

In-line coagulation assessment for ultrafiltration fouling reduction to treat secondary effluent for water reuse

Samia A. Aly, William B. Anderson  and Peter M. Huck 

ABSTRACT

Low pressure membranes are attracting attention for their potential to improve secondary effluent quality, but membrane fouling can limit their widespread applicability. In this study, in-line coagulation as pre-treatment to ultrafiltration (UF) was investigated using a bench-scale hollow fiber membrane at a constant flux of 33 L/m² h. Membrane fouling was monitored by observing change in trans-membrane pressure when the membrane was fed with secondary effluent and in-line coagulated secondary effluent over a 24-h period. The impact of four coagulants at different dosages on reversible and irreversible membrane fouling and permeate quality was studied. It was found that in-line coagulation improved UF performance to varying degrees depending on coagulant type and dosage. Generally, higher reduction of fouling was achieved by increasing coagulant dosage within the 0.5–5.0 mg/L range investigated. Ferric-based coagulants were better than aluminum-based coagulants with respect to improving membrane performance for the secondary effluent investigated, even at low dosages (0.5 mg/L). Further investigations are required to determine how in-line coagulation affects removal of organic compounds through UF membranes.

Key words | advanced wastewater treatment, fouling reduction, in-line coagulation, secondary effluent, ultrafiltration membrane

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HIGHLIGHTS

- Providing information about wastewater characteristics and how it can be improved using membranes.
- The viability of using in-line coagulation in reducing membrane fouling.
- Using low chemicals in treating wastewater can reduce total cost of treatment process and chemicals effects.
- Reusing wastewater assists in solving water shortage problems.

INTRODUCTION

Improving membrane feed water quality by pre-treatment processes is a promising strategy for fouling mitigation. Coagulation is a widely used technology in surface water and wastewater treatment, which not only reduces turbidity but under certain conditions can also remove natural organic matter (NOM) as measured by dissolved organic carbon (DOC) (Edzwald 1993; Dong *et al.* 2007; Humbert *et al.* 2007). Organics are typically negatively charged, which affects and controls the coagulation process,

especially when metal coagulants are used (Edzwald 1993). The main mechanism of DOC removal is charge neutralization (Pikkarainen *et al.* 2004; Oh & Lee 2005; and Hatt *et al.* 2011), which can be obtained using metal coagulants. DOC removal by charge neutralization occurs by direct precipitation or by adsorption onto flocculated suspended solids (Edzwald & van Benschoten 1990). The removal of NOM in water requires higher coagulant doses than those needed for turbidity reduction

only. This is because organics are highly negatively charged compounds (10 $\mu\text{eq}/\text{mg}$ DOC) when compared with suspended colloids (0.5 $\mu\text{eq}/\text{mg}$) (Edzwald & van Benschoten 1990).

Specific ultraviolet absorbance (SUVA) is used as an indicator of NOM composition as organics that have aromatic structures absorb light in UV wavelength region and is defined as the normalized UV absorbance measured at 254 nm divided by DOC concentration (mg/L). The organics removal efficiency of coagulation can be related to its SUVA value (Edzwald 1993). Waters with high SUVA values (from 4–5) contain highly hydrophobic aromatic organics of high molecular weight (humic substances). For water with high SUVA values it is expected that about 70% DOC removal efficiency can be achieved by coagulation (Edzwald 1993; Hatt *et al.* 2011). On the other hand, low SUVA values (less than 3) are indicative of the presence of low molecular weight non-humic compounds, and coagulation is not nearly as effective for DOC removal in such cases (Edzwald 1993; Hatt *et al.* 2011).

The findings described above with respect to coagulation and NOM provide important insights regarding the coagulation of treated secondary effluent, which was the focus of this study.

In the case of membrane filtration, coagulation promotes cake layer formation which protects membrane pores from smaller foulants (Haberkamp *et al.* 2007) and leads to an improvement in membrane performance (Howe *et al.* 2006). The cake layer can be easily removed by hydraulic backwashing (Zularisam *et al.* 2006).

Several studies have been conducted to evaluate pre-coagulation prior to membrane filtration. When it is applied for this purpose it is often in the form of conventional coagulation with rapid mix and a tank to allow time for floc development followed by settling basin before membrane filtration (Fan *et al.* 2008; Chon *et al.* 2012; Delgado-Diaz *et al.* 2012) or just a floc formation tank (Hillis 2006; Guo & Hu 2012; Ratajczak *et al.* 2012). As such, substantial space and energy are required. On the other hand, some studies have demonstrated the effectiveness of coagulants in reducing low pressure membrane fouling when applied as in-line coagulation (Wang & Wang 2006; Delgado-Diaz *et al.* 2012; Zheng *et al.* 2012; Buchta *et al.* 2017). In-line coagulation is defined as the continuous addition of coagulants at low doses prior to the membrane without removing particles (Wang & Wang 2006), for the purposes of changing particle and NOM characteristics (Liu & Kim 2008). This technology

has many advantages, such as the small size of its footprint relative to conventional coagulation/flocculation and/or sedimentation (Zheng *et al.* 2012), and lower coagulant dosages decreasing both cost and sludge production (Buchta *et al.* 2017).

Some studies have demonstrated that pre-coagulation is an effective method for improving performance of polymeric membranes (Dong *et al.* 2007; Humbert *et al.* 2007; Zularisam *et al.* 2008) and ceramic membranes (Li *et al.* 2011; Zhu *et al.* 2011; Abbasi *et al.* 2012; Zhao *et al.* 2019a), while others have reported little to no effect on membrane performance (Howe *et al.* 2006; Lee *et al.* 2007). Studies have been conducted to investigate the effect of coagulant type on membrane performance. Some have demonstrated that iron-based coagulants (e.g. ferric chloride) are better at reducing membrane fouling when treating surface water (Howe *et al.* 2006; Liu & Kim 2008) or secondary effluent (Haberkamp *et al.* 2007; Hatt *et al.* 2011; Acero *et al.* 2012; Wu *et al.* 2019). On the other hand, some have demonstrated that aluminum salts were more effective in improving membrane performance, in terms of high permeate quality and fouling reduction (Judd & Hillis 2001; Kim *et al.* 2005; Fan *et al.* 2008; Zheng *et al.* 2012; Zhao *et al.* 2019b).

The impact of coagulant dosage on membranes treating surface water (Ratajczak *et al.* 2012; Wray *et al.* 2014; Keucken *et al.* 2017) or secondary effluent (Liu & Kim 2008; Haberkamp *et al.* 2007; Fan *et al.* 2008; Zheng *et al.* 2012) has also been investigated, but conflicting observations have been reported. This is due to the fact that coagulation is a complex chemical process that involves multiple reactions, and there are many factors affecting its performance, especially when conducted with membrane filtration.

The primary objectives of this study were to investigate the potential of in-line coagulation as a UF pre-treatment for domestic wastewater secondary effluent and to study the effect of coagulant type and dosage for the reduction of reversible and irreversible UF fouling. A control and two dosages (0.0, 0.5, and 5.0 mg/L) were investigated for four different coagulants including aluminum sulfate (alum), polyaluminum chloride (PACl), ferric chloride, and ferric sulfate. To further investigate the impact of coagulant type and dosage on membrane performance, two coagulants (alum and ferric sulfate) were selected. Alum at dosages of 0.5, 2.5 and 5.0 mg/L and ferric sulfate at dosages of 0.5, 1.0 and 5.0 mg/L were investigated as in-line coagulation pre-treatment for UF.

METHODS

Source water

The UF was fed from the Waterloo Wastewater Treatment Plant (WWTP) secondary effluent. Waterloo WWTP treats approximately 45,000 m³/d of predominantly domestic wastewater by primary clarification (where ferrous chloride was added for phosphorus removal) followed by conventional activated sludge as a biological treatment and then secondary settling tanks. The secondary effluent was UV-disinfected before being discharged into the Grand River. Table 1 presents the quality parameters of source water during the investigated period (January to April 2015).

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

Experimental set-up

Secondary effluent was pumped to the overhead tank using a peristaltic digital drive pump (model No. 7550-50, 1.6-100 PRM, Cole-Parmer Instrument Company, Barrington, USA) (Figure 1). Coagulant was pumped in-line by a peristaltic digital drive pump (model No. 7553-70, 6-600 RPM, Cole-Parmer instrument Company, Barrington, USA) into the secondary effluent upstream of the membrane unit. The two streams (secondary effluent and coagulant) were mixed together with an in-line static mixer (Koflo Corporation, Cary, USA) and the mixture then flowed through 1.0 m tubing prior to entering the UF module). The UF membrane used in this investigation was a commercially available polyvinylidene fluoride (PVDF) membrane produced by GE Process Technologies (Oakville, Canada). The membrane module (the ZeeWeed - 1) was constructed of 15 cm long hollow fibers (500 series), and the operation mode was outside-in. The membrane had a nominal surface area of 0.047 m² with a molecular weight cut-off of 400 KDa (approximately 40 nm pore size) as delivered from the manufacturer. The set-up was designed to cycle automatically. Each cycle initiated with 30 min of permeation followed

Table 1 | Source water (Waterloo WWTP secondary effluent) quality parameters for the eight separate effluent collection events (between January and April 2015)

Parameter	Unit	Average (\pm SD)	Min	Max	Number of samples
Temperature ^a	°C	12.3 (\pm 0.23)	12.0	12.8	8
pH ^b	–	7.55 (\pm 0.09)	7.48	7.75	8
Turbidity ^b	NTU	4.98 (\pm 1.66)	2.86	7.33	8
Total organic carbon (TOC) ^b	mg/L	22.70 (\pm 0.12)	22.60	22.90	3
DOC ^b	mg/L	8.95 (\pm 0.80)	7.80	10.40	8
Biopolymers ^b	mg/L	1.94 (\pm 0.33)	1.68	2.76	8
Humics ^b	mg/L	3.32 (\pm 0.37)	2.82	4.10	8
Ultraviolet absorbance ^b at 254 nm	cm ⁻¹	0.13 (\pm 0.01)	0.11	0.16	8
Specific ultraviolet absorbance (SUVA) ^b	L/(mg/m)	1.51 (\pm 0.09)	1.30	1.59	8
Total suspended solids (TSS) ^c	mg/L	5.05 (\pm 3.09)	2.40	12.20	8
Ammonia ^c	mg/L	23.1 (\pm 2.53)	20.0	28.8	8
Nitrate ^c	mg/L	9.94 (\pm 2.46)	5.88	14.2	8
Nitrite ^c	mg/L	0.32 (\pm 0.10)	0.22	0.53	8
Total Kjeldahl nitrogen ^c	mg/L	27.0 (\pm 3.3)	23.0	33.9	8
Total phosphorus ^c	mg/L	0.26 (\pm 0.10)	0.12	0.49	8

^aMeasured in the field at time of secondary effluent collection.

^bMeasured at University of Waterloo laboratories.

^cMeasured at Waterloo WWTP laboratories.

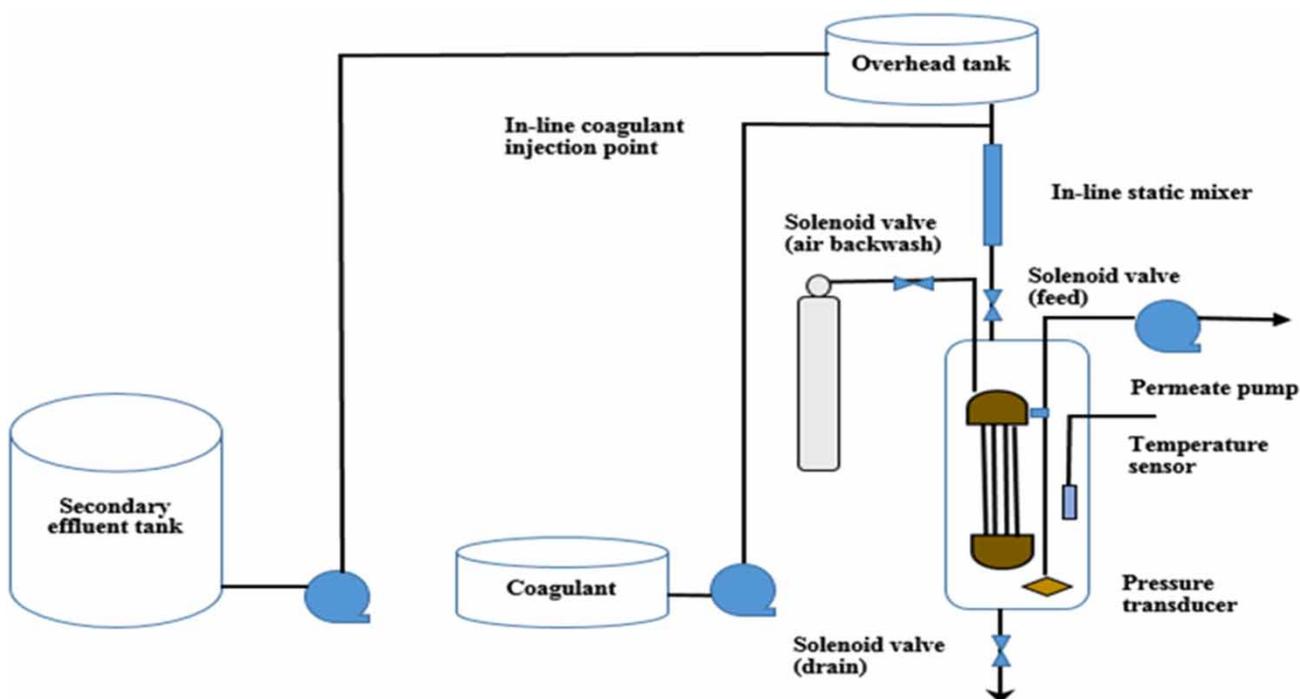


Figure 1 | Membrane and in-line coagulation bench-scale schematic.

by 20 s of air sparging backwashing. Then, the module tank was drained (30 s to empty) and refilled again with the test water (36 s to refill). To continuously monitor the temperature and the flowrate, a temperature sensor and flowmeter (model LC alpha controller, 200–500 CCM, Alicat Scientific, Tucson, USA) were connected to a data logger (HOBO Energy Logger, model H22-001, Onset, Cape Cod, Massachusetts, USA). The flow meter was used to maintain a consistent permeate flow rate throughout the whole UF experiment. It was connected with a digital permeation pump (Masterflex L/S drive model number 07550-50; Cole-Parmer, Montreal, Canada) that automatically adjusted to achieve a consistent flow (25 mL/min). The flowmeter measured the actual permeate flow rate every 10 s and data was recorded by a data logger. A pressure transducer (model 68075-02, Cole-Parmer, Montreal, Canada) was also connected to the data logger to measure the trans-membrane pressure (TMP) which was used to determine the fouling rates after correction to 20 °C. Additional details regarding the bench-scale configuration and operation are available in Aly (2015).

A permeate flux of 33 L/m² h was kept constant during all polymeric UF experiments. The run length was set to end at 24 h or when the maximum TMP (55 KPa) of the membrane was reached to measure the UF fouling rate before and after pre-treatment using the same batch of collected secondary effluent. Since the purpose of the investigation

was to screen various coagulants and examine several dosages, this run length was considered appropriate. After each experiment, chemical cleaning was performed using sodium hypochlorite (200 mg/L) for a minimum of 5 h followed by a citric acid solution (5 g/L) for another 5 h. Afterwards, the membrane was soaked in deionized water at 4 °C until usage. The UF module was integrity tested using a pressure calibrator (Meri-cal DP2001I, Meriam Instruments, Ohio, USA) prior to every experiment. The maximum allowable pressure drop through the membrane was 2.0 KPa per 2 min. More details about the procedure for integrity testing and membrane chemical cleaning are available in Aly (2015). To check cleaning effectiveness, clean water permeability tests were conducted using deionized water before each experiment (Aly 2015).

Coagulants

Four different coagulants were used in this study. They were aluminum sulfate (alum), polyaluminum chloride (PACl), ferric chloride, and ferric sulfate (Table 2). All coagulants were supplied by Kemira Water Solutions (Varenes, Quebec, Canada).

Coagulants were first optimized for the removal of DOC, biopolymers, and humic substances by preliminary jar tests that were performed at dosages of 0.0, 0.5, 1.0, 2.5, 5.0, and 10.0 mg/L (all dosages are reported as the

Table 2 | Coagulant information (as provided by supplier)

Product name/characteristics	Aluminum sulfate	Polyaluminum chloride	Ferric chloride	Ferric sulfate
Commercial name (product name)	Alum (Kemira ALS)	PACl (Stern PAC)	(PIX-111)	(PIX-312)
Concentration (as supplied)	29–50% as $\text{Al}_2(\text{SO}_4)_3 \cdot 14\text{H}_2\text{O}$	15–40% as $\text{Al}_{13}(\text{OH})_{20}(\text{SO}_4)_2\text{Cl}_{15}$	37–42% as FeCl_3	66–73% as $\text{Fe}_2(\text{SO}_4)_3$
Specific gravity	1.2–1.36	1.16–1.3	1.26–1.48	1.38–1.59
pH	<2.5	1.8–3.4	<2	<2

weight of the actual compound, without waters of hydration). All jar tests were carried out at the wastewater pilot plant in the Douglas Wright Engineering (DWE) Building, University of Waterloo, using a procedure based on Standard Practice for Coagulation – Flocculation Jar Test of Water (ASTM Int'l2). Initially raw water (secondary effluent) was mixed for 1 min prior to the addition of coagulant. Then, the appropriate dose of coagulant was added and mixing was continued at approximately 1.67 Hz for 1 min after which it was turned down to 0.005 Hz for 20 min. Finally, the flocs were allowed to settle for 30 min. Samples were taken after settling and routine analyses were conducted.

Based on the data obtained from jar tests, two dosages (0.5 and 5.0 mg/L as coagulant) were investigated as in-line coagulants to reduce UF fouling. Table 3 summarizes the dosages of coagulants and the corresponding amount added as the active metal ion. Dosage calculations for preliminary jar tests and in-line coagulation experiments are available in Aly (2015).

Analyses

Samples were collected from the inlet raw water to the membrane and from UF permeate in clean glass 1-L bottles at 25 mL/min over approximately 1 h. Turbidity, pH,

temperature, UV_{254} absorbance, and SUVA were monitored. Total organic carbon (TOC) and DOC were analyzed using an OI-Analytical TOC analyzer (Model 1030, College Station, TX, USA) by combustion as per Standard Method 5310B (Standard Methods 2012). NOM constituents were identified using liquid chromatography organic carbon detection (LC-OCD) Model 8 (DOC-LABOR, Karlsruhe, Germany) as per Huber *et al.* (2011). For DOC and LC-OCD measurements, samples were pre-filtered through pre-rinsed 0.45 μm PVDF membrane filters (Pall Supor Membrane Disk Filters, 0.45 μm , 47 mm plain, VWR International, USA). If the DOC in the sample exceeded 5 mg/L, samples were diluted with ultrapure water. Other parameters such as ammonia, nitrate, nitrite, TKN, and total P data were acquired from the City of Waterloo WWTP records. All were measured as per Standard Methods (2012).

RESULTS AND DISCUSSION

Impact of coagulant type and dosage on secondary effluent characteristics

Jar test experiments were conducted to examine the impact of four coagulants (alum, PACl, ferric chloride, and ferric

Table 3 | Dosages of the coagulants applied for in-line coagulation experiments and the corresponding amount added

Coagulant	Chemical formula	Dosage mg/L as coagulant	Amount added mg Al^{3+} or Fe^{3+} /L	Amount added mmol Al^{3+} or Fe^{3+} /L
Alum	$\text{Al}_2(\text{SO}_4)_3 \cdot 14\text{H}_2\text{O}$	0.5	0.045	1.7×10^{-3}
		5.0	0.450	1.7×10^{-2}
PACl	$\text{Al}_{13}(\text{OH})_{20}(\text{SO}_4)_2\text{Cl}_{15}$	0.5	0.125	5×10^{-3}
		5.0	1.250	5×10^{-2}
Ferric chloride	FeCl_3	0.5	0.174	3×10^{-3}
		5.0	1.740	3×10^{-2}
Ferric sulfate	$\text{Fe}_2(\text{SO}_4)_3$	0.5	0.140	2.5×10^{-3}
		5.0	1.400	2.5×10^{-2}

sulfate) on the reduction of the organic content of the selected secondary effluent. It is recognized that jar tests do not necessarily model what might be encountered in an in-line coagulation application. They could, however, provide performance information to assist with the selection of conditions for the in-line tests. A no-coagulant control and five dosages of each coagulant were investigated for the removal of DOC, humic substances, and biopolymers (0.0, 0.5, 1.0, 2.5, 5.0, and 10 mg/L). In general, increasing coagulant dosage increased the removal of all three groups of compounds.

In terms of DOC, the highest removal, 11.5%, was achieved using PACl at 10 mg/L, while alum was the least effective coagulant for the reduction of DOC (a maximum reduction of 2.0% at 5.0 mg/L). By comparison, similar higher DOC reductions were achieved by ferric chloride and ferric sulfate, where almost 7.5% reduction of DOC was observed at the highest dosage applied (10 mg/L). As expected, there was almost no impact of coagulants on humic substances removal. This was attributed to the low amounts of hydrophobic compounds in the selected secondary effluent as indicated by SUVA values, where low SUVA values (less than 3) are indicative of the presence of hydrophilic non-humic compounds, and coagulation is not nearly as effective for DOC removal in such cases (Edzwald 1993; Hatt *et al.* 2011; Yu *et al.* 2019). The pH (7.5 ± 0.3) of coagulation at the dosages employed was not sufficiently low to induce substantial enhanced coagulation DOC removal. Similar observations were reported by Paar *et al.* (2011) when studying the impact of in-line coagulation on reducing UF fouling in surface water treatment. Wray & Andrews (2014) also reported that coagulation was not efficient for removing organic compounds from lake water (Lake Ontario) that had low SUVA ($<2.0 \text{ L}/(\text{mg}/\text{m})$). There was no change observed in the low molecular weight fraction concentrations regardless of coagulant type and dosage, which is in agreement with previous studies (Haberkamp *et al.* 2007; Wray & Andrews 2014).

In terms of biopolymer removal, for all coagulants, increasing coagulant dosage increased biopolymer removal. At the highest dosage applied (10 mg/L), the highest removals of 29% and 28% were achieved by PACl and ferric chloride, respectively. The lowest biopolymer removal was 10% observed with alum at the highest dosage (10 mg/L) followed by ferric sulfate with an 18% biopolymer removal at the same dosage. The preferential removal of biopolymers by chemical coagulation has also been observed in previous studies (Haberkamp *et al.* 2007; Paar *et al.* 2011; Zheng *et al.* 2012; Wray *et al.* 2014; Deng *et al.* 2019).

In-line coagulation to control UF fouling

To examine the impact of different coagulant types and dosage on UF performance, three membrane experiments were conducted using only the secondary effluent and after in-line coagulant addition at two different dosages (0.5 and 5.0 mg/L). While 10 mg/L was preferable from the jar test results, it was decided that, for practical purposes, lower dosages made more sense in real world applications. The in-line coagulation experiments were conducted from 15 January to 11 April 2015. During this period, a no-coagulant control (0.0 mg/L) and a coagulant type at two different dosages (0.5 and 5.0 mg/L) were investigated each week (the run length was set to end at 24 h or when the maximum TMP (55 KPa) of the membrane was reached). Raw data for these experiments are available in Aly (2015).

Table 4 summarizes DOC, biopolymers, humic substances, and turbidity reduction for each of the different coagulants and dosages. Based on LC-OCD analysis, UF alone (when fed with secondary effluent without in-line coagulants) retained $73 \pm 13\%$ of biopolymers, while there was almost no removal of the remaining NOM fractions (primarily humic substances). There was a $96 \pm 2.0\%$ reduction of secondary effluent turbidity through UF. These results indicate that both biopolymers and turbidity played an important role in UF fouling.

For water analysis, in-line coagulated samples were taken immediately before entering the UF module (following 20 s of coagulant contact) at the same flow rate as was fed to the membrane (1.5 L/h). Turbidity was measured soon after the sample was collected. For DOC and LC-OCD analyses, samples were pre-filtered using a $0.45 \mu\text{m}$ PVDF membrane filter. At the highest applied dosage (5.0 mg/L), it can be seen that ferric sulfate was the most effective coagulant for reducing concentrations of organic compounds (biopolymers and humic substances), followed by PACl. The highest reduction of organic compounds at the low dose (0.5 mg/L) was achieved by ferric chloride (35% and 15% reductions of biopolymers and humics, respectively). Increasing the alum dosage from 0.5 to 5.0 mg/L had an adverse impact on biopolymers, but it provided the highest reduction in turbidity. In general, the most effective impact of in-line coagulation was observed in turbidity reduction, even at the low dosages tested. The biopolymer reduction obtained by in-line coagulants is likely attributable to phase transformation from dissolved to particulate compounds which are retained during sample filtration. The low reduction of humic substances

Table 4 | Impact of different treatment conditions on the reduction of DOC, biopolymers, humic substances, and turbidity

Coagulant	Treatment	DOC (%)	Biopolymer (%)	Humic substances (%)	Turbidity (%)
Alum	UF alone (fed with secondary effluent)	11	75	0	96
	Impact of 0.5 mg/L on UF feed ^a	12	19	5	34
	Impact of 5.0 mg/L on UF feed ^a	-10	-12	3	79
	UF after 0.5 mg/L (pre-post UF)	17	79	0	94
	UF after 5.0 mg/L (pre-post UF)	28	67	10	74
	Overall 0.5 mg/L (feed water-UF permeate)	27	83	5	96
	Overall 5.0 mg/L (feed water-UF permeate)	26	65	11	95
	PACl	UF alone (fed with secondary effluent)	9	61	0
Impact of 0.5 mg/L on UF feed ^a		17	28	21	45
Impact of 5.0 mg/L on UF feed ^a		11	22	15	60
UF after 0.5 mg/L (pre-post UF)		12	79	0	95
UF after 5.0 mg/L (pre-post UF)		2	53	0	96
Overall 0.5 mg/L (feed water-UF permeate)		27	85	17	97
Overall 5.0 mg/L (feed water-UF permeate)		11	63	5	98
Ferric chloride		UF alone (fed with secondary effluent)	26	80	4
	Impact of 0.5 mg/L on UF feed ^a	26	37	14	32
	Impact of 5.0 mg/L on UF feed ^a	17	11	7	54
	UF after 0.5 mg/L (pre-post UF)	15	82	3	94
	UF after 5.0 mg/L (pre-post UF)	22	91	6	95
	Overall 0.5 mg/L (feed water-UF permeate)	37	89	17	96
	Overall 5.0 mg/L (feed water-UF permeate)	35	92	13	98
	Ferric sulfate	UF alone (fed with secondary effluent)	7	67	0
Impact of 0.5 mg/L on UF feed ^a		20	13	16	77
Impact of 5.0 mg/L on UF feed ^a		17	58	58	43
UF after 0.5 mg/L (pre-post UF)		7	87	-15	91
UF after 5.0 mg/L (pre-post UF)		23	57	-54	96
Overall 0.5 mg/L (feed water-UF permeate)		26	88	3	98
Overall 5.0 mg/L (feed water-UF permeate)		36	82	18	98

^aCollected immediately prior to entering membrane module tank following a static mixer and 20 s contact time in influent pipe. A negative % reduction value indicates that the value was higher after treatment.

was expected as in-line coagulation was applied at pH conditions (pH >7.0) which are not favorable for enhanced coagulation.

Figure 2 illustrates the impact of coagulant type and dose on reversible UF fouling. The reversible fouling rate during a cycle 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. To determine the irreversible fouling rate, the TMP at the beginning of each cycle was averaged over the time period being investigated (Figure 3). There was a rapid increase in TMP during the first hours of the filtration of secondary effluent without coagulant addition (TMP figures are available in Aly (2015)), after which the rise in fouling rate slowed. The accelerated fouling rate at the beginning stage of the operation was attributed to membrane pore blocking (Kim *et al.* 2005) by organics or particles which were close to the diameter of membrane pores (Ma *et al.* 2013). Pore

blocking leads to the development of irreversible fouling (Juang *et al.* 2007) which is hard to recover by backwashing versus cake layer formation (Paar *et al.* 2011) which causes stabilization in the fouling rate (Mosqueda-Jimenez *et al.* 2008). The same observation was obtained by Kim *et al.* (2005) during treatment of secondary effluent and Ratajczak *et al.* (2012) treating river water (Grand River, ON) using UF.

In this study, the irreversible fouling rate was characterized by an initial rapid increase in the early stages of the UF run (10 h or less) and is described as the 'first period'. This was followed by a 'second period', where the rate stabilized or decreased (usually when a TMP of 55 KPa was approached or reached). For data interpretation, only the first period was taken into account for performance analysis (Table 5). The percentage reductions in reversible and irreversible fouling were calculated based on the average rates of reversible and irreversible fouling determined for each run (i.e. using the zero coagulant dose (raw secondary effluent)).

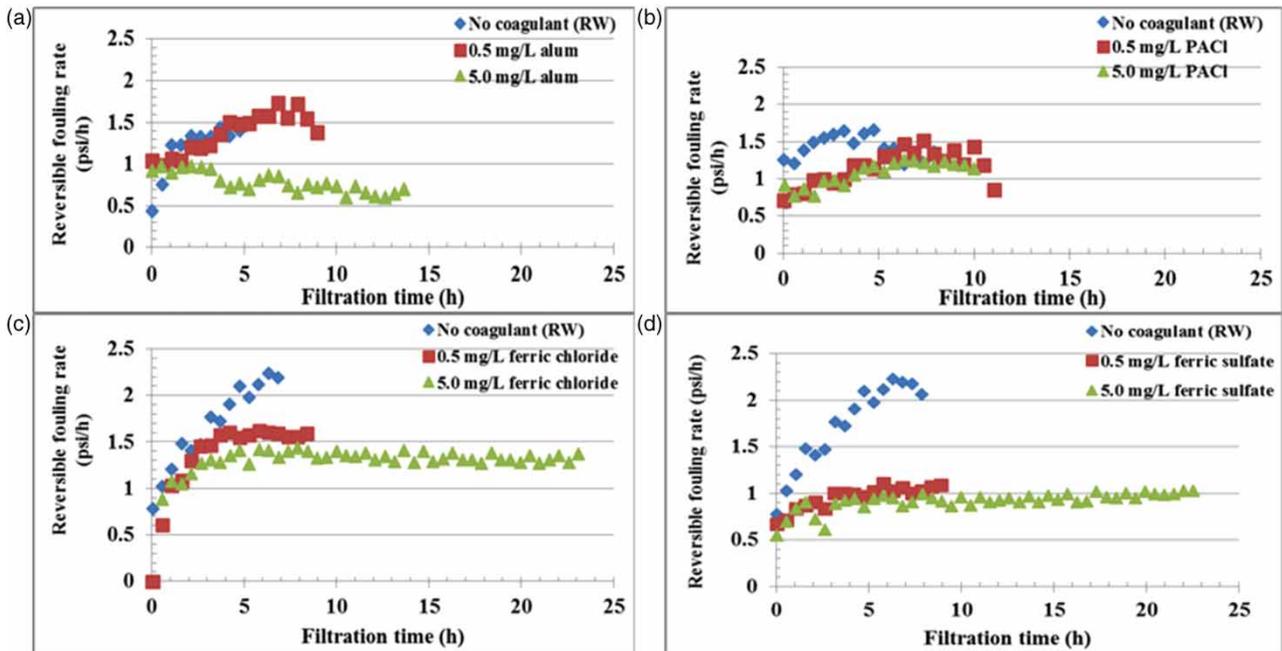


Figure 2 | Hydraulically reversible fouling rates for different coagulant types and dosages, (a) alum ($\text{Al}_2(\text{SO}_4)_3 \cdot 14\text{H}_2\text{O}$), (b) PACl ($\text{Al}_{13}(\text{OH})_{20}(\text{SO}_4)_2\text{Cl}_{15}$), (c) ferric chloride (FeCl_3), and (d) ferric sulfate ($\text{Fe}_2(\text{SO}_4)_3$).

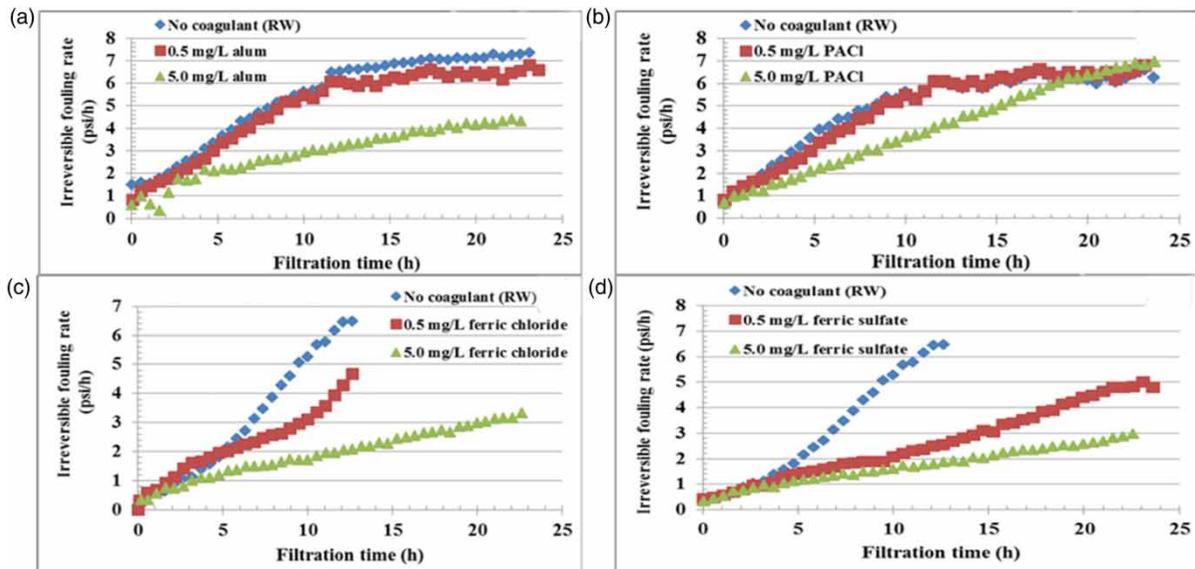


Figure 3 | Hydraulically irreversible fouling rates for different coagulant types and dosages, (a) alum ($\text{Al}_2(\text{SO}_4)_3 \cdot 14\text{H}_2\text{O}$), (b) PACl ($\text{Al}_{13}(\text{OH})_{20}(\text{SO}_4)_2\text{Cl}_{15}$), (c) ferric chloride (FeCl_3), and (d) ferric sulfate ($\text{Fe}_2(\text{SO}_4)_3$).

It has been demonstrated that coagulation leads to the rapid formation of a cake layer (Bagga *et al.* 2008) that is easily backwashed (Galvañ *et al.* 2014), and which serves as a protective layer from membrane pore blocking. It can be seen from Figures 2 and 3 that there was a significant improvement of the UF membrane performance when in-

line coagulation was applied. However, the impact on reversible and irreversible fouling reduction differed based on coagulant type and dosage. It is acknowledged that there was some difference in the observed fouling rate in each experiment (based on coagulant type) and for operational reasons each experiment was conducted from a

Table 5 | Reduction in UF reversible fouling (RF) and irreversible fouling (IRF) rates in association with coagulant addition for the whole run, and first and second periods

Coagulant	Date	Dosage mg/L	Whole run			First period			Second period		
			Run time (h)	RF	IRF	Time (h)	RF	IRF	Time (h)	RF	IRF
			% Reduction			% Reduction			% Reduction		
Alum	19-Jan-15	0.0	23			6			17		
	22-Jan-15	0.5	23.5	-6	15	6	4	5	17.5	-40	11
	15-Jan-15	5.0	23	17	66	6	11	29	17	9	44
PACl	30-Jan-15	0.0	22.5			5			17.5		
	26-Jan-15	0.5	23.5	7	-6	5	8	7	18.5	-18	-45
	28-Jan-15	5.0	23.5	11	-24	5	19	33	18.5	15	-82
Ferric chloride	6-Feb-15	0.0	22			8.5			13.5		
	2-Feb-15	0.5	24	12	40	8.5	8	34	15.5	6	-59
	4-Feb-15	5.0	23.5	22	75	8.5	14	66	15	-71	29
Ferric sulfate	13-Feb-15	0.0	18			8			10		
	11-Feb-15	0.5	23.6	32	55	8	44	57	15.6	-10	8
	9-Feb-15	5.0	22.5	36	76	8	50	77	14.5	-1	58

different secondary effluent batch. However, the intent in each experiment was to compare the pre-treatments to a base case which was the no-coagulant condition. With all coagulant types, there was a slight improvement in UF performance (especially in the case of irreversible fouling) when the dose of coagulant was increased from 0.5 to 5 mg/L. The UF membrane fouling reduction by in-line coagulation appears to be attributable to the size modification of particles that contribute to pore blocking (Zheng *et al.* 2012). The reduction in irreversible fouling observed in this study for all coagulants tested is inferred to be due to the elimination of pore blocking at the initial stages of the filtration run (Paar *et al.* 2011) because of the aggregation of colloids and organics (Howe *et al.* 2006). The same observation was reported by Yoo 2018, where the reduction in irreversible fouling only observed when flocs with a certain size (larger ones) were formed. Furthermore, increasing the coagulant dose would lead to the formation of larger particles, which further improved UF performance: the larger the flocs size that was produced, the lower the development of membrane fouling (Dong *et al.* 2012) (at least in the ranges of doses investigated here).

As can be seen in Table 5, the largest reduction in reversible and irreversible fouling was achieved by ferric sulfate at the higher of the two dosages tested (5.0 mg/L). Although PACl was the second most effective coagulant in reducing organic compounds at the high dosage, ferric chloride outperformed PACl in fouling control at the same dosage (5.0 mg/L).

Under the conditions investigated, iron-based coagulants (e.g. ferric chloride and ferric sulfate) were more effective than aluminum-based coagulants for controlling membrane fouling. A similar finding has been reported by Haberkamp

et al. (2007) and Acero *et al.* (2012) when comparing ferric chloride and alum for secondary effluent treatment by UF. A study conducted by Zheng *et al.* (2012) to compare ferric chloride, alum, and PACl as in-line coagulant pre-treatment for UF in secondary effluent found that ferric chloride generally outperformed both alum and PACl for TMP control. This may be attributed to larger floc sizes produced by iron-based coagulants than those formed by aluminum-based coagulants (Ratajczak *et al.* 2012). It is also possible that the interactions between the membrane surface and flocs formed by iron-based coagulants are weaker than those of the aluminum-based coagulants (Zheng *et al.* 2012). On the other hand, some studies (Fan *et al.* 2008; Ratajczak *et al.* 2012) reported that alum and PACl were more effective than ferric chloride for reducing membrane fouling. Zhao *et al.* (2019b) reported that PACl was better than ferric chloride in terms of fouling reduction and permeate water quality when coagulants were applied in-line with ceramic membranes for wastewater treatment. The conflicting observations may be attributable to differences in feed water characteristics (e.g. turbidity and NOM concentrations), coagulant dosages (and their calculation), membrane properties, and the flocs produced during coagulation.

It should be noted that based on data obtained from jar tests, PACl was the most effective coagulant for reducing biopolymers (organic carbon and organic nitrogen) but it was not the most effective for reducing UF fouling (as measured by change in TMP). As such, jar tests may be not be a practical predictor or indicator of membrane fouling reduction, especially when the coagulant is applied in the form of in-line pre-treatment.

Besides the impact of in-line coagulation on the reduction of UF fouling, the effect of pre-treatment on permeate quality was also monitored. Based on data summarized in Table 4, the removal of biopolymers and turbidity through UF increased (in most cases) by the application of in-line coagulation and, simultaneously, fouling was reduced. At neutral pH and low coagulant doses, the main mechanism of coagulation is charge neutralization where small particles and organic compounds aggregate to create larger compounds that easily settled on the membrane surface, preventing pore blocking. Under such conditions, in-line coagulation can assist in reducing membrane fouling and at the same time higher removal of organics and particles can be achieved.

Although combining in-line coagulation with UF appeared to result in greater reduction of DOC (Figure 4), definitive conclusions with respect to the effect of dosage could not be drawn and these experiments had only single points (no replicates). At the low coagulant dosage (0.5 mg/L) for each of the four coagulants, there was an improvement in DOC reduction by UF. Increasing the applied dosage of ferric sulfate to 5.0 mg/L yielded an additional 10 percentage points of DOC removal by UF. For alum and ferric chloride, increasing the coagulant dosage to 5.0 mg/L did not yield any additional removal of DOC. On the other hand, the removal of DOC by UF was decreased after increasing the dose from 0.5 to 5 mg/L for PACl. These observations suggest that further investigation with replicate points would be required. If it is borne out that only very small dosages are required and that higher dosages are detrimental, then coagulation optimization for in-line coagulant addition becomes critically important.

Further investigation

It is evident based on these observations that in-line coagulation can improve UF performance for secondary effluent treatment. Coagulant type and dosage impacted the reduction of reversible and irreversible fouling. To further investigate the impact of coagulant type and dosage on reducing both reversible and irreversible fouling, two coagulants (alum and ferric sulfate) were selected for further investigation. In this experiment, alum at dosages of 0.5, 2.5, and 5.0 mg/L and ferric sulfate at dosages of 0.5, 1.0, and 5.0 mg/L were investigated as in-line coagulation pretreatment for UF. Raw data for water samples and change in normalized TMP during experiments are available in Aly (2015). Figures 5 and 6 illustrate the impact of different applied dosages of alum and ferric sulfate, respectively, on the reduction of UF reversible and irreversible fouling. At low doses of alum (0.5 mg/L), the reduction of UF reversible and irreversible fouling did not exceed 10% (Figure 5). Increasing the alum dose from 0.5 to 2.5 mg/L increased the reduction of reversible and irreversible fouling to 32% and 78%, respectively. On the other hand, increasing alum dosage to 5.0 mg/L did not further measurably improve the effect. The reversible and irreversible reduction achieved at 5.0 mg/L of alum were 34% (about the same as the 2.5 mg/L dose) and 40% (half of that obtained by 2.5 mg/L), respectively. In the case of ferric sulfate, except at a dosage of 1.0 mg/L, increasing dosage had generally a positive impact in controlling fouling (Figure 6). The highest reduction of reversible and irreversible fouling was $45 \pm 7\%$ and $84 \pm 10\%$, respectively, and was achieved at 5.0 mg/L.

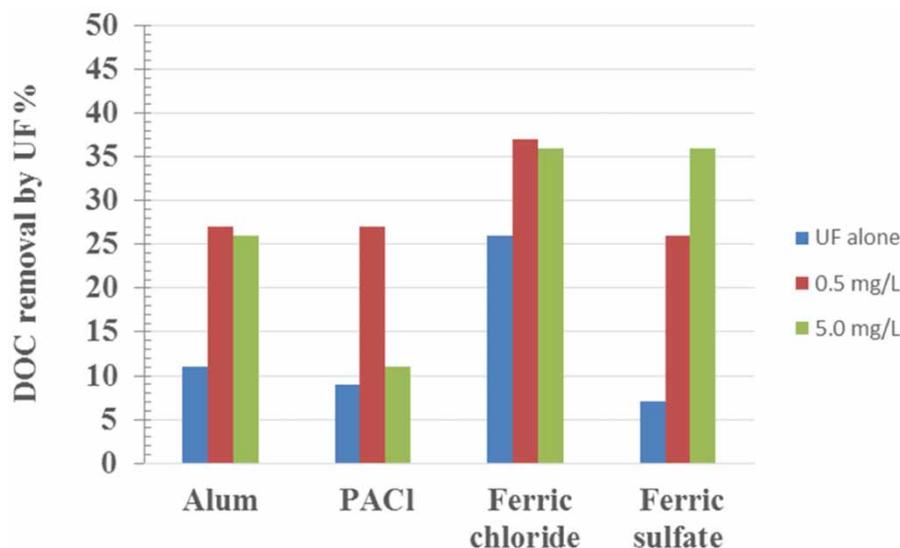


Figure 4 | The impact of combining in-line coagulation with UF for DOC reduction.

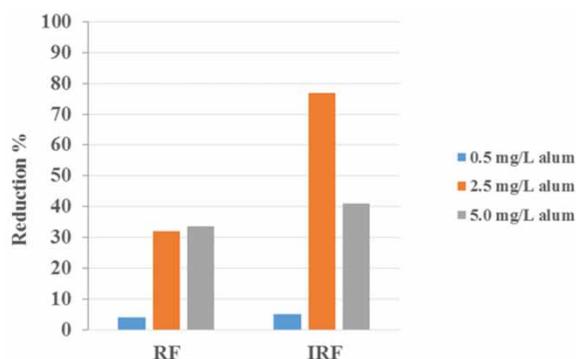


Figure 5 | Percentage reduction in reversible and irreversible UF membrane fouling using alum at three different dosages (0.5, 2.5, and 5.0 mg/L), $n = 2$ for 0.5 and 5.0 mg/L and only one point for 2.5 mg/L.

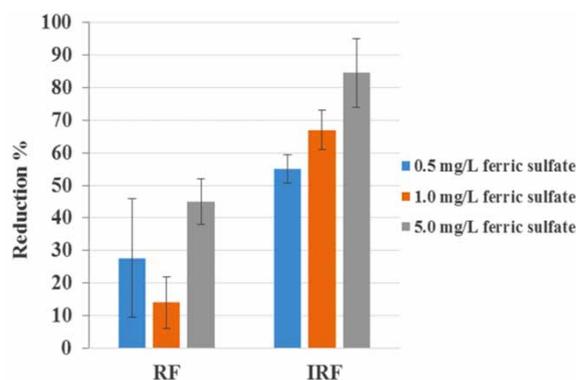


Figure 6 | Percentage average reduction in reversible and irreversible UF membrane fouling using ferric sulfate at three different dosages (0.5, 1.0, and 5.0 mg/L), $n = 4$ for 0.5 mg/L, and $n = 3$ for 1.0 and 5.0 mg/L.

In general, a more considerable impact of in-line coagulation was observed for irreversible fouling reduction, which is ultimately more important for sustainable membrane operation, as it reduces the frequency of chemical cleaning while increasing membrane life.

With respect to alum, adding more coagulant (5.0 mg/L) resulted in less improvement in membrane fouling. This may be attributable to feed water variation. The biopolymer concentration was 2.0 mg/L in coagulated secondary effluent when the 5.0 mg/L dose test was done, while it was 1.7 mg/L when 2.5 mg/L of alum was applied. Also, the turbidity was lower in coagulated secondary effluent for the 2.5 mg/L dose test (Aly (2015)). The same observation was reported by Zheng *et al.* (2012) where a lower operation time of the UF was observed with increasing alum dosage from 0.074 to 0.148 mmol Al^{3+}/L . Keucken *et al.* (2017) Doubling the coagulant dosage from 1.0 to 2.0 mg Al^{3+}/L provided a limited impact on UF fouling reduction when treating surface water. Higher deposition of aluminum hydroxide on the membrane surface (Wray *et al.* 2014), which may increase membrane

fouling (Galvañ *et al.* 2014), could have contributed to the observed phenomena.

Based on the data presented in Figure 6, it is unclear why the least reduction in the reversible fouling rate occurred at 1.0 mg/L of ferric sulfate. This suggested that there was a difference in the flocs formed or that the interaction between the formed flocs and the foulants (e.g. organic compounds) was responsible for the reduction in reversible fouling at that dosage. In a pilot plant study conducted by Paar *et al.* (2011) to investigate the impact of in-line coagulation by ferric chloride to reduce fouling of a UF membrane treating secondary effluent, dosing at 1.0 mg Fe^{3+}/L did not have any impact on the membrane performance, but this was not observed at the other investigated dosages (2.0 and 5.0 mg Fe^{3+}/L).

Although in-line coagulation improved UF performance for the treatment of the selected secondary effluent, coagulant dose should be cautiously adjusted (Galvañ *et al.* 2014). Lower dosages may not be sufficient for the transformation of particles and organics into more rejectable compounds (Ratajczak *et al.* 2012), while higher dosages may increase deposition of coagulant on the membrane surface, producing additional resistance (Galvañ *et al.* 2014; Wray & Andrews 2014). Ma *et al.* (2013) found that there was a critical coagulant dosage, impacted by feed water pH, which dramatically influenced membrane performance, leading to severe fouling. The interaction between organic compounds and particles in feed water has not been well documented (Galvañ *et al.* 2014). In addition, the data obtained from this study suggest that jar tests may be not a useful indicator of optimum coagulant type and dosage for controlling fouling. Therefore, the goals of the pretreatment (e.g. fouling reduction and/or higher permeate quality) should be carefully considered before conducting tests.

CONCLUSIONS

- This study demonstrated the viability of in-line coagulation as a pre-treatment for UF for the selected secondary effluent under the conditions investigated.
- Generally, the beneficial impact of in-line coagulation was more clearly evident with respect to irreversible fouling reduction, which is more important for sustainable membrane operation.
- Coagulant type and dosage substantially impacted the performance of UF. In some cases, an increase in coagulant dosage led to higher foulant removal, and ferric-based coagulants were better for UF fouling control than the aluminum-based coagulants.

- The reduction in UF fouling by in-line coagulation was primarily attributed to the removal of foulants (biopolymers and turbidity) and/or the size modification of particles that contributed to membrane pore blocking.
- There were no clear observations with respect to the impact of combining in-line coagulation with UF for the reduction of DOC. This will require additional investigation with replicated data points and different source waters.

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DISCLAIMER

The mention of trade names or commercial products does not constitute endorsement of or recommendation for their use.

DATA AVAILABILITY STATEMENT

All relevant data are available from an online repository or repositories (<https://uwspace.uwaterloo.ca/handle/10012/10060>).

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