

Effect of coagulation conditions on ultrafiltration for wastewater effluent

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Abstract. Low-pressure membrane filtration is increasingly used for tertiary treatment of wastewater effluent organic matter (EfOM), mainly comprising organic base/neutral compounds. In-line coagulation with underdosing, charge neutralization, and sweep floc conditions prior to ultrafiltration (UF) was studied to determine removals of the EfOM components and consequent reduction of fouling using polyethersulfone membranes. Coagulation and UF substantially reduced fouling for all coagulation conditions while removing from 7 to 38% of EfOM organic acids. From 7 to 16% of EfOM organic base/neutrals were removed at neutral pH but there was no significant removal for slightly acid coagulation conditions even though fouling was substantially reduced. Sweep floc produced the lowest resistance to filtration but may be inappropriate for in-line use due to the large added volume of solids. Charge-neutralization resulted in poor recovery of the initial flux with hydraulic cleaning. Under-dosing paralleled sweep floc in reducing hydraulic resistance to filtration (for sub-critical flux) and the initial flux was also easily recovered with hydraulic cleaning. Hydrophobic and hydrophilic base/neutrals were identified on the fouled membranes but as previously reported the extent of fouling was not correlated with accumulation of organic base/neutrals.

Keywords: effluent organic matter; in-line coagulation; ultrafiltration; fouling; membrane autopsy

1. Introduction

Ultrafiltration (UF) or microfiltration (MF) is increasingly employed for treatment of wastewater, especially for separation of mixed liquor suspended solids in membrane bioreactors (MBR) or for pre-treatment prior to reverse osmosis in the context of water reuse (Madaeni and Samieirad 2010, Sun and Liu 2013). Fouling is often the limiting factor in UF or MF, and is defined here as an increase in resistance to filtration due to the accumulation of particles or solutes on the surface of the membrane or within the membrane pores.

Hydrophilic (HPI) base/neutrals and colloidal materials have frequently been implicated as the dominant foulant in natural organic matter (NOM) or wastewater effluent organic matter (EfOM).

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NOM usually represents materials that had been in the environment and undergoing reactions for years and perhaps decades, whereas the dominant organic materials in wastewater effluent are produced via “browning reaction” transformations over a period of hours. Zularisam *et al.* (2007) used Fourier transform infrared (FTIR) to find that polysaccharide-like materials were most concentrated on fouled polysulfone membranes. More recently, Miao *et al.* (2014) also reported that HPI fraction of EfOM was important foulants in UF. Lee *et al.* (2001) reported that it was more difficult to remove hydrophilic than hydrophobic NOM from membranes, using acid or base cleaning procedures. Colloids in the base/neutral fraction from conventional fractionation procedures have often been identified as the most important foulants in NOM. Carroll *et al.* (2000) reported that the HPI neutral fraction that caused most fouling of MF membranes also contained the highest concentration of >30 kDa colloids. Fan *et al.* (2001) reported that fouling of hydrophobic polyvinylidene fluoride (PVDF) MF was in the order HPI neutrals > hydrophobic (HPO) acids > transphilic acids \approx HPI charged fraction. Zheng *et al.* (2014) also recently summarized experimental evidence that colloidal fraction of EfOM are important foulants.

HPO acids have also been implicated as the dominant foulant for various membranes. Liang and Song (2007) found that organic fouling of MBR MF membranes decreased after removal of HPO acids but was not affected by removal of particulates. Xiao *et al.* (2011) reported that higher molecular weight (MW) humic fractions were most responsible for fouling membranes. Kim (2016) reported that the permeability recovery of fouled membranes after hydraulic cleaning was directly related to the aromaticity of EfOM, as described by specific ultraviolet absorbance (SUVA). SUVA is typically highest for HPO acids. Review of the literature discloses there is justifiable disagreement and confusion about the components of NOM or EfOM that are most responsible for fouling in UF or MF. Conclusions about the nature of organic foulants are usually based on operational definitions, e.g., many investigators have used the NOM fractionation protocol of Aiken *et al.* (1992) as modified by Carroll *et al.* (2000). Colloidal or large MW organic substances as well as most of inorganic dissolved constituents can pass through the columns of resin beads (Kim and Dempsey, 2012). In our work, we avoid manipulation of pH. We remove particles (>1 μm) and then colloids (>20 nm) by filtration processes, remove HPO/HPI acids using anion exchange resin gel, and then remove HPO base/neutrals using non-ionic resin beads, leaving only HPI base/neutrals.

Coagulation has commonly been identified as a successful pre-treatment for NOM or EfOM prior to membrane filtration (Bergamasco *et al.* 2011, Kim *et al.* 2015, Yao *et al.* 2015). Fabris *et al.* (2007) showed that coagulation of lake water significantly decreased fouling of hydrophilic PVDF MF. Howe *et al.* (2006) concluded that coagulation of NOM decreased membrane fouling by removing material between 100 kDa and 1 μm . Bose and Reckhow (2007) used an extended fractionation strategy and studied adsorption of NOM onto aluminum hydroxide flocs. The humic substances were most strongly adsorbed; percent sorbed was positively correlated with SUVA and molecular size and removal of HPO/HPI acids was inversely related to the negative charge density. These results are consistent with many other investigations that have shown that coagulation was most successful in removing NOM with high MW and SUVA, especially humic materials. Haberkamp *et al.* (2007) studied coagulation of EfOM prior to UF. They reported that coagulation removed bio-colloids and humic materials better than low MW acids and low-MW neutrals were hardly removed (EfOM characterization based on HPSEC). Differences in the removal of NOM were found between charge neutralization and sweep floc conditions (Chow *et al.* 2004).

Therefore, the main objective was to investigate the effects of in-line coagulation pretreatment on filtration of wastewater effluent through 100 kDa polyethersulfone (PES) membranes, with

focus on membrane fouling and removal of EfOM. Several coagulation conditions were selected for testing, including underdosing at three pH values, charge neutralization, and two sweep floc conditions. Coagulant underdosing is defined as a condition that would typically result in poor removal of coagulated solids during passage through rapid sand or multi-media “filters”. A fractionation strategy was used to identify the components of EfOM in order to describe the effects of coagulation and to diagnose the causes of membrane fouling.

2. Material and methods

2.1 Sample collection and chemical coagulation

Fifty liters of mixed liquor were collected from an aeration tank discharge at the University Area Joint Authority (UAJA), Centre County, PA. A portion of the effluent at UAJA is treated by MF and reverse osmosis and distributed for industrial or other non-potable uses. UAJA uses an anoxic-anaerobic-oxic process for biological nutrient removal and also adds alum prior to final sedimentation (after the sampling location) for enhanced removal of phosphorus. Alkalinity and hardness are 4 meq L⁻¹. Mixed liquor was settled for 1 h and supernatant was drawn off and stored at 4°C. Total organic carbon (TOC) of the supernatant was 8.4 mg L⁻¹.

Jar tests were performed to select the different coagulation conditions and to determine removal of EfOM components. Tests were conducted using a Phipps & Bird stirrer with conventional blades (Model 7790-400), rectangular 2 L beakers, commercial liquid alum (2.17M as Al, Al₂(SO₄)₃·14H₂O) dosed from 0.6 to 12.8 mg Al L⁻¹, and pH adjusted by addition of 0.1N NaOH or HCl after coagulant addition. Rapid mix was conducted at 200 rpm for 1 min, and slow mix was sequentially completed at 30 rpm for 30 min. Zeta potential (ZP) and pH were measured at the end of the rapid mix. Turbidity was determined after 1 h of settling. Values for ZP, turbidity, and dissolved organic carbon (DOC) removal were used to select conditions for the in-line coagulation experiments. For in-line coagulation experiments, the coagulated water was mixed at 200 rpm for 2 min and then immediately fed to the membrane testing module using a peristaltic pump.

2.2 Membranes and filtration apparatus

Constant flux UF experiments were conducted as previously reported (Choi and Dempsey 2005, Kim and Dempsey 2008). Briefly, Millipore PES flat membranes had 100 kDa MW cut-off, pore size approximately 14 nm, and 40.7 cm² effective area. Retentate was recirculated to the supply vessel. Less than 40% of initial sample volume was filtered in any experiment. Permeate flux was controlled by separate peristaltic pumps. Permeate flux (by permeate mass) and trans-membrane pressure (TMP) were continuously recorded. Since concentration polarization effects in UF are relatively small (Yuan and Zydney 2000), resistance to filtration due to fouling can be determined by subtracting intrinsic membrane resistance from total resistance. The hydraulic resistance at the end of the filtration experiments was denoted R_{tot} . Resistance removed by hydraulic washing using the Jones and O’Melia (2001) method was R_{cake} . Resistance subsequently removed by soaking in 0.1N NaOH solution for 24 h (Lee *et al.* 2001) was R_{ads} . The residual resistance to filtration after chemical cleaning was the sum of the irreversible component R_{ir} and the intrinsic membrane resistance R_m . Resistance measurements except for R_{tot} were based on pure-water fluxes. These operationally-defined resistances are consistent with terminology used by Ho

and Zydney (2002) and by Choi *et al.* (2005).

2.3 EfOM fractionation

Fractionation of EfOM was performed as previously reported (Kim and Dempsey 2008, 2010, 2012). Mixed liquor was settled, particles were removed by filtration through 1.0 μm glass-fiber filters, and the filtrate was passed through three columns in series. The first column contained DEAE cellulose (diethylaminoethylcellulose, $-\text{OC}_2\text{H}_4\text{N}(\text{C}_2\text{H}_5)_2$) gel that was pre-saturated with humic acid (Aldrich Chemical, Milwaukee, WI). This 20 nm “colloids collector” was not an anion exchanger since all sites were blocked. The second column contained DEAE cellulose, a weak base anion exchange resin that retains HPO/HPI acids. The third column contained DAX-8, a non-ionic resin that retains HPO base/neutrals. Residual DOC from the last column contained only HPI base/neutrals and inorganic salts. TOC was measured after each fractionation step. Concentrations of EfOM in each fraction were determined by TOC differences from one step to the next.

2.4 Analytical methods

DOC and UV absorbance at 254 nm (UV_{254}) were measured after filtration by 0.22 μm cellulose acetate membrane filters (Shimadzu TOC-V CPN and UV-2101PC). Turbidity was measured using Hach Ratio/XR turbidimeter. ZP was measured using a Zetasizer (Malvern, Nano ZS). Conductivity and pH were measured by a conductivity meter (Orion, 115A⁺) and a pH meter (Orion, 230A).

Functional groups of EfOM on fouled membranes were analyzed by attenuated total reflectance-Fourier transform infrared (ATR-FTIR) spectroscopy (Tensor 27, Bruker, USA). Membranes were hydraulically and chemically cleaned to remove cake and reversible fouling layers, placed in sterilized Petri dishes and stored in desiccators for 48 h prior to analysis. A total of 16 scans were performed at a resolution of 4 cm^{-1} using a diamond crystal at room temperature. The measurements were repeated at 6 locations per membrane and results were averaged. All spectra were normalized on the basis of the 1151 cm^{-1} sulfone vibration peak.

Table 1 Coagulation conditions for settled mixed liquor and residual dissolved concentrations after alum coagulation. Sample sequence is from low to high coagulant dose. Values in parentheses represent removal (%) of DOC or UV_{254} due to incorporation into a filterable (0.22 μm) floc

Item	Settled mixed liquor	Under-dosing acid pH	Charge neutralization acid pH	Under-dosing neutral pH	Under-dosing alkaline pH	Sweep floc neutral pH	Sweep floc neutral pH
Sample ID	Raw	#1	#2	#3	#4	#5	#6
Alum dose (mg Al L^{-1})	0	0.6	1.3	1.3	3.8	6.4	12.8
pH	7.4	5.1	5.2	7.3	7.8	7.0	6.8
Conductivity ($\mu\text{S cm}^{-1}$)	1645	1800	1807	1652	1611	1690	1729
TDS (mg L^{-1})	808	886	889	811	790	830	849
UV_{254} (cm^{-1})	0.135	0.118 (13)	0.111 (18)	0.122 (10)	0.117 (13)	0.110 (19)	0.101 (25)
DOC (mg L^{-1})	8.0 \pm 0.2	6.9 \pm 0.1 (13)	6.6 \pm 0.2 (17)	7.1 \pm 0.2 (11)	7.3 \pm 0.2 (9)	6.2 \pm 0.2 (23)	5.5 \pm 0.1 (32)
SUVA ($\text{mg m}^{-1} \text{L}^{-1}$)	1.68	1.70	1.67	1.72	1.61	1.77	1.85

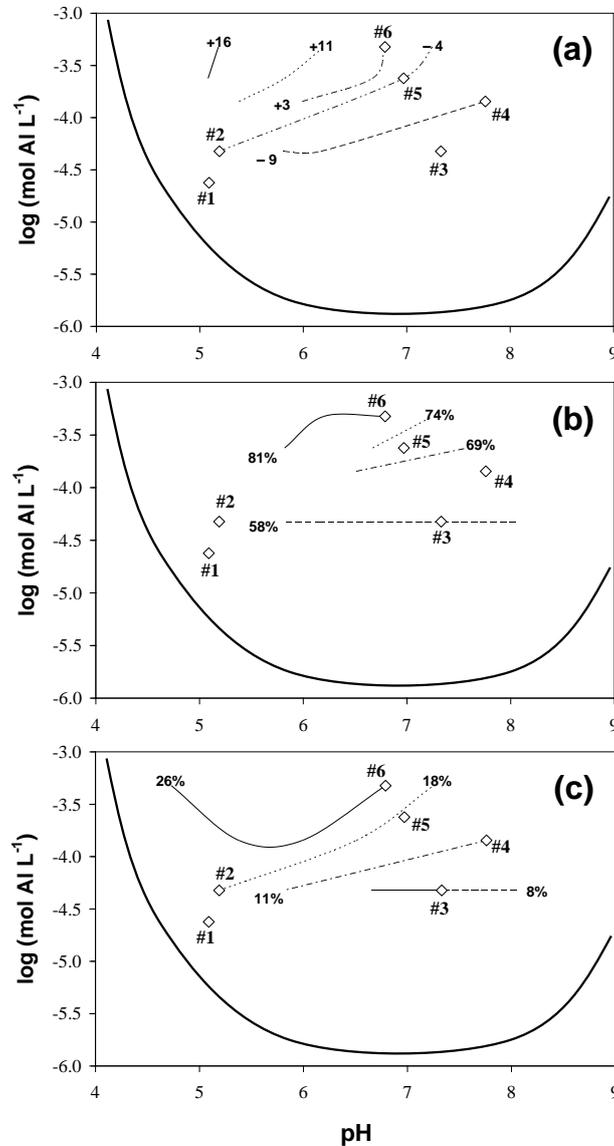


Fig. 1 (a) Zeta potential after initial mixing, (b) turbidity removal after sedimentation, and (c) UV254 removal after sedimentation and 0.2 μm filtration. The solid line represent the solubility of amorphous $\text{Al(OH)}_3(\text{s})$ at 25°C, using constants reported by Dempsey (1989). Coagulation conditions #1 to #6 are described in Table 1

3. Results and discussion

3.1 Selection of coagulation conditions

The effects of coagulation on ZP after rapid mix and turbidity and UV254 after settling are shown in Fig. 1. Sweep floc was defined as >70% turbidity removal and occurred for coagulant

dose $>3 \text{ mg Al L}^{-1}$ (i.e., $-4.0 \log (\text{M as Al})$) and $\text{pH} >6.5$. Charge neutralization was defined as ZP between $\pm 6 \text{ mV}$ and $<40\%$ turbidity removal. Underdosing was defined as a coagulant dose less than required for charge neutralization. Based on the jar test results, we selected two raw water pH conditions (pH 5 and 8), three underdosing conditions at three pH values (#1, #3, and #4), one charge neutralization condition (#2), and two sweep floc conditions (#5 and #6) for further study. DOC, UV_{254} , and SUVA after the selected coagulation conditions are also described in Table 1.

3.2 Removal of DOC by coagulation

Removal of dissolved EfOM by coagulation increased with increasing alum dose and decreasing pH. Overall DOC values are shown in Table 1. Sweep floc conditions removed 23 and 32% of DOC, charge neutralization removed 17% of DOC, and underdosing removed 9 to 13% of DOC with lowest removal at the highest pH, which was also the highest alum dose among underdosing conditions.

SUVA values for residual EfOM increased with coagulation especially under neutral pH conditions, which is different than commonly observed for NOM. The largest increases in SUVA occurred for sweep floc, precisely the conditions that are advised for greatest decrease in SUVA when treating NOM. Literature reports and data are sparse regarding changes in EfOM SUVA after coagulation, but our results seem consistent with some previous studies. Haberkamp and co-workers (2007) showed that coagulation removed a higher percentage of biopolymers than of humic substances in EfOM. Jarusutthirak and Amy (2006) reported overall SUVA values for wastewater effluent that were identical to our raw water results, but soluble microbial products that were produced in laboratory batch treatment systems had much lower SUVA values. Bose and Reckhow (1998) studied NOM from surface water and reported low SUVA for hydrophilic acids and $\text{SUVA} \geq 3$ for HPI base/neutrals.

Table 2 shows significant differences among the coagulation treatments in removals of various fractions of EfOM. All of the coagulation conditions incorporated EfOM into settleable floc but sweep floc was most successful. Only sweep floc significantly decreased colloidal EfOM. These trends are similar to those typically observed for removal of NOM from surface waters, where enhanced coagulation involves increasing coagulant dose and decreasing pH to improve removal of DOC. All coagulation conditions removed some HPO/HPI acids, with best removals using high coagulant dose and low pH. The best removals of base/neutrals occurred at neutral pH, while no base/neutrals were removed with acidic underdosing.

3.3 Resistance to filtration and transmission of DOC during UF

Acidification of the raw EfOM to pH 5 resulted in higher resistance to filtration. This is illustrated in Fig. 2 and is consistent with increased sorption of humic and fulvic acids onto most

Table 2 Effects of coagulation treatments on the removals of EfOM fractions (mg C L^{-1})

EfOM fraction	Raw	#1	#2	#3	#4	#5	#6
Settleable organics	0.45±0.04	1.41±0.08	1.71±0.06	1.25±0.08	1.08±0.07	2.14±0.07	2.88±0.04
Colloids ($1 \mu\text{m} \sim 20 \text{ nm}$)	1.18±0.09	1.25±0.06	1.16±0.07	1.13±0.06	1.01±0.08	0.62±0.07	0.28±0.04
Organic acids	3.35±0.09	2.35±0.04	2.19±0.04	3.07±0.06	3.11±0.06	2.79±0.07	2.09±0.05
Organic base/neutrals	3.37±0.16	3.34±0.22	3.29±0.13	2.90±0.20	3.15±0.16	2.80±0.16	3.10±0.08

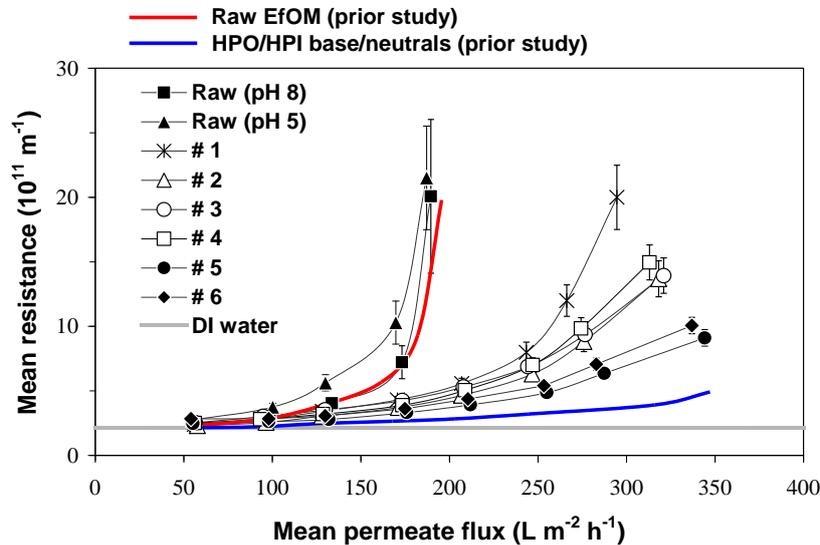


Fig. 2 Variations in resistance with permeate flux during UF membrane filtration of raw and coagulated wastewaters. #1, #3, and #4: unconventional coagulation conditions, #2: charge neutralization condition, #5 and #6: sweep floc conditions, and Raw (pH 8) and Raw (pH 5): raw wastewaters at pH 8 and pH 5, respectively. Top red line and lower blue line show our previously reported results for EfOM from UAJA before and after removal of particles, colloids, and organic acids from UAJA EfOM

solids with a decrease in pH, especially over the pH range from 8 to 4 (e.g., Aiken *et al.* 1992).

All of the coagulation conditions reduced the resistance to filtration compared to raw EfOM samples. These results are shown in Fig. 2, which also shows our previously reported results for EfOM from UAJA before (top red line) and after removal of particles, colloids, and HPO/HPI acids from UAJA EfOM (lower blue line) (Kim and Dempsey 2008). All of the decrease in resistance, in the earlier results, occurred upon removal of acids. The current results do not provide such clear evidence that all fouling was due to HPO/HPI acids, since most coagulation conditions removed some base/neutrals as well as HPO/HPI acids and since not all resistance to filtration was eliminated by these coagulation conditions. The current results indicate that a partial removal of HPO/HPI acids resulted in significant decrease in fouling; thus, it can be speculated that the formation of a porous cake layer on the surface of membrane results in increased removal of foulants before they reach the pore walls deeper inside the membrane.

Our results are also consistent with the hypothesis, supported by other work (Kwon *et al.* 2000, Li *et al.* 2000) that resistance to filtration is decreased with formation of a filtering cake layer. In our work, sweep floc conditions (highest alum doses) gave the largest reductions in resistance to filtration (Fig. 2), charge neutralization and neutral-pH underdosing used identical alum doses and gave similar reductions in resistance to filtration, and acidic underdosing (lowest alum dose) produced the smallest decrease in resistance to filtration. Thus reduction of fouling after coagulation was likely due to a combination of removal of HPO/HPI acids and formation of a filtering cake layer.

Transmission of EfOM through the membrane increased with increasing permeate flux, both for raw EfOM and after every coagulation condition. This is illustrated in Fig. 3. Increasing transmission with increasing flux indicates that the EfOM in these samples did not form a

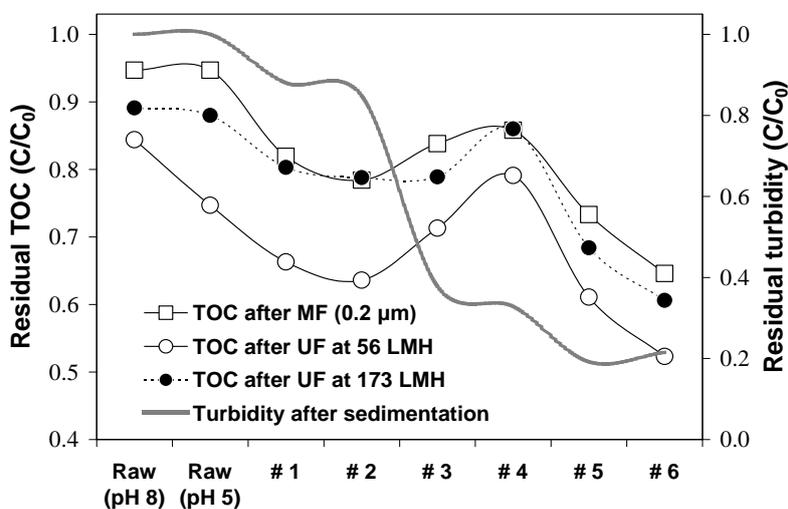


Fig. 3 Transmission of TOC through PES ultrafilters as a function of coagulation condition and settled turbidity. #1, #3, and #4: unconventional coagulation conditions, #2: charge neutralization condition, #5 and #6: sweep floc conditions

concentration polarization layer on the retentate side of the membrane sufficient to cause precipitation. Transmission decreased with increasing coagulation dose and with decreasing pH, consistent both qualitatively and quantitatively with the removals during coagulation that were reported in Table 1.

3.4 Fouling and membrane cleaning

Fouled membranes were cleaned using hydraulic and then chemical cleaning protocols. R_{cake} , R_{ads} , and R_{ir} represent the fouling that could be removed by a hydraulic cleaning, the fouling that required a chemical cleaning for removal, and the fouling that was not removed by either of those cleaning steps. Experimental values for R_{cake} , R_{ads} , and R_{ir} and their correlation to coagulation strategies are shown in Fig. 4. R_{cake} , R_{ads} , and R_{ir} for UF of raw EfOM ranged from 24.8×10^{11} to $25.5 \times 10^{11} \text{ m}^{-1}$, from 0.64×10^{11} to $1.44 \times 10^{11} \text{ m}^{-1}$, and from 0.35×10^{11} to $0.53 \times 10^{11} \text{ m}^{-1}$. These hydraulic resistance values were always higher for UF of acidic raw EfOM compared to when filtering slightly alkaline raw EfOM. All coagulation conditions resulted in decreased resistance to filtration compared to raw EfOM after UF, but which caused different flux recovery of fouled membranes after cleaning. The lowest R_{cake} values were for sweep floc conditions. The underdosing coagulation at both acidic and neutral pH levels gave the best results for R_{ir} . Increasing coagulant dose at neutral pH from 1.3 to 12.8 mg Al L⁻¹ showed an insignificant impact on R_{ads} but resulted in almost twice R_{ir} of the underdosing condition. The charge neutralization resulted in highest R_{ads} and R_{ir} . Schrader *et al.* (2005) also reported that charge neutralization resulted in high resistance to filtration. It was also noted that chemically reversible fouling (R_{ads}) was largest for the acidic pH conditions #1 and #2, suggesting increased adsorption of HPO/HPI acids onto the membrane at lower pH followed by extraction of adsorbed acids during alkaline chemical. This result also indicates that a significant fraction of each EfOM component is poorly adsorbed or perhaps not adsorbed onto Al(OH)₃ flocs. This behavior is related to the protocols for

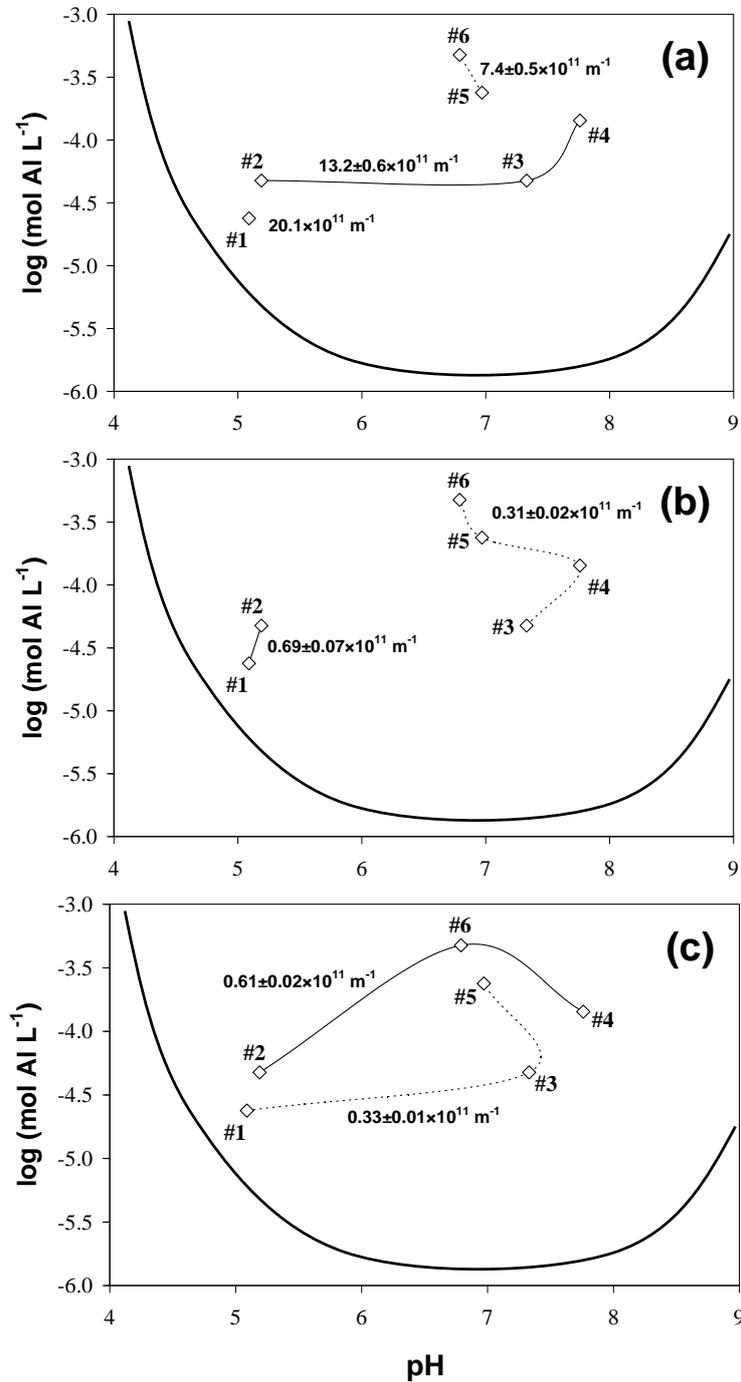


Fig. 4 Resistance to filtration after sequential hydraulic rinsing and chemical cleaning. (a) R_{cake} that could be removed by hydraulic wash, (b) R_{ads} that could only be removed by chemical cleaning, and (c) irreversible resistance, R_{ir} , still remaining after the cleanings. R_{cake} , R_{ads} , and R_{ir} for UF of raw EfOM ranged from 24.8×10^{11} to $25.5 \times 10^{11} \text{ m}^{-1}$, from 0.64×10^{11} to $1.44 \times 10^{11} \text{ m}^{-1}$, and from 0.35×10^{11} to $0.53 \times 10^{11} \text{ m}^{-1}$, respectively. The solid line represent the solubility of amorphous $\text{Al(OH)}_3(\text{s})$ at 25°C

extraction of HPO acids onto non-ionic resins (Aiken *et al.* 1992, Carroll *et al.* 2000). These results convince us that the underdosing coagulation under neutral pH conditions is most effective among the investigated coagulation strategies to minimize membrane fouling which can be chemically-reversible or -irreversible and thus reduce the use of chemicals for both pretreatment of wastewater and restoration of fouled membranes.

3.5. Spectroscopic properties of fouled and cleaned membranes

ATR-FTIR spectra for both fresh and fouled PES membranes are shown in Fig. 5. Major differences in absorbance between clean and fouled membranes were observed at 1735 cm^{-1} (C=C stretching of alkyl esters or ketones), 1070 and 1010 cm^{-1} (C-O-C and C=O ring vibrations of carbohydrate), a peak fronting around 1130 cm^{-1} (C-O-C group vibrations in the cyclic structures of carbohydrates), and 800 cm^{-1} (glycosidic linkages in polysaccharides). Assignments for these peaks were based on previous studies (Bosch *et al.* 2006, Sheng *et al.* 2006). Overall, the increases in absorbance from clean PES to fouled membranes were consistent with the dominant presence of polysaccharide-like matter and with dominant presence of HPI neutrals on the membrane surfaces.

Other investigators who have used ATR-FTIR to identify organics on fouled and chemically cleaned membranes have discovered polysaccharide-like matter or amides to be the dominant residual organic constituents. Koh *et al.* (2006) used PES colloids to pre-treat source water, thus removing NOM constituents that caused fouling of PES membranes. They identified silicates, proteins, and perhaps polysaccharide-like materials on the used PES colloids. Zularisam *et al.* (2007) also discovered polysaccharide-like matter as the dominant NOM constituent on fouled and cleaned polysulfone membranes.

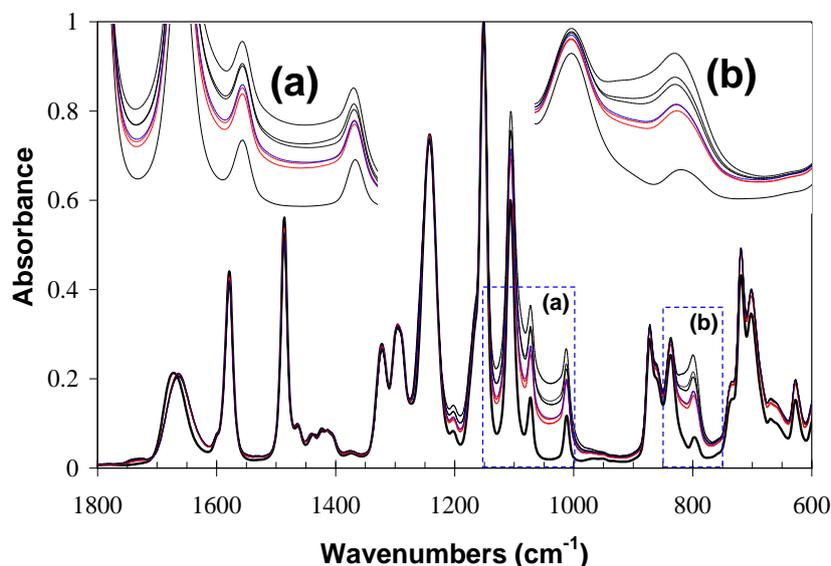


Fig. 5 ATR-FTIR spectra for the retentate side of polyethersulfone (PES) membranes after sequential hydraulic and chemical cleanings. Lines (bottom to top) represent a clean membrane, #2, #1, #4, #5, #3, Raw (pH 8), Raw (pH 5), and #6, respectively. Inserts (a) $1150\text{-}1000\text{ cm}^{-1}$ and (b) $850\text{-}750\text{ cm}^{-1}$ show regions with the greatest change in absorbance

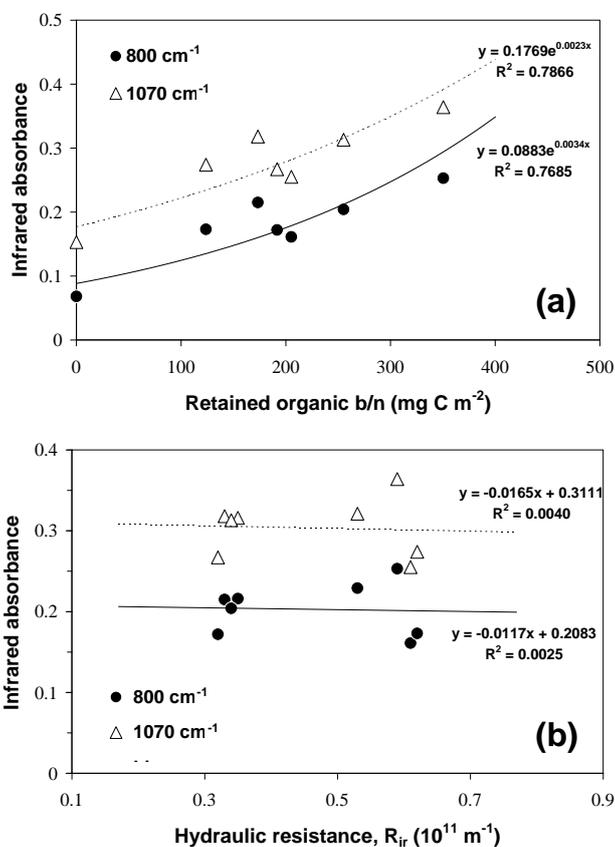


Fig. 6 IR absorbances at 800 and 1700 cm⁻¹ versus (a) retained mass of organic base/neutral fractions and (b) hydraulic resistance remaining after sequential hydraulic and chemical cleaning (R_{ir}). The increase of IR absorbances was attributed to HPO/HPI base and neutrals that would be easily retained on the top of membranes and hardly removed by alkaline extraction, while no substantial correlation between IR absorbance and membrane fouling was found

For EfOM, there seems consistency in finding residual organic matter on fouled and cleaned UF membranes that was apparently different than the EfOM constituents that caused most of the fouling. Jarusutthirak *et al.* (2002) reported that the colloid fraction (separated from EfOM by dialysis) produced the greatest flux decline, whereas polysaccharides and amino sugars were the dominant residual EfOM constituents extracted with caustic from all fouled and hydraulically cleaned polyamide UF membranes, no matter which EfOM fraction was initially filtered. Shon *et al.* (2006) reported that the HP fraction (closest to dissolved base/neutral organics in the current study) caused the least fouling of the EfOM fractions, but was the dominant material residual on sulfonated polysulfone UF membranes. Both of those studies used the Aiken strategy for separation of EfOM constituents. In our earlier work (Kim and Dempsey 2008), we reported that the base/neutral fractions did not result in fouling, but that constituents of the base/neutral fraction were the dominant residual organic material on fouled and chemically cleaned PES membranes. Our prior observation was reconfirmed as illustrated in Fig. 6(a). In the current study, there was no correlation between irreversible hydraulic resistance (R_{ir}) and intensity of absorbance in the

carbohydrate regions (Fig. 6(b)), nor was there a correlation between R_{cake} or R_{ads} and absorbance (data not shown). Taken as a group, these various results indicate that although polysaccharide constituents are dominant in most fouled and chemically cleaned membranes for either NOM or EfOM, these constituents probably do not cause the most severe fouling. This result could be due to attachment of base/neutrals to the surface of the membrane, without blockage of pores. The ATR-FTIR signal penetrates only a few microns into the sample. These results support our earlier conclusion that membrane autopsies indicating the presence of polysaccharide-like matter on fouled membranes do not necessarily implicate those materials as the most important foulants.

4. Conclusions

We investigated various in-line coagulation strategies for removal of EfOM components and also for optimization of membrane performance. This study has also provided information related to diagnosis of the causes to fouling through use of membrane autopsies. The following conclusions were drawn.

All coagulation treatments resulted in transfer of some EfOM into settleable floc, especially the highest removal of colloidal EfOM was achieved by sweep floc conditions through floc aggregates. EfOM acids were best removed by reducing pH and increasing the coagulant dose. This is a similar strategy as used for treatment of potable water. On the contrary, base/neutrals were removed best by coagulation at neutral pH. Removal of base/neutrals was relatively independent of coagulant dose. Despite not removing any EfOM base/neutrals there was still a decrease in fouling due to coagulation, and EfOM base/neutrals were found on the PES membrane but that was not correlated with fouling. All coagulation conditions resulted in decreased resistance to filtration during UF, but only a few of the coagulation treatments resulted in improved recovery of initial flux after hydraulic cleaning or after hydraulic and chemical cleanings. Decreased fouling after coagulation was related to adsorption of acids onto floc and to formation of a filter cake layer that prevents the interactions between organic acids and membrane materials. Increasing the coagulant dose at acidic (#1 and #2) or neutral (#3, #5, and #6) pH resulted in increased resistance to filtration after hydraulic cleaning. Increasing alum dose to achieve charge-neutralization conditions, at acidic pH, provided small incremental increase in removal of EfOM and specifically of HPO/HPI acids during UF, but with worse recovery of flux after cleaning operations, compared to very low alum dose. Low coagulant dose (under-dosing based on ZP values and requirements for conventional coagulation) at neutral pH (#3) provided equivalent or even better coagulation pre-treatment when compared to sweep floc conditions using up to 10 times higher dose in terms of both decreasing resistance to filtration (for sub-critical flux) and recovery of flux after hydraulic wash. Sweep floc removed more EfOM after UF than other coagulation conditions, but (as noted above) recovery of flux by hydraulic cleaning deteriorated with dose. It appears that improved removal of EfOM with sweep floc conditions would be difficult to justify due to increased chemical costs and volume of residuals. Flux recovery due to chemical cleaning (caustic) was most effective after UF of acidic samples, whether coagulated or not. This is consistent with known behavior of HPO/HPI acids, i.e. increased adsorption at lower pH and improved extraction at higher pH. Decreases in resistance to filtration were related to removal of HPO/HPI acids, but HPO/HPI base/neutrals were the dominant EfOM on fouled and sequentially cleaned membranes. Thus, discovery of hydrophilic neutrals during a membrane autopsy might not correspond to EfOM fractions that cause fouling.

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