ELSEVIER

Desalination 186 (2006) 239–249

DESALINATION

www.elsevier.com/locate/desal

Effects of dynamic or secondary-layer coagulation on ultrafiltration

M.M. Sharp, I.C. Escobar*

Chemical and Environmental Engineering, The University of Toledo, Toledo, Ohio, USA
Tel. +1 (419) 530-8267; Fax +1 (419) 530-8086; email: Isabel.escobar@utoledo.edu

Received 6 December 2004; accepted 29 April 2005

Abstract

This research focused on testing different coagulation pre-treatment techniques to improve membrane filtration in water separations, namely ultrafiltration (UF). These three techniques were 1) conventional coagulation, 2) forming a dynamic, or secondary, coagulant-based layer on the membrane, and 3) injecting the coagulant into the feed line so that it runs inline with the raw water across the membrane. Results showed that the dynamic membrane's mode of operation achieved higher steady state flux values than UF alone and than conventional coagulation pretreatment ahead of UF, while in-line coagulation displayed the worst flux decline. UF alone was ineffective in removing solids and dissolved organic carbon (DOC), while conventional coagulation and dynamic UF modes rejected solids and DOC at similar rates. Through membrane autopsies, irreversible fouling measurements for the dynamic membrane mode were significantly lower than for the conventional coagulation mode. Thus, a coagulant-based dynamic membrane has the potential to be an effective method to improve UF efficiency in water separation applications as well as to decrease pretreatment costs associated with operation. Upon reduction of associated costs, membranes can also become competitive in advanced wastewater treatment and water reuse processes.

Keywords: Coagulation; Dynamic membrane; Membrane filtration

1. Introduction

Fouling represents the major constraint to more cost-effective, and therefore expanded, application of membrane technology in drinking water and wastewater treatment. Fouling can occur in several forms and can vary from high- to low-pressure membranes. Many researchers have suggested that the humic substances fraction of natural organic matter (NOM) is a major foulant that controls the rate and extent of membrane fouling [1–9].

---

*Corresponding author.

Presented at the International Conference on Integrated Concepts on Water Recycling, Wollongong, NSW Australia, 14–17 February 2005.

However, recent studies have reported that hydrophilic (non-humic) NOM could be the more dominant foulant. In the studies performed by Lin et al. [10] and Carroll et al. [11], residual dissolved NOM composed of small, neutral hydrophilic substances is strongly implicated in controlling the rate of fouling. Associated with wastewater treated to a secondary level is effluent organic matter (EfOM). EfOM consists of NOM contributed by the drinking water source plus soluble microbial products (SMPs) produced during biological treatment, and has relevance from the perspective of effluent-impacted drinking water sources or wastewater reclamation and reuse. Based on significant chemical differences, fouling potential varies according to the type of NOM [12].

The use of low-pressure membranes, microfiltration (MF) and ultrafiltration (UF), has increased dramatically over the last decade, in response to water regulations. In the mid-1990s, low-pressure membrane technology was most often employed in a direct filtration mode, with source water applied directly to the membrane. The practice has evolved and pretreatment in the form of chemical coagulation has now become more common and has led to the hybrid technology coagulation followed by ultrafiltration (C–UF). The progression from direct to integrated treatment (C–UF) has produced benefits in terms of membrane fouling reduction by solids while only minimal benefit relative to NOM fouling.

In crossflow processes, there occurs a formation of a secondary or dynamic membrane on top of the primary membrane. Dynamic membranes are formed by initially having colloids/particulates/NOM block the support pores. Once the pores are blocked, a transition time (45–120 min) is said to have elapsed and the formation of a cake filtration layer begins. Dynamic membranes were first reported in 1965 by workers at the Oak Ridge Laboratories engaged in desalination research [13]. NOM forms cake layers that adversely affect membrane operation (i.e. irreversible fouling layers), while inorganic colloids have been observed to form desirable layers [14,15]. The presence of steady state layers of symmetric minerals of narrow particle size distribution on membranes have been associated with increased permeate volume, while the magnitude of the rejection increases with increasing the dynamic layer mass and irregularity [16]. This phenomenon is being exploited here by substituting the involuntary dynamic membrane with a layer of desirable properties.

The objective of this research was to find a method of pretreatment that would be both effective for UF membrane processes among (1) conventional coagulation, (2) dynamic membrane coagulation, and (3) in-line coagulation.

2. Methods and materials

The methods and materials used for this study were adapted from and can be found in greater detail in Peng et al. [9] and King et al. [17].

2.1. Membranes

For this study, two commercial water treatment membranes were examined. These membranes were: CQ, an ultrafiltration membrane by GE Water (Minnetonka, MN), and NTR7450, a nanofiltration membrane by Hydranautics (San Diego, CA).

2.2. Feedwater

The characteristics of the feed water used in this study can be found in Table 1.

2.3. Filtration test apparatus and procedure

Testing was conducted using the filtration assembly shown in Fig. 1. The membrane was housed in a SEPA CF filtration unit (Osmontics, Minneatonka, MN). The filtration unit was constructed out of 316 stainless steel and rated for an operating pressure up to 69 bar (1000 psi). The test unit was sealed by applying adequate

Table 1
Characteristics of feed water, average of 8 samples

Characteristic	Measurement
Turbidity, NTU	1.99
UV-254, 1/cm	0.063
TDS, ppm	235.4
Conductivity, µS/cm	353.8
pH	7.98
Hardness, mg/L as $CaCO_3$	224.7
DOC, ppm	4.61

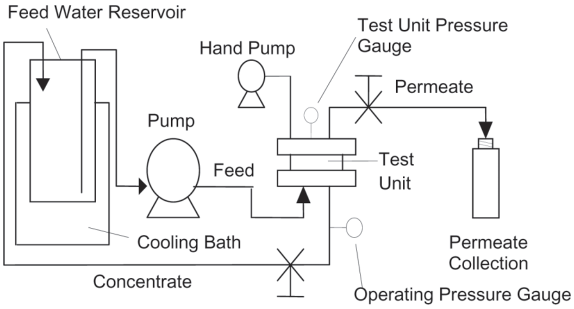

Fig. 1. Diagram of the testing apparatus.

pressure via the hand pump (P-142, Enerpac, Milwaukee, WI); this ensured water was not able to bypass the membrane. The feed stream was delivered by a motor (Baldor Electric Company, Ft. Smith, AR) and M-03 Hydra-Cell pump (Wanner Engineering, Inc., Minneapolis, MN) assembly. Flow valves controlled permeate and concentrate flow and the pressure acting on the membrane in the test unit. Due to the high pressures required by the membranes, it was necessary to use a cooling bath to control the temperature of the feed.

This testing setup was representative of actual membrane filtration, because the test unit was operated at a pressure within each membrane's recommended operating range. Additionally, the SEPA CF is a cross-flow filtration module, which is the most common mode of operation in actual membrane filtration processes.

Before use, each membrane was rinsed with deionized (DI) water and then soaked in DI water overnight [2]. The membrane was removed from the DI water and rinsed immediately before installation into the filtration cell unit. The filtration conditions (operating pressure and duration of test) depended on the physical limitations and flux of each membrane. Once the membrane was installed in the filtration cell unit, the membrane was pre-compacted with 1000 mL of DI water [2]. Immediately following the DI water, the raw water was added to the feed container. A 500 mL sample of the raw water was taken before testing and was stored for water quality analysis. The first 2000 mL of permeate from raw water filtration was discarded to ensure complete removal of DI water from the test unit. After this disposal, permeate was collected in an organic free bottle for water quality analysis. This analysis required that 1000 mL of permeate to be collected.

Throughout the test, membrane flux was measured by recording the time required to collect 50 mL of permeate. To compensate for variations in pressure and changes in feed water temperature (changes in viscosity of the water), each flux measurement was accompanied by a measurement of the operating pressure and temperature of the feed water. This allowed for normalization of the solvent mass transfer coefficient (MTC, also known as specific flux) defined as

$$\mathrm{MTC}_{25^\circ\mathrm{C}} \equiv \left[\frac{J}{\Delta P}\right]_{T(^\circ\mathrm{C})} \left[\frac{\mu_{25^\circ\mathrm{C}}}{\mu_{T(^\circ\mathrm{C})}}\right] \qquad (1)$$

where J (m/s-kPa) is flux, ΔP (kPa) is the operating pressure, and μ is viscosity ($N\cdot s/m^2$).

After collection of permeate for water quality analysis, the membrane/film assembly was removed from the SEPA CF test unit and went through water quality analysis. A 500 mL sample of the remaining raw water, further known as concentrate, was also kept for water quality analysis.

2.4. Water quality analysis

The water quality of the feed water, permeate, and concentrate was determined by TDS, pH, turbidity, conductivity, hardness, DOC, UV-254, and HPC analysis.

2.5. Membrane fouling analysis

The severity of abiotic fouling was determined by assessing the NOM accumulation on the membrane surface. This was accomplished through a membrane autopsy after filtration experimentation had been completed. The membrane autopsy was performed according to the method proposed by Hong and Elimelech [2]. A sample portion from the used membrane and an unused control were placed into separate 100 mL 0.1 M NaOH solutions overnight to dissolve the NOM. After complete removal of the NOM from the membrane surface, the resulting solutions were analyzed for turbidity, conductivity, TDS, and UV-254. The samples used for UV-254 analysis were first filtered through 0.45 μm pore size nylon filters (Whatman International Ltd., Maidstone, England); these ensured solids did not interfere with the analysis. To account for contributions in the readings from the 0.1 M NaOH solution, a clean, unused membrane sample was subjected to the same conditions and testing as the used membrane. The difference in the results of each analysis (unused membrane result subtracted from used membrane result) was considered the amount of abiotic fouling on the used membrane.

2.6. Coagulation setups

Four methods of coagulant pretreatment were tested, a conventional coagulant/settlement, two dynamic membrane, and an inline setup.

2.6.1. Conventional coagulant/settlement

For this setup, 4 L of feed water were used. A 2000 mL valved outlet reservoir bottle was filled with raw water and was stirred using a magnetic stirrer at the maximum setting of ten. At time equal to 0 s, the 5 mL of 2% ferric chloride was added into the vortex created by the mixer to ensure better and instantaneous mixing and was mixed at this setting for 2 min. At time equal to 120 s, the mixing was reduced to a setting of five for 45 s. At this time, the mixing was stopped and the floc was allowed to settle for 20 min. This procedure was repeated and after the floc was allowed to settle, the water was drained using the valve into one 4 L bottle. This was used as the raw water in the filtration process described previously.

2.6.2. Dynamic membrane

Two different setups were used to test this method of coagulation pretreatment. The first setup, called dynamic I, utilized the membrane filtration method above, but after the membrane had been pre-compacted with 1000 mL of DI water, a solution of 10 g ferric chloride/10 mL DI water was placed on the plastic film that is in direct contact with the membrane surface. To allow binding to the membrane and rinsing of excess coagulant another 1000 mL of DI water was run across the membrane before filtering the raw water. After the 1000 mL of permeate had been collected, another bottle of raw water was filtered. The first 2000 mL of permeate was again discarded and after this disposal, permeate was collected in an organic free bottle for water quality analysis.

For the second dynamic membrane setup, called dynamic II, a solution of 10 g ferric chloride/1000 mL DI water was run in a dead-end mode (0% recovery) across the membrane using the pump after the membrane had been pre-compacted with 1000 mL of DI water. An additional 1000 mL of DI water was filtered to allow the excess coagulant to be rinsed away. Two bottles of raw water were filtered with the first 2000 mL of permeate being discarded and the third 1000 mL of permeate being collected in an organic free bottle.

2.6.3. In-line testing

The original membrane filtration method was used until the 1000 mL of permeate was to be collected. At this time the pump's inlet line was replaced with the setup shown in Fig. 2. The 3/8″ tube was split with a tee and off of the tee a 3/8″ to 1/4″ reducer was coupled to valve which was then connected to 1/4″ tubing. This new line was used to introduce coagulant into the raw water before it crossed the membrane surface.

The coagulant used for this test was 500 mL of 2% ferric chloride. After the coagulant had been run in, the extra line was placed in the raw water, so that air was not sucked into the inlet line. Again the 1000 mL of permeate was collected in the organic free bottle. The same water quality testing was done on the samples as was done previously.

3. Results and discussion

3.1. Specific flux or mass transfer coefficient (MTC) results

The MTC results for each of the tests are shown in Figs. 3–6. Each figure shows the data collected during baseline testing and the data collected during each coagulant set up. Trend lines were added to indicate how each MTC was affected by the test. Fig. 3 shows the base line testing and the conventional coagulation. For the conventional coagulation, a larger MTC decline was observed.

Fig. 4 shows a comparison of the baseline data to the dynamic I data. Again, the data points are shown for each test and then trend lines are added to characterize the MTC behaviour. It was observed for the dynamic I tests that the MTC had greater overall value and although there was a decline, the ending trend was in a positive direction. Initially, the coagulant blocked the support pores, which led to a flux decline. Once the pores were blocked, a transition time elapsed and the formation of a steady-state filtration layer began, during which the flux was regained.

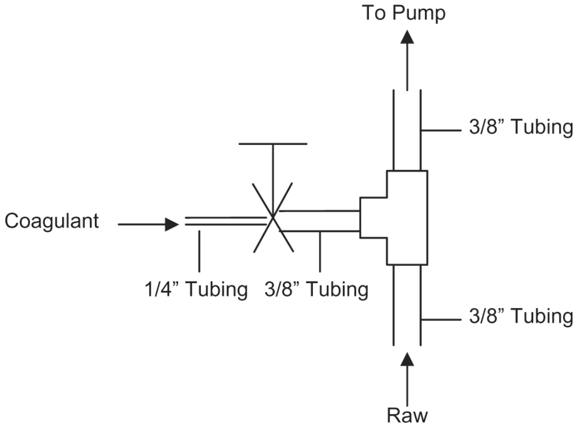

Fig. 2. Setup for inline testing.

Fig. 5 shows a comparison of the baseline data to the dynamic II membrane data. Due to its similarity to the dynamic I testing the results are comparable to the dynamic I results. There is an initial increase in MTC, then a greater decline, and then an upward trend towards the end of the test as the dynamic layer initially blocks pores and after some time forms a steady-state coagulant layer on the membrane surface.

Fig. 6 shows a comparison of the baseline to the inline coagulation data. The results show, that overall the MTC values are lower and that the inline coagulation causes a greater decrease in MTC. This decline most likely occurred because the coagulant attached to the particles that had already fouled the membrane, thereby increasing the cake layer and causing a further decline in the MTC.

3.2. Water quality

Table 2 shows a comparison between the removal percentages of TDS, hardness and DOC for the different modes of coagulation, while Figs. 7 and 8 show the graphs for turbidity and UV-254. Table 2 shows that the rejection of dissolved solids (TDS) is nearly negligible regardless of the presence of pretreatment, while dynamic I and dynamic II modes reject more hardness than

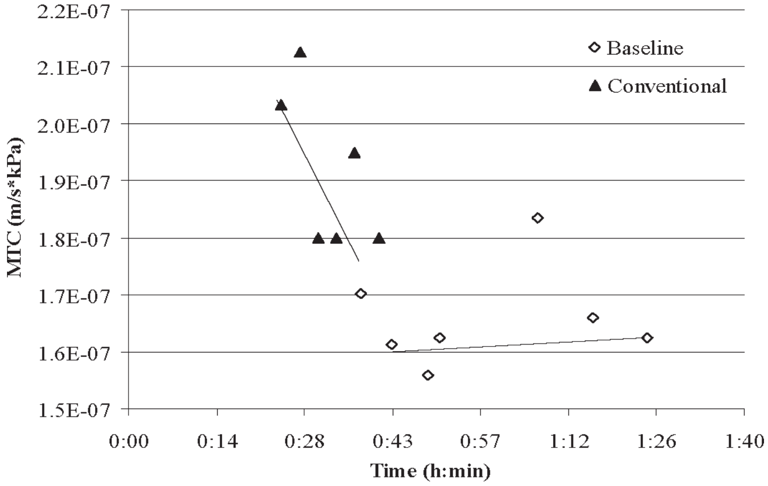

Fig. 3. Comparison of MTC values of baseline testing vs. conventional coagulation.

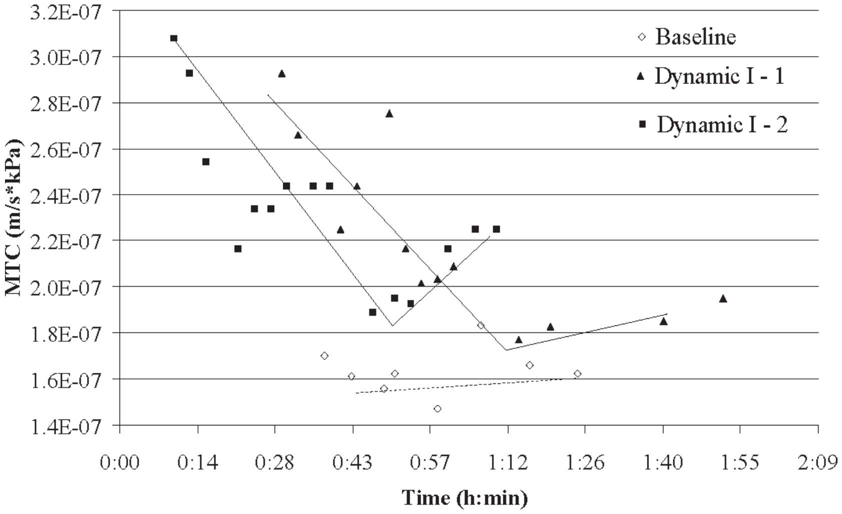

Fig. 4. Comparison of MTC values for baseline testing vs. dynamic I tests.

Table 2
Characteristics of different removal percentages for the different coagulation modes

	Baseline	Conventional	Dynamic I	Dynamic II membrane	Inline
TDS	4.9	0.0	5.2	3.2	0.0
Hardness	9.4	9.9	14.6	11.7	N/A
DOC	3.9	34.9	33.7	12.1	N/A

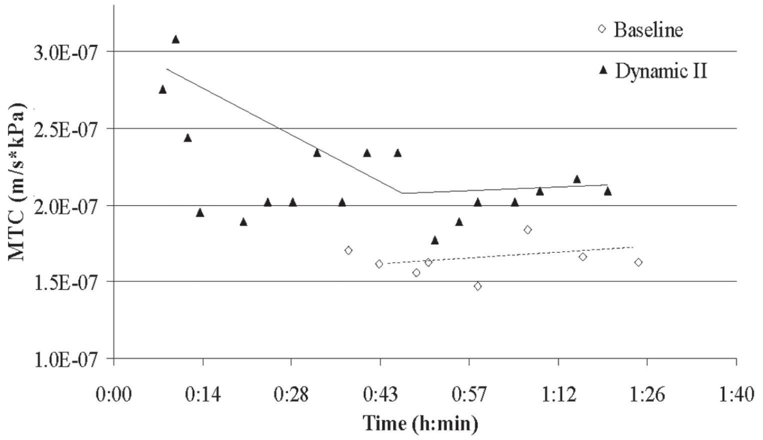

Fig. 5. Comparison of MTC values for baseline vs. dynamic II membrane.

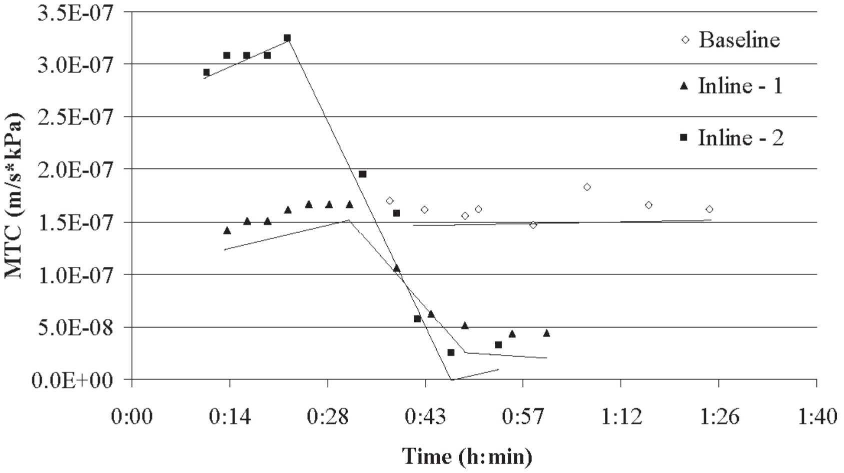

Fig. 6. Comparison of MTC values for baseline vs. in-line coagulation.

the baseline or conventional coagulation modes. Further, all coagulation modes reject more organic carbon (DOC) than the baseline, with conventional coagulation and the dynamic I displaying significantly higher rejections.

On Figs. 7, 8 the average value for the raw water and the permeate are shown using the bars. Due to the difference in raw water characteristics, the percent removal is also shown. Fig. 7 shows the values and percent removal for turbidity. It is observed that all of the tests, other than the dynamic I have above a 90% removal rate. The dynamic I removal is still above 60% with a permeate turbidity of 0.225 NTU. Fig. 8 shows the values and percent removals for UV-254. For this test, dynamic I had the highest percent of removal, with almost a 90% removal rate to less than detectable values in the permeate. Dynamic II and in-line coagulation showed no removal.

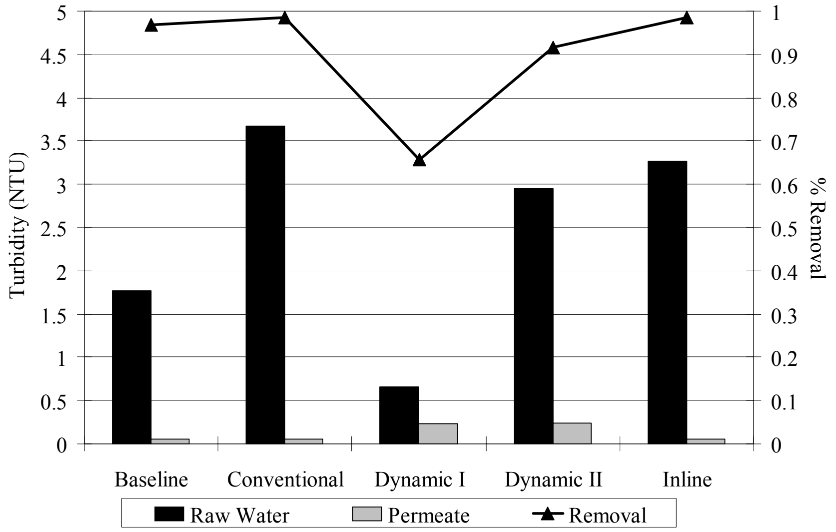

Fig. 7. Comparison of turbidity values between each test. The black bar shows the raw water and the grey bar shows the permeate values. The percent removals are shown in the line above.

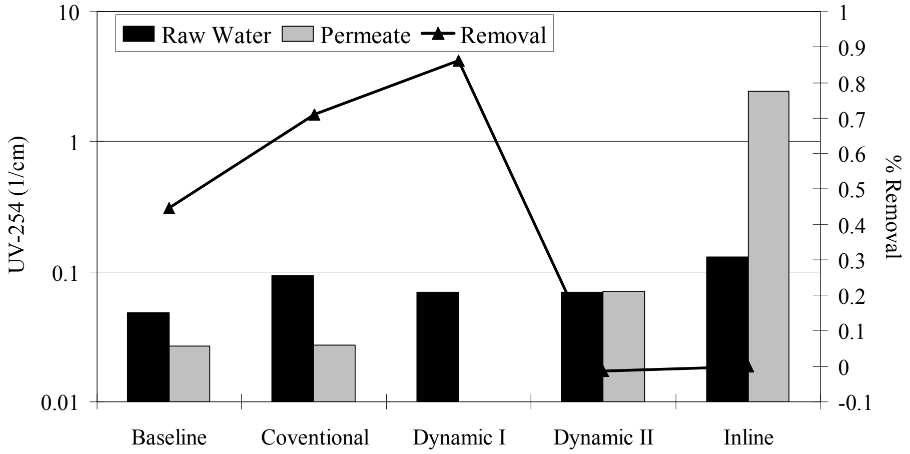

Fig. 8. Comparison of UV-254 values between each test. The black bar shows the raw water and the grey bar shows the permeate values. The percent removals are shown in the line above.

3.3. Fouling analysis

Figs. 9 and 10 are analyses of the UV-254 and solids that were built up on the membrane. Fig. 9 indicates that the conventional coagulation has the highest UV-254 values and that the dynamic I test had the lowest. Similar results are observed in Fig. 10, which shows the weights of the solids that remained on the membrane. Again conventional coagulation had the highest amount of fouling and the dynamic I had a very low amount of fouling.

Dynamic membranes are created when filtering dilute suspensions of colloidal particles of

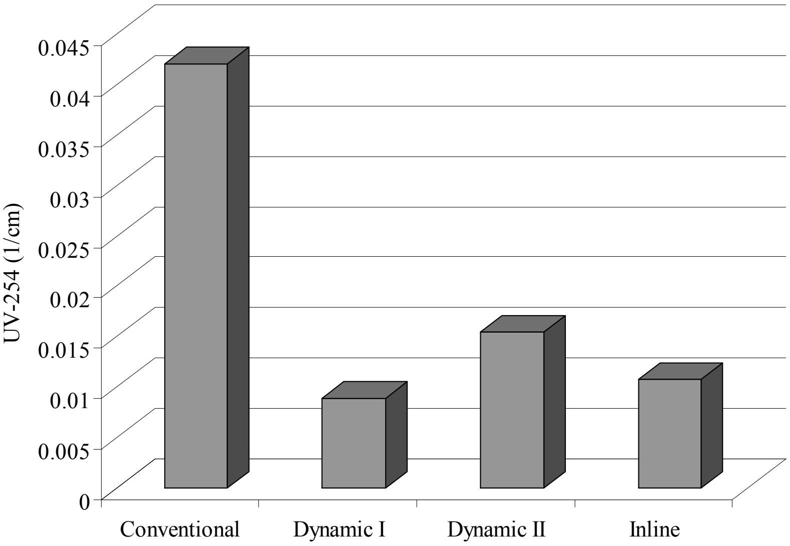

Fig. 9. Comparison of UV-254 values for membrane fouling.

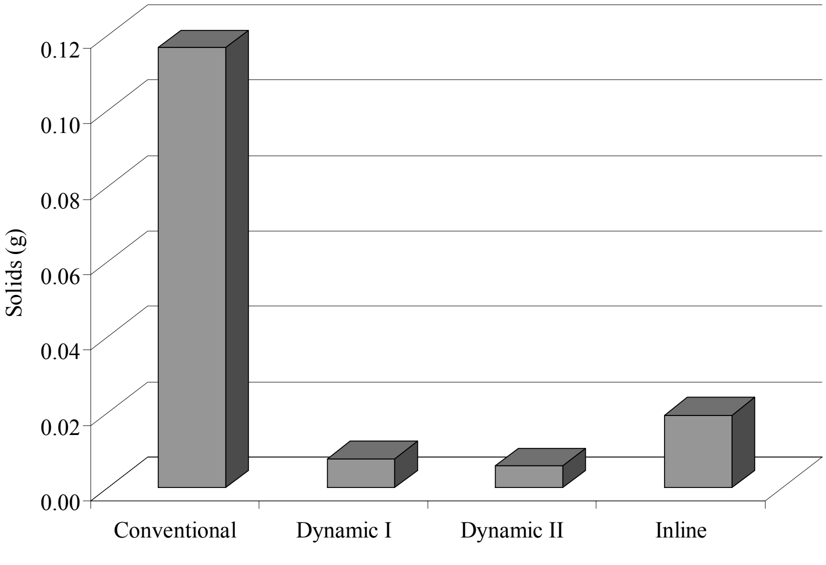

Fig. 10. Comparison of solids values for membrane fouling.

particle size much smaller than the pore size of the membrane. In this case, the flux decline mechanism behaves according to an internal pore clogging phenomenon rather than cake build-up, and it follows

$$\frac{t}{V}=\frac{1}{Q_0}+\frac{k_1 t}{2} \tag{2}$$

where V is the permeate volume, t is the filtration time, Q_o is the initial flux rate and k_1 is the filtration constant, which is proportional to the hydraulic resistance, R_m [18]. During cake formation, the classical cake filtration model describes fouling

$$\frac{t}{V} = \frac{1}{K_1}\left(V - 2V_f\right) \tag{3}$$

where V_f is the volume of permeate which produces a hydraulic resistance equal to that of the membrane, and K_1 is the cake filtration constant and inversely proportional to the cake resistance [18].

$$K_1 = \frac{2A^2\Delta P}{\mu c R_c} \tag{4}$$

where c is the colloid concentration, A is the cross sectional area, μ is the viscosity and R_c is the cake resistance.

Among the tested coagulation options, the filtration constant, k_1, decreased in the order in-line (k_1 = 1.85/mL) conventional coagulation (k_1 = 0.18/mL), dynamic I (k_1 = 0.15/mL), and dynamic II (k_1 = 0.034/mL), which shows that resistance to flow was significantly decreased by dynamic membrane operation versus other modes of coagulation. Likewise, cake filtration constant, K_1, inversely proportional to cake resistance, was highest for the dynamic II (K_1 = 3.45′10^6 mL^2/min) and lowest for in-line (K_1 = 2.50′10^4 mL^2/min).

4. Conclusion

Conventional coagulation saw significant flux decline and average removal percentages, and Figs. 9, 10 show that a considerable amount of foulants remaining on the membrane. Therefore, the matter that was removed from the water was fouling the membrane rather than being rejected to the concentrate. Dynamic I and dynamic II coagulation showed similar results with a trend towards an increasing flux and good removal percentages, and fouling data indicate a relatively low build up of solids and organics on the membrane. Thus, results indicate that dynamic I and dynamic II coagulation were both successful in removing solids and organic matter, yet they prevented them from fouling the membrane surface. Inline had the greatest amount of flux decline and had relatively high amounts of solids and organic matter left on the membrane, therefore it was not as successful in preventing fouling as were the dynamic I and dynamic II coagulation tests. This flux decline was most likely due to accumulation of organics on the membrane surfaces because of reactions between the foulants and the coagulant with the membrane surface.

After a comparison of all the data collected, it was determined that the dynamic membranes showed the most promise since they improved specific flux and the rejection of DOC, hardness and UV-254 values as compared to all other treatment alternatives. It also showed that greatest improvement with regards to fouling on the membrane along with the lowest hydraulic resistance and cake resistance. Therefore, the use of dynamic membranes was found to be effective in water separations application and to produce a higher quality permeate with lower fouling than UF alone, conventional or in-line coagulation.

Dynamic membrane using coagulants provide an improvement technique applicable to current/existing systems. The technique has the potential to significantly decrease membrane costs, to make membranes more efficient and fouling resistant and more resilient, and, therefore, applicable to a wider array of processes. As their costs decrease, membrane technologies, alone or integrated with other processes, compare favorably with other technologies suitable for wastewater treatment. Upon reduction of associated costs, membranes can also become competitive in advanced wastewater treatment and water reuse processes.

Acknowledgements

The authors would like to thank the Midwest Technology Assistance Center for the support of this project, as well as Dr. Steven Kloos from GE Water–Osmonics for the contribution of membrane and assistance.

References

[1] C. Jucker and M. Clark, Adsorption of aquatic humic substances on hydrophobic ultrafiltration membranes. J. Membr. Sci., 97 (1994) 37–52.

[2] S. Hong and M. Elimelech, Chemical and physical aspects of natural organic carbon (NOM) fouling of nanofiltration membranes. J. Membr. Sci., 132 (1997) 159–181.

[3] J.A. Nilson and F.A. DiGiano, Influence of NOM composition on nanofiltration. J. AWWA, 88 (1996) 53–66.

[4] E.M. Vrijenhoek, S. Hong and M. Elimelech, Influence of membrane surface properties on initial rate of colloidal fouling of reverse osmosis and nanofiltration membranes. J. Membr. Sci., 18 (2001) 115–128.

[5] A. Childress and M. Elimelech, Effect of solution chemistry on the surface charge of polymeric reverse osmosis and nanofiltration membranes. J. Membr. Sci., 119 (1996) 253–268.

[6] I.C. Escobar, S. Hong and A.A. Randall, Removal of assimilable organic carbon and biodegradable dissolved organic carbon by reverse osmosis and nanofiltration membranes. J. Membr. Sci., 175 (2000) 1–17.

[7] I.C. Escobar, A.A. Randall, S. Hong and J.S. Taylor, Effect of solution chemistry on assimilable organic carbon removal by nanofiltration: full and bench scale evaluation. J. Water Supply: Aqua, 51 (2002) 67–76.

[8] W. Peng and I.C. Escobar, Rejection efficiency of water quality parameters by reverse osmosis (RO) and nanofiltration (NF) membranes. Environ. Sci. Technol., 37 (2003) 4435–4441.

[9] W. Peng, I.C. Escobar and D. White, Effects of water quality and membrane properties on performance and fouling — A model development study. J. Membr. Sci., 238 (2004) 33–46.

[10] C. Lin, T. Lin and O. Hao, Effects of humic substance characteristics on UF performance. Water Res., 34 (2000) 1097–1106.

[11] T. Carroll, S. King, S. Gray, B. Bolto and N. Booker, The fouling of microfiltration membranes by NOM after coagulation treatment. Water Res., 34 (2000) 2861–2868.

[12] L. Fan, J.L. Harris, F.A. Roddick and N.A. Booker, Influence of the characteristics of natural organic matter on fouling of microfiltration membranes. Water Res., 35 (2001) 4455–4463.

[13] M. Altman, R. Semiat and D. Hasson, Removal of organic foulants from feed waters by dynamic membranes. Desalination, 125 (1999) 65–75.

[14] K. Hwang and Y. Cheng, The role of dynamic membrane in cross-flow microfiltration of macromolecules. Separ. Sci. Technol., 38 (2003) 779–795.

[15] A. Vernhet, D. Cartalade and M. Moutounet, Contribution to the understanding of fouling build-up during microfiltration of wines. J. Membr. Sci., 211 (2003) 357–370.

[16] R. Holding and R. Boston, Microfiltration using a dynamically formed membrane. Filtr. Separ., 27 (1990) 117–194.

[17] S. King, I. Escobar and X. Xu, Ion beam irradiation modifications of a polyether sulfone commercial water treatment membrane. Environ. Chem., 1 (2004) 55–59.

[18] M. Al-Malack, A. Bukhari and N. Abuzaid, Crossflow microfiltration of electrocoagulated kaolin suspension: fouling mechanism. J. Membr. Sci., 243 (2004) 143–153.