Biological filtration with and without prior in-line coagulation to reduce UF fouling by secondary effluent
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ABSTRACT

The objectives of this research were to investigate biofiltration prior to ultrafiltration (UF) for treatment of secondary effluent. Biofiltration with and without prior in-line coagulation was assessed for UF membrane fouling reduction. Two parallel pilot-scale biofilters, each with different media (sand vs. anthracite), were operated under identical conditions at a hydraulic loading rate of 0.75 m/h. A component of this investigation included the in-line application of a 1.0 mg/L dose of ferric sulfate prior to an anthracite biofilter. All UF membrane fouling experiments were conducted at bench-scale at a constant flux of 32 L/m²h (LMH). The sand (BF1) and anthracite biofilters (BF2) removed on average 25 and 20%, respectively, of the biopolymer fraction of the effluent organic matter. Humic substances were less well removed at about 10%, while biofilter influent turbidity was reduced by 75 and 70% through BF1 and BF2, respectively. Feeding the UF membrane with biofilter effluent (no prior coagulant addition) substantially reduced both hydraulically reversible and irreversible membrane fouling by up to 60 and 80%, respectively. Hydraulically reversible and irreversible fouling were further reduced (up to 69 and 87%, respectively) by the integration of the in-line coagulation/biofiltration pre-treatment processes compared to biofiltration alone.

Key words | advanced wastewater treatment, biofiltration, fouling reduction, secondary effluent, ultrafiltration membrane

INTRODUCTION

While biological treatment processes are capable of substantial removal of organics found in wastewater, reusing secondary effluent requires some form of additional advanced treatment. Low pressure membrane filtration can play an important role in such additional treatment. It can produce water that may either be suitable for reuse in some non-potable applications, or be fed to downstream processes for even further treatment (e.g. nanofiltration, reverse osmosis) for other higher quality reuse applications. Interest in the application of low pressure membranes as an advanced wastewater treatment has increased the number of research initiatives being conducted and reported upon (Haberkamp et al. 2008; Zheng et al. 2010; Filloux et al. 2012; Pramanik et al. 2014). Despite the expansion in the use of membranes in water and wastewater production, membrane fouling is still an important shortcoming of this technology.

It has been previously suggested that humic substances substantially contribute to membrane fouling (Jucker & Clark 1994; Shon et al. 2006). However, most recent studies have reported that the biopolymer (BP) fraction is responsible for polymeric ultrafiltration (UF) membrane fouling (Fan et al. 2008; Zheng et al. 2010; Peldszus et al. 2011; Filloux et al. 2012; Rahman et al. 2014). Due to the complex and variable composition of effluent organic matter (EfOM), complicated fouling mechanisms, and conflicting
observations related to the identification of foulants of low pressure membranes, further investigation is required.

Fouling affects membrane filtration adversely by reducing permeate flux, increasing energy requirements, decreasing intervals between cleaning, and reducing membrane life (Hatt et al. 2011). Therefore, the mitigation and control of membrane fouling is an important consideration for the effective operation and economic feasibility of the technology. To reduce the concentration of organic foulants in treated wastewater, several pre-treatment processes have been investigated. Biofiltration has some benefits which make it safer and more environmentally-friendly than existing treatment technologies including no chemical addition and less sludge production (if upstream coagulation not practiced). Biofiltration has only relatively recently been investigated as a low pressure membrane pre-treatment for drinking water production (Peldszus et al. 2011; Filloux et al. 2012; Rahman et al. 2014). In those studies, biofiltration was investigated in dual media form (anthracite over sand) at short empty bed contact times (EBCTs) (5–10 min), corresponding to hydraulic loading rates (HLRs) on the order of 5 m/h. There are far fewer studies examining biofiltration to reduce membrane fouling in wastewater for water reuse applications and those were conducted at HLRs in the range of slow sand filtration. Zheng et al. (2009) investigated biofiltration as a pre-treatment to UF for secondary effluent treatment with sand as the support media. In their study, biofiltration was operated at slow sand filtration HLRs (0.25 and 0.5 m/h). Biofiltration has also been investigated as a microfiltration pre-treatment for treating secondary effluent at an EBCT of 40 min corresponding to a HLR of 0.2 m/h (Pramanik et al. 2014), where biological active carbon was employed to provide a higher effective surface area for biofilm development and some absorptive capacity for EfOM removal. Investigation of the performance of biofiltration as a pre-treatment for UF for the treatment of secondary effluent with different organic composition at higher HLRs than those investigated by Zheng et al. (2009) is necessary to demonstrate the viability of the technology. Also, study is needed to determine if differences between non-adsorbing media (e.g. sand and anthracite) exist as it relates to the rate of removal and type of specific organic fractions that contribute most to UF fouling when treating secondary effluent.

Recently, some studies have demonstrated the effectiveness of low coagulant dosages for reducing low pressure membrane fouling (Wang & Wang 2006; Delgado-Diaz et al. 2012; Zheng et al. 2012; Wray et al. 2014). In those applications, coagulants were continuously added in-line prior to the membrane without removing particles (Wang & Wang 2006) or altering feed water composition (Liu & Kim 2008). A small footprint is required for in-line coagulation in comparison to conventional coagulation-flocculation with or without sedimentation (Zheng et al. 2012), and lower coagulant dosages decrease both cost and sludge production making in-line coagulation an attractive and competitive alternative. Given these observations, it is possible that a combination of in-line coagulation and biofiltration pre-treatments has the potential to better achieve two important treatment targets (fouling mitigation and high permeate quality). Azzeh et al. (2015) reported the effectiveness of combining in-line coagulation (<0.5 mg/L alum) prior to biofiltration for reducing UF fouling treating river water (Otonabee River, Ontario, Canada). The investigation of such combinations for secondary effluent treatment by membrane filtration is needed.

The initial work in this study characterized the secondary effluent being used, including determining the concentrations of the organic fractions that have been found in previous investigations to be responsible for reversible and irreversible UF fouling. The study then investigated sand vs. anthracite biofiltration as a pre-treatment for UF as it relates to reversible and irreversible fouling reduction. The impacts of in-line coagulation prior to anthracite biofiltration on biofilter performance and the subsequent reduction of UF fouling were also examined.

**METHODS**

**Source water**

The secondary effluent investigated in this study was collected from the Waterloo wastewater treatment plant (WWTP), which treats approximately 45,000 m³/d of predominantly domestic wastewater from about 137,000 residents in the City of Waterloo, Ontario, Canada. The raw sewage was treated by primary clarification where ferrous chloride was added for phosphorus removal. This was followed by...
conventional activated sludge as a biological treatment and then secondary settling tanks. The secondary effluent is UV-disinfected before being discharged into the Grand River.

Secondary effluent following UV exposure was collected around 9:00 a.m. twice per week in three 200 L polyethylene drums and immediately transferred to the University of Waterloo (approximately 3.5 km from the WWTP) and stored in a holding tank. Pumping to the biofilters was immediately initiated. Water in the tank was continually mixed and allowed to increase to room temperature (23°C).

**Experimental set-up**

The biofiltration set-up was constructed and operated in a wastewater pilot plant on the campus of the University of Waterloo. It consisted of two parallel glass columns 5.1 cm in internal diameter and 2.1 m high with an effective bed depth of 75 cm supported by 10 cm of (3 mm) gravel (Figure 1). There was 125 cm of water above the media in each column and the overflow was 200 cm from the base of the column. The biofilters were fed with a peristaltic digital drive pump (model No. 7550-50, 1.6–100 rpm, Cole-Parmer Instrument Company, Barrington, USA) and backwashed with a model No. 7553-70, 6–600 rpm pump (Cole-Parmer Instrument Company, Barrington, USA). To monitor water flow rate through the biofilter, flowmeters (Model 2L09, 5–50 cm³/min water, VWR International, USA) were located in the effluent tubing. An air flowmeter was used to adjust the air flow rate during backwashing (Model 2L09, 10–400 CCM air, VWR International, USA). Polyethylene tanks were used for feed water storage and effluent water collection. Sand and anthracite were compared as biofilter media (BF1 and BF2, respectively). The uniformity coefficient of both media was 1.5 while the
effective size was 0.5 and 1.0 mm for sand and anthracite, respectively. The biofilters were operated in down flow mode (at constant head, constant rate) under the same operating conditions in order to compare the two media. The EBCT of each biofilter was 60 min corresponding to a HLR of 0.75 m/h. During the first 6 months of biofilter operation they were backwashed with their own effluent once per week. The backwash frequency was then twice weekly until the end of the experimental period.

The membrane module (ZeeWeed-1®, GE Water and Process Technologies, Oakville, Ontario, Canada) contained a bundle of 15 cm long polyvinylidene fluoride hollow fibers (500 series), and the operation mode was outside-in at a constant permeate flux of 32 L/m² h (LMH). The inner fiber diameter was 0.8 mm and the outer diameter was 1.95 mm. The membrane module had a nominal surface area of 0.047 m² and the MWCO was 400 KDa (approximately 40 nm pore size). The UF module was positioned vertically in a clear polyvinyl chloride cylindrical tank. The setup was designed to cycle automatically with 30 min permeation followed by backwashing with water and air sparging for 20 sec. The module tank was then drained (30 sec) and refilled again with the investigated water (36 sec). For continuous measurement during the experiments, a temperature sensor and flowmeter monitor (Model LC alpha controller, Alicat Scientific, Tucson, USA) were connected to a data logger (HOBO Energy Logger, model H22-001, Onset, Cape Cod, Massachusetts, USA). A digital flowmeter was used to maintain a constant pre-determined permeate flow rate through the whole UF experiment. It was connected to a digital permeation pump (Masterflex® L/S® drive model number 07550-50; Cole-Parmer Canada) that was programmed to operate at a constant flow rate (25 mL/min). The flowmeter measured the actual permeate flow rate every 10 sec and the data were recorded by data logger. Transmembrane pressure (TMP) was measured using a pressure transducer (model 68075-02, Cole-Parmer, Montreal, Canada) which was connected to the data logger as well. Fouling rates were determined using TMP data after correction for temperature to 20 °C. Additional details regarding the bench-scale configuration and operation are available in El-Hadidy (2011) and Rahman (2013).

To measure the UF fouling rate before and after pretreatment using the same batch of collected secondary effluent, the run length was set to end at 24 h or when the TMP reached 8 psi (55.2 kPa). Chemical cleaning was performed after each experiment by soaking the membrane in sodium hypochlorite (200 mg/L) for a minimum of 5 h, followed by a citric acid solution (5 g/L) soak for another 5 h. If the membrane was not immediately placed back into use following chemical cleaning, it was stored in a glass jar containing deionized water at 4 °C. The UF module was integrity tested using a pressure calibrator (Meri-cal DP20011, Meriam Instruments, Ohio, USA) prior to every experiment. The maximum allowable pressure drop through the membrane was 0.5 psi (2.1 kPa) over a period of 2 min (based on the manufacturer’s recommendation). To check cleaning effectiveness, clean water permeability tests were conducted using deionized water before each experiment.

For the in-line coagulation experiments, a dose of 1.0 mg ferric sulfate/L was pumped into the influent tubing prior to BF2 (anthracite media) by a peristaltic digital drive pump (Masterflex® L/S® model no. 7550-50, 1.6–100 rpm, Cole-Parmer Instrument Company, Barrington, USA) (Figure 2). The secondary effluent and coagulant then passed through an in-line static mixer (Koflo Corporation, Cary, IL). Following the static mixer, 1.0 m of tubing remained before the inlet of the biofilter. The contact time between the addition of the coagulant and entry into the biofilter was 20 sec.

Analyses

Water samples were collected once every 2 weeks from the inlet raw water (RW) and the outlet of each biofilter (sand media [BF1], anthracite media [BF2]) and from UF permeate in clean glass 1 L bottles before backwashing the biofilter. Samples were collected at 25 mL/min, the same flow rate as the biofilters, over approximately 1 h to avoid unnecessarily disturbing the media. Several water quality parameters including turbidity, pH, temperature, UV₂₅⁴ absorbance, and specific UV absorbance (SUVA) were monitored. Total organic carbon (TOC) and dissolved organic carbon (DOC) were analyzed using an OI-Analytical TOC analyser (Model 1030, College Station, TX, USA) by combustion as per Standard Method 5310B (APHA/AWWA/WEF 2012). Natural organic matter (NOM) constituents were identified using liquid chromatography–organic carbon detection (LC-OCD).
Model 8 (DOC-LABOR, Karlsruhe, Germany) as per the method of Huber et al. (2011). Before analysis, samples were pre-filtered for DOC and LC-OCD through pre-rinsed 0.45 μm PVDF membrane filters (Pall Supor® Membrane Disc Filters, 0.45 μm, 47 mm plain, VWR International, USA). Samples were diluted with ultrapure water if the DOC in the sample exceeded 5 mg/L. Ammonia, nitrate, nitrite, total nitrogen, and total phosphorus data were acquired from the City of Waterloo WWTP records. All were measured as per APHA/AWWA/WEF (2012).

RESULTS AND DISCUSSION

Secondary effluent composition

The secondary effluent ranged in temperature from 10.0 to 25.0 °C averaging 16.0 ± 3.5 °C at the time of collection. Experiments were conducted at room temperature (~23 °C). The selected secondary effluent quality as monitored during the investigated period from January 2014 to April 2015 is presented in Table 1. The data show that there was no substantial variability in DOC and the major NOM fractions (BP and humics) measured by LC-OCD throughout this long-term study. The humic substances, hydrophobic compounds with high molecular weight (1,000–20,000 Da), made up the largest fraction in all samples accounting for an average of 34% of the DOC while BP, proteins and polysaccharides materials (over 20,000 Da), accounted for 18% of the DOC. The remaining 30% of the DOC consisted of low molecular weight (LMW) acids (16%) and LMW neutrals (14%). The BP maximum concentration is a single relatively high value (2.8 mg/L) observed on March 26, 2015. The next highest concentration was 1.8 mg/L. The average BP concentration was 1.3 mg/L which is relatively high when compared with BP concentrations of secondary effluents investigated previously in the literature (Zheng et al. 2010; Pramanik et al. 2014). No seasonal impact on BP concentrations were observed during the investigated period (data not shown). UV_{254} absorbance ranged from 0.108 to 0.167 cm⁻¹ and SUVA values were less than 2.0 L/(m/mg). SUVA reflects the aromatic content of organic matter and a low value (<3.0) indicates that the secondary
DOCS was relatively hydrophilic and less aromatic (Edzwald 1993). There was substantial variability in TOC, turbidity, nitrate, and TKN during the investigated period. Higher turbidities were encountered in colder water at least in the early stage of this study.

Rejection of NOM constituents and turbidity by UF

Figure 3 illustrates the average percentage removal of NOM constituents and turbidity rejection by UF. It can be seen that the average rejections of DOC through UF were relatively low (around 17%) while there was almost no rejection of humic substances (less than 5%). By contrast, the average rejections of BP and turbidity through the UF were 70 and 95%, respectively. Some previous studies (e.g. Shon et al. 2006) have reported that hydrophobic organics (e.g. humic substances) were the largest contributors to membrane fouling. Other recent studies have reported BP as being the most important low pressure membrane foulants when treating drinking water (Amy 2008; Hallé et al. 2009; Peldszus et al. 2012; Rahman et al. 2014). Similar findings with respect to BP have been reported by other authors (Fan et al. 2008; Haberkamp et al. 2008; Zheng et al. 2010; Pramanik et al. 2014) when treating domestic wastewater by low pressure membranes. Based on the data presented in Figure 3, it can be seen that BP are likely to be a significant contributor to UF fouling when treating secondary effluent (at least for the type of UF membrane studied here). This interpretation is supported by Figure 4 as discussed below. In addition, particulate substances (measured as turbidity) in secondary effluent may play an important role in UF fouling and when combined with organic components, can lead to excessive fouling as reported by Hallé et al. (2009) and Peldszus et al. (2011) using river water.

| Parameter       | Unit    | Average (±SD) | Min  | Max  | Number of samples |
|-----------------|---------|---------------|------|------|-------------------|
| Temperaturea    | °C      | 16.0 (± 3.5)  | 10.3 | 25.0 | 41                |
| pHb             | –       | 7.5 (± 0.3)   | 7.1  | 8.4  | 32                |
| Turbidityb      | NTU     | 4.5 (± 5.6)   | 1.1  | 10.3 | 32                |
| TOCb            | mg/L    | 14.6 (± 5.6)  | 5.6  | 24.0 | 16                |
| DOCb            | mg/L    | 8.9 (± 1.1)   | 6.2  | 11.0 | 41                |
| BPb             | mg/L    | 1.3 (± 0.4)   | 0.6  | 2.8  | 41                |
| Humicsb         | mg/L    | 3.1 (± 0.3)   | 2.2  | 3.6  | 41                |
| UVb             | cm⁻¹    | 0.158 (± 0.020) | 0.108 | 0.167 | 40                |
| SUVAb           | L/(mg/m) | 1.5 (± 0.2)  | 1.2  | 2.0  | 38                |
| TSSc            | mg/L    | 4.2 (± 2.5)   | 1.6  | 12.2 | 44                |
| Ammoniac        | mg/L    | 20.6 (± 5.8)  | 8.6  | 35.0 | 44                |
| Nitratec        | mg/L    | 9.5 (± 4.5)   | 2.0  | 20.8 | 44                |
| Nitritec        | mg/L    | 0.7 (± 0.4)   | 0.2  | 1.8  | 44                |
| TKNc            | mg/L    | 25.0 (± 6.7)  | 11.9 | 38.0 | 44                |
| Total Pc        | mg/L    | 0.3 (± 0.1)   | 0.12 | 0.5  | 44                |

*aMeasured in the field when collecting secondary effluent.
*bMeasured at University of Waterloo laboratories.
*cMeasured at Waterloo WWTP laboratories. TSS, total suspended solids. TKN, total Kjeldahl nitrogen.
Impact of biofiltration on feed water (secondary effluent) quality

Figure 4 shows the LC-OCD chromatogram for secondary effluent, UF permeate when treating secondary effluent directly, as well as biofilter effluents. The figure illustrates that BP – appearing as the first peak at elution times from 20–40 min – were the most rejected by UF, while the retention of humic substances (second peak) and other DOC fractions through UF was significantly lower. The figure also illustrates the removal of different DOC fractions through the biofilter and the principal change during biofiltration of secondary effluent is occurring in the BP fraction (first peak). On the other hand, the proportional removals of humic substances and LMW compounds were much lower. The removal of BP through aerobic biodegradation is well documented in surface water treatment (Hallé et al. 2009; Rahman et al. 2014; Siembida-Lösch et al. 2015) as a biofiltration process and in secondary effluent treatment (Zheng et al. 2010; Pramanik et al. 2014) using slow sand filtration. The average BP concentrations in effluents of BF1 and BF2 were 0.8 and 1.0 mg/L, respectively, compared with the average concentration in secondary effluent of 1.3 mg/L ($n = 41$). In general, the lowest concentrations of organic compounds were measured in the effluent of BF1 (sand). A total of 44 samples were collected from secondary effluent and biofilter effluents between January 2014 and April 2015. A summary of organic compound and turbidity removal through the biofilters is shown in Figure 5. Reductions of $18 \pm 10\%$ (mean $\pm$ standard deviation) and $26 \pm 10\%$ in DOC and BP, respectively, were observed through BF1 while slightly lower reductions ($16 \pm 8$ and $19 \pm 12\%$) of...
DOC and BP, respectively, were observed through BF2 ($n = 44$). The differences between BF1 and BF2 in terms of removal of BP were statistically significant (paired $t$-test, $\alpha = 0.05$). While humics make up the dominant DOC fraction in secondary effluent, they were not well removed through biofiltration. This has been observed previously in drinking water pre-treatment (e.g. Hallé et al. 2009; Rahman et al. 2014). The average humic substance removals through BF1 and BF2 were $14 \pm 11$ and $11 \pm 10\%$, respectively. The average turbidity reduction achieved by BF1 and BF2 was $76 \pm 15$ and $70 \pm 19\%$, respectively. Statistically there was no difference between BF1 and BF2 in the reduction of turbidity or humic substances (paired $t$-test, $\alpha = 0.05$).

**Impact of biofiltration on UF fouling**

The performance of UF treating secondary effluent and biofilter effluents (BF1 and BF2) was investigated in four replicate experiments (January–May, representing three seasons). Each experiment was conducted with the same batch of secondary effluent. They were evaluated by plotting the change in TMP vs. filtration time. Figure 6 provides an example of a UF fouling experiment comparing secondary effluent and biofilter effluents (conducted from February 27 to March 5, 2015). During the filtration of secondary effluent, a rapid increase in TMP was observed, reaching 6.0 psi (41.4 kPa) after only 12 h of filtration. On the other hand, operating the UF with effluent from BF1 or BF2 substantially improved performance and there was a clearly-observable lower rate of fouling development. After a filtration time of 23 h, the maximum normalized TMPs reached by BF1 and BF2 effluents were 3.0 and 4.0 psi (20.7 and 27.6 kPa), respectively. Similar results were obtained for the remainder of the experiments that were conducted from January to May 2015 (four in total) (Aly 2015). Comparing the change in TMP for the secondary effluent and biofilter effluents demonstrated the impact of the dissolved organic compounds and the particulate matter on the development of UF fouling. The BP and turbidity in secondary effluent in the experiment illustrated in Figure 6 were 1.5 mg/L and 3.5 NTU. The removal of BP through BF1 and BF2 averaged 32 and 30\%, respectively, which led to a less rapid TMP increase compared with the direct filtration of secondary effluent (no pre-treatment before UF). The concentrations of BP in the effluents of BF1 and BF2 were virtually identical at 1.05 and 1.03 mg/L, respectively, while the turbidity values were 0.5 NTU in BF1 effluent compared with 1.2 NTU in the effluent of BF2 (in the experiment illustrated in Figure 6). Based on these data, it can be seen that the deposition of particles (not only BP) appear to have had an effect on UF fouling. Hence, the TMP improvement obtained by using BF1 effluent (when compared with BF2 effluent) appears to be the result of lower particulate amounts, not differences in BP concentrations, at least for this example.

Figure 6 | UF TMP when fed with RW (secondary effluent) vs. when fed with biofilter effluent (experiment conducted from February 27 to March 5, 2015).
It is well known that increasing TMP during filtration cycles is attributable to the development of hydraulically reversible and/or irreversible fouling. In the experiment illustrated in Figure 6, the use of BF1 effluent yielded 62 and 83% reductions in reversible and irreversible fouling, respectively, during the first 12 h of filtration time. The use of BF2 effluent also improved the UF performance, where 48 and 80% reductions in reversible and irreversible fouling, respectively, were observed. The reductions in reversible and irreversible fouling rates were calculated based on average values of reversible and irreversible fouling determined for each run (e.g. secondary effluent vs. BF1 and BF2 effluents). Hydraulically reversible fouling values were calculated as the average ΔTMP from all filtration cycles in each experiment, whereas ΔTMP in any cycle (30 min) was calculated by subtracting the TMP measured at the start of the cycle from the TMP measured at the end of the previous cycle before backwashing. The values of TMP were taken every 2 min after the start and 2 min before the end of the filtration cycle (i.e. the TMP value at t = 0.0 min was not used). Hydraulically irreversible fouling is defined as the difference in the TMP at the start and the end of each experiment and can be calculated by subtracting the initial TMP of the last cycle from the initial TMP of the first cycle of the experiment divided by the filtration time (h). When using the secondary effluent as UF feed, there was a dramatic increase in hydraulically reversible fouling reaching 1.5 psi/h (10.3 kPa/h) within the first 6 h. Using the effluents from BF1 and BF2 as feed for UF reduced the rate at which hydraulically reversible fouling occurred. The hydraulically reversible fouling values reached 1.0 psi/h (6.9 kPa/h) at the end of the experiment (24 h) for both BF1 and BF2, however, lower values were observed using BF1 effluent during different cycles. Hydraulically irreversible fouling was also reduced when the UF was fed with biofilter effluents (additional details can be found in Aly (2015)).

BP are comprised of a mixture of polysaccharides and protein-like materials (Huber et al. 2011). Based on the nitrogen/carbon (N/C) ratio obtained from the organic carbon detector (OCD) and organic nitrogen detector (ONC) obtained from the LC-OCD, approximate values of the protein content of the BP can be estimated (Filloux et al. 2012; Siembida-Lösch et al. 2015). In addition to the quantitative removal of particulates and BP through biofiltration, there was a dramatic reduction of proteins as well (raw data not shown). The concentration of proteins in secondary effluent ranged from 0.05 to 0.31 mg/L, constituting about 13% of the BP (on average). The concentration of proteins in BF1 effluent varied between 0.02 and 0.20 mg/L and in BF2 effluent varied between 0.04 and 0.20 mg/L. In general, BF1 (sand) removed more protein than BF2 (anthracite) at 62 ± 17% and 49 ± 18%, respectively, with these removals being significantly different (paired t-test, α = 0.05). In this study, there was an average reduction of 85 ± 9% of protein through UF, regardless of the type of feed water (e.g. secondary effluent or biofilter effluent), which reflected the importance of those compounds with respect to UF fouling. The significance of protein-like materials present in secondary effluent in UF fouling has been previously reported (Haberkamp et al. 2008; Henderson et al. 2011; Filloux et al. 2012). Despite the fact that biologically treated wastewater (e.g. secondary effluent) generally contains a higher protein content than that in surface water, the same phenomena was observed when UF membranes were used in surface water treatment (Hallé et al. 2009; Peldszus et al. 2011). However, Pramanik et al. (2014) reported that polysaccharides (carbon-like materials) were retained more than proteins, causing severe membrane fouling when treating biologically treated wastewater.

Since UF fouling reduction with biofiltration is attributable to the removal/transformation of BP and particulates, the relationship between their concentrations and UF fouling merits investigation. Figures 7 and 8 plot BP concentrations, humic substance concentrations, and turbidity in UF feed water (from both biofilter effluents) vs. hydraulically reversible and irreversible fouling rates, respectively. As expected, there was no relationship observed between humic substances and reversible or irreversible fouling for UF (p > 0.05, t-test). A potential correlation between turbidity in biofilter effluent and reversible fouling may exist (R² = 0.44), while turbidity was not correlated with irreversible fouling. Further analysis of data illustrated in Figures 6 and 7 revealed that a statistically significant correlation between turbidity in the biofilter effluent and reversible fouling did exist (r = 0.67, p < 0.001, t-test). This observation is consistent with previous drinking water studies (Hallé et al.
where most particulate compounds deposit on the membrane surface producing a cake layer which can be removed through backpulsing/flushing with water (Howe & Clark 2002; Gao et al. 2011). The fact that the correlation observed between turbidity and reversible fouling was not higher implies that particulate compounds alone may not be directly responsible for the reversible fouling production.

The results shown in the two figures indicate that BP concentrations in UF feed water (biofilter effluent) were positively correlated with both reversible ($r$ [df = 7] = 0.78, $p < 0.001$, t-test) and irreversible fouling ($r$ [df = 7] = 0.81, $p < 0.001$, t-test). In a recent study conducted by Wang (2014) to investigate the impact of ozonation-biofiltration pre-treatment in controlling UF fouling in a full-scale drinking water treatment plant, no correlation was found between BP and hydraulically irreversible fouling, while BP in feed water were linearly correlated with hydraulically reversible fouling. Hallé et al. (2009) reported similar findings in a bench-scale UF experiment treating surface water. Similarly, Haberkamp et al. (2011) reported a high correlation between hydraulically reversible fouling of UF membranes and BP content in secondary effluent. On the other hand, Rahman et al. (2014) reported that BP concentration in UF feed water (surface water or biofilter effluents) was highly correlated ($R^2 = 0.95$) with hydraulically irreversible fouling. Also, Peiris et al. (2010) and Peldszus et al. (2011) observed a high correlation. 

Figure 7 | Relationship between BP, humics, and turbidity in membrane feed (biofilter effluent) vs. reversible UF fouling. $n = 9$ for turbidity and 8 for humics and BP.

Figure 8 | Relationship between BP, humics, and turbidity in membrane feed (biofilter effluent) vs. irreversible UF fouling. $n = 9$ for turbidity and 8 for humics and BP.
between protein content in the BP fraction and irreversible fouling of UF membranes. In these two studies, a weak correlation between BP and hydraulically reversible fouling was observed.

It is important to mention that, in the current study, when the membrane was fed with secondary effluent without pretreatment, there was no correlation between BP concentration in secondary effluent and reversible or irreversible fouling. However, irreversible fouling was correlated with the particulate matter (measured as turbidity) in secondary effluent (additional detail can be found in Aly (2015)).

It has been reported that the fouling mechanism of BP is primarily attributable to pore blocking (Zheng et al. 2009). In the early stages of filtration, open pores are first blocked by molecules equivalent in diameter to the membrane pores. As more molecules accumulate on the membrane surface, a cake layer then forms (Haberkamp et al. 2008). It has been suggested that a combined fouling layer of BP and particulate matter can change the reversible fouling to irreversible fouling (Hallé et al. 2009; Peldszus et al. 2011) or change the membrane separation characteristics (Haberkamp et al. 2011), which in turn can provide unexpected/unusual correlations between compounds present in UF feed water and UF fouling. Figure 9(a) and 9(b) show the correlation between turbidity and BP concentrations with the irreversible fouling of the UF membrane when fed with secondary effluent and biofilter effluents, respectively. Since investigating the combined impact of BP and turbidity on UF fouling was not within the scope of the current study and there was no way to perform an independent experiment, Figure 9(a) and 9(b)

![Figure 9](https://iwaponline.com/jwrd/article-pdf/8/2/176/240637/jwrd0080176.pdf)
was drawn based on the data obtained from UF experiments that were conducted to investigate the impact of biofiltration as a UF pre-treatment. It was observed that both BP and turbidity impacted membrane fouling and any increase in these compounds substantially increased reversible (data not shown) and irreversible fouling. Also, the combined impact of BP and particles on UF fouling appeared to have more impact when the membrane was fed with secondary effluent. These observations help to explain why BP in this study were correlated with both reversible and irreversible fouling when the membrane was fed with biofilter effluents. Due to the high BP content of the investigated secondary effluent (1.8 ± 0.1 mg/L) (even after biofiltration, 1.4 ± 0.2 mg/L vs. about 0.1–0.5 in surface water), most of the UF membrane pores can be rapidly blocked. With more BP delivered to the UF surface a cake layer forms which is likely accompanied by the particulate matter present in the feed water (secondary effluent or biofilter effluents). These fundamentals can also explain why only turbidity correlated with reversible and irreversible UF fouling when fed with secondary effluent without any pre-treatment.

**Impact of in-line coagulation on biofilter performance**

An investigation of the impact of in-line coagulation on biofiltration was conducted from April 13 to May 30, 2015. The biofilter containing anthracite media was selected for this experiment as only one could be tested and the impact of feeding a coagulant on headloss was uncertain (the anthracite effective size was 1.0 mm vs. 0.5 mm for the sand). The experiment began 15 months after this biofilter was brought on-line. Figure 10 summarizes the average removal of DOC, BP, humic substances, and turbidity through the biofilter alone and following the combination of in-line coagulation addition (1.0 mg/L ferric sulfate) and subsequent biofiltration. The coagulant and dose were selected based on a comparison of four different coagulant types and several feed concentrations for this particular secondary effluent (Aly 2015).

Biofiltration alone improved the secondary effluent quality by reducing the concentration of organics and particles. The average DOC removal through the biofilter was 13 ± 6%, which is comparable to removals reported in previous studies investigating biofiltration for river water treatment (Hallé et al. 2009; Peldszus et al. 2012; Rahman et al. 2014). The average BP removal was 29 ± 5%, while a slight reduction of humic substances (14 ± 3%) was observed through the biofilter. The average removal of turbidity achieved by the biofilter was 77 ± 6%.

A ferric sulfate dose of 1.0 mg/L (5.0 × 10⁻³ mmole Fe³⁺/L) prior to biofiltration further improved the performance of the biofilter for the reduction of organics and particles. At this low dosage of applied coagulant, an additional 3 and 6 percentage points of DOC and humic substances removals were observed, respectively. A statistically significant difference (paired t-test, α = 0.05) in the reduction of BP and turbidity was found to be attributable to in-line coagulant addition, where the average removals of BP and turbidity increased to 40 ± 4 and 88 ± 0.6%, respectively. Azzeh et al. (2015) reported that the application of alum doses of 0.1 and 0.25 mg/L (3.0 × 10⁻⁴ and 8.0 × 10⁻⁴ mmole Al³⁺/L, respectively) prior to biofiltration in river water treatment removed an additional 3 and 4 percentage points of BP, respectively. In the present study, the application of ferric sulfate at 1.0 mg/L resulted in an additional 10 percentage points of BP removal. This observation emphasizes the impact of coagulant type and dosage on biofiltration performance. Despite the improvement in organics and particle removal, which is attributed to size modification by coagulant addition (Zheng et al. 2012), no adverse impact was associated with in-line coagulant addition with respect to biofilter head loss. However, this observation would require further investigation to confirm if this would apply in real-world scenarios.
Impact of the pre-treatment combination on UF performance

When the UF membrane was fed with secondary effluent, fouling rapidly developed, while there was a substantial reduction in fouling development when the UF membrane was operated with biofilter effluent without coagulant or after in-line coagulant addition prior to the biofilter. Figures 11 and 12 illustrate the change in reversible and irreversible fouling, respectively, for a UF experiment conducted from April 21 to 25, 2015 for secondary effluent and biofilter effluents (with and without prior in-line coagulant). Membrane filtration of BF2 effluent (no coagulant) resulted in 31 and 74% reductions in the reversible and irreversible fouling, respectively, following 12 h of filtration time. At a ferric sulfate dose of 1.0 mg/L, added prior to BF2, reductions in the reversible and irreversible fouling of 69 and 87%, respectively, were observed. When using secondary effluent as UF feed, the hydraulically reversible fouling reached 1.5 psi/h (10.3 kPa/h) within the first 12 filtration cycles (one cycle = 30 min permeation). The hydraulically irreversible fouling values reached 1.5 psi/h (10.3 kPa/h) at the end of the experiment (24h) for BF2 (no coagulant), however, even lower values were observed for BF2 effluent with prior in-line coagulant addition (0.5 psi/h (5.4 kPa/h) after 24 h). The hydraulically irreversible fouling rate can be determined by monitoring the progressive increase of the initial TMP at the beginning of each filtration cycle (Figure 12). Hydraulically irreversible fouling rapidly increased to reach almost 6.0 psi/h (41.4 kPa/h) at the end of the experiment (24 h) when the secondary effluent was used as UF feed. On the other hand, the values at the end of the 24 h experiment were 2.7 and 2.0 psi/h (18.6 and 13.8 kPa/h) for BF2 effluent and BF2 effluent with coagulant addition, respectively.

The pre-treatment strategy combination of in-line coagulation at 1.0 mg/L ferric sulfate prior to biofiltration removed more of the NOM fractions (e.g. BP and humic substances) and turbidity which impacted the overall process and produced better quality permeated water (Table 2). On the other hand, there was no impact of this combination (in-line coagulation prior to biofiltration) on the reduction of turbidity through the UF membrane likely due to the already low permeate turbidities which never exceeded 0.2 NTU (with or without pre-treatment). The DOC removals (from RW) through the UF with prior biofiltration and with prior in-line coagulation/biofiltration were 32 and 44%, respectively. The TOC values measured in parallel with the DOC results are considered anomalous, for reasons that are not entirely clear but may relate to an analytical issue. These data may be found in Aly (2015). Since the focus of this investigation was the reduction of UF foulants (e.g. BP fraction and particles), the potential problem with the TOC data was, however, not considered crucial to the interpretation of the overall results.

Extended run experiment

A 48 h run was conducted in the period from May 4 to 9. The UF was operated under the same conditions (i.e. flux and at room temperature) as in the previous experiments. Figure 13
illustrates the change in the irreversible fouling rates for two different UF experiments using biofilter effluent (with and without prior in-line coagulant addition). One was conducted for the usual filtration time (24 h) from April 21 to 25, 2015 and the other was conducted for the extended filtration time (48 h) from May 4 to 9, 2015. In each of the two experiments, there was a reduction in reversible fouling development when the UF was fed with the biofilter effluent with prior in-line coagulant addition, however, the greater reduction was observed during the shorter (24 h) experiment (data not shown).

Hydraulically irreversible fouling was also reduced when the UF was fed with biofilter effluent with prior in-line coagulant addition. The hydraulically irreversible fouling values reached 2.5 psi/h (17.2 kPa/h) at the end of the two experiments (24 and 48 h) for biofilter effluent (no coagulant). After 48 h of filtration run, the hydraulically irreversible fouling values were 4.5 and 1.0 psi/h (31.0 and 6.9 kPa/h) when the UF was fed with biofilter effluent (no coagulant) and biofilter effluent when preceded by 1.0 mg/L ferric sulfate addition, respectively. Slowing the rate of irreversible fouling can reduce the frequency of chemical cleaning leading to the extension of membrane service life.

In-line coagulation enhanced the conditions for the subsequent removal of particles and organics through the biofilter providing additional improvement in the performance of the UF. At such low dosages, coagulants alter the characteristics of colloids and organics by reducing surface charge through charge neutralization leading to the production of aggregates of fine particles and organic material. The aggregated compounds can then be more easily rejected through biofiltration by straining, providing additional removal of organics in addition to biodegradation by attached filter biomass.

**CONCLUSIONS**

This study investigated the pre-treatment of secondary effluent for reuse by biofiltration and, in-line coagulation and biofiltration in series, prior to UF. Two parallel pilot-scale

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**Table 2** Average concentration and standard deviations for selected parameters for RW and following various treatment processes, when comparing biofiltration pre-treatment with and without prior coagulation ($n = 4$)

| Parameter       | Unit       | RW (secondary effluent) | BF2 effluent | In-line coagulation + BF2 | BF2 + UF | In-line coagulation + BF2 + UF |
|-----------------|------------|-------------------------|--------------|---------------------------|----------|-------------------------------|
| DOC (LC-OCD)    | mg/L       | 9.8 ± 0.8               | 8.5 ± 0.8    | 7.4 ± 1.6                 | 6.7 ± 0.5| 5.5 ± 1.0                     |
| BP              | mg/L       | 1.8 ± 0.1               | 1.4 ± 0.2    | 1.1 ± 0.1                 | 0.6 ± 0.3| 0.5 ± 0.3                     |
| HS              | mg/L       | 3.5 ± 0.6               | 3.2 ± 0.3    | 2.9 ± 0.4                 | 2.8 ± 0.3| 2.3 ± 0.2                     |
| UV$_{254}$      | cm$^{-1}$  | 0.14 ± 0.01             | 0.13 ± 0.01  | 0.11 ± 0.01               | 0.12 ± 0.01| 0.09 ± 0.01                     |
| Turbidity       | NTU        | 5.0 ± 1.3               | 1.2 ± 0.6    | 0.6 ± 0.1                 | 0.2 ± 0.1| 0.2 ± 0.1                     |

HS, humic substances.

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Figure 13 | Hydraulically irreversible fouling rates for a UF membrane fed with BF2 effluent and in-line coagulant prior to BF2 in 24 and 48 h experiments.
biofilters (BF1-sand and BF2-anthracite) were operated under identical conditions at an HLR of 0.75 m/h and were followed by a bench-scale UF membrane operated at a constant flux of 32 L/m² h (LMH). In some experiments, ferric sulfate was applied as an in-line coagulant prior to the anthracite-containing biofilter. Based on this experimental configuration and the secondary effluent utilized, the following can be concluded:

- Biofiltration improved secondary effluent characteristics by reducing organic compound concentrations and turbidity. BP (polysaccharides and proteins) were the largest group of DOC constituents removed through the biofilters with higher removals being obtained by the sand biofilter, 26 vs. 19% in the anthracite biofilter. Humic substances were less well removed through either of the two biofilters (14 and 11%, for BF1 and BF2, respectively).
- Biofiltration dramatically improved the performance of downstream UF membranes by slowing the development of fouling. BF1 effluent feed yielded 62 and 83% reductions in reversible and irreversible fouling, respectively, while BF2 effluent as a feed led to 48 and 80% reductions in reversible and irreversible fouling, respectively. The observed reduction in the UF fouling rate is attributed to the removal/transformation of BP (especially proteins) and turbidity through biofiltration. Both reversible and irreversible fouling were correlated with BP concentrations in biofiltered secondary effluent. Particulate matter was weakly correlated with UF reversible fouling. This study demonstrated that a combined layer of organic compounds (e.g. BP) and particulate matter can develop leading to an increase in irreversible fouling.
- In-line coagulation prior to biofiltration further improved the performance of an anthracite media-containing biofilter by reducing organic matter concentrations and particulates without any adverse impact of in-line coagulant addition on filter operation. The most dramatic impact of in-line coagulation prior to biofiltration was observed in the reduction of irreversible fouling (especially over time) which is ultimately more important than reversible fouling for sustainable membrane operation. For example, a ferric sulfate dose of 1.0 mg/L, added prior to the anthracite biofilter, reduced the reversible and irreversible fouling by 69 and 87%, respectively.
- Substantially improved UF permeate quality resulted from the integrated in-line coagulation and biofiltration processes.

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