MEMBRANE CLEANING:FROM THEORY TO PRACTICE

Flexiable cleaning regimes promote membrane permeability

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ABSTRACT

Microfiltration and ultrafiltration are increasingly replacing conventional water treatment processes as a result of more stringent regulations and greatly improved competitive pricing. The most common operating issue of membrane plant operation is to control membrane fouling. Although the impact of fouling may be mitigated via the modification of pretreatment process, inefficient cleaning is the leading cause of irreversible permeability loss, resulting in premature replacement of membranes.

Membrane fouling is fundamentally the result of interfacial interactions between membrane and fouling substances, and between different constituents of fouling materials. Different fouling materials interact to form fouling layers with different structures that may impact the cleaning efficacy and require particular cleaning sequences. The complexity and dynamic nature of membrane fouling make it challenging for plant operations.

A membrane cleaning study with various cleaning regimes provides a practical means to elucidate the nature of fouling and to devise effective cleaning regimes. By correlating the recovery in membrane permeability to specific cleaning steps, as well as the quantity of contaminants on the membrane surfaces, the cause for fouling could be elucidated and the most effective cleaning regimes could be determined. Several case studies are selected to illustrate the complexity of membrane fouling in real world applications.

INTRODUCTION

Membranes have several distinctive features such as providing superior quality of filtered water, robust operation, and small footprint. However, a commonly recognised problem of operating membrane processes is control of membrane fouling. Membrane fouling is omnipresent and can severely affect plant operation. If not cleaned effectively, membrane fouling can lead to a downward spiral of plant performance and premature replacement of membranes. Given its importance, however, the studies specifically addressing membrane cleaning in water treatment are generally limited (Al-Amoudi and Lovitt, 2007; Chen et al., 2003; Lee et al., 2001; Lee et al, 2007; Lee and Elimelech, 2007; Li and Elimelech, 2004; Liikanen et al., 2002; Nyström and Zhu, 1997; Porcelli and Judd, 2010a, 2010b; Strugholtz et al., 2005; Zondervan et al., 2007; Zondervan and Roffel, 2007).

At a fundamental level, membrane fouling is the result of interfacial interactions between fouling materials and membrane surface, and that between different fouling materials. Fouling occurs when the sum of adhesion forces exceeds the sum of repulsion forces. Those interfacial forces can be electrostatic, hydrogen bonds, steric, van der Waals, and hydrophobic / hydrophilic (Gregory, 2006). The extended Derjaguin, Landau, Verwey, and Overbeek (eDLVO) theory describes the double layer electrostatic force, van der Waals force, and acid-base interaction. Research has been conducted using DLVO theory or its extended version to understand membrane fouling mechanisms (Bhattacharjee et al., 1996; Brant and Childress, 2002; Contreras, 2011; Kim and Hoek, 2007; Lee et al., 2007). Expanding this model to include other interactions may provide a useful theoretical framework for describing membrane fouling phenomenon, if each interfacial force can be qualified and quantified. Membrane fouling in real-world applications is often more complex, and it is difficult to delineate the impacts from various interactions. Recognising the limitations due to complexity of fouling, however, models can still provide insights for the nature of dominating interactions as well as the physiochemical factors affecting fouling.

From a more practical perspective, developing a procedure to evaluate the nature of fouling in general, and the most effective cleaning regime for a specific application in particular is imperative for troubleshooting the membrane plants that encountered the fouling issues. Membrane fouling can be very dynamic due to the temporal and spatial variations of incoming water quality, changes in pretreatment processes, and accumulative impact from long-term ineffective cleaning. This dynamic nature of fouling, as well as the synergetic interactions of different foulants, can lead to changes in the nature of fouling and form varied structures of fouling layer (Kim et al., 2009). Therefore, periodic reevaluation of cleaning regimes may be necessary. Concentration of chemicals, different sequence of cleaning steps, the length of cleaning for each steps, and solution temperature are key variables affecting cleaning (Porcelli and Judd, 2010). Although possible combinations of those variables seem endless, many practical considerations, such as chemical compatibility of membrane materials, availability of cleaning chemicals that have proper regulatory approval, permissible length of cleaning operation without impacting the plant production, and sometimes the restrictions imposed on the disposal of spent cleaning solutions, all limit the options of cleaning operation. Therefore, the selection of a cleaning regime often is merely "workable", not necessarily optimal. Compromises have to be made to accommodate different needs.

MEMBRANE FOULING AS AN INTERFACIAL PHENOMENON

Membrane fouling refers to the accumulation of certain constituents ("foulants") on the membrane surfaces and/or within membrane media. As a result of fouling, permeability of membranes declines significantly, which leads to the increased energy consumption in the form of higher trans-membrane pressure (TMP), decreased plant productivity due to plant shutdown for cleaning, and increased chemical consumption.

Membrane fouling is the result of interfacial interactions between foulants and membranes, and between foulants and foulants (Contreras, 2011; Contreras et al., 2009; Kim and Hoek, 2007, Lee et al., 2007). Those interactions include electrostatic, hydration, steric, van deer Waals, and hydrophilic/hydrophobic, and they are either attractive or repulsive (Gregory, 2006). Table 1 summarises the characteristics of these interactions (Liu, 2014). The sum of those interactions would determine if the adhesions between foulants and membranes, and between foulants and foulants are predominating, i.e., membrane fouling occurring.

The eDLVO theory describes the particle-to-surface or particle-to-particle interfacial interactions including electrostatic, van der Waals, and acid-base interactions (Hunter, 1984). It has been used for investigating membrane fouling (Bhattacharjee, 1996; Brant and Childress, 2002; Contreras, 2011). Contreras (2011) concluded that specific interactions that are not included the eDLVO could play more significant roles in membrane fouling. Therefore, constructing a model including more interfacial interactions than those described by eDLVO can provide a more accurate and comprehensive description for membrane fouling.
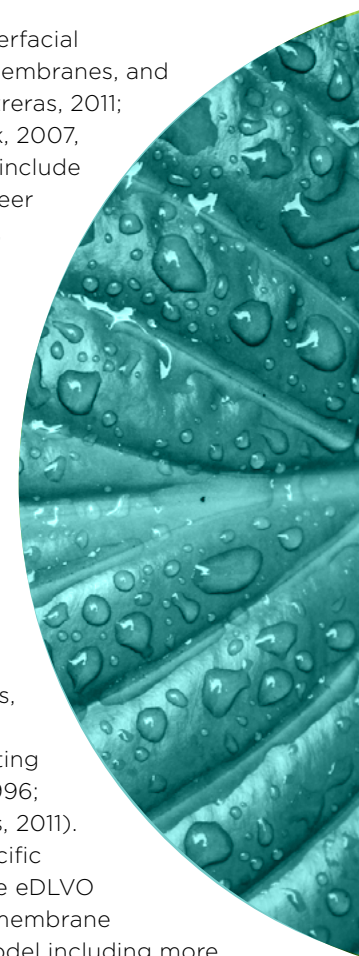
Table 1. Interactions Affecting Membrane Fouling

Interactions	Nature	Energy Level (KJ/mol.)	Range of Influence
Electrostatic	Attractive or repulsive	$\leqslant 30$	Intra- and inter-molecular, $\propto r^{-2}$
Hydration	Generally repulsive	Specific to molecular structure	Inter-molecular
Steric	Repulsive	Specific to molecular structure	Inter-molecular
Van der Waals	Attractive	$\leqslant 1$	Inter-molecular, $\propto r{-6}$
Hydrophobic	Attractive	~ 2.5 /mol. $-CH_2$	Inter-molecular

The difficulty is to qualify and quantify every interfacial interaction for any given condition. However, with the advances in analytical techniques such as atomic force microscope (AFM) and quartz crystal microbalance with dissipation (QCM-D), and creative ways to employ them in the study of membrane fouling, the progress in better understanding membrane fouling can be expected. Even with an incomprehensive picture, the models based on the eDLVO can still provide useful insights and understanding for membrane fouling in a simplified manner. One example is a study on the impact of polymeric coagulants and flocculants on fouling of microfiltration membranes (Wang et al., 2011). In a simplified case where the primary metal-salt coagulant was not used, membrane fouling had been found to be primarily dominated by electrostatic interaction. The normalised fouling rate was correlated well with the charges carried by both polymers and membranes, as showing in Figure 1. The charge characteristics of membranes and polymers as a function of pH are shown in Figure 2.

All three membranes used in the experiments are rated as 0.2 micron and are negatively charged in pH range 3 – 10 (Figure 2(a)). Supor-200, a polyethersulfone membrane, is the most negatively charged, and HT-200, a cellulose acetate (CA) membrane, is the least negatively charged. The polymers tested were cationic (pDADMA 400 – 500 kD), nonionic (PAM 5,000 kD), and anionic (PAA 520 kD), respectively in the pH range of 3 - 10 (Figure 2(b)). The cationic and anionic polymers had similar molecular weight, and nonionic polymer had a molecular weight about 10 times higher than the other two. Therefore, the eDLVO theory would predict that the adhesion of the cationic polymer (pDADMA 400 – 500 kD) on the most negatively charged membrane (Supor-200) would be the most significant due to electrostatic attraction, and consequently causing the most severe fouling. This is exactly what exhibited in Figure 1 in which the degree of fouling is characterised by the normalised fouling rate. As indicated above, the eDLVO theory may have capacity to predict the outcomes qualitatively under well-defined and simple conditions.

However, in practice polymeric coagulant and flocculants are rarely used alone, and more often in company of a primary coagulant such as iron- or aluminum-based metal salt coagulants, or inorganic polyelectrolytes such as polyaluminum chloride (PACl). The addition of the primary coagulant greatly complicates the situation: the two-member (polymer-membrane) system becomes a three-member system (membrane – polymer – primary coagulant). With the presence of a primary coagulant, the patterns of membrane fouling become rather complex. The normalised fouling rate of a PVDF membrane from various polymers is plotted in Figure 3.
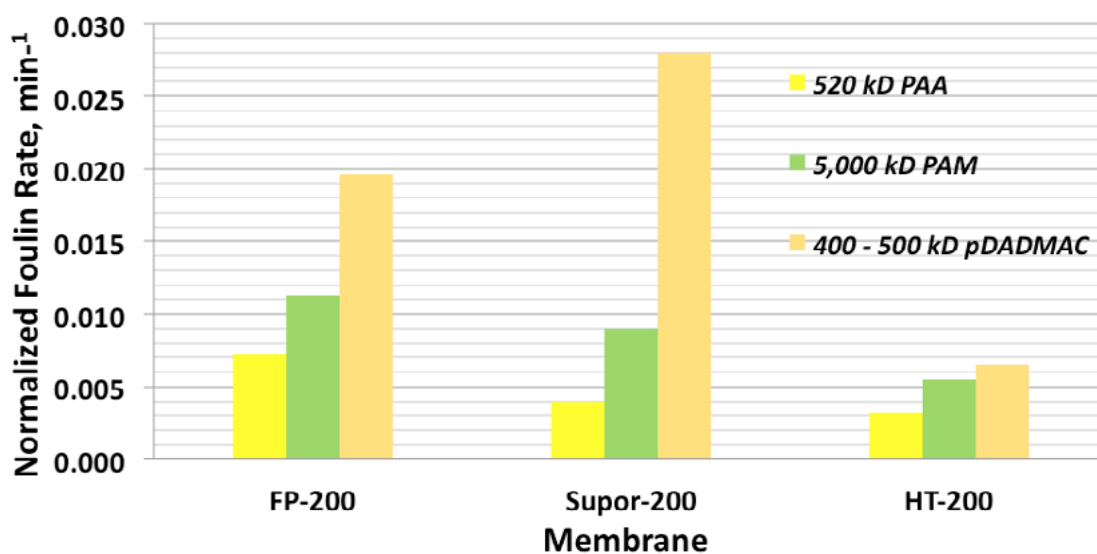

Figure 1. Normalised fouling rates of membranes by different polymers (pH = 7.2) (Wang et al., 2011)
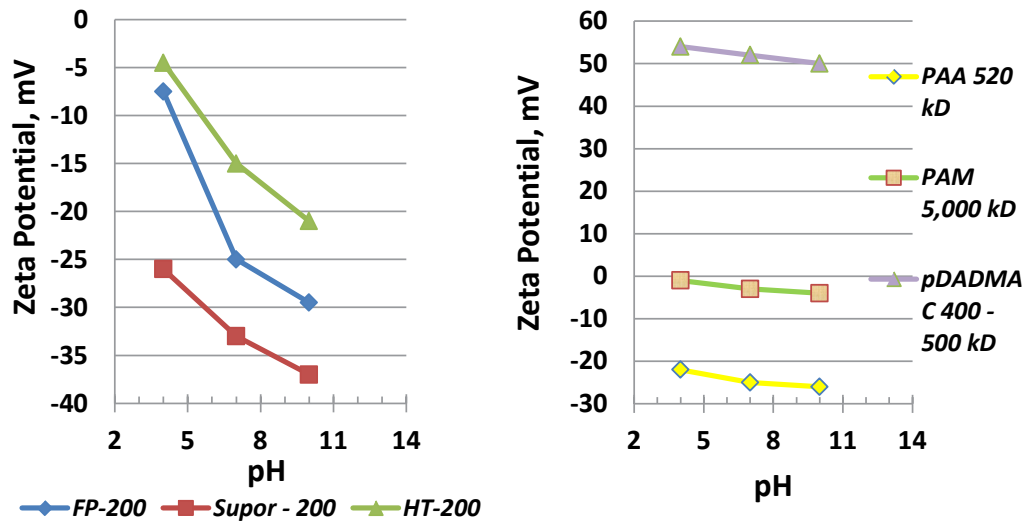
Figure 2. Charge characteristics of (a) different membranes, (b) various polymers (Wang et al., 2011)
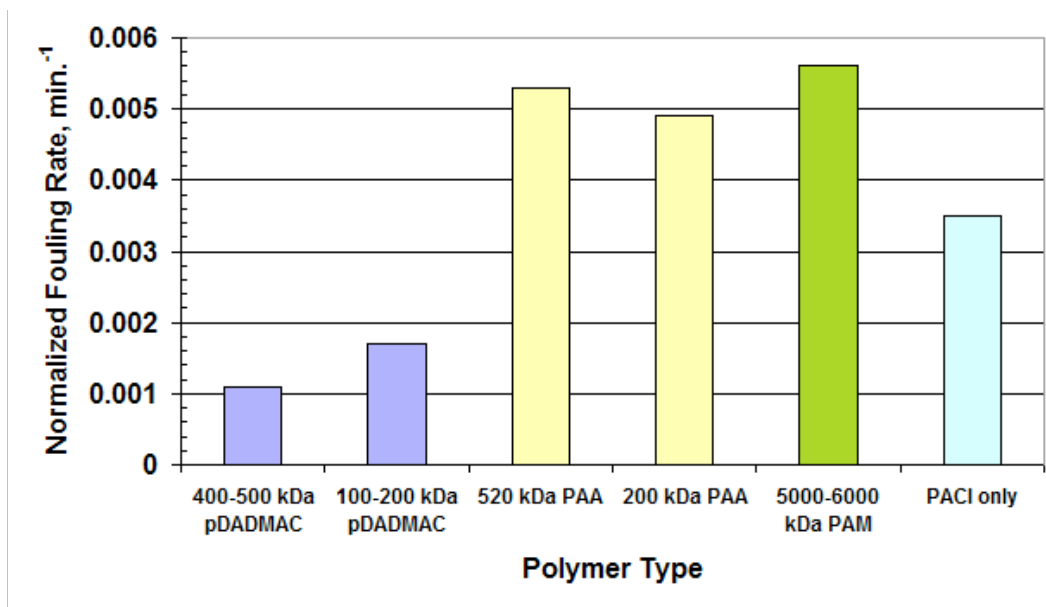

Figure 3. Effect of polymers on membrane fouling rate of a PVDF membrane after 1 hour sedimentation. PACl: 15 mg/L, polymers: 1 mg/L

In Figure 3, while the negatively charged anionic polymer (PAM) showed the most fouling, cationic polymers actually exhibited significantly lower normalised fouling rates when compared with the control, i.e., using a primary coagulant only (Liu, et al., 2011). The lower fouling rate of cationic polymers may be attributed to several possible reasons:

▸ The flocs from the primary coagulants formed a cake layer on the membrane surfaces, which shielded the electrostatic interactions between polymer molecules and the membrane surface;

◗ Flocs adsorbed free-floating polymer molecules, and embedded them in the flocs structures. Consequently it reduced the adhesion of polymers on either membrane surfaces or the outer surfaces of flocs;

◗ The addition of a primary coagulant reduced both bulk quantity and certain fractions of natural organic matter (NOM) contributing to the membrane fouling. The testing results indeed indicated that the removal of UV_{254} was the most effective by cationic polymers (Wang et al., 2013).

The first two scenarios are supported by the fact that increasing the mass ratio of primary coagulant (PACl) to polymer generally decreased the normalised fouling rate (Liu et al., 2011).

This example illustrates the complicated relationships of various factors contributing to membrane fouling. The addition of a primary coagulant into the system changed the interactions by limiting the direct adhesion of polymer molecules to the membrane surfaces, which rendered the surface charge of membranes playing less important roles in fouling.

Another factor that can significantly affect the effectiveness of membrane cleaning, but has not been researched in detail, is the structure of the fouling layer (Contreras et al., 2009). Although membrane fouling is typically classified into different categories, such as inorganic colloidal fouling, organic fouling, biofouling, and scaling, etc., such categories are more out of convenience. In reality, various foulants form fouling layers with different structures. The interactions of different foulants can either elevate or reduce the overall fouling of membranes (Contreras et al., 2009; Li and Elimelech, 2004). Depending on how the different foulants are distributed, fouling layers formed on membrane surfaces can be stratified or mixed (partially or completely). The structure of fouling layers is not well understood and it may be the result of physicochemical interactions between different foulants, or temporal change in feed water quality. Nevertheless, it could have implications on membrane cleaning strategies. For example, the stratified structure of a fouling layer may lead to sequential cleaning with cleaning steps aimed to remove the stratified sub-layers one by one. On the other hand, cleaning strategy for the fouling layer with a mixed structure may target the foulants responsible for physical integrity of the fouling layer at first, so as to loosen up the entire fouling layer to allow better access of cleaning solutions penetrating into the layer.

MEMBRANE CHEMICAL CLEANING: PRACTICAL CONSIDERATIONS

Chemical cleaning is critical for the operation of membrane plants. Cleaning not only restores membrane permeability to meet the plant production, but also has important implications for maintaining long-term membrane permeability (Liu et al, 2015). The accumulated effect of inefficient cleaning seems to "harden" the fouling materials remaining on the membranes and makes the subsequent cleaning even more ineffective.

Chemical cleaning is carried out via chemical reactions between cleaning chemicals and foulants. Those reactions may change the structure and/or property of foulants, alter the surface chemistry of fouling layers, and weaken the adhesions between foulant-foulant and foulant-membrane interfaces (Li and Elimelech, 2004). The effectiveness of membrane cleaning is measured by (a) how much membrane permeability can be restored; and (b) how fast the restoration of membrane permeability can occur. The major variables contributing to the effectiveness of membrane cleaning include the types and concentration of cleaning reagents, the temperature and ironic strength of cleaning solutions, the frequency of cleaning, duration of the cleaning operation, the sequence of cleaning steps, and hydrodynamic conditions during the cleaning (Al-Amoudi and Lovitt, 2007; Chen et al., 2003; Lee et al., 2001; Liikanen et al., 2002; Liu, 2017; Porcelli and Judd, 2010b; Strugholtz et al., 2005; Tragårdh, 1989; Zondervan and Roffel, 2007). Many of those variables are interdependent. For example, both the concentration and temperature of cleaning solution can affect reaction rate, which in turn affects the duration of cleaning operation. Fundamentally, the objective of a membrane cleaning study is to select a set of variables of cleaning operation to restore membrane permeability to an acceptable level in a reasonable time frame. There are several practical constraints to achieve this objective:

1. Is the chemical formulation of cleaning solution compatible to the membranes to be cleaned?

2. Are the chemicals used for cleaning locally available?

3. Is there any regulation against the use of any chemical in the formulation of cleaning solutions?

4. Can the spent cleaning chemicals be disposed of in a safe and environmentally acceptable manner?

These constraints can limit the options for membrane cleaning. Chemical compatibility is especially important because credible data on the effect of long-term exposure of membranes to chemicals is not always available. Chain breaking in polysulfone molecules after extended exposure to hypochlorite was observed (Gaudichet-Maurin and Thominette, 2006; Rouaix et al, 2006). The decrease in elongation of a polyethersulphone (PES) membrane after exposure to hypochlorite was also reported (Thominette et al. 2006). The deterioration in mechanical strength of hypochlorite-treated membranes leads to the loss of membrane integrity (Arkhangelsky et al., 2007). It is also known that the overexposure of PVDF membranes to alkaline conditions can lead to dehydrofluorination – a process that makes PVDF membranes lose elasticity and become brittle (Liu, 2013).

LAB MEMBRANE CLEANING STUDY

Although it is possible to conduct field cleaning via trial-and-error at the membrane plants, it is often more efficient and practical to conduct a lab cleaning study using fouled membrane samples to compare the cleaning efficacy of different cleaning regimes. The lab cleaning study involves several steps:

5. Measuring of baseline membrane permeability (i.e., the permeability of membrane samples as received);

6. Cleaning membrane samples with multiple cleaning steps;

7. Measuring the membrane permeability following each cleaning step;

8. Comparing the membrane surfaces before and after cleaning via analytical techniques such as Scanning Electronic Microscopy (SEM), X-ray Energy Dispersion Spectroscopy (EDX), Fourier Transform Infrared Spectroscopy (FTIR).

Figure 4 depicts a bench-top device for lab cleaning study of hollow fiber membrane samples. The stand has a five-station for testing five hollow fiber samples simultaneously. Filtered compressed air at a constant pressure (1 bar) is used to push deionised water in a reservoir flowing from the fiber lumen to the outer

surfaces, or in "inside-out" mode (one end of hollow fibers is sealed by inserting a stainless steel pin into the fiber lumen). Filtrates are collected in containers and the volume of the filtrate in a given time is measured to generate permeability data. After the measurement of the baseline permeability, samples are divided into different groups of five samples, each with similar mean value of permeability. Each group of samples is cleaned with a multiple-step cleaning regime, by soaking in the chemical solutions for a pre-determined length of time at the ambient temperature (~21oC). After each cleaning step, samples are thoroughly rinsed and permeability is measured again.

The permeability of membrane samples is expressed as the percentage of permeability for new membrane by averaging five replicates. Due to the heterogeneous nature of both membrane surfaces and adhesion of fouling materials, replicate samples are tested and statistical analyses (e.g., t-test) are carried out to determine if the changes in permeability between cleaning steps and among the different cleaning regimes are statistically significant.

Figure 4. The bench-top testing stand for cleaning study of hollow fiber membrane samples

The key to a successful design of a cleaning study is to differentiate the effect of cleaning steps/regimes, and to confirm these effects in subsequent cleaning steps. The causes for fouling of microfiltration (MF) and ultrafiltration (UF) membranes generally include natural organic matter (NOM), iron, precipitates of metals, and scaling. The results of membrane autopsy on samples (70% from surface water filtration plants) indicated that the predominant causes for fouling were NOM, and then some combinations of iron and NOM (Liu et al., 2015). A good understanding on the nature of the raw water and pretreatment processes also helps in designing the cleaning study plan. It should be noted that the design of cleaning regimes is a dynamic process: selections of subsequent cleaning steps depend on the responses of membranes (i.e., the change in permeability) to previous cleaning steps.

The improvement in membrane permeability can be related to a specific cleaning regime and/or step to interpret the nature of fouling or even possibly the structure of fouling layers by comparing the sequence of cleaning steps in different regimes. Surface analytical techniques, such as Scanning Electronic Microscopy (SEM), X-ray Energy Dispersion Spectroscopy (EDX), Fourier Transform Infrared Spectroscopy (FTIR), are often employed to detect the changes in properties of membrane surfaces before and after cleaning. Whenever possible, these changes should also correlate to the improvement in membrane permeability to elucidate the possible cause of fouling.

INTERPRETING THE RESULTS

Two examples provided below are used to illustrate how the results of a cleaning study could be used to elucidate the causes of membrane fouling.

Example 1

The plant is a microfiltration plant filtering surface water. The source water contains high TOC (>10 mg/L), moderate to high hardness and alkalinity. The pretreatment includes coagulation with ferric sulfate, flocculation, and sedimentation prior to microfiltration. The operator of the plant reported the rapid increase in trans-membrane pressure (TMP) and the decline in cleaning effectiveness. A membrane autopsy was performed and the significant solid accumulation was noted in the membrane module. A dark brown color on membrane surfaces was observed, which was consistent with the cases where iron was present.

A membrane cleaning study was performed and the results of the study are presented in Figure 5. The cleaning results are expressed as the average percent permeability of five replicates (where the permeability of the new membrane is 100%) and illustrated using a bar graph. Bars for each cleaning regime are grouped together and the colours of bars in a group relate to a particular cleaning step (e.g., before cleaning, 1st Step, 2nd Step, and so on). The details for each cleaning regime are summarised in the table below the bar graph. In the table, Super Iron-out is a household rust cleaner (Summit, Fort Wayne, ID) that has been proved to be very effective to remove the deposition of iron hydroxide on the membranes.

The permeability for the samples as received was only 14% of that for new membranes, indicating a rather severe fouling. After three-step cleaning, the permeability was recovered from 83% to 97% of that for new membranes for Regimes B and A, respectively. It is interesting to note that sequence of the cleaning steps played an important role in recovering the permeability. Regime A was cleaned with caustic/chlorine mixture first and achieved the overall highest recovery. Although the cleaning step with the mixture of caustic/chlorine did not appear to be very effective at the first glance when compared to the other two regimes, it seemed to help the subsequent cleaning tremendously. The reason for the enhanced cleaning by applying the mixture of caustic and chlorine is not clear. However, it was possible that caustic/chlorine solution might have modified the properties of a fouling layer, making subsequent cleaning steps more effective. It has been reported that NOM adsorbed on silica colloids enhanced the adhesion between colloids and colloids and membrane surfaces (Contreras et al., 2009). The caustic/chlorine mixture could reduce or modify the NOM molecules adsorbed on colloids and thus the adhesion of those particles.

Example 2:

The source water is industrial wastewater produced at a chemical manufacturing plant. The available water quality indicated the potential for organic and biofouling (BOD_5: 8 - 15 mg/L; SS: 13 – 38 mg/L; TOC: 24 – 136 mg/L, pH: 8.1 – 8.3).
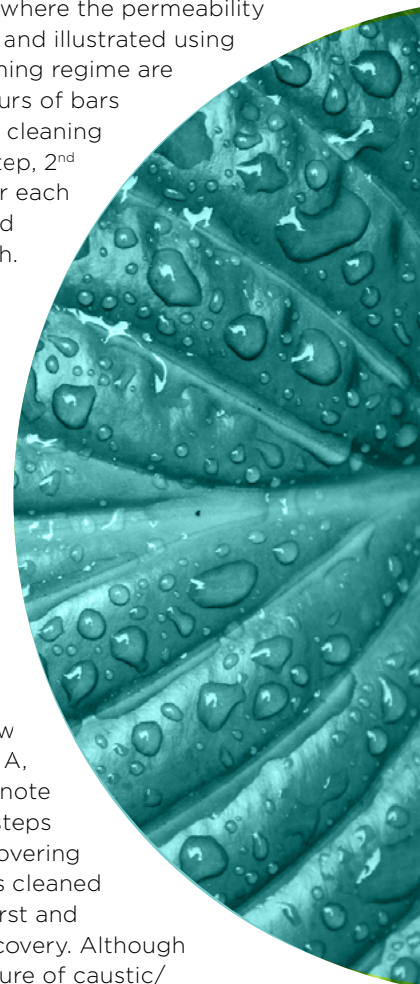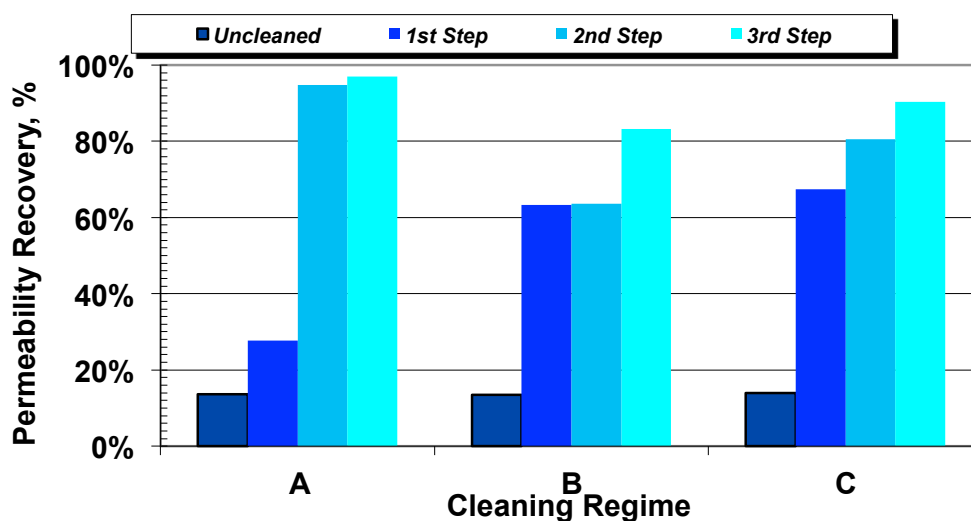
I. D.	Step 1 (16 hrs)	Step 2 (4 hrs)	Step 3 (16 hrs)
A	5000 ppm NaClO + 1% NaOH	1% Super Iron-out [b]	5000 ppm NaClO + 1% NaOH
B	2% citric acid	1% Super Iron-out [b]	5000 ppm NaClO + 1% NaOH
C	1% Super Iron-out [b]	5000 ppm NaClO + 1% NaOH	5000 ppm NaClO + 1% NaOH

Figure 5. Membrane permeability recovery before and after each step of cleaning (average value of five fiber samples) for a MF plant filtering coagulated and settled surface water.

Three mobile microfiltration units deployed at the plant site for treatment of the industrial effluent while plant's own wastewater plant shutdown for repairs and upgrade. A membrane cleaning study was performed to optimise the operation of the microfiltration filters and the results of the study are presented in Figure 6.

The permeability of the membrane samples as received showed a value of 28% of that for new membranes. After two-step cleaning, membrane permeability for Regime A, B, and C is 67.1%, 95.3%, and 98.6% of those for new membranes, respectively. Contrary to what the water quality data indicated, the results of the cleaning study showed that membrane fouling was primarily caused by foulants inorganic by nature, as both citric acid and Super Iron-out in the first step of cleaning outperformed the mixture of caustic and chlorine, and they contributed the majority of permeability recovery. More intriguingly, the first step cleaning with the mixture of caustic and chlorine in Regime A seemed to hinder the subsequent cleaning with citric acid, leading to a lower overall recovery of membrane permeability when compared to Regimes B and C.

The analyses of membrane surfaces with SEM and EDX are presented in Figure 7. Prior to cleaning, both outer and inner surfaces showed heavy deposits of solids, and significant amounts of metal elements such as Mn, Fe, Cu, Al, as well as non-metal elements such as O, Si, and S in addition to C and F (which might be part of the membrane medium).

The deposition of solids on membrane surfaces might have actually functioned as a barrier for direct adhesion of organic foulants via adsorption in this case. Therefore, the cleaning step with the mixture of caustic and chlorine had only limited contribution to the overall recovery of membrane permeability.
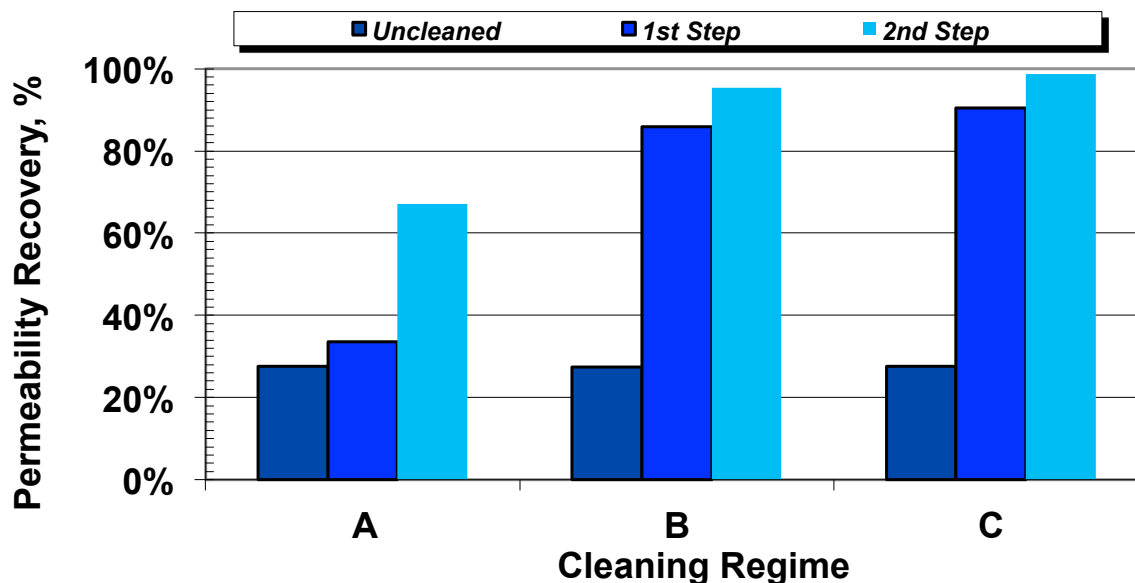
I. D.	Step 1(16 hrs)	Step 2 (16 hrs)
A	5000 ppm NaOCl + 2% NaOH	2% citric acid
B	2% citric acid	5000 ppm NaOCl + 2% NaOH
C	1% Super Iron-out [b]	5000 ppm NaOCl + 2% NaOH

Figure 6. Membrane permeability recovery before and after each step of cleaning (average value of five fiber samples) for a MF plant filtering industrial effluent.

After cleaning, the SEM images of membrane surfaces appeared free of most deposits and element analysis by EDX also showed absent or greatly reduced non-medium elements, which are consistent with the nearly complete recovery of membrane permeability shown in Figure 6.

CONCLUDING REMARKS

Given the importance of membrane chemical cleaning, it is unfortunate that there has not been more research on the subject. The understanding of the fouling phenomenon is the basis for deriving more effective strategies for chemical cleaning. Constructing models beyond the eDLVO theory may provide a theoretical framework for understanding membrane fouling, which requires the incorporation of interfacial interactions in addition to electrostatic, van der Waals, and acid-base interaction into the model. Balancing the conflicting needs of being simple and easy to understand on one hand, while keeping it sufficiently realistic on the other, requires both theoretical development and experimental validation for the model. For practical applications, rapid determinations for the causes of fouling and effective cleaning regimes are imperative, and can be done using a lab cleaning study with relatively ease. Designing a plan for a membrane cleaning study requires not only considering practical constraints, but also a good understanding on the nature of source water and pretreatment processes. An interactive approach to account for the response of a membrane to initial cleaning steps is often helpful to quickly lock to the responsible foulants. Although not always obvious, the sequence of cleaning steps often plays an important role in restoring membrane permeability. As fouling nature may change over time, reevaluation and adjusting the cleaning regime is necessary to maintain long-term permeability of membranes.
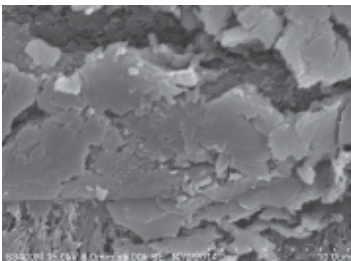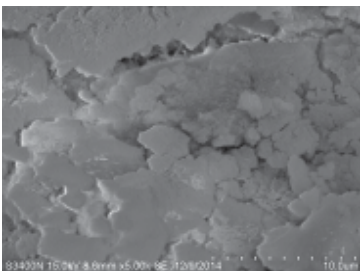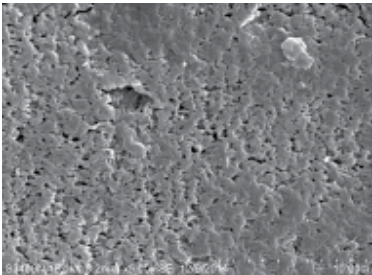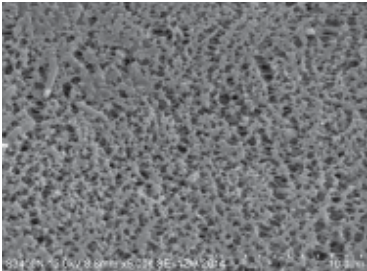
SEM	EDX
Uncleaned (outer surface) 	<table><tr><td>Elt.</td><td>Line</td><td>Intensity (c/s)</td><td>Error 2-sig</td><td>Atomic %</td><td>Atomic Ratio</td><td>Conc</td><td>Units</td><td>Error 2-sig</td></tr><tr><td>C</td><td>Ka</td><td>207.79</td><td>3.413</td><td>57.677</td><td>3.0250</td><td>36.867</td><td>wt.%</td><td>0.606</td></tr><tr><td>O</td><td>Ka</td><td>152.89</td><td>3.173</td><td>19.067</td><td>1.0000</td><td>16.235</td><td>wt.%</td><td>0.337</td></tr><tr><td>Na</td><td>Ka</td><td>13.81</td><td>3.072</td><td>0.514</td><td>0.0269</td><td>0.629</td><td>wt.%</td><td>0.140</td></tr><tr><td>Mg</td><td>Ka</td><td>18.41</td><td>3.257</td><td>0.482</td><td>0.0253</td><td>0.624</td><td>wt.%</td><td>0.110</td></tr><tr><td>Al</td><td>Ka</td><td>156.92</td><td>4.352</td><td>3.374</td><td>0.1770</td><td>4.845</td><td>wt.%</td><td>0.134</td></tr><tr><td>Si</td><td>Ka</td><td>383.74</td><td>5.359</td><td>7.696</td><td>0.4036</td><td>11.503</td><td>wt.%</td><td>0.161</td></tr><tr><td>S</td><td>Ka</td><td>145.67</td><td>4.306</td><td>2.735</td><td>0.1435</td><td>4.668</td><td>wt.%</td><td>0.138</td></tr><tr><td>Cl</td><td>Ka</td><td>20.63</td><td>3.575</td><td>0.386</td><td>0.0203</td><td>0.729</td><td>wt.%</td><td>0.126</td></tr><tr><td>Mn</td><td>Ka</td><td>44.69</td><td>2.868</td><td>1.595</td><td>0.0836</td><td>4.663</td><td>wt.%</td><td>0.299</td></tr><tr><td>Fe</td><td>Ka</td><td>151.09</td><td>3.523</td><td>6.473</td><td>0.3395</td><td>19.238</td><td>wt.%</td><td>0.449</td></tr><tr><td></td><td></td><td></td><td></td><td>100.000</td><td></td><td>100.000</td><td>wt.%</td><td></td></tr></table>
Uncleaned (inner surface) 	<table><tr><td>Elt.</td><td>Line</td><td>Intensity (c/s)</td><td>Error 2-sig</td><td>Atomic %</td><td>Atomic Ratio</td><td>Conc</td><td>Units</td><td>Error 2-sig</td></tr><tr><td>C</td><td>Ka</td><td>11.53</td><td>0.864</td><td>39.262</td><td>4.4840</td><td>15.585</td><td>wt.%</td><td>1.168</td></tr><tr><td>O</td><td>Ka</td><td>7.54</td><td>0.711</td><td>8.756</td><td>1.0000</td><td>4.630</td><td>wt.%</td><td>0.436</td></tr><tr><td>F</td><td>Ka</td><td>6.39</td><td>0.692</td><td>7.468</td><td>0.8529</td><td>4.689</td><td>wt.%</td><td>0.508</td></tr><tr><td>Al</td><td>Ka</td><td>16.71</td><td>1.146</td><td>6.305</td><td>0.7201</td><td>5.623</td><td>wt.%</td><td>0.386</td></tr><tr><td>Si</td><td>Ka</td><td>5.34</td><td>0.996</td><td>1.769</td><td>0.2021</td><td>1.642</td><td>wt.%</td><td>0.306</td></tr><tr><td>S</td><td>Ka</td><td>7.68</td><td>1.120</td><td>2.037</td><td>0.2326</td><td>2.159</td><td>wt.%</td><td>0.315</td></tr><tr><td>Mn</td><td>Ka</td><td>29.11</td><td>2.226</td><td>13.342</td><td>1.5238</td><td>24.225</td><td>wt.%</td><td>1.852</td></tr><tr><td>Fe</td><td>Ka</td><td>20.19</td><td>2.204</td><td>10.921</td><td>1.2472</td><td>20.155</td><td>wt.%</td><td>2.200</td></tr><tr><td>Cu</td><td>Ka</td><td>9.19</td><td>2.000</td><td>10.139</td><td>1.1579</td><td>21.292</td><td>wt.%</td><td>4.632</td></tr><tr><td></td><td></td><td></td><td></td><td>100.000</td><td></td><td>100.000</td><td>wt.%</td><td></td></tr></table>
Cleaned (outer surface) 	<table><tr><td>Elt.</td><td>Line</td><td>Intensity (c/s)</td><td>Error 2-sig</td><td>Atomic %</td><td>Atomic Ratio</td><td>Conc</td><td>Units</td><td>Error 2-sig</td></tr><tr><td>C</td><td>Ka</td><td>925.97</td><td>6.752</td><td>61.593</td><td>8.1171</td><td>48.963</td><td>wt.%</td><td>0.357</td></tr><tr><td>O</td><td>Ka</td><td>135.69</td><td>3.767</td><td>7.588</td><td>1.0000</td><td>8.035</td><td>wt.%</td><td>0.223</td></tr><tr><td>F</td><td>Ka</td><td>914.09</td><td>6.841</td><td>26.427</td><td>3.4827</td><td>33.230</td><td>wt.%</td><td>0.249</td></tr><tr><td>Al</td><td>Ka</td><td>62.27</td><td>4.725</td><td>0.532</td><td>0.0701</td><td>0.950</td><td>wt.%</td><td>0.072</td></tr><tr><td>Si</td><td>Ka</td><td>183.55</td><td>5.185</td><td>1.417</td><td>0.1868</td><td>2.634</td><td>wt.%</td><td>0.074</td></tr><tr><td>S</td><td>Ka</td><td>275.79</td><td>5.222</td><td>1.961</td><td>0.2584</td><td>4.162</td><td>wt.%</td><td>0.079</td></tr><tr><td>Cu</td><td>Ka</td><td>13.98</td><td>2.439</td><td>0.481</td><td>0.0635</td><td>2.025</td><td>wt.%</td><td>0.353</td></tr><tr><td></td><td></td><td></td><td></td><td>100.000</td><td></td><td>100.000</td><td>wt.%</td><td></td></tr></table>
Cleaned (inner surface) 	<table><tr><td>Elt.</td><td>Line</td><td>Intensity (c/s)</td><td>Error 2-sig</td><td>Atomic %</td><td>Atomic Ratio</td><td>Conc</td><td>Units</td><td>Error 2-sig</td></tr><tr><td>C</td><td>Ka</td><td>1,449.40</td><td>9.744</td><td>56.709</td><td>7.0914</td><td>45.426</td><td>wt.%</td><td>0.305</td></tr><tr><td>O</td><td>Ka</td><td>218.36</td><td>5.061</td><td>7.997</td><td>1.0000</td><td>8.533</td><td>wt.%</td><td>0.198</td></tr><tr><td>F</td><td>Ka</td><td>1,700.73</td><td>10.521</td><td>33.700</td><td>4.2140</td><td>42.699</td><td>wt.%</td><td>0.264</td></tr><tr><td>Al</td><td>Ka</td><td>31.12</td><td>5.287</td><td>0.197</td><td>0.0247</td><td>0.355</td><td>wt.%</td><td>0.060</td></tr><tr><td>S</td><td>Ka</td><td>274.55</td><td>6.135</td><td>1.397</td><td>0.1747</td><td>2.987</td><td>wt.%</td><td>0.067</td></tr><tr><td></td><td></td><td></td><td></td><td>100.000</td><td></td><td>100.000</td><td>wt.%</td><td></td></tr></table>

Figure 7. SEM images of elemental analyses by EDX for samples before and after cleaning (Samples for SEM/EDX were from those cleaned with Regime C in Figure 6)

THE AUTHORS

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He is a member of AWWA. He serves on Membrane Process Committee of AWWA. He also served on several project-advisory committees of American Water Works Research Foundation (AWWARF) and is a member of the peer-review panel of USEPA's Membrane Filtration Guidance Manual. His publications include one book, two book chapters. He also authored and co-authored over thirty articles.

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