Microfiltration of different surface waters with/without coagulation: Clear correlations between membrane fouling and hydrophilic biopolymers

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Abstract

Although low-pressure membranes (microfiltration (MF) or ultrafiltration (UF)) have become viable options for drinking water treatment, problems caused by membrane fouling must still be addressed. The objective of this study was to compare five different surface waters and to identify a relevant index of water quality that can be used for prediction of the fouling potential of the water. Bench-scale filtration tests were carried out with commercially available hollow-fiber MF membranes. Fairly long-term (a few days) filtrations in the constant-flow mode were carried out with automatic backwash. Membrane fouling in this study was shown to be irreversible as a result of the periodic backwash carried out throughout of the operation. Easily accessible indexes of water quality including dissolved organic carbon (DOC), UV absorbance, Ca concentration and turbidity could not explain the degree of fouling encountered in the filtration tests. Fluorescence excitation-emission matrix (EEM) could provide information on the presence of protein-like substances in water, and peaks for protein showed some correlation with the membrane fouling. Biopolymer (characterized by high molecular weights and insensitivity to UV light absorption) concentrations in the five waters determined by liquid chromatography with organic carbon detection (LC-OCD) exhibited an excellent correlation with the fouling rates. Coagulation with polyaluminum chloride could mitigate membrane fouling in all cases. The extent of fouling seen with coagulated waters was also correlated with biopolymer concentrations. The relationship between biopolymer concentrations and the fouling rates established for the raw waters could also be applied to the coagulated waters. These results suggested that the contribution of biopolymers to membrane fouling in the present study

was significant, an observation that was supported by the analysis of foulants extracted at the termination of each test. Biopolymer concentrations determined by LC-OCD might be used as a key indicator of fouling potential of water for low-pressure membranes.

Keywords

Microfiltration; irreversible membrane fouling; biopolymers; coagulation

1. Introduction

Membrane fouling, which causes the decline of membrane permeability, elevation of energy consumption and cleaning frequency, and reduction of membrane lifetime, still remains a major obstacle to wider application of membrane processes in drinking water treatment. For mitigation of membrane fouling and optimization of membrane processes such as selection of membranes or pre-treatment methods, identification of major foulants is indispensable. Natural organic matter (NOM) has been considered to be a major foulant in low-pressure membrane (microfiltration (MF) and ultrafiltration (UF)) processes used for drinking water treatment. Hydrophobic humic substances generally account for a large fraction of the NOM in many aquatic systems (McKnight and Aiken, 1999) and have been considered as major foulants, particularly in early studies of MF/UF for drinking water treatment (Jucker and Clark, 1994; Yuan and Zydney, 2000 and 2001). Contrasting results have recently been reported: hydrophilic organic matter such as polysaccharides can also be a major foulant. Kimura et al. (2004) demonstrated that polysaccharide-like organic matter was responsible for the evolution of the irreversible fouling in the long-term operation of a UF membrane. Lee et al. (2004) noted that macromolecular compounds and/or colloidal organic matter in the hydrophilic NOM fraction may be a foulant in low-pressure membranes. The importance of relatively large organic components in membrane fouling in low-pressure membranes was pointed out in some early reports (Yuan and Zydney, 1999; Howe and Clark, 2002). Yamamura et al. (2007) suggested that hydrophobic (humic-like) components with low molecular weight are first adsorbed on the membrane and then hydrophilic NOM with a higher molecular weight accumulates

on/in the membrane. Peldszus et al. (2011) showed that the content of protein-like substances was highly correlated with fouling in a UF membrane. Hydrophilic organic matter may cause severe membrane fouling in hydrophobic membranes via pore blockage associated with large (macromolecular) hydrophilic molecules (Lee et al., 2004) and/or hydrogen bonds (Yamamura et al., 2008).

Advances in analytical techniques allow us to analyze NOM more efficiently. Among these advanced characterization techniques, high performance liquid chromatography with on-line organic carbon detection (LC-OCD) seems to be promising. Using LC-OCD, NOM can be quantitatively fractionated into biopolymers, humic substances, building blocks, low molecular weight acids and neutrals (Huber et al., 2011). Tian et al. (2013) suggested that the biopolymer fraction quantified by LC-OCD can be correlated with membrane fouling in UF. However, their results were obtained by using an unstirred membrane cell, which is different from the configurations used in pilot/full-scale operations. Additionally, their experiments were rather short (~several hours with a single backwash), which limits the applicability of the results. Nguyen et al. (2011) suggested that fairly long-term testing (at least a few days) is necessary to provide a better assessment of longer-term membrane performance observed in a full-scale utility. Hallé et al. (2009) reported that the biopolymer fraction of NOM determined by LC-OCD played an important role in the evolution of membrane fouling in a UF membrane. However, they examined only a single drinking water source (the Grand River, Ontario, Canada).

Reversibility of fouling (i.e., physically or hydraulically reversible versus irreversible

fouling), which has often been neglected in related studies, should also be a focus. Physically or hydraulically reversible and irreversible fouling are hereafter designated as reversible and irreversible fouling. Irreversible fouling is defined as the fraction in the total fouling that is not cancelled after physical or hydraulic cleaning (e.g., backwash). Irreversible fouling increases operational costs and energy consumption even with the routine backwash that is normally carried out in full-scale operations and should therefore be focused on (Kimura et al., 2004). An experimental framework filtering multiple types of samples for fairly long durations (i.e., at least a few days (Nguyen et al., 2011)) and focusing on irreversible fouling is therefore necessary.

The objective of this study was to check the correlation between the biopolymer fraction in natural waters as characterized and quantified by LC-OCD and membrane fouling in a commercially available hollow-fiber MF membrane. Filtration experiments were continuously carried out for fairly long periods with periodic backwash, and the results obtained in this study are therefore realistic. Additionally, the effectiveness of pre-coagulation was investigated in this study. The results obtained suggest that the biopolymer content in water as determined by LC-OCD can be a universal indicator for assessing the membrane fouling potential of surface water in MF processes used for drinking water treatment.

2. Materials and methods

2.1 Raw waters

Water samples (~300 L) were collected from 5 different drinking water sources in

various parts of Japan and used for experiments: the Toyohira River, the drinking water source for the majority of Sapporo; the Hoshioki River, the drinking water source for a part of Sapporo; the Chitose River, drinking water source for Ebetsu city, which is impacted by agricultural activities, peat bogs and municipal wastewater effluent; the Yodo River, drinking water source for Osaka, which is impacted to an extent by municipal wastewater effluent and the Shira River, drinking water source for Arita Town. These samples were shipped with cooling to our university laboratory. Sodium azide (2 mg/L) was added to the samples on arrival to inhibit biological activity. Samples were kept in a refrigerator until use, and the temperature was adjusted to 20 °C prior to use. Table 1 summarizes the water quality of the samples. All waters were low in DOC and reasonable in turbidity.

2.2 Bench-scale filtration experiments

Tiny membrane modules were fabricated in the laboratory using hollow fiber membranes made from PVDF polymer (Asahi Kasei, Tokyo, Japan). The area of the membrane in each membrane module and the pore size of the membrane were 0.0128 m² and 0.1 µm, respectively. A single membrane module was immersed in the filtration tank in each experiment, and membrane filtration was carried out in outside-in mode. The filtration system was operated with automatic backwash. Trans-membrane pressure was monitored continuously and recorded using a digital pressure meter (Nagano Keiki, Tokyo, Japan). A constant membrane flux of 62.5 LMH was maintained by a peristaltic pump (EYELA, Tokyo, Japan). Periodic backwash (every 30 minutes for 15 seconds, at 94 LMH) was conducted using a separate backwashing

pump from the inside to the outside of the membrane. Permeate was used for backwashing. New membranes were used in each experiment. The operation was usually continued until TMP reached an excessive level (40 kPa). As described later, some operations had to be terminated within 10 hours due to severe membrane fouling, whereas others could be continued for >100 hours.

For each water sample, both raw water and pre-treated water (coagulation) were examined. Polyaluminum chloride (PACl) was used as a coagulant. The coagulant dose was 2 mg Al/L. For filtration of coagulated water, raw water was mixed with PACl at a G value of 100 s⁻¹. The coagulated water was then delivered to the filtration tank without sedimentation.

2.3 Fouling index

The use of a standardized fouling index has emerged over the past several years (Huang et al., 2008; Nguyen et al., 2011; Myat et al., 2012). The rates of TMP increases observed in this study were used to calculate the fouling index. Specific flux is calculated as follows:

$$J_s = \frac{J}{\Delta P} = \frac{1}{\mu(R_m + k_{total}V)} \quad (1)$$

where J_s = specific flux, J = water flux, ΔP = transmembrane pressure, μ = viscosity of water, R_m = resistance of clean membrane, k_{total} = total rate constants for resistances

and V = specific volume (permeate volume/membrane area). Membrane performance can be normalized by dividing $J/\Delta P$ at any specific volume by the initial condition as follows:

$$J'_s = \frac{(J/\Delta P)_V}{(J/\Delta P)_0} = \frac{1}{1 + \frac{k_{total}}{K_{mem}} V} \text{ or } \frac{1}{J'_s} = 1 + \frac{k_{total}}{K_{mem}} V \quad (2)$$

where J'_s is normalized specific flux. The slope in a plot of $(1/J'_s)$ versus (V) data represents the fouling index.

2.4 Assessment of membrane fouling

Pure water permeability of fouled membranes was assessed after several steps of cleaning. Types of fouling (i.e., reversible versus irreversible), the effectiveness of membrane cleaning (physical and chemical) and the features of the foulants were investigated. When each operation was terminated, fouled membranes were taken out of the filtration tank. Pure water permeability of the fouled membrane was measured before and after wiping manually with a sponge and rinsing thoroughly with distilled water, which was performed to assess the degree of the reversible and irreversible fouling that had developed in the continuous operation. Sponge wiping was performed to thoroughly remove the cake from the membrane surface, although routine backwashing was carried out in the continuous operations. The extent of permeability restored by the physical cleaning reflects the reversible fouling. The difference in pure water permeability between a new membrane and the fouled membranes wiped with a

sponge indicates the degree of irreversible fouling.

After the assessment of irreversible fouling by the method described above, membrane modules were disassembled to fabricate three tinier membrane modules. The membranes were cut and re-potted as shorter fibers. The three tinier modules were then soaked separately in three different chemical solutions at 20 °C for 24 hours. The chemical solutions used were NaClO (1000 ppm as free available chlorine), NaOH (pH 12) and HCl (pH 2). Recoveries of pure water permeability due to the chemical cleaning were evaluated, and the chemical solutions containing the foulant desorbed from the membranes were analyzed further.

2.5 Analytical methods

The concentrations of dissolved organic carbon (DOC), biopolymers and humic substances were determined using an LC-OCD system (Model 8, DOC-LABOR, Karlsruhe, Germany). UV absorbance at 254 nm was measured by a spectrophotometer (UV-1800, Shimadzu, Kyoto, Japan). Before UV absorbance and DOC measurements were performed, the samples were filtered with 0.45-μm hydrophilic PTFE membranes (Advantec Toyo, Tokyo, Japan). It was confirmed that adsorption of organic matter to the membranes was negligible. Turbidity measurements were performed using a turbidity meter (SEP-PT-706D, Mitsubishi Chemical Analytech, Mie, Japan). The concentrations of calcium were determined without filtering by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) (ICPS-7500, Shimadzu, Kyoto, Japan). Fluorescence EEMs of samples were generated using a fluorescence

spectrophotometer equipped with a 15 W ozone-free xenon lamp (RF-5300PC, Shimadzu, Kyoto, Japan). The interval of excitation and emission wavelengths was 5 nm. Excitation and emission wavelengths between 220 nm and 550 nm were measured. Prior to fluorescence analysis, samples were filtered with the 0.45- μ m filters.

3. Results and discussion

3.1. Filtration of raw surface waters

3.1.1 Correlation between the fouling rates and general water quality indexes

Figure 1 plots the inverse of normalized specific flux versus specific volume to calculate the fouling index. According to Nguyen et al. (2011), the fouling index determined in this study is termed “hydraulic-irreversible fouling index (HIFI)”. Coagulation was not carried out in these experiments. Significant fouling occurred for Yodo River water, Chitose River water and Shira River water.

Figure 2 shows the relationships between the HIFI calculated and the general water quality indexes including DOC concentration, UV absorbance, turbidity and Ca concentration. As Figure 2 clearly shows, correlations between the HIFI values and these easily accessible water quality indexes did not exist.

Very weak correlations between DOC and the fouling index were not surprising based on the assumption that hydrophilic NOM is mainly responsible for membrane fouling (Kimura et al., 2004; Lee et al., 2004; Yamamura et al., 2007; Peldszus et al., 2011). As shown later, humic substances comprised >50% of the organic matter in waters tested

in this study, whereas hydrophilic NOM (i.e., biopolymers) constituted a minor fraction. Humic substances absorb UV light due to the presence of double/triple bonds and aromatic rings in their structures. UV can therefore be a good surrogate parameter for humic substances in most cases. UV absorbance could also not be correlated to the HIFI values in this study. These results imply that humic substances were not critical in the evolution of membrane fouling, although they have been considered to be major foulants (Hao et al., 2011; Sutzkover-Gutman et al., 2010). Although the importance of Ca in membrane fouling was suggested in a few studies (Jermann et al., 2007; Yuan and Zydney, 2000), no clear correlation was found between Ca concentrations and membrane fouling in this study. Turbidity (particulate matter) can also cause membrane fouling, mainly reversible fouling. Reversible fouling was effectively controlled by periodic backwashing in this study. The absence of a correlation between turbidity and the HIFI values was therefore reasonable.

3.1.2 Fluorescence EEM analysis of the raw waters

Figure 3 shows fluorescence EEMs of the 5 water samples examined in this study. Fluorescence EEM provides information on the characteristics of organic matter in samples: a peak found near Ex/Em of 320 nm/430 nm indicates the presence of humic-like substances, whereas a peak near Ex/Em of 270 nm/320 nm is an indicator of protein-like substances (Chen et al., 2003). Quantitative interpretation of EEM data is still difficult, although some studies have recently attempted to interpret EEM data using principal component analysis or the PARAFAC model (Peiris, 2010; Murphy et al., 2011). Such advanced statistical analyses were not performed in this study.

However, the data shown in Figure 3 suggest that humic substances were the major components in all samples. Additionally, the major peaks in the EEM of Yodo River water, Chitose River water and Shira River water extend over the region of protein-like substances, suggesting an abundance of protein-like substances in the three samples, which caused severe membrane fouling in the filtration tests (Figure 1).

3.1.3 LC-OCD analysis of the raw waters

Figure 4 shows LC-OCD chromatograms of the raw waters filtered in this study. The peaks at a retention time of approximately 30 minutes and 40-50 minutes are defined as peaks related to biopolymers (e.g., polysaccharides and proteins) and humic substances, respectively (Huber et al., 2011). As in previous studies using LC-OCD, peaks of biopolymers did not exhibit strong UV responses (data not shown). Although EEM is not sensitive to a major component of biopolymers (polysaccharides), the speculation made on the basis of results of EEM analysis is supported by results of LC-OCD analysis: humic was found to be dominant in the LC-OCD chromatograms in all cases. Examination of the LC-OCD data shown in Figure 4 also suggests that humic substances are not good indicators of fouling potential of a feed water. The concentration of humic substances in the Toyohira River water was fairly high and comparable to the concentration of humic substances in the Yodo River water. As shown in Figure 1, however, the fouling rate observed with Toyohira River water was much less than the fouling rate observed with Chitose River water. The opposite case is found with the Shira River water. Although the concentration of humic substances in the Shira River water was relatively low, membrane fouling occurred rapidly.

Concentrations of biopolymers seem to be related to the fouling rates. The concentrations of biopolymers were significantly high in the Yodo River water, Chitose River water and Shira River water, and the HIFI values were very high in the filtration tests.

3.2 Filtration resistance of the fouled and cleaned membranes

In this study, pure water permeabilities of the fouled and cleaned membranes were measured and were converted to the filtration resistances of the membranes. The conversion was made using the following formula:

$$J = \frac{\Delta P}{\mu R_t} = \frac{\Delta P}{\mu (R_m + R_f)} \quad (3)$$

where R_t is the total membrane filtration resistance, and R_f is the fouling resistance. Comparison between the filtration resistances measured at the termination of the continuous operations and those determined after physical cleaning (wiping with a soft sponge in this study) allows us to know the degree of reversible fouling. The physically cleaned membranes were subsequently cleaned with chemical reagents. Restoration of membrane permeabilities seen with chemical cleaning provides information on the degree of irreversible fouling.

Figure 5 shows filtration resistances of the fouled and cleaned membranes. For comparison, the filtration resistance of a new membrane is also shown in Figure 5. The

degree of reversible fouling is represented by differences between the black and white bars in Figure 5. Reversible fouling that could be cancelled by physical cleaning was found to be a minor component in the total filtration resistance in all cases. Rather, irreversible fouling, represented by the difference between the resistance determined after physical cleaning and the resistance of a new membrane, accounted for the major part of the fouling in all cases. Observation with scanning electron microscopy (SEM) revealed that the fouled membranes were still covered by deposits even after sponge cleaning (Figure S1 of the Supporting Information). These deposits and foulants accumulating in the internal pores caused irreversible fouling. Three different chemicals were tested to cancel the irreversible fouling in this study. The effectiveness of the chemical reagents in terms of mitigation of irreversible fouling followed the order, NaClO > NaOH > HCl. Acid was the least effective, but NaClO could almost completely cancel the irreversible fouling. In all cases, membranes cleaned with NaClO exhibited a permeability that was as high as the permeability of a new membrane. Alkali was fairly effective but inferior to NaClO. These results suggested that organic matter was mainly responsible for the irreversible fouling in this study.

3.3 Analysis of extracted foulants

To obtain information on organic matter that caused the irreversible fouling in this study, foulants extracted after physical cleaning were analyzed by fluorescence EEMs and LC-OCD. Foulants extracted by NaOH were used for this purpose instead of the NaClO extracts. This decision was made because NaClO (an oxidizing agent) was likely to degrade the organic matter and to significantly alter its properties. The

effectiveness of HCl cleaning was limited (Figure 5), and HCl was therefore excluded from the analysis. Figure 6 shows the EEM fluorescence spectra measured for the foulants extracted from the fouled membranes. In all of the EEM fluorescence spectra obtained for the foulants, a peak that can be attributed to a protein-like substance at $\text{Ex/Em} = 270 \text{ nm}/320 \text{ nm}$ dominates. The shapes of the EEM fluorescence spectra obtained for the foulants were obviously different from the EEM fluorescence spectra for the raw waters in which the peak of humic substances was dominant (Figure 3). Figure 7 shows the LC-OCD chromatograms of the extracted foulants. Similar to the results of the EEM analysis, LC-OCD chromatograms of the raw waters and those of the extracted foulants were significantly different. The LC-OCD chromatograms of the raw water (Figure 2) showed that humic substances were the major components in the raw waters, in accordance with the fluorescence EEMs for the raw waters (Figure 3). However, in the LC-OCD chromatograms of the extracted foulants, the peak for the biopolymer (retention time of approximately 30 minutes) became significant. In the case of the foulant that was extracted from the membrane fouled by Toyohira River water, the peak of humic substances was still dominant in the LC-OCD chromatograms of the extracted foulant. However, the relative amount of biopolymer compared to the humic substances in the foulant significantly increased even in the case of Toyohira River water, compared with the raw water (Figure 4). Both the fluorescence EEM analysis and LC-OCD analysis for the extracted foulants agree with our assumption based on the previous studies (Kimura et al., 2004; Yamamura et al., 2007) that hydrophilic NOM was mainly responsible for the evolution of irreversible fouling. Hydrophilic NOM or biopolymers seem to be selectively trapped on/in the membranes and caused irreversible fouling in this study. Hydrogen bonds between biopolymers

and the membranes (Yamamura et al., 2008) might explain the result. Additionally, plugging of the micropores of the membrane should be considered because the size of the biopolymers might be as large as the micropores of the MF membranes (Kimura et al., 2005; Rosenberger et al., 2006).

3.4 Filtration of pre-coagulated water

Figure 8 plots the inverse of normalized specific flux versus specific volume to calculate the fouling index for pre-coagulated water. Coagulation was effective for mitigation of membrane fouling in this study: the HIFI values were somewhat suppressed in all cases. Coagulation significantly mitigated the membrane fouling in the case of Shira River water. In contrast, the HIFI values were still relatively high even after coagulation in the cases of Yodo River water and Chitose River water. Degrees of reversible fouling and irreversible fouling were assessed at the termination of filtration of the coagulated waters as well. Similarly to the case of filtration of non-coagulated waters, irreversible fouling was dominant whereas reversible fouling was minor in all cases (data not shown).

As stated in the previous sections, biopolymers were thought to be mainly responsible for membrane fouling in this study. Coagulation reduced the concentrations of biopolymers to some extent, which might explain the mitigation of membrane fouling. Figure 9 summarizes the relationship between the HIFI calculated and the concentrations of biopolymers in the feed water in the series of filtration experiments. Figure 9 includes the data obtained in both experiments with coagulation (Figure 8)

and those without coagulation (Figure 1). As illustrated in Figure 9, a remarkable correlation between the fouling index and biopolymer concentration was found, suggesting that biopolymer concentration could be used to assess the fouling potential of a feed water. Although it was not confirmed in this study due to insufficiency of data, the raw water data and the pre-coagulated water data might eventually exhibit different slopes: the pre-coagulated water data might have lower fouling rates for the same amount of biopolymer concentration. If the two lines diverge, this would suggest that humic substances, which are preferentially removed by coagulation, also play a supporting role in fouling. The regression line suggested in Figure 9 perhaps needs refinements by other studies.

3.5 Suggestions for future studies

As described above, concentrations of hydrophilic biopolymers in the feed waters could clearly be correlated with the (irreversible) fouling rates in this study. Hallé et al. (2009) reported that biopolymer concentrations were not directly correlated to irreversible fouling, which contradicts the results obtained in this study. Hallé et al. (2009), however, also mentioned that biopolymer composition must play an important role in irreversible fouling. The biopolymer composition in their study might be unique. They examined only one river water, whereas 5 different surface waters with significant diversity were tested in this study. Detailed compositions of biopolymers (i.e., polysaccharides and proteins) in various types of waters are certainly worth investigation. Advanced analytical techniques that would allow us to investigate the details of polysaccharides and proteins have recently been proposed (Kimura et al.,

2012; Miyoshi et al., 2012). Tian et al. (2013) recently reported a remarkable correlation between biopolymer concentrations and membrane fouling in UF of three water sources impacted by municipal wastewater. There might be a boundary where biopolymer concentration can be used as a key water quality index to predict membrane fouling. More data are apparently necessary to establish the relationship between biopolymer concentration in surface water and membrane fouling.

Assuming that biopolymer concentration is a good indicator of membrane fouling, identification of methods for better removal of biopolymers would be very important. Conventional water treatment processes such as coagulation or activated carbon adsorption are not necessarily good at removing hydrophilic organic matter (Tambo and Kamei, 1978).

4. Conclusions

A remarkable relationship between the fouling index calculated from fairly long-term microfiltration experiments and concentrations of biopolymers in the feed waters collected from various parts of Japan was demonstrated in this study. The relationship was maintained for the pre-coagulated waters as well. Concentrations of biopolymers may be a new useful indicator of the fouling potential of feed water in microfiltration. Analysis of the extracted foulants supports the importance of the contribution of biopolymers to the evolution of membrane fouling, particularly irreversible fouling.

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Table 1. Water quality indexes of the collected samples.

	DOC (mg/L)	Turbidity (TU)	UV absorbance at 254 nm (abs)	Ca concentration (mg/L)
Toyohira River	1.0	1.9	0.019	7.5
Hoshioki River	0.5	1.3	0.007	8.7
Chitose River	2.0	2.4	0.047	10.8
Yodo River	1.6	2.1	0.038	11.1
Shira River	1.0	0.7	0.007	1.9

Figure 1. Plot of the inverse of normalized specific flux versus specific volume for raw waters.

Figure 2. Relationships between hydraulic-irreversible fouling index (HIFI) and general water quality indexes.

Figure 3. Fluorescence EEMs of the raw waters.

Figure 4. LC-OCD chromatograms of the raw waters.

Figure 5. Filtration resistances of the fouled and cleaned membranes.

Figure 6. Fluorescence EEMs of the foulants extracted by NaOH after physical cleaning.

Figure 7. LC-OCD chromatograms of the foulants extracted by NaOH after physical cleaning.

Figure 8. Plot of the inverse of normalized specific flux versus specific volume for coagulated waters.

Figure 9. The relationship between HIFI calculated and concentrations of biopolymers in the feed water.

Graphical Abstract (for review)