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Impact of backwash water composition on ultrafiltration fouling control

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ABSTRACT

This paper investigates the impacts of different components in backwash water on ultrafiltration (UF) fouling control. Natural surface water was used as feed water, different backwash waters with different Ca^{2+} and Na^+ concentrations were prepared by dosing $CaCl_2$ and NaCl into demineralized water. Furthermore, UF permeate containing mainly natural organic matter (NOM) with minimal cations (Ca^{2+} and Na^+) was produced by dialysis and used for backwashing as well. Thus, the efficiency of different backwash waters on UF fouling control was evaluated. Results show that the presence of both divalent (Ca^{2+}) and monovalent cations (Na^+) in backwash water reduces the fouling control efficiency. Since the negative charges of UF membranes and NOM compounds are screened by the cations during filtration, NOM can easily deposit on the surface of the UF membrane, causing fouling. When the mono- and divalent cations are absent in the backwash water, the charge-screening effect around the negatively charged UF membrane and NOM is reduced, increasing the repulsion force between them. In addition to the charge-screening effect, the absence of calcium in backwash water can also reduce the calcium-bridging effect between the membrane and NOM, increasing the fouling control efficiency of the backwash. Measurements of the streaming potential indicate that backwashing with demineralized water can maintain the negative charge of the membrane. Organic compounds in the backwash water do not influence the fouling control efficiency of the backwash.

1. Introduction

Ultrafiltration (UF) is now recognized as a proven technology in water treatment. In the past two decades, UF has developed rapidly due to the progress of both membrane fabrication and operational techniques. UF is mainly applied for surface water treatment and as a pretreatment for reverse osmosis in desalination and treatment of filter backwash water [1]. However, fouling is still a persistent problem in the operation of UF. Fouling results in water loss due to the need for regular backwashing. Some researchers have reported that fouling in surface water treatment is mainly caused by natural organic matter (NOM) [2–4]. NOM is a complex mixture composed of different organic components, such as polysaccharides and humic substances. The macromolecular compounds in the NOM are usually reported as the main fouling factors [3,5,6].

In order to control membrane fouling, different pretreatments have been investigated [7–9]. The most commonly used pretreatment for ultrafiltration of surface water is in-line coagulation. Kabsch-Korbutowicz [10] found that in-line coagulation resulted in a better removal of NOM and less membrane fouling. However, the problem with in-line coagulation is that a large amount of backwash-derived waste sludge containing dosed coagulants is produced. This waste sludge can contain high concentrations of iron or aluminum. Therefore, the backwash waste stream has to be treated before it is discharged, which is expensive. Panglisch et al. [7] claimed that the cost of treating the backwash waste stream can be up to 20% of the total production cost. Besides in-line coagulation, backwashing with Milli Q water has recently been proven to be a good method to control UF fouling [9]. Abrahamse et al. [9] shown that fouling can be almost completely prevented by backwashing with Milli Q water. It was argued that the absence of ions in backwash water results in a reduction of the screening of the membrane charge, thereby creating higher repulsion forces between the foulants and the UF membrane (due to the increased surface charge: ~zeta potential). However, as the water compositions of normal backwash water (UF permeate) and Milli Q water are totally different, it is not clear which component in the backwash water actually control the fouling removal.

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At least three types of substances in backwash water can affect fouling control efficiency: divalent cations (calcium), monovalent cations (sodium), and organic matter. Many studies have investigated the impact of these substances on the fouling of UF membranes when they are present in the feed water [9,11–19]. Hong and Elimelech [11] systematically investigated the role of chemical and physical interactions in the NOM fouling of nanofiltration membranes, and they found that this fouling is low when the feed water has a low ionic strength, contains low levels of divalent cations, and has a high pH. It is believed that the presence of divalent cations (calcium) in the feed water significantly reduces the charge of the membrane and NOM, not only by effective charge screening but also by complex formation, whereby calcium can simultaneously bind to the carboxyl functional groups of the membrane and NOM molecules through specific complex formations, thereby enhancing membrane fouling. Jermann et al. [17] investigated the impact of molecular interactions between different NOM compounds on ultrafiltration fouling mechanisms. An aggravated fouling was also observed with the presence of calcium in a humic acid feed solution, and the fouling was found to be irreversible. The impact of calcium on fouling was attributed to: the reduction of electrostatic repulsion between membranes and NOM molecules (due to a screening of the membrane and NOM surface charge); complexation between the membrane and the NOM molecules; and/or, complexation among the NOM molecules themselves. Several studies also indicate an increase in fouling with an increase in the calcium concentration [12–14].

In contrast to these findings, Katsoufidou et al. [16] showed that with an increase in calcium concentrations, the fouling of UF membranes by alginate becomes more reversible. However, at a concentration of 2 mM calcium, irreversible fouling was not found. They argued that this was caused by the formation of a highly permeable hydrogel layer which forms when calcium binds to alginate.

However, most of the previous studies have focused on the impact of divalent cations, monovalent cations and organic matter on UF fouling when they are present in the feed water. Limited literature is available regarding the impact of these substances in backwash water. Since backwashing with demineralized and Milli Q water has been proven to be a good method to control UF fouling [9], it is important to understand the mechanisms behind this and to understand which components in normal backwash water (i.e., UF permeate) decrease the efficiency of fouling removal, compared to demineralized and Milli Q water. Therefore, the objective of this study was to investigate the separate impacts of divalent and monovalent cations (calcium and sodium) and NOM in backwash water on the foulant removal of UF membranes. Moreover, online streaming potential measurements were conducted out to study the influence of different types of backwash water on the charge of the UF membrane surface, in order to elucidate the mechanisms by which backwashing with demineralized and Milli Q water improve fouling control.

This paper will thus be divided into three major sections:

1. A study of the impact of mono- and divalent cations in backwash water on UF fouling control.
2. A study of the impact of organic matter in backwash water on UF fouling control.
3. A study of the effects of different types of backwash water on the UF membrane's surface charge (and the charge in the membrane's pores).

2. Materials and methods

2.1. Impact of cations in backwash water

2.1.1. Feed water

Most research on UF membrane fouling has been conducted with artificial water types containing commercial model organic compounds such as humic acid and sodium alginate [13,16,20]. However, the question is how representative these commercial compounds are for the natural organic matter in natural water. In this study, the goal was to mimic real situations. Therefore, 400 l of raw surface water (batch 1) was taken from the Schie Canal in summer (Delft, The Netherlands) and used in this study as the feed water for the ultrafiltration. The surface water was stored in a climate-controlled room with a constant temperature of 12 °C to limit the biological activity. The quality of feed water and permeate was determined with single analysis and listed in Table 1. For each UF experiment, 35 l of feed water was taken from the climate-controlled room and put in an 80-l feed vessel equipped with a stirring device. The feed water was used at room temperature (19–20 °C) for the UF experiments.

2.1.2. Backwash water

Backwash water with different concentrations of monovalent and divalent cations was prepared by adding calcium (as $CaCl_2 \cdot 2H_2O$) and sodium (as NaCl) to demineralized water (NaCl and $CaCl_2$ were obtained from Sigma–Aldrich and were both reagent grade). The concentrations of calcium and sodium were checked using a flame Atomic Absorption Spectroscopy (AAS) after

Table 1
Water quality of feed, permeate and backwash water used in three different experiment runs.

	pH	Turbidity (NTU)	Conductivity (μs/cm)	Ca^{2+} (mmol/l)	Na^{+} (mmol/l)	DOC (mg/l)
Cation experiments						
Feed (Schie water batch 1)	8.1	9.15	882	2	2.5	25
Backwash water 1 (UF permeate 1)	8.1	0.155	878	2	2.5	16
Backwash water 2	N/A	N/A	N/A	<0.1	<0.1	0.5
Backwash water 3	N/A	N/A	N/A	3	<0.1	0.5
Backwash water 4	N/A	N/A	N/A	6	<0.1	0.5
Backwash water 5	N/A	N/A	N/A	<0.1	6	0.5
Backwash water 6	N/A	N/A	N/A	<0.1	12	0.5
NOM experiments						
Feed (Schie water batch 2)	8.5	4.5	836	2.5	2.5	20
UF permeate 2	N/A	N/A	N/A	2.5	2.5	18.9
UF permeate after dialysis	N/A	N/A	N/A	0.5	0.37	17
Demineralized water	N/A	N/A	N/A	<0.1	<0.1	0.5
SPC measurements						
Feed (Utwente water)	7.7	N/A	N/A	1.9	1.4	13
UF permeate 3	8	N/A	N/A	1.88	1.4	11.6

SPC: streaming potential coefficient. DOC: dissolve organic carbon.
N/A: not available.

Table 2
Characteristics of RX-300 membrane module provided by manufacturer.

Type of membrane fiber	UFC M5 0.8
Membrane material	PES/PVP
Molecular weight cut-off	100 kDa
Filtration mode	Inside-out
Internal fiber diameter (mm)	0.8
Length of module (cm)	30
Number of fibers	120
Surface area (m^2)	0.07

dosing. Six different types of backwash water were used, with different concentrations of divalent and monovalent cations (as shown in Table 1). 3 mmol/l Ca is often observed in Schie Canal water, so this concentration was used in this study. In order to see the impact of a higher concentration, 6 mmol/l was tested as well to see the impact of a high calcium concentration. Because divalent cations have stronger influences on electrical double layer, the tested concentrations for sodium were doubled.

2.1.3. *Chemical cleaning solution*

Because all cation experiments were carried out with a single membrane module, a chemical cleaning was conducted after each experiment. The chemical solution used in this study was a combination of 0.4 g/l NaOH and 120 ppm NaOCl. After each experiment, the fouled membrane was backwashed with the chemical solution for 5 min, and then it was soaked for 15 min before a thorough rinsing with demineralized water. If one chemical cleaning was not sufficient to recover the membrane's initial permeability, another chemical cleaning was conducted. All the cation experiments were started with an initial transmembrane pressure (TMP) around 130 mbar at a flux of 85 l/(m^2 h).

2.1.4. *Membrane*

A commercially available, polymeric hollow fiber ultrafiltration membrane module (RX-300, X-Flow) was used in this study. The characteristics of this membrane module are shown in Table 2. These membranes are made of a mixture of polyethersulfone (PES) with a small amount of polyvinylpyrollidone (PVP). Based on the streaming potential measurements, van der Ven [21] reported that the streaming potential coefficient of the same ultrafiltration membrane was constant at −24 mV/bar in a pH range between 3.5 and 10 by using an electrolyte solution of 10 mM KCl; the charge of the membrane, therefore, is negative at the pH of the feed water (around 8).

2.1.5. *Ultrafiltration setup and filtration protocol*

Many studies on UF fouling control are conducted in a constant-pressure mode and/or only one filtration cycle is carried out [11,16,17]. However, because all full-scale ultrafiltration plants are operated under a constant-flux mode and with a regular backwash, the results from these experiments are not representative for full-scale operations. Therefore, the ultrafiltration setup used in this study (Fig. 1) was designed for constant-flux experiments [22]. Furthermore, backwashing was incorporated in the setup, and software was added to run the setup continuously with a program of several operational cycles of filtration and backwashing. The constant flux of the setup was maintained by a Verder VG 1000 Basic gear pump which was controlled by a flow meter (Endress & Hauser). Flow rate, temperature and TMP were continuously logged with a time interval of 8 s during the experiments. Flow rate and TMP were also measured with Endress & Hauser equipment.

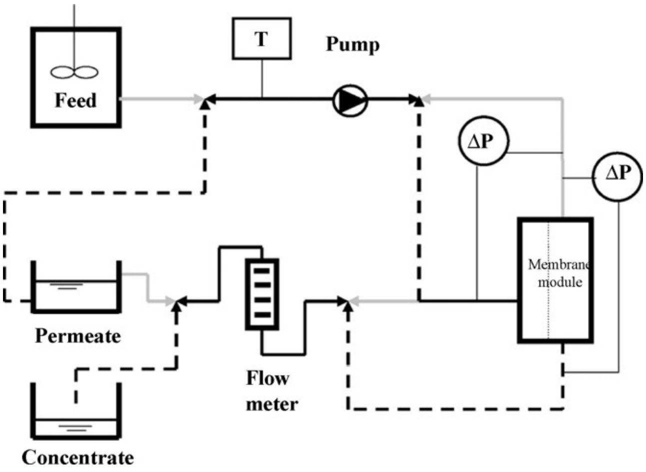

Fig. 1. Scheme of the ultrafiltration setup [22].

All experiments were carried out in a dead-end operation mode. Before each experiment (and after each chemical cleaning), the setup was thoroughly flushed with demineralized water in filtration mode and backwash mode to remove the chemical residues and air in the system. Afterwards, the setup was operated at a flux of 85 l/(m^2 h) for half an hour to determine the initial permeability of the membrane. Each fouling experiment, with a different type of backwash water used each time, consisted of 14 operational cycles. Each cycle was composed of three phases: (1) filtration at a flux of 85 l/(m^2 h) for 15 min; (2) purging the setup at a flow of 4 l/h for 1 min to clean the tubes before backwashing; (3) backwashing at a flux of 170 l/(m^2 h) for 1 min. All these setting points were programmed into the setup's controller before starting the experiment. The duration of each experiment (the full 14 cycles) was about 4 h. After the experiment, the setup was shut down and all logged data were taken from the logger for analysis.

2.2. *Impact of NOM in backwash water*

2.2.1. *Feed water*

A new batch of 300 l of Schie Canal water (batch 2) was taken in autumn for the NOM experiments. Because a different batch of raw water was taken than the batch used in the cation experiments, the feed water composition is not exactly the same (due to seasonal varieties). However, since each batch was used to make a relative comparison of the influence of a single component in the backwash water, the difference between the two batches is not relevant. The water quality of the second batch of raw water is listed in Table 1.

2.2.2. *Backwash water*

To study the influence of the NOM in backwash water on UF fouling control, three types of backwash water were compared: (1) UF permeate; (2) demineralized water; and, (3) UF permeate after dialysis. UF permeate after dialysis (as shown in Table 1) was prepared using a 20-h dialysis. Five liters of UF permeate was poured into dialysis bags (Spectrum Europe BV, The Netherlands) with a molecular weight cut-off (MWCO) of 3.5 kDa and the filled bags were put in a vessel with 80 l of demineralized water. The demineralized water in the vessel was recirculated with an aquarium pump. The ions in the UF permeate diffused through the dialysis bags into the demineralized water, until equilibrium was reached. Most of the organic matter in the UF permeate was retained in the dialysis bags, because its molecular weight was higher than the MWCO of the bags. The water remaining in the dialysis bags was then used for backwashing.

2.2.3. *Chemical cleaning*

A new membrane module was used after each experiment and therefore no chemical cleaning (see Section 2.1.3) was carried out.

2.2.4. Membrane

The same type of hollow fiber ultrafiltration membrane modules (X-Flow UFC M5, see Table 2) was used in this set of experiments.

2.2.5. Setup and filtration protocol

The UF setup was already described in Section 2.1.5. Moreover, most of these settings were the same as in the experiments studying the influence of cations. The only differences were the operational flux and the backwash flux: in this set of experiments, the fluxes for filtration and backwashing were 120 and 240 l/(m^2 h), respectively. Since several trial experiments did not show efficient fouling (85 l/(m^2 h)), a higher flux was used in these experiments to ensure a high enough increase in TMP.

2.3. Measurements of streaming potential

The charge of the membrane surface can be quantified using the zeta potential. Based on the well-known Helmholtz–Smoluchowski equation, the zeta potential can be calculated from streaming potential measurements. Because the emphasis of this experiment is to evaluate the changes in the membrane charge under two different backwash conditions, the exact values of the zeta potential are not necessary, only the relative changes. Therefore, the streaming potential coefficient (SPC) was used in this study to evaluate the change in membrane charge (Eq. (1)).

$$\mathrm{SPC} = \frac{\Delta\phi}{\Delta P} \qquad (1)$$

2.3.1. Feed water

Raw natural water on the campus of the University of Twente was used in this study as feed water. The water quality of the raw water is listed in Table 1.

2.3.2. Backwash water

The purpose of the SPC's determination is to demonstrate that backwashing with demineralized water can maintain the original negative charge of the UF membrane (improving fouling control), so only two types of backwash water were compared. They were UF permeate and ultrapure water (demineralized water purified by a Synergy Water Purification System from Millipore).

2.3.3. Membrane

Since the experimental setup is not designed for an X-Flow RX-300 membrane module, two homemade membrane modules containing RX-300 hollow fibers were prepared. Ten 1-m fibers were potted in an 8 mm PVC pipe (using a polyurethane potting resin) to represent one module with a surface area of 0.025 m^2.

2.3.4. Determination of SPC

The SPC over the membrane's surface (axial SPC) and through its pores (radial SPC) was determined. Five pressure differences between two measuring points were applied by using five different flow rates. Under each pressure difference, the streaming potential between the measuring points was measured using a Keithley 2000 multimeter with two homemade Ag/AgCl electrodes. By plotting the streaming potential as a function of pressure a linear relationship was obtained. The slope of this line was the SPC.

2.3.5. Filtration/streaming potential setup and filtration and streaming potential measuring protocol

The experimental setup, as shown in Fig. 2, was designed for long-term and automated process operations [13]. It can be operated under constant-pressure and in a constant-flux mode. The system contains a feed pump and a backwash pump (Ismatec, Reglo-Z). Feed and backwash flows are measured by two mass flow controllers (Bronkhorst, NL, Cori-Flow M53C and M54C). The internal PID controllers of these two instruments directly control the pumps to achieve a constant flux. During the streaming potential measurements, a background electrolyte solution for the measurements is taken from the backwash tank. By opening solenoid valves 4 and 5 (Plast-o-matic), as shown in Fig. 2, the streaming potential of the UF membrane surface can be measured. On the other hand, the streaming potential measurements of the membrane pores are enabled by opening valves 3 and 5.

Twenty-five liters of raw water was taken from a campus pool and filtered with a coarse (40 μm) metal filter. The membrane module was thoroughly rinsed with ultrapure water before use (under the filtration and backwash mode). Afterwards, the permeability of the membrane was determined with ultrapure water. Following this, the SPC of the clean membrane surface and its pore walls was determined. Streaming potential measurements were carried out in a 1 mM KCl background electrolyte solution in ultrapure water. The pH and conductivity of this solution were 6.5 and 178.8 μs/cm, respectively. A fouling experiment was conducted after the determination of their initial streaming potentials. The fouling experiment consisted of 14 cycles, each cycle had a 15-min filtration at a flux of 120 l/(m^2 h) and a 1-min backwash at a flux of 240 l/(m^2 h). After the fouling experiments, the SPC of the fouled membrane surface and its pore walls was again determined.

3. Results and discussion

3.1. Impact of mono- and divalent cations in backwash water on UF fouling control efficiency

In field practice, most UF membranes are hydraulically cleaned by reversing the water flow after a short period of filtration (backwashing). The part of the fouling that can be removed by a hydraulic backwash is defined as reversible fouling. On the other hand, the fouling that cannot be removed by a hydraulic backwash and remains on the membranes after backwashing is defined as hydraulically irreversible fouling.

The term “fouling control efficiency” refers to the extent of the recovery of the membrane's permeability by means of hydraulic backwashing (i.e., high fouling control efficiency corresponds to a high recovery of membrane permeability after consecutive backwashings). Since one usually distinguishes reversible and irreversible fouling, high fouling control efficiency in this study refers to a low irreversible fouling after consecutive backwashings.

3.1.1. Effect of backwashing with demineralized water

In Fig. 3, the increase in relative TMP (TMP/TMP$_0$) as a function of time is plotted for a constant-flux experiment when backwashed with UF permeate and demineralized water. It is clear from this graph that the relative TMP only increased slightly when backwashed with demineralized water. However, when backwashed with UF permeate, the measured relative TMP increased much faster. This indicates that higher fouling control efficiency can be achieved by backwashing with demineralized water, which agrees with the finding of Abrahamse et al. [9]. The increased fouling control efficiency when backwashed with demineralized water compared with backwashing with UF permeate can result from the absence of either monovalent cations, divalent cations, or the NOM in the demineralized water compared to UF permeate. The increase in TMP for backwashing with UF permeate is a bit higher than that of backwashing with synthetic sodium spiked demineralized water. That is probably because of the presence of calcium in UF permeate which has a stronger influence on the electrical double layer and consequently the charge of NOM and UF membranes than sodium.

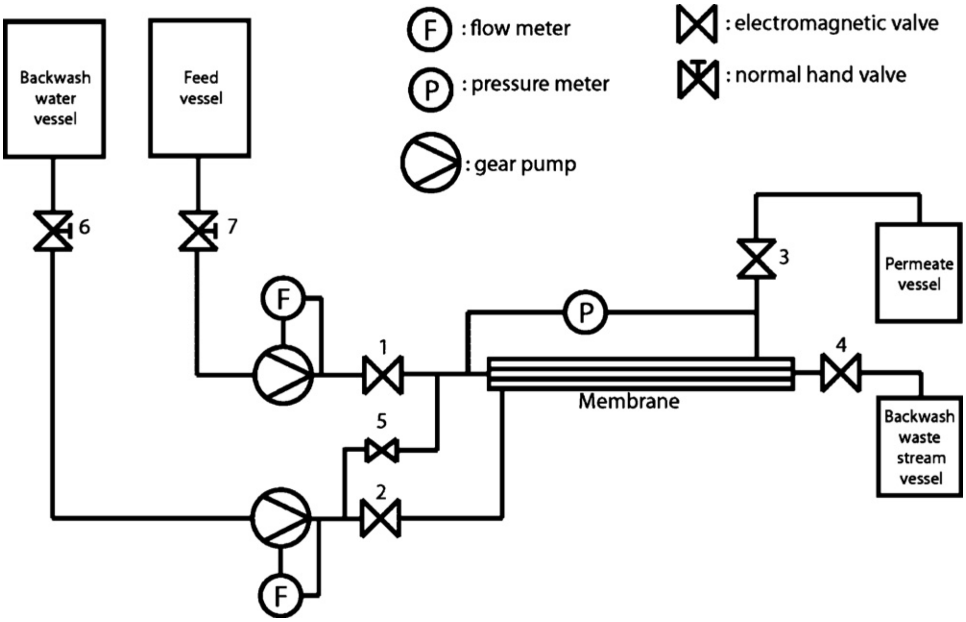

Fig. 2. Scheme of experimental setup for streaming potential measurement [13].

3.1.2. Impact of monovalent cations in backwash water on fouling control

Three types of backwash water were compared in this study: demineralized water, demineralized water with 6 mmol/l Na^+ added, and demineralized water with 12 mmol/l Na^+ added. In Fig. 4, the relative TMP as a function of time for constant-flux experiments is plotted for these three types of water. Only a minor increase in irreversible fouling (a 30% relative TMP increase, from 1 to 1.3) could be observed when backwashed with demineralized water, indicating high fouling control efficiency. For the water types containing NaCl, however, the relative TMP after several backwashings increased by 130% within 14 operational cycles for both types of backwash water with sodium.

The UF membrane used in this study is negatively charged at the feed water pH, due to the dissociation of carboxyl functional groups on the membrane surface. A large number of NOM molecules present in the feed water are also negatively charged at the feed water pH. Both calcium and sodium ions are present in the feed water. Calcium can either bridge the negatively charged membrane and NOM molecules, or screen their negative charge by compressing their electrical double layers. However, since sodium is monovalent, it is not capable of bridging the negatively charged UF membrane and the negatively charged NOM via complexation. Therefore, the most logical explanation for the decrease in permeability during the filtration phase, when Na^+ is present in the water, is a charge-screening effect of the negatively charged UF membrane and the negatively charged NOM, due to the compression of their electrical double layers in the presence of Na^+. As a result of this charge screening, the electrostatic repulsion force between the UF membrane and the NOM is reduced, thereby enhancing deposition of NOM molecules on the membrane's surface (Fig. 5a).

When backwashing the fouled membrane with backwash water containing high concentrations of sodium (Fig. 5b), the compressed electrical double layer formed during the filtration phase is maintained during the backwash and, therefore, the adhesion between the NOM fouling layer and the membrane is maintained. In this case, a vigorous agitation is required to remove it from the membrane surface, and the hydraulic forces induced by the backwash are not sufficient to remove this layer. However, when the membrane is backwashed with demineralized water (Fig. 5c), the sodium concentration in the NOM fouling layer on the membrane surface is lowered and a lower sodium concentration is established, leading to a relaxation of the compressed electrical double layer. The negative charge of the membrane and the NOM and the electrostatic

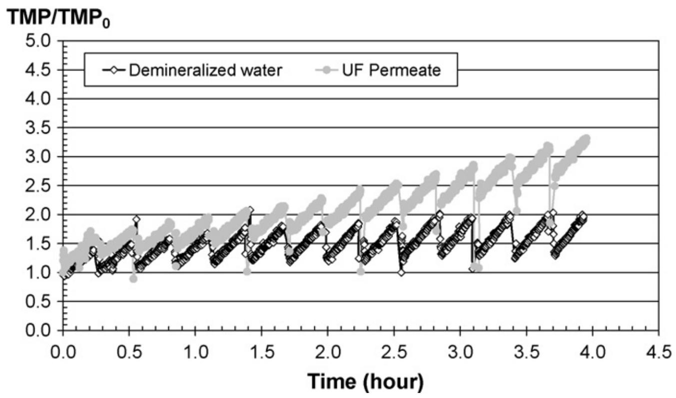

Fig. 3. Relative TMP as a function of time for two different backwash waters in cation experiments: demineralized water and UF permeate.

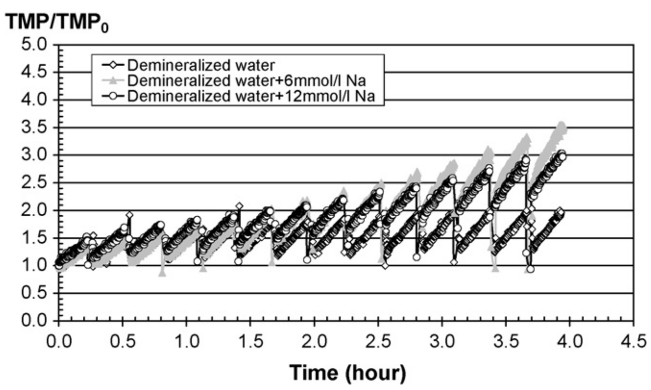

Fig. 4. The relative TMP as a function of time during constant-flux fouling experiments for the three types of backwash water: demineralized water, demineralized water with 6 mmol/l Na^+, and demineralized water with 12 mmol/l Na^+.

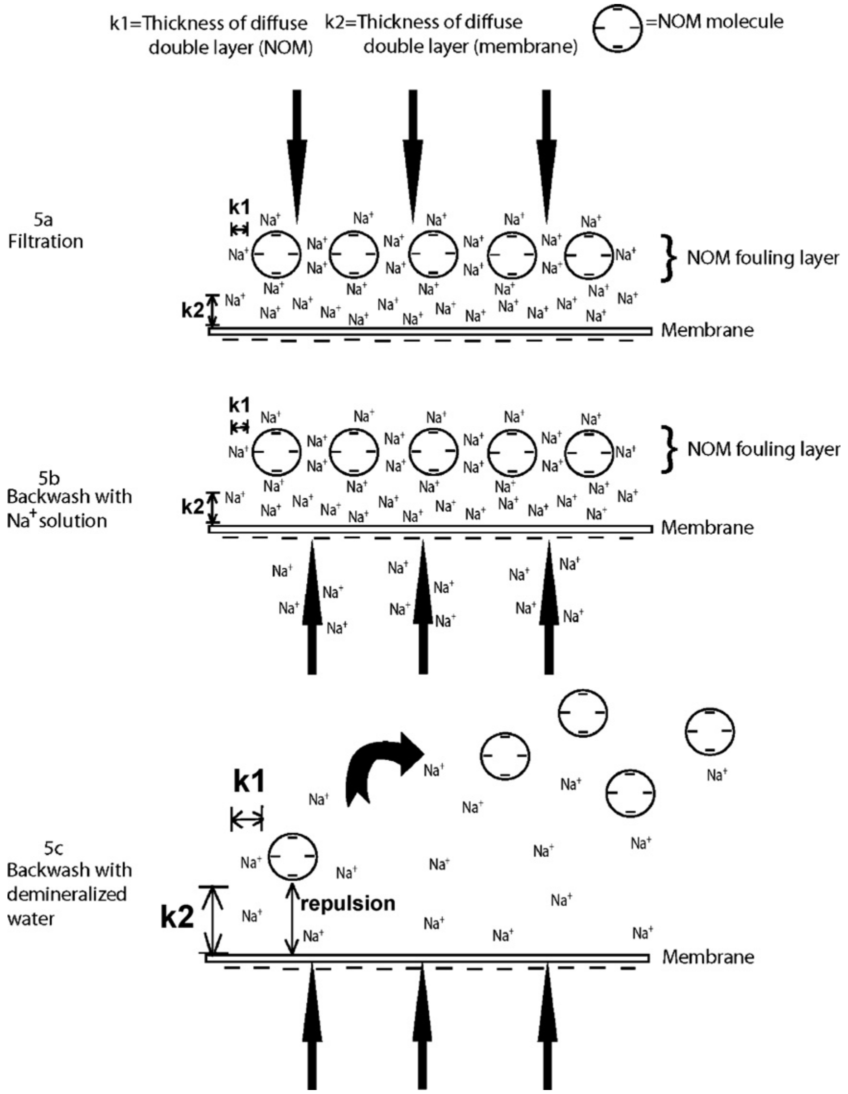

Fig. 5. Proposed mechanism regarding charge-screening effect caused by sodium ions in: (a) filtration; (b) backwash with Na^+ solution; (c) backwash with demineralized water.

repulsion force between the two are restored, resulting in an easier removal of the fouling layer.

There is a change in TMP increase tendency at the 10th cycle between two sodium added demineralized water (Fig. 4). The increase tendency for 6 mmol/l sodium added water is a bit higher than that for 12 mmol/l sodium added, which is not matched with the hypothesis. However, that might be due to the reduction of colloids in feed water. There was a weekend break between experiments of backwashing with 6 and 12 mmol/l sodium added demineralized water. There might be some biological activities happened during the weekend and reduce the amount of foulants in feed water, leading to the change in TMP increase. The absolute value of the negative membrane charge (determined by measurements of zeta potential) increases with the dilution of the background electrolyte solution, indicating that the membrane charge decreases with increasing ionic strength (and thus the sodium concentration). However, this increase is not linear and the increase in the membrane charge is low for sodium concentrations between 10^{-2} and 10^{-3} M. This would explain why there is no big difference between backwashing with 6 and 12 mmol/l sodium, in terms of the fouling control efficiency.

Since UF membranes cannot reject sodium, the sodium concentration in the UF permeate is equal to that in the feed water. Therefore, when the UF membranes are used as a pretreatment for seawater or brackish water desalination, the sodium concentration in the permeate is very high and this can seriously affect the fouling control efficiency in these applications, if the permeate is used as backwash water.

3.1.3. Impact of divalent cations in backwash water on fouling control

Again, three types of backwash water (demineralized water, demineralized water with 3 mmol/l Ca^{2+} added and demineralzied water with 6 mmol/l Ca^{2+} added) were compared for their effect on fouling control efficiency. Fig. 6 displays the relative TMP as a function of time for constant-flux fouling experiments using the three types of backwash water. As before, when the membrane is backwashed with demineralized water, the relative TMP after several backwashings only slightly increases. However, its increases for backwash waters containing 3 and 6 mmol/l Ca^{2+} are 150% and 180%, respectively. The presence of calcium ions in backwash water, therefore, appears to reduce the UF fouling control efficiency.

The thickness of a diffuse double layer of particles and the membrane surface can be determined. Not only the concentration of the electrolyte in solution, but also the valence of the electrolyte in solution influence the charges of the membrane and the NOM particles.

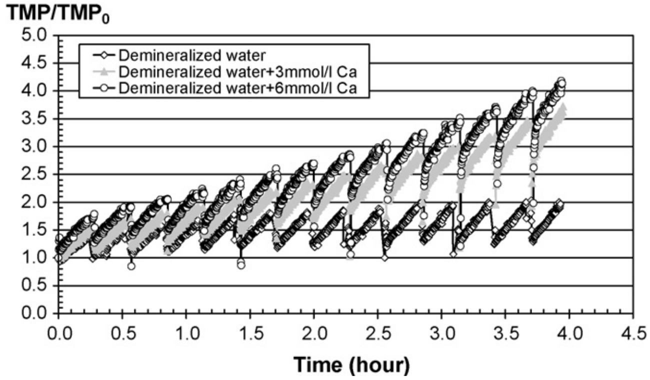

Fig. 6. The relative TMP as a function of time during constant-flux fouling experiments for three types of backwash water: demineralized water, demineralized water with 3 mmol/l Ca^{2+}, and demineralized water with 6 mmol/l Ca^{2+}.

At a constant electrolyte concentration, compression of the electrical double layer increases with increasing valence of ions in the electrolyte solution. Therefore, as shown in Fig. 7a, divalent cations have a stronger influence than monovalent cations on the compression of the electrical double layer, and the charge-screening effect becomes more severe. As a result, the electrostatic repulsion force between the membrane and NOM decreased even more when Ca^{2+} was present in the feed water. Moreover, it is likely that calcium ions also cause complexation of NOM macromolecules and bridging between NOM molecules and the membrane surface. The negatively charged functional groups of the membrane and the NOM can be bound by calcium via a complexation during the filtration phase, which is generally called a ‘Ca-bridging effect’. These deposited NOM molecules form a compact fouling layer on the membrane surface, which is difficult to reverse by backwashing.

In Fig. 7b, the process of backwashing with a solution containing Ca^{2+} is displayed. The bound NOM fouling layer is not removed by backwashing. The presence of calcium ions in the backwash water maintains the charge-screening effect and the Ca-bridging effect between the membrane and the NOM, and acts against the hydraulic shearing force of the backwash. Therefore, the adhesion force between the membrane's surface and the NOM is maintained, leading to a less efficient NOM fouling removal. When the membrane is backwashed with demineralized water (Fig. 7c), the calcium concentration near the membrane surface is lowered, thus reducing the charge screening and restoring the electrostatic repulsion force between the membrane and the NOM molecules. Some of the calcium ions contributing to the Ca-bridging effect and the complexation between NOM molecules are also removed when

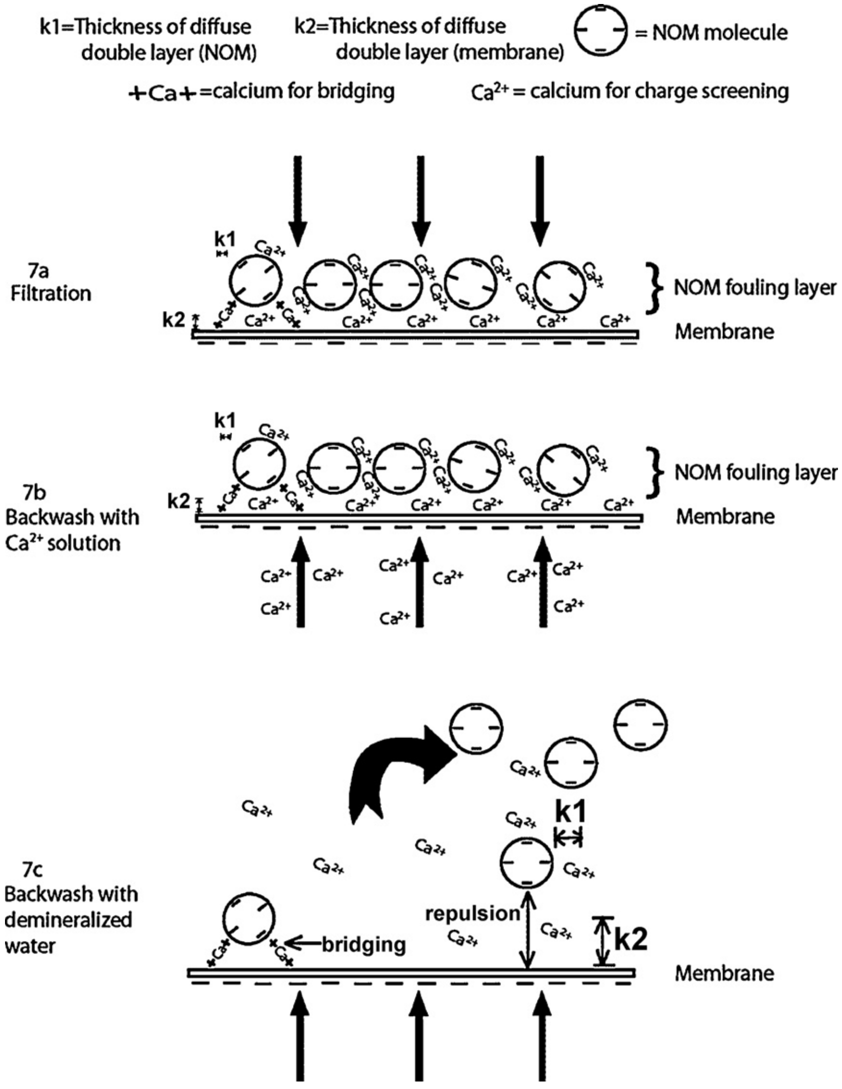

Fig. 7. Proposed mechanisms caused by calcium ions in: (a) filtration; (b) backwash with Ca^{2+} solution; (c) backwash with demineralized water.

Table 3
Streaming potential coefficients of the UF membranes under different conditions.

	Ultrapure water		UF permeate	
	Before fouling experiment	After the 14th backwashing	Before fouling experiment	After the 14th backwashing
SPC along fiber (mV/bar)	−17.7	−18.0	−19.5	−14.1
SPC through pore (mV/bar)	−47.8	−47.6	−66.3	−35.4

backwashed with demineralized water. The main findings of this study can be used to improve the fouling control strategies as full-scale.

3.2. Impact of organic matter in backwash water

Fig. 8 shows the relative TMP as a function of time during constant-flux fouling experiments using three different types of backwash water: demineralized water, the UF permeate and the UF permeate after dialysis (containing mainly organic matter). The composition of backwash water is displayed in Table 1. The relative TMP increased by 80% after 14 cycles when backwashed with demineralized water, a higher increase than in the previous experiments (30%). This is probably due to the higher flux used in this set of experiments compared to the cation experiments. When the membrane was backwashed with the UF permeate, the relative TMP after several backwashings increased by 500% after 14 cycles, which is also higher than in the previous experiments (also probably caused by the higher operating flux). Surprisingly, when the membrane was backwashed with UF permeate after dialysis (which contains a limited amount of calcium and sodium ions, but most of the organic matter present in the UF permeate), the increase in the relative TMP was similar to the increase when backwashed with demineralized water. Based on the findings of cation experiments in Section 3.1, the presence of calcium and sodium ions was found to reduce the fouling control efficiency. However, calcium (0.50 mmol/l) and sodium (0.37 mmol/l) ions in the UF permeate after dialysis are much lower than the values in cation experiments: 3 and 6 mmol/l for calcium and 6 and 12 mmol/l for sodium. There might be critical cation concentrations in backwash water regarding the fouling control. On the other hand, because the organic matter in the UF permeate can pass through the membrane, the organic matter does not cause pore blocking or fouling of the membrane. Furthermore, because of the low concentration of cations in the backwash water, the adsorption of these small NOM molecules on the membrane surface via complexation can also be neglected. Therefore, it can be concluded that organic matter in the UF permeate alone does not result in irreversible fouling.

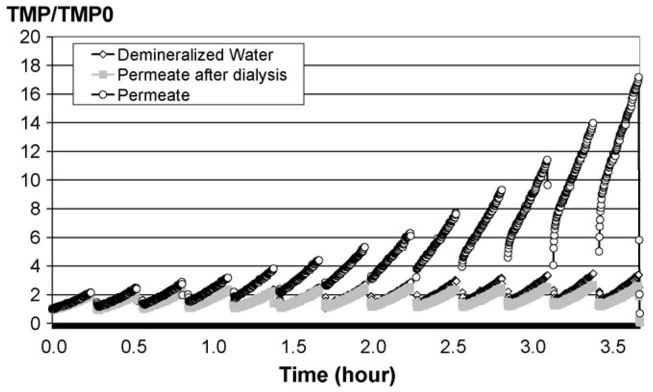

Fig. 8. The relative TMP as a function of time during constant-flux fouling experiments for three types of backwash water: demineralized water, UF permeate and the UF permeate after dialysis (with mainly organic matter).

3.3. Effect of backwash water composition on UF membrane surface and pore wall charge

The improved fouling control when backwashed with demineralized water and the impact of different components (i.e., mono- and divalent ions and NOM molecules) in backwash water on fouling control efficiency have been investigated and proven. The main explanation for the improvement in fouling control when backwashed with demineralized water was said to be the recovery of the negative charge of the UF membrane during a backwash. In order to confirm this explanation, measurements of streaming potential were carried out.

Table 3 shows the streaming potential coefficients of the UF membrane before the constant-flux fouling experiments and after backwashings at the 14th cycle of the fouling experiments with the UF permeate and ultrapure water as backwash waters. The initial SPC through pore is rather different between the ultrapure water and UF permeate backwashing experiments. It might be due to the left negatively charge residuals during membrane manufacturing, which was not flushed out during the pre-cleaning before experiments. When backwashed with UF permeate, both the SPCs over the membrane surface and through the membrane pore wall become less negative. The SPC of the membrane's surface increases from −19.5 to −14.1 mV/bar after 14 operational cycles, while the increase in the SPC through the membrane's pore wall is even higher, from −66.3 to −35.4 mV/bar. The reason for this is that the fouled membrane is covered by a negatively charged NOM fouling layer whose negative charge is reduced by the cations in feed water, and backwashing with the UF permeate could not remove this layer. Consequently, the membrane charge after the 14-cycle fouling experiment becomes less negative compared to the clean membrane charge. In contrast to the UF permeate, backwashing with ultrapure water was able to remove the NOM fouling layer by decreasing the concentration of cations near the membrane surface, thus restoring the negative charge of the UF membrane. The SPC of the membrane after a backwashing at the 14th cycle of the fouling experiment is almost identical to that of the clean membrane. Therefore, it can be concluded that the negative charge of the UF membrane can be recovered by backwashing with ultrapure water.

4. Conclusion

The experiments' results confirm that backwashing of UF membranes with demineralized water is much more efficient than with UF permeate, in terms of the removal of irreversible fouling. Both sodium and calcium ions in backwash water reduce the fouling control efficiency of the UF membrane, and calcium ions have a double stronger impact on fouling control than sodium ions at the same concentration. That is probably because their presence in the backwash water maintains the charge-screening effect, preventing the restoration of the electrical repulsion force between the UF membrane and NOM. Since calcium has a stronger impact on electrical double layer, its influence on fouling control is stronger than sodium. Furthermore, the presence of calcium ions can result in calcium complexation with the membrane and the NOM. The finding about the impact of sodium ions on fouling control is useful when backwashing with demineralized water is applied on UF pretreatment of RO desalination. On the other hand, the organic matter itself in backwash water does not influence the removal of irreversible fouling. Measurements of the streaming potential also confirmed that the charge of the UF membrane becomes less negative when it is backwashed with the UF permeate, while backwashing with ultrapure water can maintain the original negative charge of the UF membrane. This is essential to prevent the NOM fouling.

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