

Ceramic microfiltration – influence pretreatment on operational performance

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SUMMARY

A sustainable membrane operation often requires pretreatment to improve the technical and economical feasibility. This paper reports the impact of pretreatment on the performance of ceramic microfiltration for several pilot studies at different locations. Four different pretreatment processes were investigated:

- 1) in-line coagulation (for the removal of high molecular weight, HMW, dissolved organic carbon, DOC);
- 2) ion exchange (for the removal of low molecular weight, LMW, DOC);
- 3) ozone (for disinfection, taste and odor control and modifying the character of DOC)
- 4) ion exchange followed by in-line coagulation (for almost complete removal of DOC.)

Pretreatment in all the cases studied was needed to control membrane fouling to establish a technically and economically feasible process. In these studies, it seems that the HMW fraction of the DOC, which includes biopolymers, in combination with the LMW fraction, which includes humics/acids, are primarily responsible for the increase in TMP after a filtration cycle followed by a backwash (irreversible fouling). Removing one of these organic fractions often results in a more stable operation. Ozonation in all studied cases led to a better or superb operation, but ozone application is not always economically feasible. The feasibility of ozone as pretreatment depends largely on the initial ozone demand and whether or not there are secondary treatment targets (e.g., higher virus removal, taste, odor).

KEYWORDS

Ceramic microfiltration, fouling mechanism, DOC characterization, pretreatment, ion exchange, ozone and in-line coagulation

INTRODUCTION

Ceramic microfiltration

In the past decade, there has been an increasing need to treat surface water for drinking water production and to treat wastewater for reuse. For those applications, removal of suspended and biological colloidal matters is a necessity. Micro- and ultrafiltration (MF and UF) are often used because they provide an absolute barrier against particles greater than the pore size. Polymeric membranes still dominate this sector of the water industry; however, ceramic membranes have some unique resilient properties which make them a favorable option. Ceramic membranes are less fragile than polymeric membranes, have a longer and possibly indefinite life, and can withstand heavy pollutant and solid loads, vigorous backwash and a variety of chemical types and concentrations. This makes the ceramic membrane a promising alternative.

Membrane fouling

For membrane application, a major obstacle is always the potential for membrane fouling. A sustainable membrane operation often requires pretreatment to reduce the fouling potential of the treated water. A critical review from Huang et al. summarized the pretreatment technologies as: coagulation, adsorption, pre-oxidation, pre-filtration, dissolved air flotation, ion exchange, or a selected combination of the above [Huang 2009]. Coagulation is by far the most widely adopted pretreatment technology for membrane filtration. Coagulated water causes less fouling as compared to uncoagulated water in most applications; however sometimes the opposite happens and coagulation leads to a higher level of irreversible fouling. The fouling mechanism seems not to be the same at each location and it is, therefore still not completely understood. Most of the studies suggest that coagulation controls colloidal fouling (i.e., pore blockage) and removes the HMW fraction of natural organic matter (NOM) and therefore reduces NOM fouling. But Gray et al. argued that the mechanism of fouling control for coagulation was the removal of LMW organics (with an adsorption peak at 220 nm) that were responsible for 'gluing' colloids to the membrane surface [Gray 2008]. Galjaard et al. proposed that coagulation removes HMW organics, but coagulation also introduces or forms metal organic complexes. These complexes could interact with smaller organics and the membrane resulting in film formation on the membrane surface and irreversible fouling [Galjaard 2005].

Full scale application of other pretreatment techniques like adsorption, ion exchange and pre-oxidation is still very limited, and it requires further assessment. One of the purposes of this study is to compare the impact of various pretreatment methods on the fouling of ceramic membranes.

Problem description

A better understanding of the mechanism of membrane fouling is crucial when determining the optimal pretreatment strategy for a particular water. After years of experience treating the IJssel Lake water, a surface water in the Netherlands, Galjaard et al. suggested that the irreversible fouling (i.e., the fouling that is not removed with backwashes and chemically enhanced backwashes) is caused by attachment of a NOM-film on the membrane surface [Galjaard 2005]. This hypothesis proposes that HMW organics interact at high concentrations at the membrane surface forming long "polymers". The LMW organics like carboxylic acids and humics combine with the HMW organics by electrostatic forces, and this interaction accelerates the formation of the a film in the same way that organic metal complexes do. This can result in rapid irreversible fouling if the formed film and the membrane are oppositely charged, because the film is then adsorbed by the membrane. According to this hypothesis, two solutions exist to reduce the fouling potential of IJssel lake water: 1) remove humics and carboxylic acids with ion exchange and avoid the formation of metal organic complexes by not using coagulants; and, 2) reduce the negative surface charge of the membrane or create an opposite surface charge to promote electrostatic exclusion of the formed film. The strategy led to the development of a novel ion exchange technology called suspended ion exchange (SIX®) and the development of a ceramic membrane process called CeraMac®. Water sources are, however, unique and have their own fouling characteristics. It is of great interest, therefore, to verify this fouling hypothesis for other source waters and to study how different pretreatment strategies impact the feasibility of using ceramic MF.

This paper presents results of several pilot studies using ceramic MF. At each location at least two different pretreatment strategies were investigated. The membrane performance with these pretreatments is discussed in comparison to the "NOM film" fouling hypothesis. Besides sharing these findings with the water and membrane community, this paper aims to initiate a discussion about the fouling mechanism and pretreatment strategies when using ceramic MF.

METHODS

Ceramic membrane and membrane process

The ceramic MF membrane is a monolith membrane provided by Metawater (Japan). The nominal pore size of the membrane separation layer is 0.1 μm , and the membrane has a very narrow pore size distribution. Two sizes of membrane elements, 0.4 and 25 m^2 surface area were used during these studies. Two different types of modules were also evaluated in these studies. The first type of module housed one element in one module, and the second type of module, CeraMac® (see figure 1), housed multiple elements in one membrane vessel.

The CeraMac® process is developed by PWN Technologies. The CeraMac® design greatly reduces the installation cost of a ceramic membrane system to a level which is cost competitive with a polymeric membrane system. Rather than having ceramic membrane modules in individual stainless steel casings, up to 192 ceramic modules can now be housed in a single stainless steel vessel. This results in a significant reduction in the amount of stainless steel and the number of valves, while increasing productivity (i.e., all elements are backwashed at the same time which reduces the downtime during a backwash, BW, from 10 minutes to a few seconds).

In all cases the ceramic microfiltration is operated in the dead-end mode. The water is fed vertically from the bottom into a vertically set module. After a prescribed operating time, the BW occurs. This BW water is forced through the membranes by air-pressure and not by a BW pump. This pressure is built up in the BW tank by pumping the water in the BW tank against a certain initial air-pressure.



Figure 1, CeraMac® vessel system with 192 ceramic elements and a backwash tank

This creates an air-spring effect when the valve opens, and the BW water rushes out of the vessel and then the valve closes, but the tank remains under pressure. This means that virtually no air volume is lost during a BW (apart from that which is dissolved in the water). The BW occurs over a few seconds, and forces the water from the permeate side of the membrane through to the feed side. The BW water exits the vessel through a separate backwash water port at the bottom of the vessel. The flow used for a BW is (3 L/m²). This occurs over 3 to 5 seconds when the membrane is clean, but the time increases up to 30 seconds when the membrane is fouled. After a BW, there is an automatic forward flush (FF), from the top to the bottom of the feed channels of the membrane module. This FF is also forced over the membrane by air. This air, however is generated by a compressor and stored in a separate FF tank. The air pushes a fixed amount of flush water (stored on top of the modules and in the membrane feed channels) out, thus emptying the whole feed side volume of the membranes.

There are two types of chemically enhanced backwash (EBW) trialed during these studies: a chlorine EBW and a low pH /peroxide EBW. These occurred at prescribed intervals (e.g., after a fixed number of backwashes), and the chlorine EBW generally occurred more frequently than the low pH/peroxide EBW. A typical pattern of EBWs was a chlorinated EBW after every five to 15 BWs, and a low pH/peroxide EBW after every five chlorinated EBWs.

For the EBW, the flow used was the same as for a normal BW, but chemical was added while the BW tank was filling. During the EBW, the BW tank drained over four 4 minutes through a separate smaller EBW outlet. Then, while the BW tank was re-filling, the membrane(s) soaked in the EBW solution for approximately five minutes. The sequence ends with a standard BW and FF. The whole EBW sequence is approximately 10 minutes in duration.

Locations and water sources

The pilot studies were performed at different locations treating different sources, three surface waters and one secondary effluent of a municipal waste water treatment plant.

Andijk, Netherlands

The first pilot study was conducted on IJssel Lake water for drinking water production in Andijk, the Netherlands. The IJssel Lake is fed by the river Rhine and is the biggest fresh water lake in the Netherlands. For the Andijk pilot work, in-line coagulation and ion exchange were trialed as pretreatments. As a coagulant ferric chloride was used. The ion exchange process was SIX® with LanXess VPOC 1071 anion resin.

Singapore

The second pilot was at the Choa Chu Kang Waterworks (CCKWW) in Singapore. The CCKWW receives raw water from three sources, via Kranji, Pandan and the Western Catchments Reservoirs which include the Tengeh, Poyan, Murai and Sarimbun Reservoirs. For this pilot, the membrane system treated clarified water with and without pre-ozone. The clarified water was raw water treated by screening, aeration, coagulation and clarification in the existing full scale plant.

The target contact time to dissolve the ozone was as short as possible to reduce the volume of the contactors and to dose as little ozone as possible. Because the maximum capacity was not known during the design of the ozone contactors, a conservative value was chosen of around five minutes at a maximum capacity of 110 m³/h before the water entered the membrane vessel. This yielded an initial ozone dose of approximately 1.3 to 1.5 mg/L, which is similar to the current ozone dose at CCKWW after the existing sand filters. The target ozone concentration on the membrane surface was 0.8 to 1.1 mg/L.

Plymouth, United Kingdom

The third pilot was at Crownhill Water Treatment Works (WTW) of South West Water (SWW) in the United Kingdom. The raw water was from the Burrator Reservoir, combined occasionally with pumped water from the River Tamar and the River Tavy. Four pre-treatments were included in the study: 1) suspended ion exchange (SIX®, by PWN Technologies); 2) clarification (from the existing Crownhill WTW); 3) clarification by the WTW followed by SIX®; and, 4) SIX® followed by pilot-scale in-line coagulation. The anion resin used at this location was LanXess S5128 (Germany).

Secondary effluent

The last pilot study was treating secondary effluent with a ceramic membrane for a confidential client. The secondary effluent water was first strained and chlorinated. Four pretreatments were evaluated, direct treatment (no pretreatment), in-line coagulation, ozonation, and ozonation followed by in-line coagulation.

For all the pilot studies, the operational parameters were logged automatically including but not limited to the following parameters: time, feed water temperature, flow rate, membrane feed side pressure and membrane permeate side pressure. The transmembrane pressure (TMP) was calculated based on the difference between the feed pressure and the permeate pressure. The membrane operational conditions were different for each pilot. But it will be outlined in the next section when presenting the operational results. More details of the pilot studies can also be found in previous publications [Galjaard 2013; Shorney-Darby 2014; Zheng 2013].

DOC-characterization and particle charge

The organic matter was analyzed via SEC-LC-OCD method (size-exclusion chromatography – liquid chromatography - organic carbon detection) at 'Het Water Laboratorium HWL' (the Netherlands). The SEC-LC-OCD method itself was developed by DOC Lab in the Germany and the principle of this method is described by Huber [Huber 2011]. The zeta potential measurements were made in the University of Twente (the Netherlands). The instrument was a Malvern Zetasizer nano.

RESULTS AND DISCUSSION

Raw water organic matter analysis

Table 1 gives an overview of the TOC and DOC concentration and the UV Transmission at 254nm (UVT) of the four different sources. The TOC and DOC data for the clarified surface water in Singapore was measured with the US EPA 415.1 method. The other TOC and DOC concentrations were obtained with the SEC LC-OCD method.

Table 1. Organic carbon concentrations of the four different water sources

	TOC (ppm)	DOC (ppm)	UVT (%)
Andijk, NL	5.5 ~ 6.4 (5.9)	5.4~6.3 (5.8)	72.6 ~ 80.2 (76.3)
CCKWW, SG	2.2 ~ 6.7 (3.3)	1.8 ~3.4 (2.4)	79.8 ~ 89.0 (86.5)
Plymouth, UK	1.6 ~ 4.4 (2.4)	1.4 ~4.4 (2.3)	74.9 ~ 90.6 (82.4)
Secondary effluent	8.5 ~ 10.5 (9.8)	8.4 ~ 10.3 (9.5)	66.6 ~ 73.1 (68.7)

The SEC-LC-OCD method is a powerful tool to characterize organic matter. The SEC broadly groups the organics into five fractions: biopolymers, humics, building blocks, LMW acids and LMW neutrals (in the order of retention time). Two detectors, organic carbon detector (OCD) and ultraviolet detector (UVD) are equipped to detect the organics. The OCD spectrum is used to determine the total mass of organic carbon, whereas the UVD spectrum counts only the UV adsorbing species (i.e., double bond carbon). Figure 2 shows the OCD signal of three raw water samples which are representative of three different resources, the IJssel lake water, the Burrator reservoir water and the secondary effluent wastewater. Figure 2 shows that the secondary effluent wastewater had the highest concentration of DOC, as quantified by the surface area under the graph, followed by the IJssel lake water and the Burrator reservoir water. The secondary effluent compared to the others had very high concentrations of biopolymers and LMW components. These fractions could be biologically active and this matches their origin as a wastewater. For the two surface waters, humics was the main fraction. The DOC concentration in the IJssel lake water was higher than in the Burrator reservoir water. This can be attributed to the fact that IJssel lake water is fed by the river Rhine, which is heavily polluted.

Figure 3 illustrates the UVD spectra for the same three water samples. Surprisingly, it shows that the "biopolymer" fraction from Burrator reservoir has the highest UV peak, although it has the lowest concentration detected by the carbon detector. Generally, it was thought that the biopolymer fraction does not adsorb UV light at that wavelength; therefore, the high UV adsorbing properties of the biopolymer fraction from Burrator reservoir water suggests that there are other chemical/biological origins for the organics. This remains an open question for future study. A huge humics peak can be observed for the IJssel lake water. For the secondary effluent, the low molecular weight fractions show high UV adsorbing properties. Combining the observations from figures 1 and 2, it shows the organic matter in different water resources was very different, not only their quantity, but also in their composition and the properties of each composition. LC-OCD analyses were performed regularly however only three samples are shown as representatives. For IJssel lake water and the secondary effluent, there is some variability over time according to the spectra, but overall the results are fairly consistent. For the Burrator reservoir water, the fluctuation is much more significant, especially with in concentration and the UV absorbance of the biopolymer fraction.

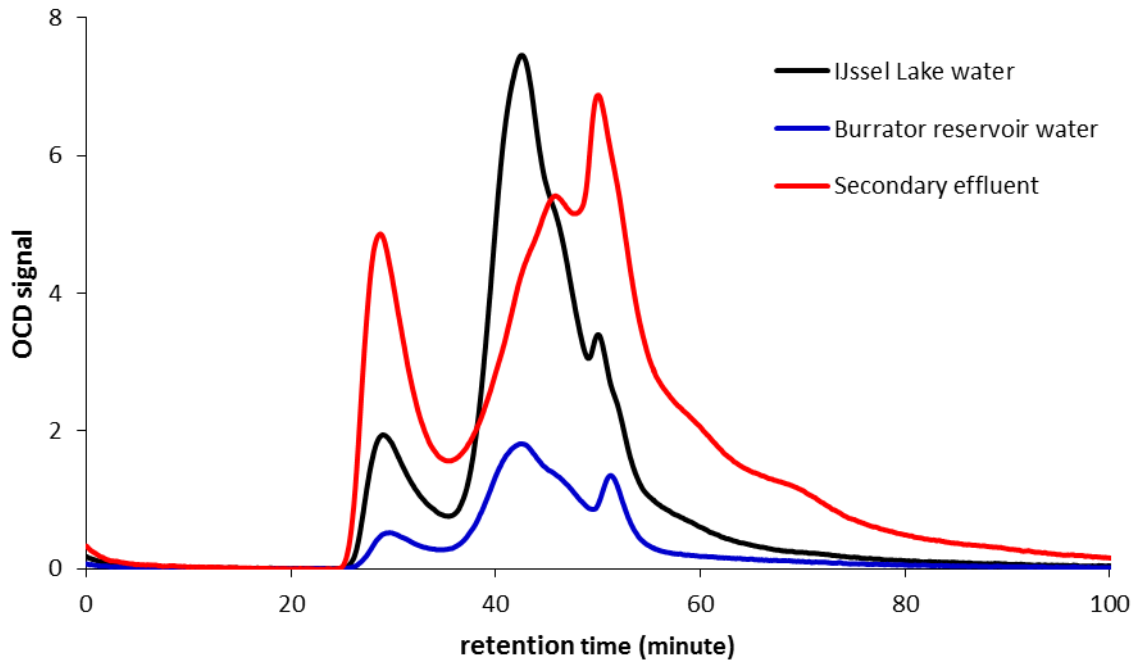


Figure 2, SEC-OCD chromatogram of three water samples including IJssel Lake water, Burrator water and a secondary effluent.

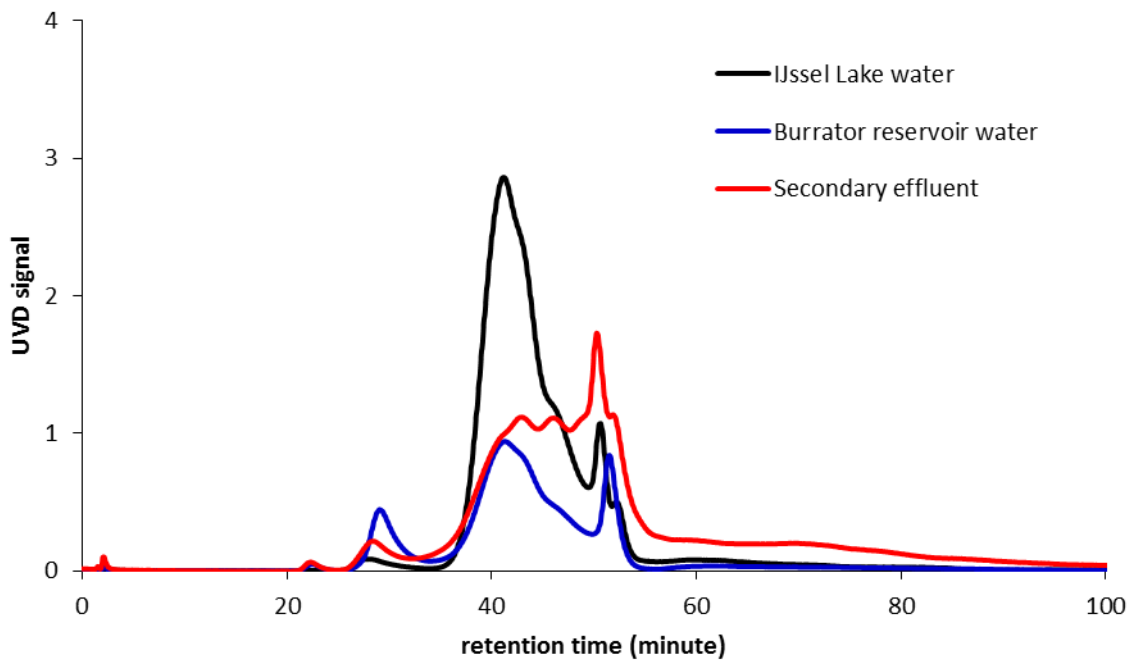


Figure 3, SEC-UVD chromatogram of three water samples including IJssel Lake water, Burrator water and a secondary effluent.

Membrane performance pilot Andijk, the Netherlands

For the filtration of IJssel lake water with the ceramic MF membrane, two pretreatment methods have been tested: in-line coagulation and ion exchange. The DOC concentration of the coagulated water and the ion exchanged water was similar, typically between 2 to 3 ppm, depending on the season [Galjaard 2005], but the compositions are quite different. NOM analysis (figure 4) indicated that in-line coagulation removes a part of the biopolymer fraction and a small portion of humics. The ion exchange removed most of the humics and LMW fractions but it has almost no impact on biopolymer removal.

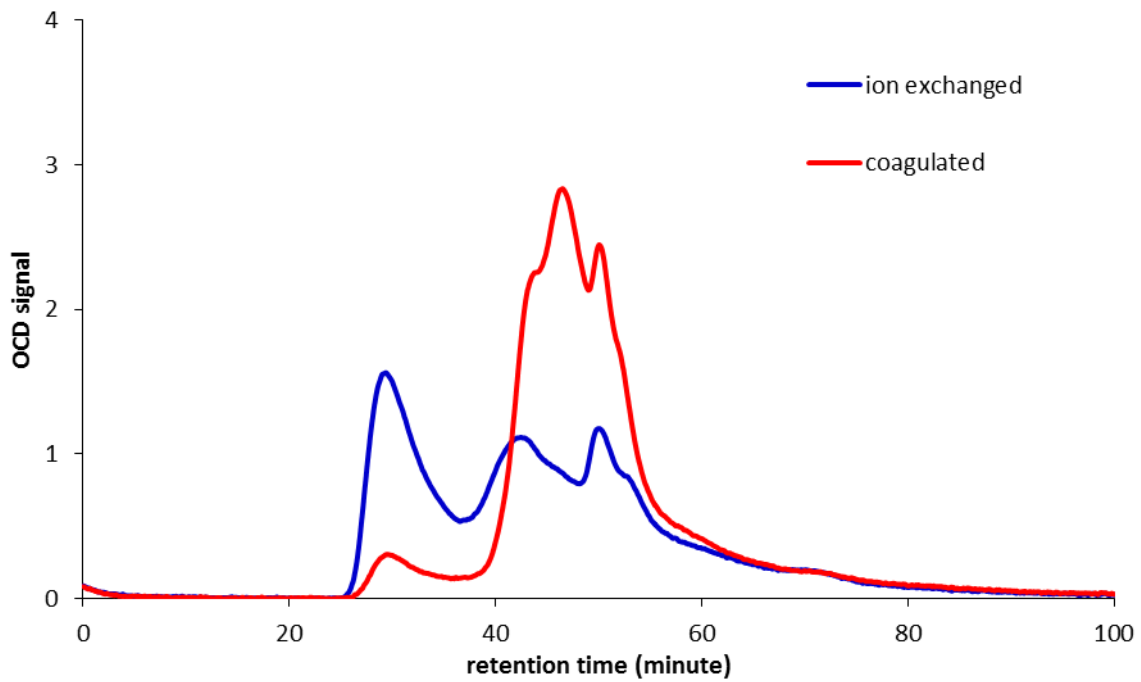


Figure 4, SEC-OCD chromatogram of ion exchanged and in-line coagulated IJssel Lake water

Figure 5 illustrates the difference in transmembrane pressure (TMP) development during a filtration cycle. In this figure, TMP is plotted as a function of the water volume being treated. The flux for the coagulated water and ion exchange treated water was 100 LMH. The starting TMP after a BW is higher for the coagulated water.

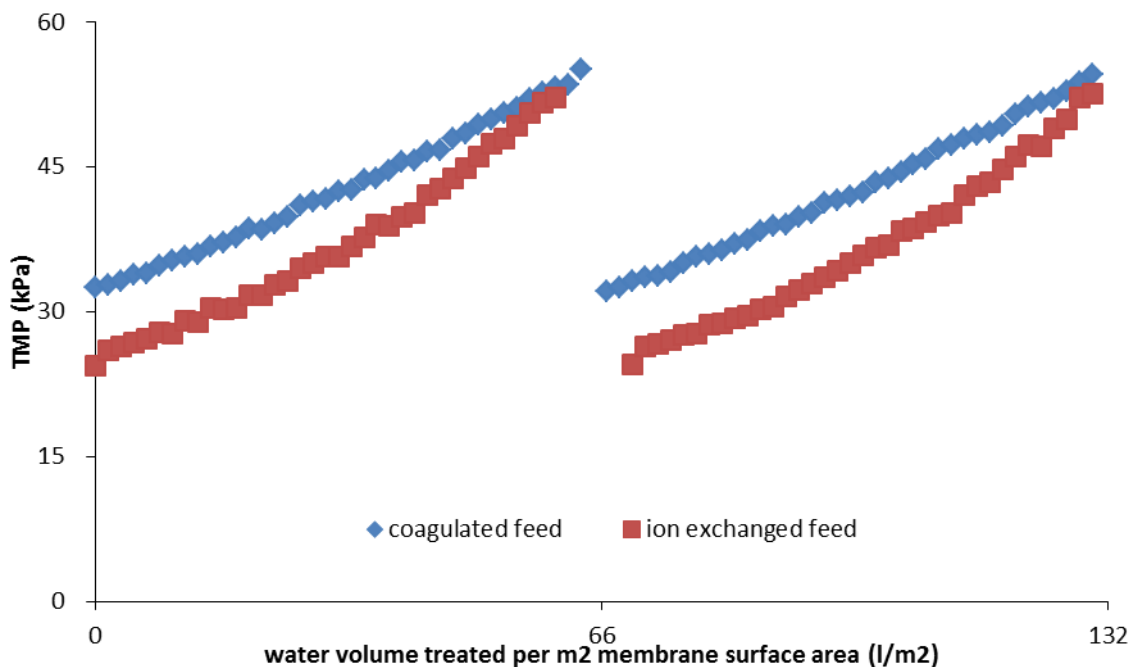


Figure 5, TMP development for treating coagulated and ion exchanged IJssel lake water; membrane feed flux 100 LMH

This is caused by a small difference in irreversible fouling. For the both pretreatments the TMP increased relatively quickly indicating quite some removal of suspended matter. For IJssel lake water, the biopolymers are difficult to coagulate, because they are 100 percent hydrophilic, thus requiring a relatively high amount of ferric at a relatively low pH (to enhance the coagulation, Galjaard 2005). It

looks as if there is no significant difference in the TMP build up for the two different pretreatment strategies. Long term operation, however reveals a big difference. In-line coagulation was not able to control the irreversible fouling, even with the applied EBWs. Even under optimized coagulation conditions, the fouling rate observed was 0.5 kPa/day. In contrast, the ion exchange treated water allowed a very stable membrane operation and almost no irreversible fouling was observed. Figure 6 illustrates TMP development over almost 12 months of continuous testing. The data was obtained at a lower flux of 68 LMH, filtration time 30 minutes and EBWs after nine BWs. The flux was limited by water availability from the SIX® pilot which was the pretreatment.

Figure 6 shows fluctuation in the TMP, attributed to the seasonal change and operational mistakes (e.g., no EBWs by accident in January), but overall it was very stable, with a TMP increase of 0.01 kPa/day. It is necessary to mention that the first increase in TMP (in June) was caused by moving the upstream peroxide dosing of 6 ppm, necessary for the advanced oxidation process with UV downstream of the membrane [Galjaard 2011] (the ceramic membrane can withstand high concentrations of peroxide).

This immediately resulted in a TMP increase. During several experiments, it was observed that dosing peroxide prior to the ceramic membranes could increase the membrane permeability by around 20 percent [Zheng 2013]. The ion exchange pretreatment has been selected as pretreatment for the full scale plant, mainly because of its ability to remove not only DOC but it also removes nitrate which are both favorable for the operation of the membrane and downstream AOP process [Martijn 2012].

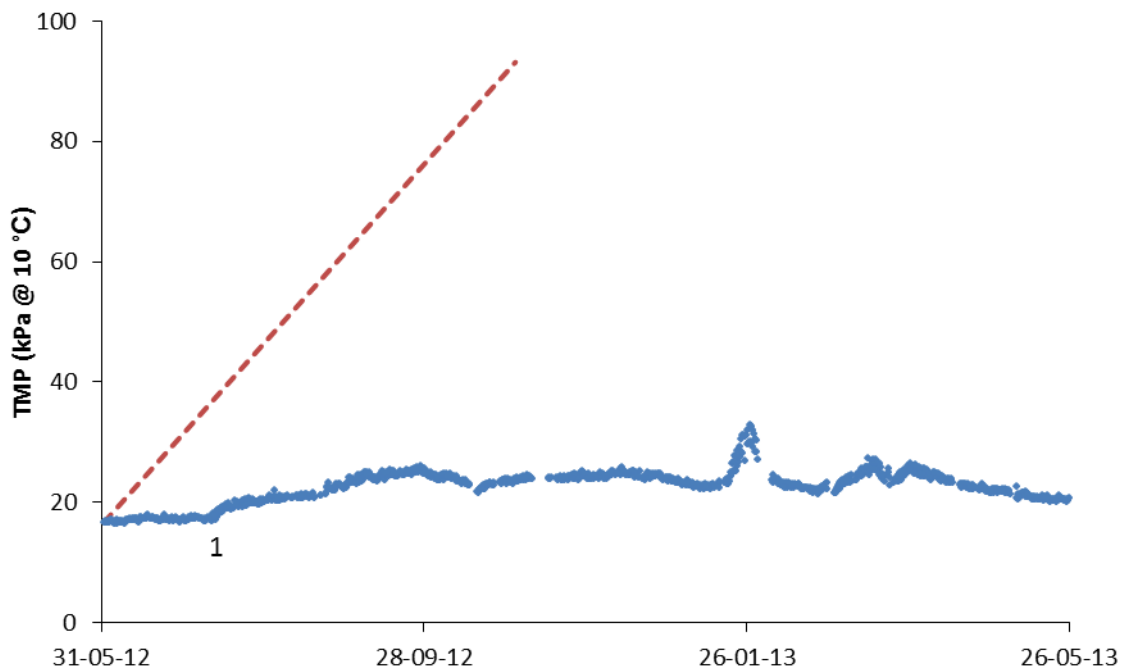


Figure 6, TMP development for treating ion exchanged IJssel lake water; membrane feed flux 68LMH and filtration time 30 minutes. The dashed line indicates the TMP increase treating in-line coagulated water (0.5 kPa/day TMP increase in an optimized situation).

Membrane performance pilot CCK Singapore

For the CCK CeraMac® demo-plant [Galjaard 2013] in Singapore, the ceramic membrane treated in a first stage clarified water which was produced by the existing plant. The DOC concentration of the clarified water was between 2 and 3 ppm, and was thus comparable with the DOC concentration after pretreatment in Andijk. The DOC was measured in a local lab with the US EPA 415.1 method. No LC-OCD analysis were conducted during for this pilot study.

The hybrid ozone/ceramic MF process was operated by maintaining 0.8 ppm ozone concentration at the feed side of the membrane. The ozone was always present during filtration. Figure 7 shows TMP development during two filtration cycles with a BW in between. The operation conditions are the same, with a flux of 200 LMH and a filtration time of 30 minutes. A big difference in the TMP build up can be

observed with and without ozone. When no ozone was applied, the overall TMP is higher and the TMP increases during the filtration cycle. When ozone was applied, permeability almost immediately increases [Galjaard 2013] resulting in an overall lower TMP and negligible TMP increase during a filtration cycle.

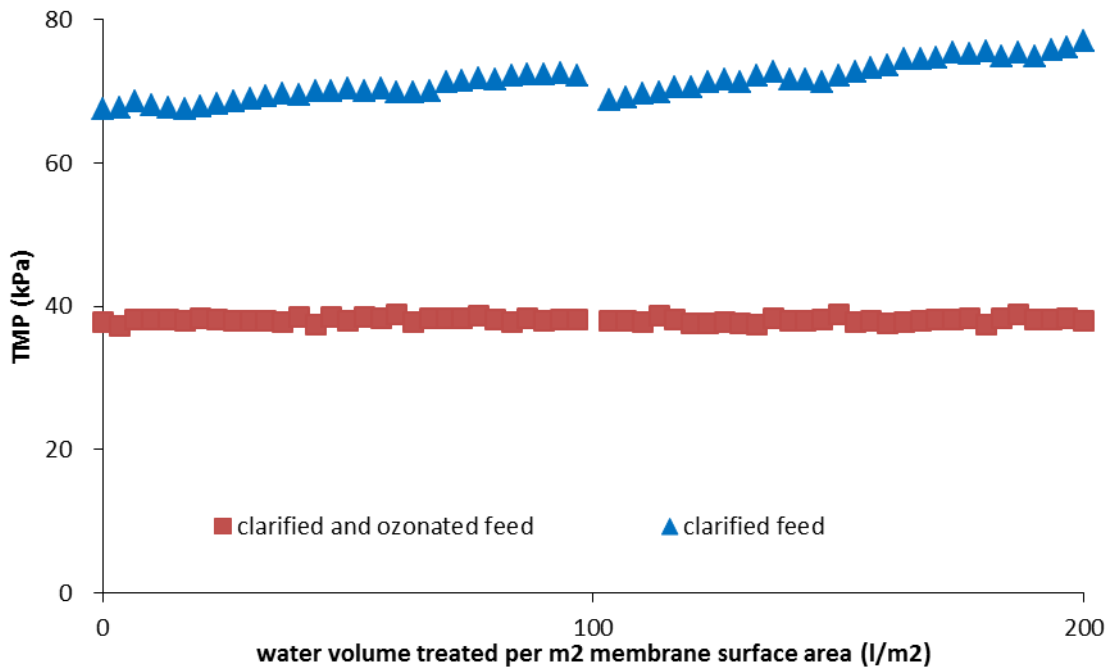


Figure 7, TMP development for treating clarified and ozonated clarified water at Choa Chu Kang Waterworks; membrane feed flux 200 LMH and filtration time 30 minutes for both the clarified feed and the ozonated clarified feed.

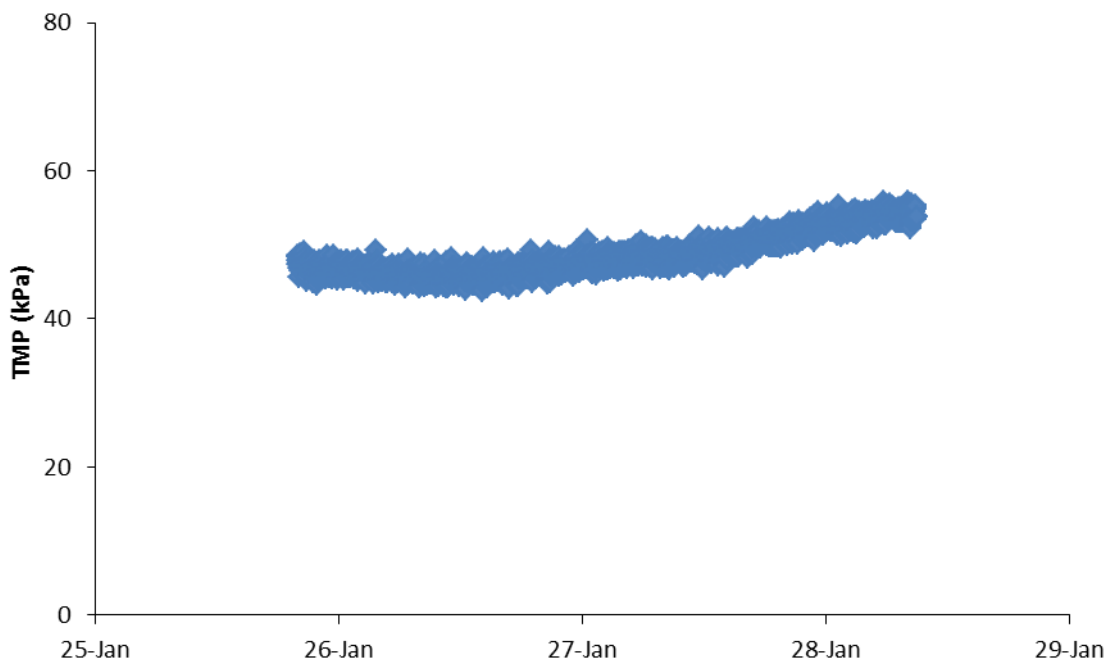


Figure 8, TMP development for a hybrid ozone/ceramic MF process for treating clarified water, feed flux 315 LMH, 61 hours continuous filtration without BW.

The study showed also a stable operation on the clarified water without ozone at a flux of 200 LMH. However, fluctuation in TMP and permeability were also observed, mainly caused by fluctuations in feed water quality. The hybrid ozone/ceramic MF significantly improved the system's performance,

with stable operation, higher flux, lower TMP, increased permeability, and increased recovery. The hybrid process could operate at a feed flux of 315 LMH. During the filtration experiments, there was an time when no BW or any other cleaning was performed for 61 hours due to a drained permeate storage tank. During these 61 hours, there was minor TMP increase (Figure 8). This demonstrates the superior robustness of the hybrid ozone/ceramic MF process.

Membrane performance pilot Plymouth, United Kingdom

During this pilot study many different pretreatment options were investigated including coagulation and clarification, ion exchange and the combination of ion exchange and in-line coagulation. LC-OCD analysis (figure 9) revealed that coagulation and clarification was efficient in removing biopolymers and ion exchange was efficient in removing humics. This matches with what was observed in Andijk. If the clarification and ion exchange were combined, both biopolymer and humics were removed and the DOC of the treated water became extreme low [Shorney-Darby 2014]. What also can be seen is that the membrane is not retaining any DOC which lowers the fouling potential of the feed water for this membrane.

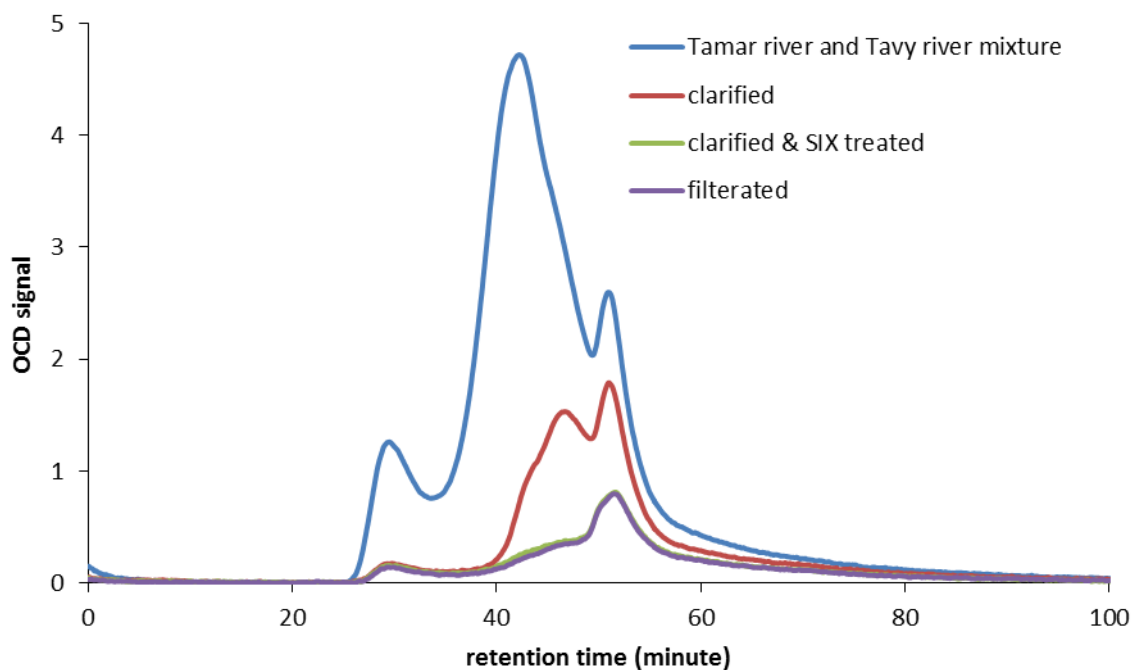


Figure 9, SEC-OCD chromatogram of raw, clarified, clarified followed by SIX® and membrane permeate on raw feed water in Plymouth

Figure 10 shows the TMP during 2 filtration cycles with three different pretreatments. The membrane operational conditions were the same, feed flux of 150 LMH and filtration time 30 minutes. With only ion exchange treatment, the starting TMP was low but the increase was high. The BW could not restore the TMP completely. For the coagulated and clarified feed, the overall TMP was high with only a slight increase in TMP. Also for this pretreatment the BW was not capable of restoring the membrane completely leading to an instable operation. For the ion exchanged followed by in-line coagulation the TMP was much lower and there was almost no TMP increase during the filtration. In this case, the BW was able to keep the operation stable (Figure 11) This is most likely caused by almost the complete removal of the biopolymers and a large part of the humics as well as introducing microflocs on the membrane. Besides binding the biopolymers, these microflocs also protect the membrane surface and can be easily backwashed.

Membrane performance pilot secondary effluent

Four pretreatment methods were tested in a pilot study treating secondary effluent of a waste water treatment plant, namely: no pretreatment, in-line coagulation, ozonation and a combination of pre-ozonation and in-line coagulation. NOM analysis indicated that in-line coagulation worked fairly well to

remove part of biopolymer and humics. Ozonation alone had a minor impact on the total amount of the biopolymer concentration in the feed water of the membrane (Table 2) but it did alter the characterization of the organic matter (according to the LC-UVD). This can also be seen in a change in the total amount of biopolymers in the permeate. The retention by the membrane of these biopolymers became higher compared to in-line coagulation. Ozonation combined with in-line coagulation largely enhanced organic removal. More details about the NOM analysis of the raw water is not include here, but will be published in later paper.

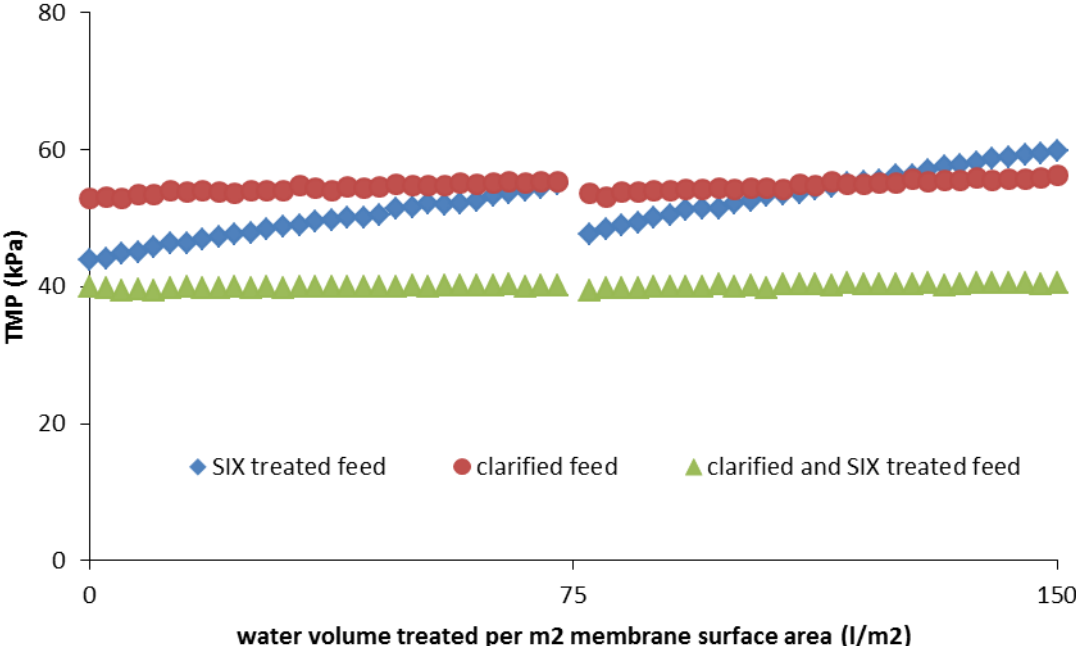


Figure 10, TMP development for three different pretreatments; membrane feed flux 150 LMH and filtration time of 30 minutes

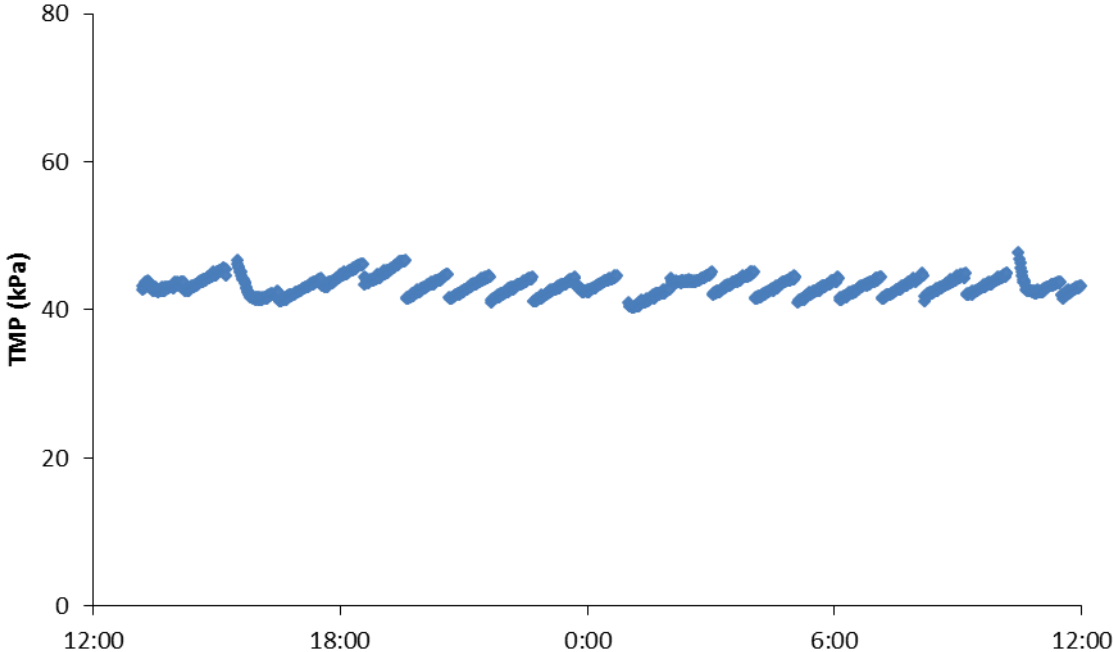


Figure 11, TMP development for a pretreatment of ion exchanged followed by in-line coagulation; flux 100 LMH, filtration time of 60 minutes.

Table 2. Charge properties and biopolymer concentration in the membrane feed and filtrated streams under four different pretreatment methods.

	no pretreatment	coagulation	ozonation	ozonation & coag.
ZP membrane feed (mV)	-16.9	-17.1	-18.2	-15.1
ZP membrane filtrated (mV)	-9.84	-16.5	-12.1	-14.7
Absolute ZP change (mV)	7.1	0.6	6.1	0.4
biopolymer con. feed (ppb)	1338	1362	1365	922
biopolymer con. filtr. (ppb)	291	677	300	561
biopolymer rejection (%)	78	50	78	39

Table 2 shows different biopolymer rejections for the different pretreatment steps. The membrane rejects more biopolymer when filtering untreated and ozonated secondary effluent, however, a remarkably low rejection of biopolymer was observed when filtering in-line coagulated water. At the same time, a significant similar change in the zeta potential was observed, largely depending on if in-line coagulation was used or not.

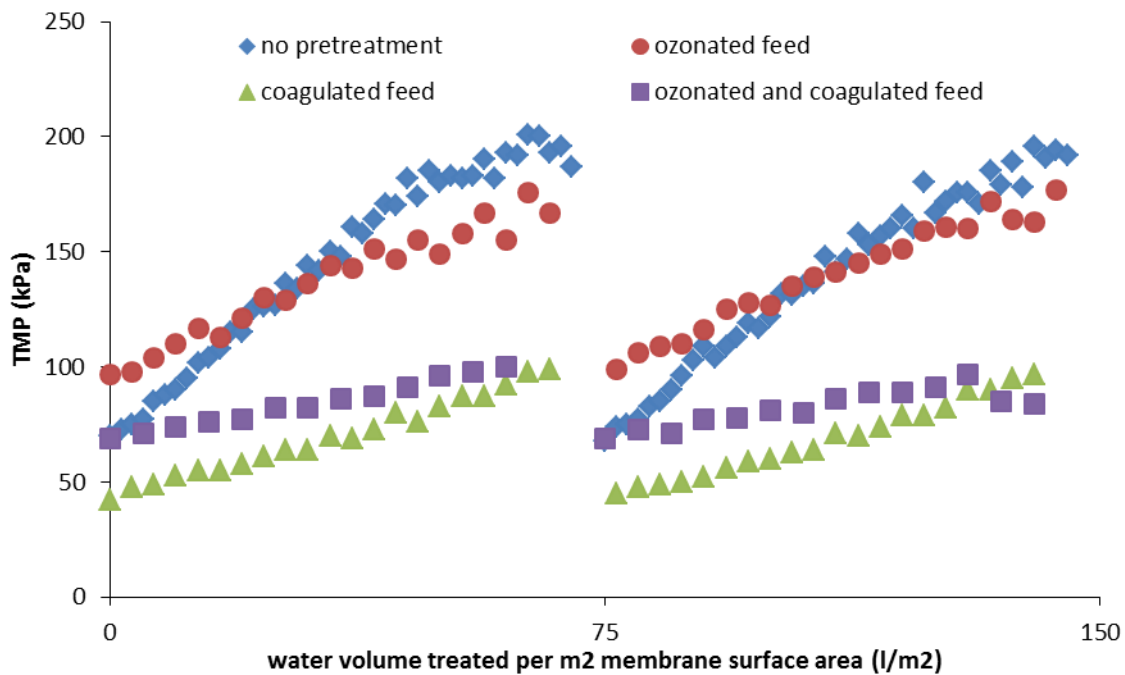


Figure 12, TMP development after different pretreatments when treating secondary effluent; feed flux 100 LMH and filtration time of 45 minutes for no pretreatment; flux 200 LMH and filtration time of 22.5 minutes for in-line coagulation and ozone; flux 300 LMH and filtration time of 15 minutes for ozone followed by in-line coagulation.

Figure 12 presents the TMP development after four different types of pretreatment. The fluxes were different but the filtration time was changed so that each set of data is for the same amount of water per m² of membrane surface in one filtration cycle. It is interesting that the permeability of the membrane is highest for ozone followed by in-line coagulation. That pretreatment also led to the most stable operation at a relatively high flux (300LHM). The high initial demand of ozone due to the high concentration of DOC rendered this option to be not economically feasible. Neither no pretreatment nor ozone alone led to a stable process. In-line coagulation led to a technically and economically feasible process.

Fouling discussion

For the fouling of low pressure membranes, it is often described that the fouling is attributed to the deposition of dissolved HMW organic carbon like polysaccharides and polyhydroxyaromatics on the membrane surface. However, as shown in the case study of treating IJssel lake water, it is not a necessity to remove the HMW NOM fraction for obtaining a sustainable membrane operation. In the ion exchange and ceramic MF process, the physical picture of the fouling looks like the biopolymer fractions were rejected by the membrane. The biopolymers were not glued/linked together and could be removed easily by a BWs. This is contributed to the pre-removal of the humics and LMW acids by ion exchange. Kim et al. also found that, by removing organic acid with ion exchange, nearly no fouling occurred when treating secondary effluent [Kim 2008; 2010]. How humics and LMW acids affect the membrane fouling still remains unclear. Direct adsorption of these LMW organics onto the membrane surface could be the case. However this group is in mass percentage very small (<10%) and in size often smaller than the pores of the membrane and therefore is unlikely to be solely responsible. Most likely the humics and LMW acids could work as “linkers” to “glue” the HMW organics, similarly to the divalent and trivalent cations. The “crosslink” effect of metal ions in developing irreversible fouling has been demonstrated in the works of Elimelech and coworkers [Hong 1997; Li 2004] for nanofiltration and by Li for ultrafiltration [Li 2011].

For the CCK demo-plant in Singapore, it was observed that combination of ozonation with ceramic MF significantly improved the system's performance. By treating the clarified water, the fouling film could be gradually formed from organic and inorganic substances. Ozone can affect/break the fouling film by reacting with the organic and inorganic components. Once the fouling film became loose, it was easily washed off of the membrane surface. This can be considered as the scrubbing/cleaning effect [Sartor 2008]. After the membrane became clear, the permanent presence of ozone prevented the formation of the fouling film.

In the Plymouth case, the biopolymer fraction can be considered as the primary foulant. This is because the biopolymer is sticky and it is difficult to remove with a BW. Remarkably the removal of the LMW fraction with ion exchange alone did not lead to the same stable performance as in Andijk. The nature or origin and properties of the biopolymers seems to be different. This is so far only evident due to the data from the LC-OCD in comparison to the LC-UVD. In the case of Plymouth, in-line coagulation for the removal of this fraction seems to be essential to control fouling.

For the secondary effluent, the biopolymer concentration is relatively very high compared to the other sources. In this case, removal of this biopolymer fraction by coagulation seems essential. In treating the secondary effluent, it seems different pre-treatments lead to different biopolymer rejection. A high rejection of biopolymer was observed for untreated and only ozonated water (78% rejection in both cases), and a moderate rejection of the biopolymer by coagulated feed (50 %), and low rejection of biopolymer for ozonated water followed by in-line coagulation. This could be caused by electrostatic exclusion between the membrane and the biopolymer. As a consequence of charge exclusion, the fouling was reduced.

CONCLUSIONS

Pretreatment is in all the locations of this study needed to control membrane fouling and to establish a technically and economically feasible process. In all cases, it seems that the HMW fraction of the DOC such as biopolymers are primarily responsible in combination with the LMW fraction such as humics/acids for the increase in TMP after a filtration cycle followed by a BW (i.e., irreversible fouling). Removing one of these fractions often results in a more stable operation. The decision which organic fraction to remove (i.e. ion exchange to remove humics or in-line coagulation to remove a part of the biopolymers) is often determined by secondary needs or other restrictions (e.g., conditioning for downstream processes or removal of other species besides suspended matter). Ozone in all studied cases led to a better or superb operation, but in some cases it is not cost effective. The feasibility of ozone as pre-treatment depends largely on the initial ozone demand and whether or not secondary treatment targets are present (i.e., higher virus removal, taste, odor). SEC/LC-OCD method is considered as a powerful tool for the water analysis in combination with UV detection, because it provides not only quantity but also characteristics of the organic matters.

The slow implementation of ceramic membranes offers new opportunity in developing new pre-treatment technologies or cleaning strategies, especially in combination with strong oxidants and in-line coagulation. This is possible because of the membrane's superior ability to withstand strong oxides or heavy solids loads.

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