circuiting. The columns were operated at two gpm/ft² with an empty bed contact time of 15 minutes, and all samples analyzed and presented in results were taken after 10 bed volumes of treatment to ensure stability. The column operation was performed in a 20°C constant temperature room for consistency (Figure 4).

Figure 3. IDITM collimated beam unit and mixing plate with separate IL Radiometer™

Figure 4. Packed column with glass beads, biologically active GAC and transfer pump

Results and discussion
High quality waters
The results of UV photolysis experiments at 254 nm in Type 1 lab water are shown in Figure 5. At a UV dose of 600 mJ/cm² the average percent remaining for each compound analyzed in duplicate samples was 63% for norfloxacin, 75% for 17β-estradiol and essentially 100% for sucralose. When the UV dose was increased to 1200 mJ/cm², the percent remaining of norfloxacin dropped to 18% and 17β-estradiol to 48%, but the sucralose remained at 100%. Very similar results were observed for the drinking water samples (not shown). Since the delivered UV dose accounts for background UV absorbance, this similarity is not surprising. These data are consistent with the absorbance results for each compound shown in Figure 2, and prior literature for the estradiols showed a wide range of removals with direct UV photolysis²,⁷,¹².
Figure 6 shows the results for the UV-H\textsubscript{2}O\textsubscript{2} studies conducted on the treated drinking water samples spiked with the three micropollutants. Control runs (0 mJ/cm\textsuperscript{2} and 0 mg/L H\textsubscript{2}O\textsubscript{2}) show good recovery and quality control in the experiments. Results of experiments using a UV dose of 600 mJ/cm\textsuperscript{2} and 12 mg/L H\textsubscript{2}O\textsubscript{2} showed about 80% removal of norfloxacin, 43% removal of 17β-estradiol and 38% removal of sucralose. Further reductions in the micropollutants were achieved when using a UV dose of 1200 mJ/cm\textsuperscript{2} and 12 mg/L H\textsubscript{2}O\textsubscript{2}.

The overall treatment performance at practicable full-scale UV-H\textsubscript{2}O\textsubscript{2} conditions of 1200 mJ/cm\textsuperscript{2} and 12 mg/L H\textsubscript{2}O\textsubscript{2} were 98% removal of norfloxacin, 83% removal of 17β-estradiol and 55% removal of sucralose. The effectiveness of UV-H\textsubscript{2}O\textsubscript{2} found for these three micropollutants are typical of the ranges reported in the literature for compounds of similar chemical structures and reactivity\textsuperscript{2,7,12}. The combined results for studies in laboratory water and in treated drinking water are shown in Figure 7 with respect to compound and likely mechanism of degradation. Norfloxacin is primarily removed by photolysis with additional removal by radical oxidation, 17β-estradiol removal is dependent upon both photolysis and radical oxidation, and sucralose removal is almost entirely dependent upon radical oxidation.

Given the recalcitrant nature of the 17β-estradiol and sucralose following UV-H\textsubscript{2}O\textsubscript{2}, studies were undertaken to examine the effects of UV-H\textsubscript{2}O\textsubscript{2} followed by biofiltration with biologically active GAC preconditioned through operation in a filter at a full-scale drinking water treatment facility. GAC following UV-H\textsubscript{2}O\textsubscript{2} serves several synergistic benefits since the GAC reduces the residual H\textsubscript{2}O\textsubscript{2} yielding oxygen as a terminal electron acceptor which can enhance the biological activity on the GAC. Results shown in Figure 8 for 17β-estradiol indicate that greater than 90% removal was achieved by the combination of UV-H\textsubscript{2}O\textsubscript{2} followed by biofiltration. Removals of 17β-estradiol with UV alone and UV-H\textsubscript{2}O\textsubscript{2} were comparable to those found previously. UV photolysis with biofiltration, biofiltration alone and biofiltration with H\textsubscript{2}O\textsubscript{2} addition all demonstrated about 35% removal, and UV-H\textsubscript{2}O\textsubscript{2} alone demonstrated about 75% removal, which is consistent with prior studies.

Figure 9 shows results of comparable biofiltration studies using sucralose. These data also suggest that the combination of UV-H\textsubscript{2}O\textsubscript{2} and biofiltration was the best multiple barrier treatment demonstrating 88% removal. As observed previously, direct photolysis, direct photolysis with biodegradation and H\textsubscript{2}O\textsubscript{2} with biofiltration did not produce significant removals of sucralose. Addition of UV-H\textsubscript{2}O\textsubscript{2} alone resulted in a 48% reduction in sucralose.
Wastewaters
Results of micropollutant removals in conventional (activated sludge) wastewater treatment were studied to examine the impacts of a more complicated background water matrix with a UV-T of 55%. This matrix, since it had very low bromide levels, was used also to challenge an Ozone-H\(_2\)O\(_2\) advanced oxidation treatment so it could be compared as a feasible and common alternative to the UV-H\(_2\)O\(_2\) process. Experimental results for norfloxacin are shown in Figure 10, 17β-estradiol in Figure 11, and sucralose Figure 12. For all three compounds the best removals are achieved by ozone alone and Ozone-H\(_2\)O\(_2\), respectively. The UV photolysis and the UV-H\(_2\)O\(_2\) experiments produced reductions on the order of 20% for all three compounds, which is likely the result of the 55% UV-T of the wastewater effluent samples. For all three micropollutants, the reduction achieved by simulating the six-hour activated sludge contact followed by the two-hour settling was not significant.

Statistical significance
Often, mechanistic studies on oxidation/treatment of micropollutants employ concentrations in the mg/L range or solely in laboratory prepared waters to control and eliminate undesirable matrix interferences. Experiments that seek to reach practical levels involve low µg/L levels and complex natural water matrices. Therefore, it is important when data sets are limited to develop quantifications of variability prior to drawing meaningful conclusions and recommendation. Selected high-quality water experiments were duplicated as a check on the data, and all wastewater experiments were run in duplicate and basic statistical analyses were performed using JMP software on micropollutant concentrations resulting in the error bars shown on graphs. Experiments in high-quality waters without biofiltration were found to have a maximum standard deviation of 7%. Experiments in high-quality waters with biofiltration had a maximum standard deviation of 11%. Wastewater experiments had a maximum standard deviation of 21%. Estimated standard deviations for the high-quality water experiments and actual standard deviations for the wastewater experiments are shown on all graphs for comparative purposes.

Conclusions and recommendations
The following messages can be taken from the experimental results of this study:
• Sucralose was significantly more difficult to remove than other compounds.
• In high quality waters (high UV-T) UV-H\(_2\)O\(_2\) followed

![Graph of 17β-estradiol removal experiments pH 7, 60 mg/L DIC tap water (UV-T 90%)](image)

![Graph of Sucralose removal experiments pH 7, 60 mg/L DIC tap water (UV-T 90%)](image)

![Graph of Norfloxacin in wastewater experiments pH 7, 60 mg/L DIC (UV-T 55%)](image)
by GAC biofiltration was highly effective at removing all compounds tested.

- In wastewaters with low UV-T (55%) the most promising treatment was the radical oxidation generated by the ozone-$\text{H}_2\text{O}_2$ process. Ozone alone (although, in this wastewater matrix, it is likely that both the direct and indirect ozone pathways were occurring) performed well for norfloxacin and $17\beta$-estradiol with less removal of sucralose. The low UV-T in the wastewater effluent rendered UV alone and UV-$\text{H}_2\text{O}_2$ far less effective.
- In general, AOPs were very promising in the treatment of emerging micropollutants.
- Experimental variability must be considered when drawing meaningful conclusions especially at low concentrations in complex matrices. The experiments reported in this study ranged from seven to 21%.

Experimental findings in this study led to the following recommendations:

- Attempts to determine mechanisms or measure breakdown products were not performed in this study so percent reductions should not be used to infer reduced toxicity or risk in the treated samples. Additional analysis to determine breakdown products or cumulated toxicity of the treated samples should be performed.
- Studies using additional water qualities, additional compounds and additional treatment scenarios should be performed to extend these results to emerging applications.
- The applications of UV-$\text{H}_2\text{O}_2$ and ozone-$\text{H}_2\text{O}_2$ should be compared in more detail to identify more specifically which applications would suggest selection of one process over another. Bromate formation was not a factor evaluated in this study since the only wastewater used was very low in bromide.
- The benefits of following AOPs with a biologically active filtration were clear and should be carefully studied in future pilots due to a variety of additional benefits.
- Efforts to improve the sustainability of these advanced processes (by reducing costs, reducing carbon footprint, reducing chemical generation, transport and use) warrants further research.

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