Ozone Enhanced Biofiltration for Municipal Wastewater Use

ABSTRACT

With climate change, population growth and water scarcity, there is a growing demand to manage water resources in a sustainable approach. Recently, ozonation followed with biologically active filtration (BAF) drew interests due to their synergistic effects at reduced operating cost in terms of performance, media replacement, and ozone dosage. To investigate these operating parameters of the combined ozonation and BAF process for guiding future process design, a comprehensive pilot study was planned and started in January 2014, the process of which included an ozone contactor, and biological active filters at Hammarby Sjöstadsverk Wastewater Treatment Plant, Stockholm, Sweden. Anthracite and granular activated carbon (GAC) produced similar results in terms of COD and ammonia removal, achieving approximately 50% COD removal and reducing ammonia nitrogen to less than 0.2 mg/L. Ozone plays an important role in oxidizing micropollutants. GAC showed additional polishing effect for residual micropollutants while anthracite showed little removal.

INTRODUCTION

With climate change, population growth and water scarcity, there is a growing demand to manage water resources sustainably. Municipalities and industries are now faced with the prospect of further treating, or deep polishing, water and wastewater prior to use as potable water, direct or indirect water reuse or for effluent discharge to sensitive surface waters. Indirect and direct potable reuse (IPR and DPR) are water recycling applications developed largely as a result of advances in treatment technology that enable the production of high quality recycled water at increasingly reasonable costs and reduced energy inputs. In DPR, treated water is introduced directly into a potable water supply distribution system or into the raw water supply immediately upstream of a water treatment plant without the need for an extended residence time in an environmental buffer. In IPR, municipal wastewater is highly treated and discharged directly into groundwater or surface water sources with the intent of augmenting drinking water supplies. Total organic carbon (TOC) and micropollutants, including endocrine disrupting compounds (EDCs) and pharmaceutical and personal care products (PPCPs), are of concern to reduce epidemiological and (eco-) toxicological risks. The EPA defines environmental EDCs as exogenous agents that interfere with the "synthesis, secretion, transport, binding, action, or elimination of natural hormones in the body that are responsible for the maintenance of homeostasis, reproduction, development, and or behavior" (Crisp et al. 1998). The unexpected consequences of trace concentrations of EDCs on wildlife raised concerns about the potential effects of these chemicals on humans. Prior research has shown that there are few inexpensive methods that can remove or destroy all of the required micropollutants such as EDCs, PPCPs, and industrial recalcitrant Chemical Oxygen Demand (COD) from effluent that must be deep polished. Reverse osmosis has

commonly been used but is expensive and concentrates these micro-pollutants into a side stream that requires further treatment. Publications in the past indicated ozone can effectively remove micropollutants including EDCs and PPCPs. In recent years, interest has focused on ozonation enhanced biologically active filtration (BAF) due to the synergistic effects that enhance perfomance and reduce operating cost by extending media life, controlling oxidation byproducts, and reducing ozone dosage. Biofiltration was used as an operational practice of managing, maintaining, and promoting biological activity on granular media in the filter to enhance the removal of organic and inorganic constituents. Combined ozone and BAF has the potential to completely or partially replace the reverse osmosis membrane process, which was commonly applied to indirect or direct water reuse. Table 1 summarizes the literature reports of the removal of organic matter and ammonia nitrogen with ozone enhanced biofiltration to treat secondary effluents. Review of the studies showed that few focused on design parameters, especially the effect of ozone doses on the removal of organics and oxidation by-products, media differentiation between anthracite and granular activated carbon (GAC), and the selection of downsteam process units. Because of the insufficient information to guide the design, piloting was usually needed. Therefore, in this study, we investigated the performance of anthracite and GAC as biofiltration media in terms of the removal of selected micropollutants, organic matter, ammonia nitrogen, total suspended solids (TSS), turbidity, and the improvement of ultravoilet (UV) transmittance in order to provide fundamental design guidance for ozone enhanced biofiltration systems for specific treatment goals.

Table 1: Summary of literature reports for secondary effluent treatment using ozone enhanced biofiltration

References	Efficiencies	EBCT (minutes)	Ozone Dosage (mg/L)
(Reaume et al. 2012)	43% DOC removal with GAC (0.8-1.0 mm) and 17% DOC removal with sand.	40	3.5
(Kalkan et al. 2011)	45.9% and 37.8% DOC removal was achieved with PK1-3 (ES 1.2 mm) and CAgran, respectively, on 170th day operation.	18	NA
	Similar performance was achieved at the 8.3 minutes EBCT ports indicating the bio-activity was in the upper layer.	8.3	NA
(Ho et al. 2011)	DOC removal was less than 10% with the biologically active sand; less than 20% after 200 days of operation with GAC. Biologically active sand removed little Atrazine, Estrone (E1), 17a-ethynylestradiol (EE2), Nnitrosodimethylamine (NDMA), Nnitrosomorpholine (NMOR) and Nnitrosodiethylamine (NDEA).	15	NA
(Halle et al. 2015)	DOC removal was less than 15% with the biologically active dual media (anthracite and sand).	5 and 14	NA
(Levine et al. 2000)	Pre-ozonation favored the breakdown of high-molecular-weight organic matter (> 1000 daltons [Da]). DOC removal 20-30% for ozonation and GAC.	15	15
(Wang et al. 2008)	COD, NH3-N, and TOC were removed from 40–52, 10–19, and 9–13 mg/L to 18–23, 0.5–1.5, and 7–8.5 mg/L respectively (removal efficiency were 58, 89, and 25%, respectively). Media was clay-based, approximately 2-4 mm diameter.	55-223	10
(Li et al. 2006)	Without ozone, BAC removed average 14% DOC. O_3 followed by BAC removed DOC by 34% (3 mg/L O_3); 40% (6 mg/L O_3); 45% (9 mg/L O_3); and 48% (12 mg/L O_3)	15	3, 6, 9, 12
(Reungoat et al. 2010)	10% DOC removal by ozonation and 20-30% removal by GAC	18	5
(Li et al. 2005)	Without ozone, BAC removed average 14% DOC after maturation. DOC removal 34% (3 mg/L O_3) for the system (O_3+BAC) and oxidation alone 12%.	15	3, 6, and 9
GAC, granular activated carbon; BAC, biologically activated carbon; TOC, total organic carbon; DOC, dissolved organic carbon; COD, chemical oxygen demand; EBCT, empty bed contact time.			

MATERIALS AND METHODS

To investigate the operating parameters of the combined ozonation and BAF process for guiding future process design, a comprehensive pilot study was planned and started in January 2014 at Hammarby Sjöstadsverk Wastewater Treatment Plant, Stockholm, Sweden.

The ozone pilot consisted of two contact columns operated in series (Figure 1). To maintain reaction time and facilitate mixing, the first column was operated in a downstream mode, and the second column was operated in an upstream mode. Each column had a water fill level of 3.6 m (11.8 feet) with an inner diameter of about 0.19 m (0.62 feet). The ozone gas was continuously bubbled into the water through the ceramic diffusor built in the bottom of each column. The ozone effluent was then fed to the downstream filters. The heart of the ozone treatment system was a MODULAR HC8 generator (nominal ozone production 8 g/h) (WEDECO, Herford, Germany).

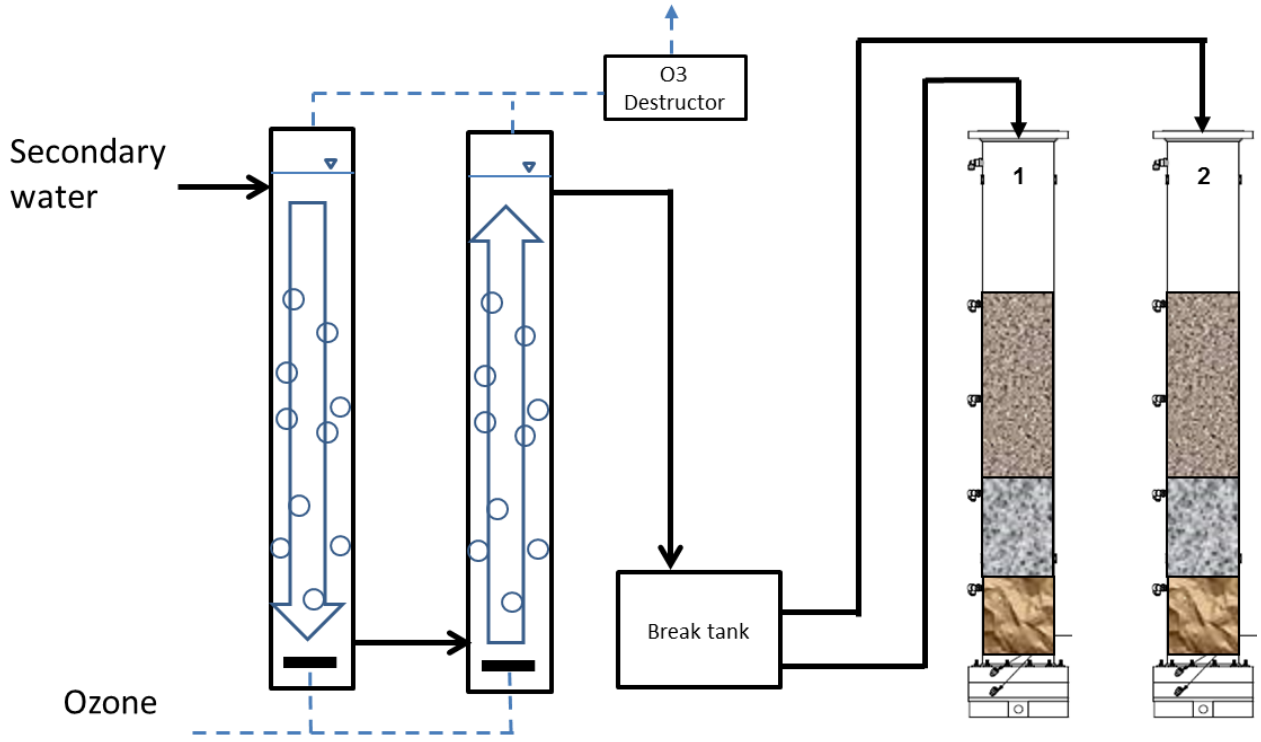


Figure 1: Schematic diagram of ozonation and biologically active filtration

The filter pilot unit was a self-sustained and self-controlled automatic system. It was mounted on a welded stainless steel skid with an instrument panel on one side. The unit was equipped with two tertiary filters of 20.3 cm (8 inches) diameter and 3.66 m (12 feet) tall with a cross section area of 0.0325 m^2 (0.35 ft^2), with independent control systems. The online data acquisition included influent and effluent turbidity measured by VisoTurb® 700IQ (YSI, Yellow Springs, OH), temperature, pH, and differential pressure of the filter media. Table 2 shows the media configuration and sizes. The filter loaded with anthracite was referred as BAF 1 and the filter loaded with GAC was referred as BAF 2.

Table 2: Media configuration and sizes

	BAF 1	BAF 2
Top layer	0.61 m (2 feet) anthracite (ES 1.0 mm UC 1.4)	0.61 m (2 feet) spent GAC (ES 1.0-1.2 mm UC 1.7)
Bottom layer	0.305 m (1 foot) sand (ES 0.5 mm UC 1.4)	0.305 m (1 foot) sand (ES 0.5 mm UC 1.4)
ES, effective size; UC, uniformity coefficient.		

The source water was effluent from a secondary biological treatment process. The filter was allowed to achieve microbial acclimation during the period from January 16, 2014 to March 10, 2014, with an ozone dose maintained at 0.6 mg O_3/mg TOC. The study period for ozone enhanced biofiltration ran from March 10, 2014 to April 13, 2014. During this period, the systems received effluent directly from the secondary biological treatment process. Ozone doses were varied from 0.6 O_3/TOC to 1.2 O_3/TOC during the study period. Both filters were maintained at a flow rate of 1.96 L/min (0.52 gpm), corresponding to 15 minutes empty bed contact time (EBCT), maintaining this contact time until the end of the study.

RESULTS AND DISCUSSION

Table 3 shows the secondary effluent characteristics during the study period. The TSS in the ozone influent averaged 7.9 mg/L (standard deviation 1.9 mg/L). It was interesting to see that the average TSS concentrations were reduced to 4.7 mg/L (standard deviation 3.1 mg/L) after ozone, for approximately 40% reduction. Additional TSS reduction was achieved in the BAF effluents, where TSS levels were maintained at less than 1.0 on the average.

Table 3: Secondary effluent characteristics during the period of the study

Parameter	Inlet Ozone system	Ozone Effluent	BAF 1 Effluent	BAF 2 Effluent
TOC (mg/L)	12.6	11.8	9.1	8.5
COD (mg/L)	41.9	32.2	20.3	21.2
BOD_5(mg/L)	7.3	8.0	3.0	2.7
UV Transmittance (%)	53.8	73.0	77.4	77.9
NH4-N (mg/L)		0.79	0.05	0.03
TSS (mg/L)	7.9	4.67	0.47	0.66

Both filters behaved similarly for turbidity removal. Turbidity was reduced from an average of 3.03 NTU down to 0.58 NTU and 0.53 NTU (average) for BAF 1 and BAF 2 (Figure 2), respectively, according to online turbidity sensors. The readings from the online turbidity sensors were confirmed

with lab analysis.

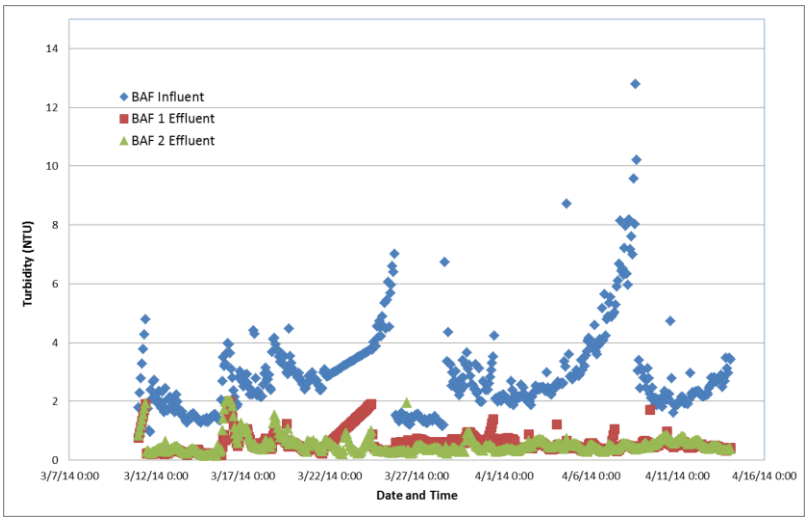


Figure 2: Turbidity trending of BAF 1 and BAF 2 from March 10, 2014 to April 13, 2014

The COD concentrations averaged 40.7 mg/L (standard deviation 6.8 mg/L) in the ozone influent and 31.7 mg/L (standard deviation 6.2 mg/L) in the ozone effluent (Figure 3).

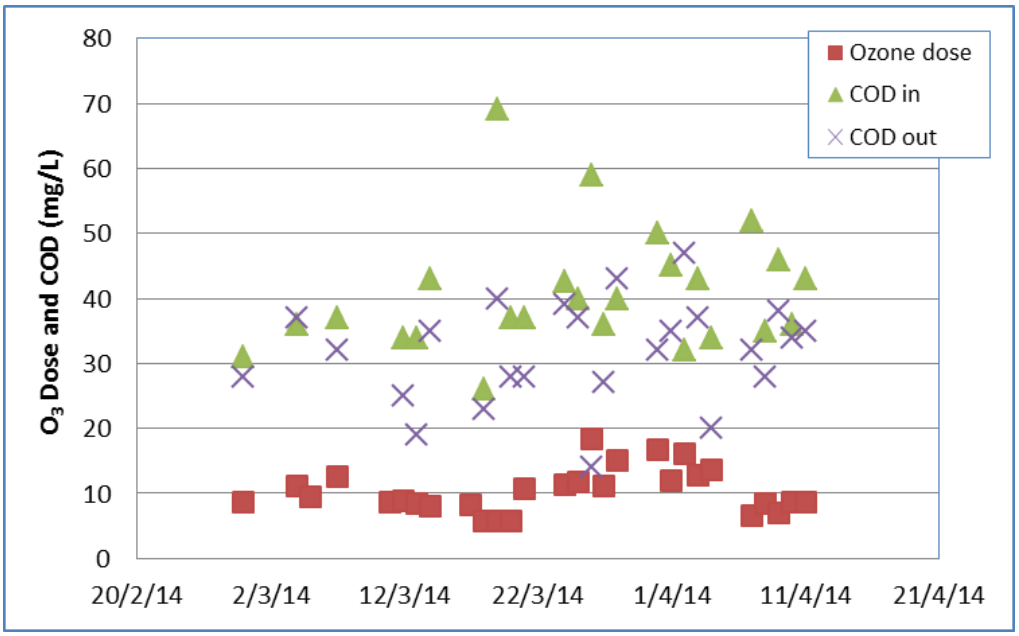


Figure 3: Actual ozone dosages and the COD changes before and after ozonation

Both BAFs showed similar COD removal efficiencies at a fixed ozone dose (Figure 4). When considering the overall efficiencies of the combined ozone and BAF, about 40% COD removal on an average basis was achieved at the O3/TOC ratio 0.6, and about 50% removal was achieved at the O3/TOC ratios of 0.8, 1.0, and 1.2 on an average basis. At the ratio of 0.8, the COD removal appeared to reach a plateau. This suggests that the optimal O3/TOC ratio for the overall O3 and BAF system was 0.8. This ratio is consistent with a previous report that 45.9% and 37.8% of dissolved organic carbon (DOC) removal were achieved with two different activated carbons PK1-3 (ES 1.2 mm) and CAgran, respectively, on 170th 150 day operation (Kalkan et al. 2011). In another study, it was found that GAC (average 43% removal) was much better for DOC removal than sand (average 17% removal) when both filters operated with empty bed contact times of 40 minutes (Reaume et al. 2012). Li et al. (2005) observed that BAC only removed on average 14% DOC without ozone, while ozone enhanced BAC removed 34% DOC, even though analysis of the ozonation effluent (3 mg/L O3 dosed in front of BAC) indicated that ozone alone had removed only 12% DOC. This finding demonstrates the benefit of placing ozone in front of biofiltration.

Other benefits of the combined ozonation and biofiltration include the reduction of biodegradable disolved organic carbon (BDOC) and oxidation by-products such as N-nitrosodimethlyamine (NDMA), and potentially extending the media life to avoid frequent regeneration (Gerrity et al. 2015). The removal of BDOC increases biostability of downstream pipeline by preventing the bacterial re-growth. It was reported that the carbon had only been replaced twice in 27 years of operation in biologically active carbon filters following ozonation at Fred Hervey Water Reclamation Facility, El Paso, TX (Trussell et al. 2013).

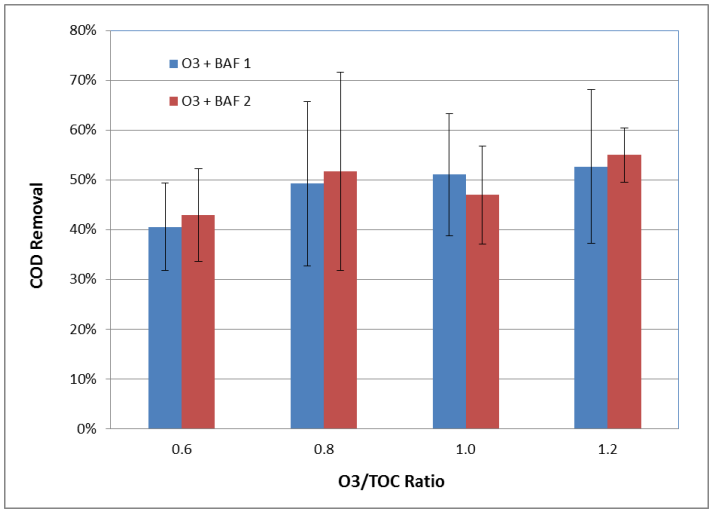


Figure 4: COD removal efficiencies of the combined O_3 and BAF from March 10, 2014 to April 13, 2014

Ammonia nitrogen was maintained at less than 0.1 mg/L in the effluents, with biofilter influent ammonia nitrogen varying from 0.2 to 1.2 mg/L. Kalkan et al. (2011) also observed that ammonia nitrogen was reduced to 0.2 mg/L with two different activated carbons, PK1-3 and CAgran, predominatly due to biological nitrification.

Figure 5 shows the UV transmittance improvement by ozonation. The UV transmittance (254 nm) of the secondary effluent averaged 53.9% (standard deviation 3.1%) and never exceeded 60%. The UV transmittance after ozonation averaged 71.9% (standard deviation 3.4%). This was a significant increase. After biofiltration, UV transmittance averaged 76.4% (standard deviation 3.3%) with BAF 1 and 77.9% (standard deviation 2.5%) with BAF 2. The improvement of UV transmittance is beneficial for sizing UV systems if UV disinfection is employed downstream.

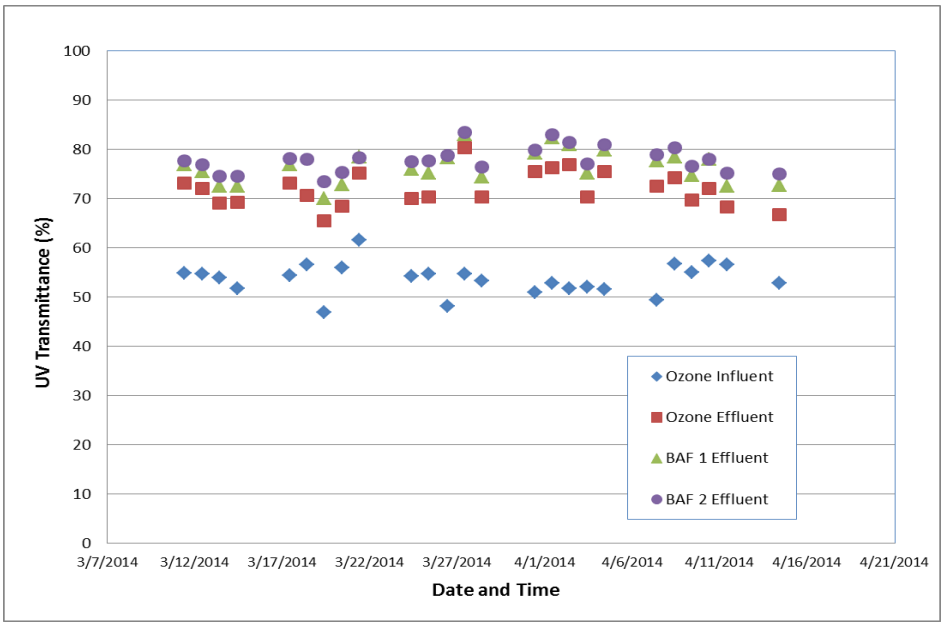


Figure 5: Improvement of UV Transmittance by ozone and biofiltration from March 10, 2014 to April 13, 2014

The concentrations of the selected micropollutants varied depending on the inlet concentration in the raw water and the operating conditions of the upstream biological treatment process (Figure 6). Figure 6 shows the variation of concentrations at the inlet of the ozone system. Most micropollutants were present in lower concentrations, from 30 – 400 ng/L, and most are pharmaceuticals. Some micropollutants used more frequently can be found at higher concentrations in the ozone influent. For example Benzotriazole is widely used as a corrosion inhibitor in dish washer products in households. The ozonation reduces the concentrations of most of these micropollutants by more than 80% (Table 4). The average ozone dosage is approximately 10 mg/L or 0.8 g O3/ g TOC. Several micropolluatnts are oxidized down or close to their specific detection limits, such as carbamazepine and diclofenac.

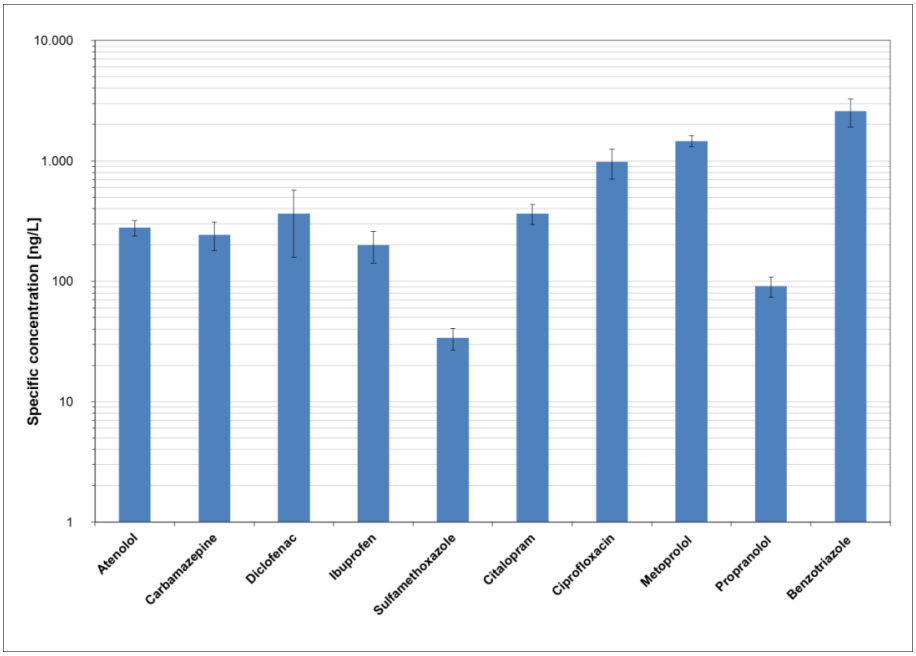


Figure 6: Variation of micro-pollutant concentrations at the inlet of ozonation

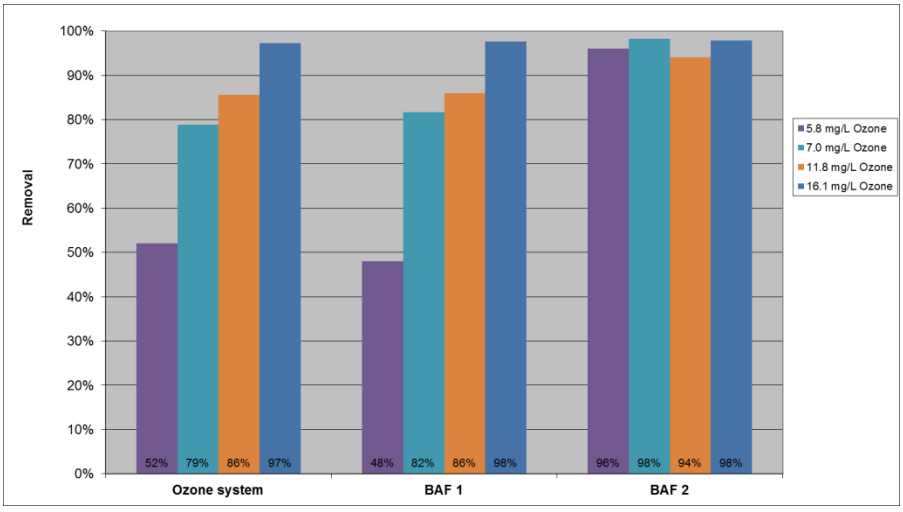
Table 4: Summary of the removal efficiencies of selected micro-pollutants

Compound	LOQ	Before Ozonation	After Ozonation	After BAF 1	After BAF 2	Elimination Ozonation	Elimination BAF 1	Elimination BAF 2
	[ng/L]	[ng/L]	[ng/L]	[ng/L]	[ng/L]	[%]	[%]	[%]
Atenolol	10	315 ± 89	54 ± 50	42 ± 40	15 ± 4	39 ± 4	2 ± 3	6 ± 7
Carbamazepine	15	265 ± 57	15 ± 0	15 ± 0	15 ± 0	94 ± 1	0 ± 0	0 ± 0
Diclofenac	25	507 ± 218	25 ± 0	25 ± 0	25 ± 0	69 ± 8	0 ± 0	0 ± 0
Ibuprofen	40	366 ± 415	42 ± 4	40 ± 0	40 ± 0	7 ± 7	0 ± 0	0 ± 0
Sulfamethoxazole	15	53 ± 28	15 ± 0	15 ± 0	15 ± 0	16 ± 9	0 ± 0	0 ± 0
Citalopram	3	364 ± 53	32 ± 33	26 ± 28	3 ± 1	68 ± 41	2 ± 3	8 ± 10
Ciprofloxacin	20	1269 ± 426	30 ± 23	44 ± 54	20 ± 0	21 ± 8	0 ± 1	0 ± 0
Metoprolol	5	1590 ± 448	225 ± 214	202 ± 198	43 ± 12	73 ± 36	2 ± 4	12 ± 15
Propranolol	3	103,5 ± 30	3 ± 0	3 ± 0	3 ± 0	97 ± 1	0 ± 0	0 ± 0
Benzotriazole	30	2180 ± 680	565 ± 420	560 ± 462	103 ± 57	57 ± 26	1 ± 3	24 ± 19

Comparing the removal rates of single micropollutants with their reaction kinetic rate constants revealed that substances showed higher removal rates if their specific rate constants are high. Those micropollutants

with lower rate constants exhibited lower removal rates. The BAF 1 (anthracite) showed relatively low reduction for atenolol, citalopram, ciprofloxacin, metoprolol, propranolol and benzoltriazole. BAF 2 (GAC) showed higher removal of these micropollutants, likely because of both adsorption and biodegradation. The removal of other micropollutants through biofiltration was close to zero because they were oxidized to the detection limits with ozonation. In a full scale pilot study, 13 of 34 trace compounds studied had removals less than 15% under a stead state in a biological active sand filter with EBCT 7.5 minutes, and were classified as recalcitrant to biodegradation (Zearley and Summers 2012). Similarly, in a pilot study at Southern Nevada Water Authority (SNWA), 23 of 36 micropollutants were removed by no greater than 15% with biologically active anthracite; and meanwhile, these micropollutants were removed by greater than 70% with biologically active carbon in parallel (Snyder et al 2007), likely due to the adsorption properties (higher specific surface area) of carbon and biological removal. The low removals in biologically active sand or anthracite filters were likely due to low biodegradation rates of these micropollutants and much lesser specific surface area of sand and anthracite media for adsorption (Zhu and Bates 2013).

The ozone dosage also influenced the removal efficiencies (Figure 7). Figure 7 shows that the removal of benzotriazole increased with an increasing ozone dose (mg/L), while carbamazepine was reduced at high efficiencies even at low ozone doses. This indicated that benzotriazole has a much lower ozone rate constant than that of carbamazepine. The filter with granular activated carbon further removed benzotriazole and reduced the concentration down to the detection limit. However, the anthracite filter did not show considerable reduction. The removal of metoprolol showed a similar trend after biofiltration. Carbamazepine, diclofenac, and hormonally active substances such as estradiol were oxidized to the detection limit even at the lowest dose of ozone.



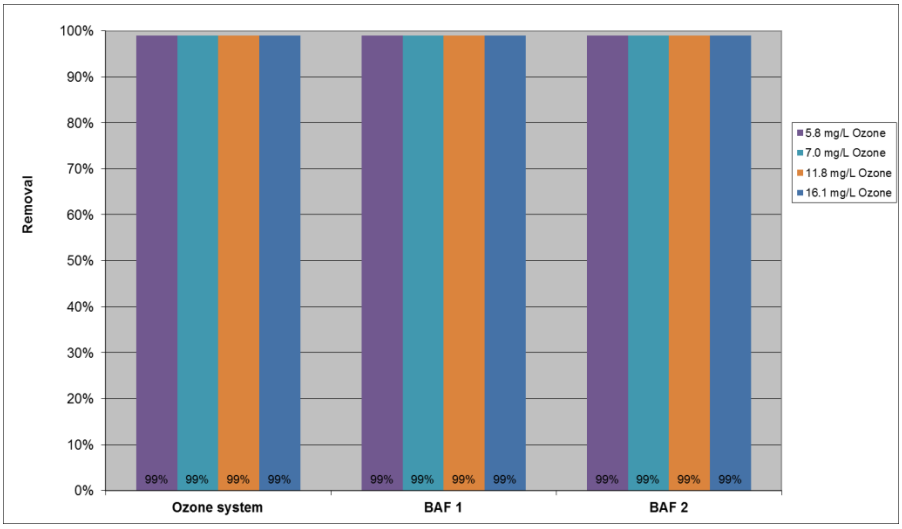


Figure 7: Specific removal for Benzotriazole (upper) and Carbamazepine (lower) at different ozone dosages

In summary, the combination of ozone oxidation and biofiltration systems can achieve an almost complete reduction of various micropollutants. As a result, this combined process effectively protects receiving waters against the negative impacts of micropollutants. Ecotoxicological tests (YES/YAS, Microtox) showed no abnormalities, either after the ozone stage or after the filter stages, demonstrating that the estrogenic effects were reduced by ozonation to an acceptable level (data not shown).

CONCLUSIONS

The ozone enhanced bio-filtration system provides a multi barrier solution (oxidation, biological and physical filtration) for treating multiple parameters including COD, ammonia, micropollutants and oxidation by-products. Anthracite and GAC produced similar results in terms of COD and ammonia removal, achieving approximately 50% COD removal and reducing ammonia nitrogen to less than 0.2 mg/L. Turbidity was reduced from an average of 3.03 NTU down to less 0.58 NTU and 0.53 NTU (average) for BAF 1 (anthracite) and BAF 2 (GAC), respectively. Ozone enhanced biofiltration improved UV transmittance. Ozone plays an important role in oxidizing micropollutants. GAC showed additional polishing effect for residual micropolluants while anthracite showed little removal.

Future work will concentrate on the effects of temperature, nutrients such as phosphorus, TSS, and EBCT on the process performance, and comparison of media (such as GAC, antharacite, sand, and expanded clay) over an extended period of time (i.e., over one year) and the investigation of media service life.

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