**Title** Impact of coagulation on biofiltration: removal of trace organic contaminants to mitigate the effects of wastewater reuse on drinking water treatment

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**Abstract** Biofiltration has been assessed for the removal of several types of trace organic contaminants (TrOCs), including endocrine-disrupting compounds, pharmaceuticals and personal care products, and taste and odor compounds. Biofiltration is often preceded by the unit processes of coagulation, flocculation, and sedimentation. Maximizing the simultaneous removal of multiple TrOCs via independent optimization of each such unit process in a treatment train ignores synergism and antagonism among the processes. Thus, a holistic consideration of contaminant removal by biofiltration must include examination of common upstream processes, such as coagulation. Overall, coagulation will impact the amount and composition of natural organic matter in the biofilter influent; this could influence microbial community structure and biodegradation capability, with implications for the removal of TrOCs, total organic carbon, biodegradable dissolved organic carbon, and assimilable organic carbon. In this study, we examine the impact of coagulant type, coagulant dose, and coagulation pH on the simultaneous removal of multiple TrOCs in downstream biofiltration. Synthetic water was prepared for these experiments using natural organic matter concentrated from Lake Austin in Austin, Texas. Four parallel bench-scale biofilter trains were operated. One granular activated carbon (GAC) biofilter train and one sand biofilter train were operated as controls, using non-coagulated synthetic water. One GAC biofilter train is being operated with alum-coagulated synthetic water, and one GAC biofilter train is being operated with ferric-coagulated synthetic water. A suite of nine common TrOCs was selected to cover a range of chemical classes, product applications, and relative biodegradabilities. The TrOCs are added to the synthetic water after coagulation, each at a concentration of 0.5 µg/L. Coagulation doses and optimum coagulation pH were determined via jar-testing to be 50 mg/L at

pH 6.5 for alum and 60 mg/L at pH 5.5 for ferric chloride. As expected, iron coagulation removed more dissolved organic carbon than did alum coagulation. Atenolol, caffeine, DEET, naproxen, diclofenac, and gemfibrozil all showed the highest removal in the biofilter train receiving ferric-coagulated water, which had the highest removal of dissolved organic carbon as compared to the other biofilter trains. For 2-MIB and geosmin, the highest removal was observed in the GAC biofilter receiving non-coagulated water as compared to the other biofilter trains. The sand biofilter only removed atenolol, but at a low percent removal (10%). Thus far ferric chloride may be more beneficial to use during treatment since it appears to have better removal of a greater variety of TrOCs in treatment train 4 and removes a greater amount of DOC during coagulation, which can be beneficial to the operational parameters of biofilters at a water treatment plant.

**Problem and Research Objectives**

A key problem in the drinking-water industry is to find effective treatment processes to remove an increasing variety and concentration of trace organic compounds (TrOCs), such as endocrine-disrupting compounds (EDCs), pharmaceuticals and personal care products (PPCPs), and taste and odor compounds, many of which occur due to increased wastewater influence. As water scarcity continues, the number of wastewater-impacted drinking water treatment plants likewise will increase. Thus, indirect and direct potable reuse will become more commonplace. The 2012 Texas State Water Plan predicts that water reuse will provide approximately 1.53 million acre-feet per year of water supply statewide by 2060 and will meet 18% of the projected water needs. During low-flow conditions in the summer, the influent to drinking water treatment plants in many Texas cities consists mainly, if not 100 percent, of wastewater from upstream cities (Rice et al., 2015). The increase in reuse, application of more conservation measures, and longer drought periods means that drinking water treatment plants will see both a greater variety and increasing concentration of TrOCs. Therefore, the drinking-water industry needs to find effective treatment processes to remove this increasing variety and concentration of TrOCs. The multi-barrier benefits of biofiltration, including particle removal, biodegradation, and adsorption, make this an attractive process for addressing the TrOC problem.

Biofiltration has been assessed for the removal of several types of TrOCs, including EDCs (Zearley & Summers, 2012); PPCPs (Zearley & Summers, 2012); and taste and odor compounds (Nerenberg et al., 2000). Biofiltration is often preceded by coagulation, flocculation, and

sedimentation. Maximizing the simultaneous removal of multiple TrOCs via independent optimization of each unit process in a treatment train ignores synergism and antagonism among the processes. Thus, a holistic consideration of contaminant removal by biofiltration must include examination of common upstream processes, such as coagulation.

Coagulation, flocculation, and sedimentation reduce particle loading to the biofilter and can remove a portion of natural organic matter (NOM) from the water (reviewed by Matilainen et al., 2010). To help minimize disinfectant byproduct (DBP) concentrations in finished drinking water, U.S. Environmental Protection Agency regulations specify the removal of total organic carbon (TOC) by enhanced coagulation, where the required TOC removal depends on the TOC and alkalinity of the source water. Coagulation and biofiltration should be used in concert with one another to minimize effluent organic carbon and DBP formation potential. Lauderdale and Brown (2013) demonstrated that purposefully decreasing TOC removal via coagulation (by halving the coagulant dose) could be offset by increased TOC removal via biofiltration, resulting in similar overall TOC removals by coagulation/biofiltration under both coagulant conditions. These results suggest that shifting greater burden for TOC removal to the biofilters, which are operationally less expensive than is coagulation, could provide cost-savings to a utility.

Some studies have noted greater NOM removal with ferric- as compared to aluminum-based coagulants (e.g., Bell-Ajy et al., 2000). The hydrophilic neutral fraction of NOM, which strongly contributes to biodegradable dissolved organic carbon (BDOC), tends to remain at a higher concentration in the water after alum coagulation (Soh et al., 2008) as compared to ferric coagulants, which generally removed up to 20% more BDOC(Volk et al. 2000). ; however, removal within these processes is highly dependent on pH (Matilainen et al., 2010). Hence, when coagulation occurs upstream of biofiltration, the coagulant choice and pH selection must be made in light of how those choices will impact overall NOM and TrOC removal. In particular, the influent BDOC concentration to the biofilter must be sufficient to sustain the biomass needed for TrOC removal because TrOCs are likely to be secondary microbial substrates due to their low concentrations.

Several studies have suggested that the amount of biomass in a biofilter, as long as it is above some critical minimum amount, does not impact the overall removal of biodegradable organic matter in a biofilter (e.g., Urfer et al., 1997). However, Urfer et al. (1997) also suggest that the critical minimum amount of biomass might be higher for more slowly biodegradable

components as compared to the amount of biomass necessary for more easily biodegradable components. Thus, the biodegradation of some TrOCs (e.g., sulfamethoxazole) could be improved by increased biomass concentrations in the biofilter. Overall, coagulation will impact the amount and composition of NOM in the biofilter influent; this could influence microbial community structure and biodegradation capability, with implications for the removal of TrOCs, TOC, BDOC, assimilable organic carbon, and DBP formation potential.

The goal of this project was to develop a holistic understanding of coagulation-biofiltration, such that the removal of TrOCs can be maximized. Specific objectives are as follows:

1. Examine the impact of coagulant type, coagulant dose, and coagulation pH on the simultaneous removal of multiple TrOCs in downstream biofiltration;
2. Examine the impact of coagulant type, coagulant dose, and coagulation pH on the microbial community in downstream biofiltration.

**Materials/Methodology**

*Synthetic water*

The first task was to design the synthetic water, concentrate NOM from Lake Austin, and choose a diverse set of TrOCs. The final synthetic water parameters are as follows: alkalinity=100 mg/L as $CaCO_3$, pH=8.2, TOC=5 mg/L, and hardness=20 mg/L as $CaCO_3$. The synthetic water is supplemented with nitrogen ($NH_4Cl$) and phosphorus ($KH_2PO_4$) prior to biofiltration to prevent nutrient limitation, and the pH of the biofilter influent is adjusted to 8.2, for both non-coagulated and coagulated waters, to prevent phosphate adsorption in case of floc carryover to the biofilters. NOM has been extracted and concentrated from 9000 L of Lake Austin water (Austin, TX) to 90 L. The NOM concentration process includes filtration through two progressively smaller filters, the first 5 micron Pentek PD-5-934 filter to remove all suspended particles greater than 5 microns and finally a 0.5 µm Pentek 155403-75 filter, followed by cation exchange with the Ambersorb 200H resin (a strong-acid cation-exchange resin) and reverse osmosis with a Dow Filmtec spiral-wound TW30 membrane (Pressman et al., 2010, Barrett et al., 2014). The water was run repeatedly through a reverse osmosis membrane, rejecting the "clean" water, and retaining the concentrated organic-rich water until the desired volume was reached. A suite of nine common TrOCs was selected to cover a range of chemical classes, product applications and relative biodegradabilities (Table 1). The nine chosen TrOC are added to the synthetic water after coagulation (just before entering the biofilter), each at a concentration of 0.5 µg/L.

**Table 1. Suite of diverse TrOC and their associated analytical methods**

| *Compound* | *TrOC category* | *Chemical class* | *Method* |
|---|---|---|---|
| 2-MIB | microbial derived odor | borneo | Gas chromatograph/mass spectrometer (GC-MS )Martínez (2013) |
| Geosmin | microbial derived odor | bicyclic alcohol | |
| Diclofenac | pharmaceutical/ nonsteroidal anti-inflammatory drugs (NSAID) | phenylacetic acid | Liquid chromatograph/mass spectrometer (LC-MS) Vanderford et al. (2012) |
| Naproxen | pharmaceutical/NSAID | propionic acid | |
| Gemfibrozil | pharmaceutical/ anti-convulsant | fibric acid derivative | |
| Atenolol | pharmaceutical/ cardiovascular | isopropylamino-propanol derivative | |
| Caffeine | food product | xanthines | |
| Thiabendazole | pesticide/fungicide | benzimidazole | |
| N,N-Diethyl-meta-toluamide (DEET) | pesticide | aromatic amide | |

*Biofilters*

Assembly: Eight glass columns with 1.5-cm diameters were used for the biofilters. The columns were set up in 4 parallel treatment trains (with 2 biofilters in series) and filled with media to a height of 5 cm. Two different types of media were studied, exhausted granular activated carbon (GAC) taken from a water treatment plant in Arlington, TX, and silica sand (Sigma Aldrich, St. Louis, MO). Many conventional plants are now using GAC as the media of choice because it provides excellent mechanical filtration of particulate matter, in addition to providing a large

amount of surface area for bacterial growth and removing organic compounds. Exhausted GAC was chosen to reduce the amount of TrOCs and dissolved organic carbon (DOC) lost to adsorption on the media and focus on removal by biodegradation (Volk 2009). Sand was chosen to be a nonadsorptive control. Each filter will have an empty bed contact time (EBCT) of 3 minutes, for a total contact time of 6 minutes for the 2 columns in series.

The columns were sized by using a scaling model (Manem and Rittmann 1990) to simulate a full scale biofilter. A summary of the full-scale and bench-scale biofiltration parameters is provided in Table 2.

**Table 2 -** Biofilter Parameters

| | **Full Scale** | **Bench Scale** |
|---|---|---|
| Diameter (cm) | 34.4 | 1.5 |
| Height (cm) | 260 | 5 |
| EBCT (min) | 10 (X2 columns) | 3 (X2 columns) |
| Flowrate (L/min) | 253 | 0.003 |

Operation: After designing and constructing the biofilters (Figure 1), each train was run for one week with raw Lake Austin water to seed the filters with local microorganisms. Trains 1 and 2 are operated as controls with uncoagulated synthetic water. Additionally, Train 1 is operated with silica sand as the non-adsorptive control. Train 3 was run sequentially using synthetic water coagulated under the optimized conditions for alum. Train 4 will be run sequentially using synthetic water coagulated under the optimized conditions for ferric chloride.

The suite of TrOCs is spiked to the synthetic water after the coagulated synthetic water wastransfer to the glass carboy to prevent loss of TrOCs thorugh coagulation and through sorption in case of floc carryover into the final storage containers. The biofilter influent for each train is housed in an individual 20-L glass carboy that is covered with aluminum foil to minimize loss of volatile components. The influent, columns, and tubing were kept in darkened room to prevent photodegradation of contaminants and algal growth. The columns are run upflow via peristaltic pumps, and the total EBCT of each train is 6 min to simulate a 20-min full-scale EBCT (Manem and Rittmann 1990). The flow rate, pH and dissolved oxygen concentration were measured in the influent and effluent.

Samples were analyzed for pH, heterotrophic plate counts, DO, and DOC(Table 3). The suite of TrOCs was measured monthly.

**Table 3. Water quality analyses**

| Parameter | Method No. | Method Title | Source |
|---|---|---|---|
| pH | 4500-H+ | pH Value | Standard Methods (2005) |
| TOC/DOC | 5310 B | Total Organic Carbon: High T Combustion | Standard Methods (2005) |
| DO | 4500-O G | Membrane Electrode Method | Standard Methods (2005) |
| HPC | 9215 | Heterotrophic Plate Count | Standard Methods (2005) |

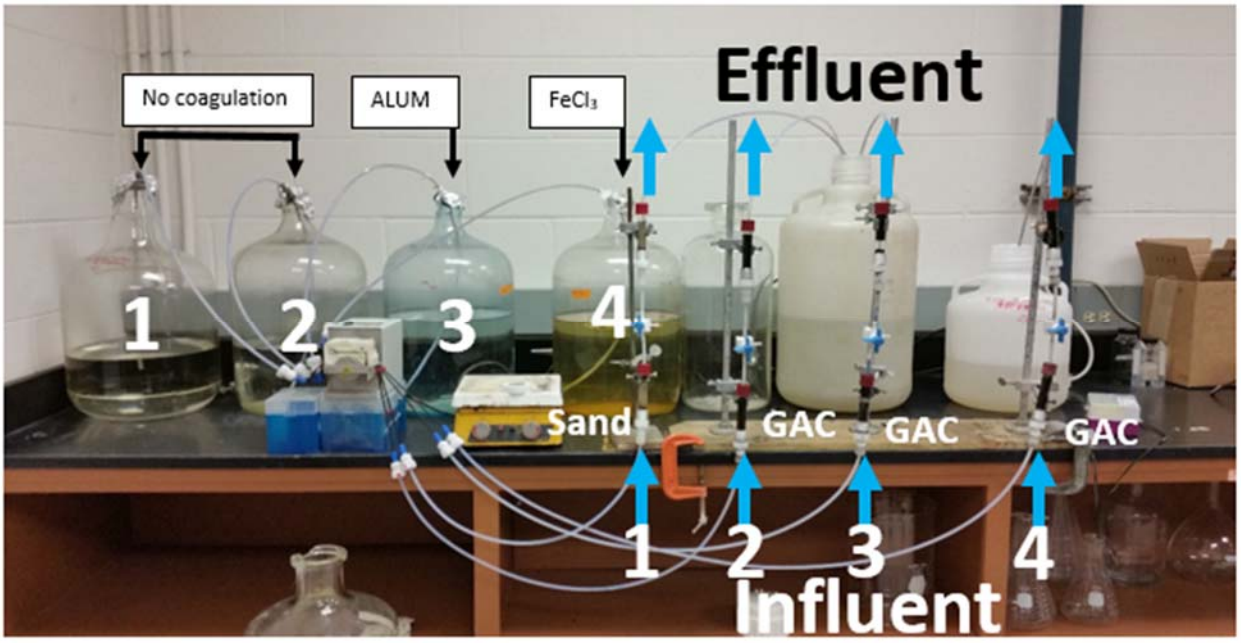


Figure 1. Bench-scale biofilter setup.

*Coagulation*

Optimization: Coagulation dosage and optimum pH were determined by performing jar tests on a range of concentrations for both coagulants following the jar-test procedure in Bell-Ajy et al. (2000). Briefly, 200 mL of raw (non-coagulated) water were added to a jar and dosed with the same concentration of appropriate coagulant. The pH was adjusted in each jar using 1 N $HNO_3$ or 1 N NaOH. The water was then rapidly stirred (250 rpm) for 2 minutes, stirred slowly (20 rpm) for 30 minutes, and then flocs were allowed to settle for 40 minutes. Each sample was filtered through a 0.45-μm Gelman Supro filter, and DOC was analyzed using a Shimadzu TOC analyzer in non-purgeable organic carbon mode. At the optimum pH, the same coagulation procedure was repeated except that the coagulant dose was varied such that the optimum dose for each coagulant was determined.

Bench scale: For the control columns 20 L of Millipore water are used to prepare the synthetic water. After mixing the salts and trace metals to the appropriate concentrations (Table 4), the solution is transferred to a glass carboy (carboys 1 and 2 in Figure 1), and the final pH is brought to 8.2. For the other biofilter trains, 20 L of synthetic water are prepared prior to starting the coagulation process. For train 3, 50 mg/L of alum is added to the synthetic water, and, for Train 4, 60 mg/L of ferric chloride is added to the synthetic water. The water is rapidly stirred using a paddle impeller (250 rpm) for 2 minutes, stirred slowly (20 rpm) for 30 minutes, and then flocs are allowed to settle for 40 minutes. The supernatant is then transferred to a glass carboy (carboys 3 and 4 in Figure 1), and the final pH is brought to 8.2.

Table 4. Synthetic water salts and trace metal final concentrations

| CO3 & Salts | mg/L |
|---|---|
| NaHCO3 | 168.01 |
| Na2SO4 | 17.75 |
| NaCl | 13.68 |
| CaCl2*2H20 | 2.81 |
| MgCl2*6H20 | 3.88 |
| NH4Cl | 0.45 |
| KH2PO4 | 0.11 |
| CH3COONa | 10 |

| Trace Metals | mg/L |
|---|---|
| AlCl3*6H2O | 0.2 |
| CoCl2*6H2O | 0.0382 |
| CuSO4*5H2O | 0.0574 |
| FeSO4*7H2O | 0.7016 |
| H3BO3 | 0.0303 |
| MnCl2*4H2O | 0.2807 |
| Na2MoO4*2H2O | 0.0254 |
| Na2SO4 | 0.142 |
| NiCl2*6H2O | 0.0216 |
| ZnSO4*7H2O | 0.288 |

*TrOC Analyses*

LC-MS: TrOCs are concentrated using solid phase extraction (Waters Oasis® HLB™, 200 mg resin/6cc cartridge) and then analyzed with a TS Ultimate 3000 liquid chromatograph connected to a TSQ Quantiva tandem mass spectrometer (Thermo Fisher LC-MS/MS). The SPE cartridge is first conditioned with 3.0 mL of LCMS grade dichloromethane (DCM), 5.0 mL of LCMS grade methanol, and then 7.0 mL of LCMS grade water. Using a vacuum flask, 200 mL of sample is loaded through the cartridge at approximately 10 mL/min. When the loading is complete, the columns are rinsed with 3.0 mL of deionized (DI) water and then rinsed with 4.0 mL of a methanol/water solution (95/5 v/v). The columns are then dried under vacuum using a vacuum manifold for 40 minutes, after which they are sequentially eluted with 6.0 mL of methanol followed by 4.0 mL of methanol/DCM (70/30 v/v). The eluted samples are then concentrated via evaporation using a 35ºC water bath, under an ultra-pure nitrogen stream, down to approximately 0.5 mL. The samples are then brought to a final volume of 1 mL using LC/MS grade methanol (Honeywell).

Two separate analyses are conducted on the same extract: one in positive electrospray ionization mode [(+) ESI] and the other in negative electrospray ionization mode [(-) ESI]. For the (+) ESI, 2.0 µL of the sample extract is separated on a high pressure liquid chromatography (HPLC) system incorporating a reversed phase C18 column, using formic acid 99.5+% and ammonium formate ≥99.0% as solvent A, and methanol/acetonitrile with 0.1% formic acid as solvent B. For the (–) ESI: 3.0 µL of the extract is separated on an HPLC system incorporating a reversed phase C18 column, 40 mg/L ammonium acetate as solvent A, and LCMS grade methanol as solvent B.

GC-MS: 2-MIB and geosmin are concentrated using solid phase microextraction fibers (SPME) from 10 mL of sample and then analyzed with an Agilent 5977A gas chromatograph/mass spectrometer (GC-MS).

**Principal Findings**

Coagulation Optimization: Based on the jar-test results (Figure 2), a dosage of 50 mg/L at pH 6.5 was chosen for alum and 60 mg/L at pH 5.5 was chosen for ferric chloride.

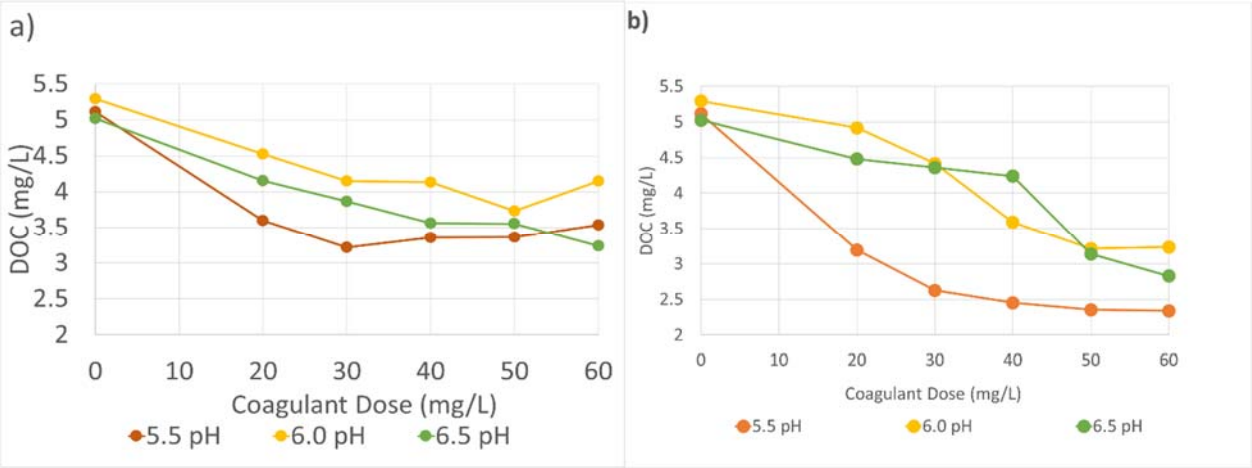


Figure 2. Jar test results for (a) alum and (b) ferric chloride coagulation.

Initial results for TrOC removal in the biofilter trains are shown in Figure 3. Atenolol, caffeine, DEET, naproxen, diclofenac, and gemfibrozil all showed higher removal in the biofilter train receiving ferric-coagulated water (Train 4). For both 2-MIB and geosmin, higher removal was observed in the GAC biofilter receiving non-coagulated water (Train 2). The sand biofilter (Train 1)only showed removal of atenolol, at less than 10% removal.

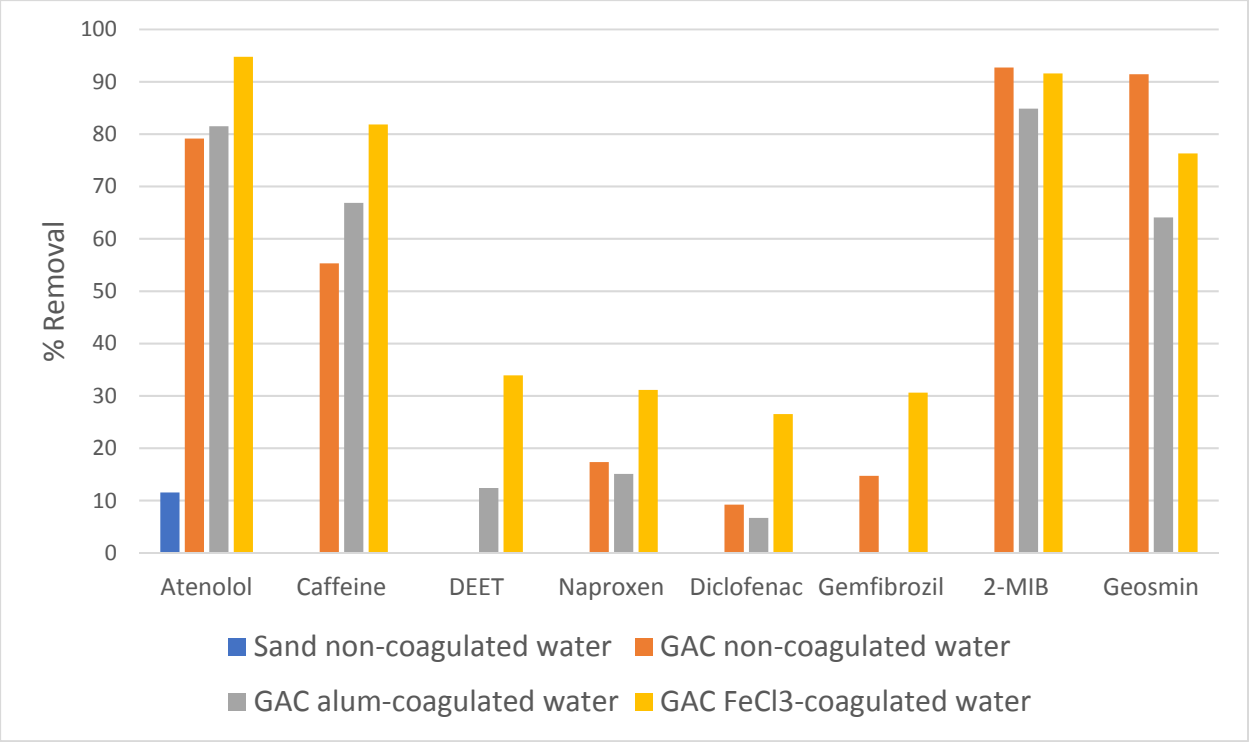


Figure 3. GC-MS and LC-MS/MS data for TrOC removal in the biofilter trains (6 months after start up). Each train was fed synthetic water with 0.5 µg/L of each TrOC.

**Significance**

In coagulation, ferric chloride removed more DOC than did alum. Atenolol, caffeine, DEET, naproxen, diclofenac, and gemfibrozil all showed the highest removal in the biofilter train receiving ferric-coagulated water as compared to the other biofilter trains. For both 2-MIB and geosmin, the highest removal was observed in the GAC biofilter receiving non-coagulated water as compared to the other biofilter trains. The sand biofilter showed removal only of atenolol, but at less than 10%. For TrOC removal, the ferric biofilter train, which had the lowest influent DOC, appears to have better removal. Further sorption studies will be made to determine how much is due to biodegradation versus sorption. The bench-scale columns will continue to be operated under optimized coagulation conditions and their performance will continue to be assessed to see if the trend continues. Additionally, the NOM fractionation will be analyzed for all three cases to compare similarities and differences.

To date this study suggests that optimized ferric chloride coagulation appears to have better removal of a greater variety of TrOCs. Ferric chloride may be more beneficial to use during

treatment since some studies have shown it removes a greater amount of NOM and thus through flocculation and sedimentation reduces particle loading and backwashing of the biofilters

**References Cited**


*Standard Methods for Examination of Water & Wastewater*. 2005. Washington, DC: APHA.

Bell-Ajy K., Abbaszadegan M., Ibrahim E., et al. 2000. *JAWWA* 92(10), 44-58.

Barrett, M., Katz, L., and Taylor, S. 2014 *Transportation Research Record* 2436, 131-138.

Lauderdale, C., Brown, J. 2013.. *WRF, Denver, Colorado*. TC 4346

Manem, J.A. and Rittmann, B.E., 1990. *Water Sci Technol* 22(1-2), pp.329-346.

Martínez, C., Ramírez, N., et al. 2013. *Talanta* 116:937-945.

Matilainen, A., Vepsäläinen, M., Sillanpää, M. 2010. *Adv Coll Interf Sci* 159(2), 189-197.

Nerenberg, R., Rittmann, B.E., Soucie, W.J. 2000. *JAWWA* 92(12), 85–95.

Pressman, J.G., Richardson, S.D., Speth, T.F., Miltner, R.J., Narotsky, M.G., Hunter, III, E.S., Rice, G.E., Teuschler, L.K., McDonald, A., Parvez, S. and Krasner, S.W., 2010.. *Environmental science & technology*, *44*(19), pp.7184-7192.

Rice, J., Via, S.H., Westerhoff, P. 2015. *JAWWA,* 107(1), E571-E581.

Soh Y.C., Roddick F.A., van Leeuwen J.A. 2008. *Water Sci Technol* 58(6), 1173-1179.

Urfer, D., Huck, P.M., Booth, S.D.J., Coffey, B.M. 1997. *JAWWA* 89(12), 83-98.

Vanderford, B.J., Drewes, J.E., et al. 2012. *Water Research Foundation. Report 4167.*

Volk, C.J., Bell, K., Ibrahim, E., et al. 2000. *Water Res* 34(12), 3247-3257.

Zearley, T.L., Summers, R.S., 2012. *Environ Sci Technol* 46(17), 9412–9419.