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Fouling control in ceramic nanofiltration membranes during municipal sewage treatment

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ABSTRACT

Using ceramic nanofiltration membranes for treatment of municipal sewage is upcoming. However, the knowledge on fouling control methods for this application are very limited. The most commonly used fouling control method, chemical cleaning, has disadvantages. Chemical cleaning negatively impacts (i) the glass seal layer of tubular ceramic nanofiltration membranes and (ii) the environment, especially when using sodium hypochlorite for removal of organic fouling. Therefore, the use of chemical cleaning should be limited as much as possible. In this research, first, the well-known fouling control methods for polymeric micro- and ultra-filtration membranes, were studied on ceramic nanofiltration membranes: hydraulic backwash and forward flush. Second, a precoat method was combined with a chemical reaction to aid the detachment of the formed cake layer. In this method, a precoat layer was filtered atop of the membrane surface before the start of filtration. The precoat layer then acts as a barrier between the foulants and the membrane surface. After filtration, the precoat layer reacts with the cleaning reagent underneath the fouling layer to enable fast removal of fouling. Results showed that hydraulic backwash was not effective to be used for this type of membranes. Forward flush was able to maintain a higher flux but the relative production downtime was high. Reaction based precoat was most effective in maintaining a high flux and resulted in the highest net water production. Two reaction based precoat methods were tested of which the reaction of calcium carbonate with citric acid was more effective than a Fenton reaction.

1. Introduction

Worldwide water scarcity creates a need for different water sources such as municipal sewage [1–3]. Since two decades, the interest for ceramic nanofiltration (NF) has emerged for this purpose. Several characteristics make ceramic membranes suitable for municipal sewage: its resistance to high temperatures, pressures, and concentrations of chemicals [4–7]. Furthermore, ceramic NF membranes are less susceptible to organic fouling than polymeric NF [8,9].

One of the largest challenges of using membranes for treatment of municipal sewage is controlling fouling on the membrane surface in order to produce as much water as possible. The two most important performance indicators for fouling control strategies are: (i) keeping the filtration downtime as low as possible and (ii) maintaining a high flux during filtration. Both of these aspects contribute to a higher water production.

Fouling can be divided into two main categories: reversible and irreversible fouling. Reversible fouling is defined as fouling that settles atop the membranes surface and can, therefore, easily be removed with various fouling control methods. Whereas, irreversible fouling is fouling that blocks the pores of the membrane. The irreversible fouling is usually strongly attached to the pore which makes it difficult to remove this fouling. Irreversible fouling can only be removed by chemical cleaning.

The most common cleaning method used for ceramic membrane filtration is by chemicals which removes the reversible and irreversible fouling [4,10–13]. Depending on the type of fouling, sodium hypochlorite, acid solutions, and/or base solutions are the most commonly used chemicals to clean the membranes. Chemical cleaning is effective for the removal of (ir)reversible fouling. However, when only applying chemical cleaning the permeability is, on average, low during the filtration cycle; resulting in a low water production. Moreover, from a sustainability point of view fouling control methods with a lower chemical consumption are preferred. Previous research showed that long term use of chemical cleaning, such as sodium hypochlorite, damages the glass seal layer at the edges of tubular ceramic NF membranes [14]. Therefore, chemical treatment using sodium hypochlorite should be avoided.

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In literature, research on alternative fouling control method using ceramic and polymeric NF is limitedly available. Especially since a limited amount of papers describing sewage treatment using ceramic or polymeric NF. Sayed et al. reported that using polymeric NF for the treatment of municipal sewage was not feasible when using chemical cleaning as fouling control method due to the extensive downtime required [15]. However, for polymeric ultrafiltration (UF) and microfiltration (MF). Backwash and forward flush are the most commonly used methods for polymeric UF and MF to remove hydraulic reversible fouling [16]. Applying hydraulic backwash or forward flush has the benefit of keeping the permeability higher compared to regular filtration. The advantage of forward flush over backwash is that feed water can be used to flush the membrane without produced water loss which results in a higher net water production. Much variation in backwash and forward flush methods can be found for polymeric UF and MF, e.g. using a combination of backwash and forward flush, cross-flushing with pressure pulsing [17], air-enhanced backwashing [18,19]. The filtration layer of polymeric NF membranes is thin and fragile which makes them not suitable for these methods. However, these methods could have potential for removal of organic fouling during ceramic NF, since these membranes are more robust.

Ghadimkhani et al. reported that defouling of ceramic UF flat sheet membranes by air Nano Bubbles holds potential as an innovative sustainable technology [20]. Fujioka et al. used ozonated water flushing as fouling control method using ceramic NF membranes during secondary wastewater effluent treatment [21]. They found that the progression of fouling was limited to 35% in transmembrane pressure increase over five filtration cycles [20]. However, application of ozone is energy intensive and the by-products need to be treated with consideration.

The most recent development in the field of membrane development are carbon nanotube (CNT) based composite membranes. These membranes offer enhanced membrane properties such as lower fouling potential than polymeric or ceramic membranes [22]. Fan et al. [2016] developed a superhydrophobic CNT hollow fibre membrane and found that when using electrochemical assistance lower fouling potential occurred: the flux remained high during treatment of natural organic matter contain water for 36 h of operation [23,24]. However, these membranes need to be developed further before they can be applied for water treatment, e.g. the potential toxicological effect of CNT in the environment is not studied yet [22].

Another fouling control method found in literature is enhanced precoat engineering (EPCE®) used for polymeric UF and MF [25,26]. In this method, a suspension is dosed on the membrane (the precoat layer) to form an easily removable and permeable layer on the membrane. During filtration the fouling attaches or adsorbs onto the precoat layer instead of on the membrane. When the threshold pressure is reached, the membrane will be hydraulic backwashed. Then, during backwash the cake layer detaches easily from the membrane [25,26]. Alternatively, precoating using coagulants has been used to enable UF membranes to remove natural organic matter [27]. These methods have not been tested on ceramic NF membranes so far.

Therefore, several fouling control protocols were studied to control fouling in ceramic NF membranes, filtering high municipal sewage. First, several commonly known methods for polymeric UF membranes were tested on ceramic NF membranes: hydraulic backwash and forward flush. Second, a reaction based precoat was tested, where a precoat was filtered on the surface layer of the membrane. Then, after regular filtration, a chemical was dosed to initiate a chemical reaction to enhance the detachment of the cake layer, followed by a forward flush. Both the Fenton reaction and a calcium carbonate reaction with acid were used, where iron(III) chloride flocs and calcium carbonate particles were used as precoat.

The experiments were realised under lab conditions using the model compound sodium alginate to mimic fouling on the membranes. Sodium alginate is commonly used as a surrogate for extracellular polymeric substance (EPS) which is one of the largest contributors to fouling in organic loaded waste streams [28–34].

2. Materials & methods

2.1. Membranes

Filtration experiments were performed using ceramic NF membranes with a filtration layer of titanium oxide, a molecular weight cut-off (MWCO), as indicated by the manufacturer, of 450 Da, a mean pore size of 0.9 nm, and an open porosity of 30–40%. The actual MWCO was measured regularly, the results follow later in this paper. These ceramic NF membranes have a negative surface charge. Previous research showed that the zeta potential of the membranes was negative, −8 to −22 mV for pH 4–9, respectively [35].

Two different membrane configurations were used; consisting of (i) four large membranes in a tandem, and (ii) one small membrane. First, the hydraulic backwash experiments were executed with the large membranes. However, these membranes were damaged during the tests (described in Section 3.1), and could not be used for further studies. Therefore, the alternative membrane configuration, with smaller membranes, was used for the other experiments. The large membrane consisted of a 19 channel tube with a length of 1200 mm and an effective membrane area of 0.25 m^2. The small membrane has a single-channel, tubular configuration with a length of 100 mm and an effective filtration area of 0.163 dm^2 (Inopor GmbH, Germany).

2.2. Filtration setup

Ceramic NF membranes experiments were performed with a cross-flow filtration system using a pneumatic diaphragm pump (Hydra-cell) with a pulsation dampener. The feed water was recirculated; both the permeate and the concentrate were fed back into the feed tank, except for the sampling volume which was a negligible amount (< 0.1%) (Fig. 1). In order to ensure that the feed water quality remained constant during the experiment, feed water samples were analysed regularly.

The experiments using small and large membrane configurations were conducted with slightly different conditions at room temperature. When using the small configuration, the single pass water recovery was < 1% and the flux was 50–60 L·(m^2·h)$^{-1}$, unless otherwise specified, and a cross-flow velocity of 1.0–1.2 m·s^{-1} (Fig. 1). In the experiments using the configuration with the large membrane, a recirculation pump was added to the setup to reach a cross-flow velocity of 1.0–1.2 m·s^{-1}. The flux of these membranes was between 15 and 40 L·(m^2·h)$^{-1}$, unless otherwise specified, and the water recovery 50%. The experiments with both configurations were conducted at a transmembrane pressure (TMP) of 4.5–5.5 bar. All experiments were executed at least twice to ensure repeatability of the results. An experiment was considered as repeatable when the standard deviation between the results was less than 5%.

2.2.1. Temperature correction of permeability

In order to correct for the temperature, the following equation (Eq. (1)) was used to calculate the permeability of the membrane:

$$L_{20°C} = \frac{J \cdot 9e^{-0.0239 \cdot (T-20)}}{\Delta P} \tag{1}$$

where $L_{20 °C}$ is the temperature-corrected permeability at 20 °C (L·(m^2·h·bar)$^{-1}$), T is temperature of water (°C), J is membrane flux (L·(m^2·h)$^{-1}$), and ΔP is transmembrane pressure (bar). All permeability values were temperature-corrected to 20 °C [36].

2.2.2. Hydraulic permeability of clean membranes

A demineralised water filtration test was performed after chemical cleaning and before each filtration experiment to determine the hydraulic permeability. The hydraulic permeability indicates if the (ir)
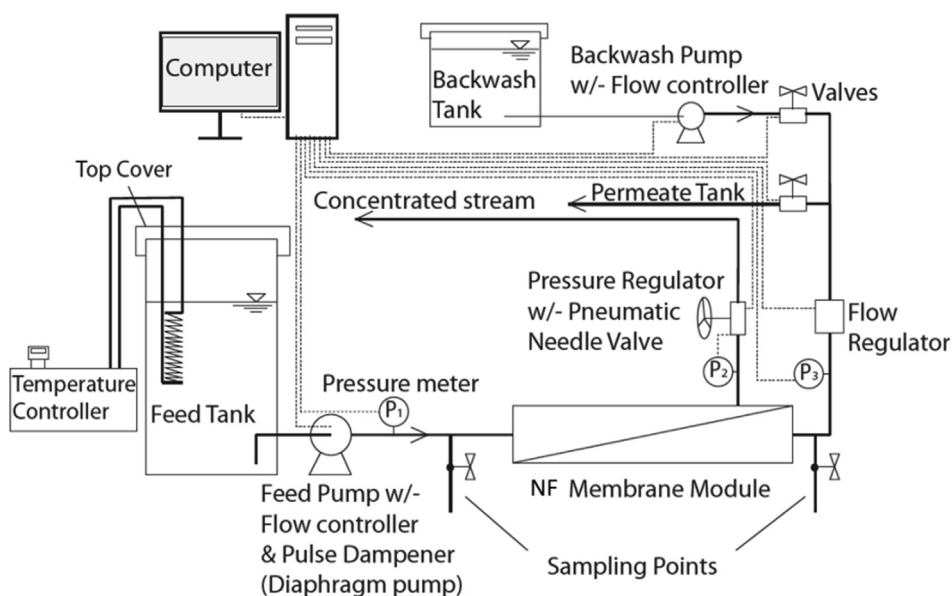
Fig. 1. Schematic representation of the small membrane configuration of the cross-flow ceramic NF filtration system.

reversible fouling was removed during chemical cleaning. These hydraulic permeability tests were executed under similar conditions as the filtration tests with a duration of 1 h.

2.2.3. Relative production downtime

The relative production downtime (*RPD*) (min·h^{-1}) was calculated using Eq. (2).

$$RPD = \frac{t_{cleaning}}{t_{filtration} + t_{cleaning}} \left(\frac{min}{h} \right)$$

(2)

where $t_{cleaning}$ is the duration of the cleaning and/or precoating and $t_{filtration}$ is the filtration time between cleaning two cleaning intervals (Table 2).

2.3. Model sewage

Fouling tests were performed using sodium alginate as model compound for sewage [28,31]. The feed water composition consisted of 0.8 g·L^{-1} sodium alginate (Sigma-Aldrich), 1 mM NaCl (Sigma-Aldrich) as background salt concentration, 1 mM NaHCO$_3$ (Sigma-Aldrich) as buffer, and 3 mM CaCl$_2$ (Sigma-Aldrich) adjusted to pH of 7. Sodium alginate is known to form a gel in the presence of calcium; sodium alginate aggregates according to the so called egg-box model which promotes cake development during filtration [28,32,37,38]. The model sewage contains a higher organic load than municipal sewage: with the model sewage a pre-sieved municipal sewage experiment of five days could be simulated in two hours [13].

2.4. Fouling control methods

2.4.1. Hydraulic backwash

The effect of hydraulic backwash was tested using the large membrane configuration. The experiment was performed at a constant flux of 30 L·(m^2·h)$^{-1}$ using permeate water as backwash water. The hydraulic backwash was initiated when the permeability reached 10 L·(m^2·h·bar)$^{-1}$: the hydraulic backwash pressure was 6 bar with a duration of 5 min. This process was repeated four times.

2.4.2. Forward flush

Forward flush cleaning was studied using the small membrane configuration. During forward flush the pressure on the membranes was released and feed water was used to flush away the cake layer. Moreover, the valve at the permeate side was closed to prevent flow through the membrane during forward flush. Preliminary results showed that forward flush was most effective with an interval of 20 min and a forward flush duration of 3 min; these conditions were used in this research. The influence of cross-flow was determined using four different cross-flow velocities: 0.4, 1.1, 2.2 and 4.3 m·s^{-1} corresponding to Reynolds numbers of 2100, 4200, 6300, 12,600, and 25,300, respectively.

2.4.3. Reaction based precoat

Two different reactions were tested using the reaction based precoat method; a reaction to initiate a Fenton reaction and a reaction to create carbon dioxide vapour using calcium carbonate and acid. These experiments were performed using the small membrane configuration.
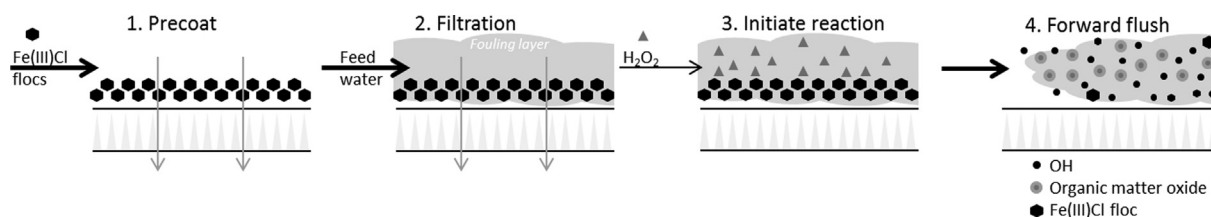
Fig. 2. Conceptual illustration of reaction based precoat method using the Fenton reaction. The precoat, consisting of iron(III) chloride flocs, was filtered on the membrane surface (step 1), followed by regular filtration of model sewage water (step 2). After filtration, hydrogen peroxide was added to initiate the Fenton(like) reaction (Eqs. (3)–(5)), where organic matter will oxidise (step 3). Finally, the precoat and oxidised organic matter will enable the fouling layer to detach more easily from the membrane surface and will be removed by forward flush (step 4).

2.4.3.1. Reaction based precoat using a Fenton reaction. Iron(III) chloride flocs were used as precoat, after filtration hydrogen peroxide was dosed to initiate the Fenton reaction (see Fig. 2). In a Fenton reaction iron works as a catalyst for hydrogen peroxide, resulting in an advanced oxidation reaction. Free radicals are formed being able to degrade organic matter (OM). Both iron forms, iron(II) and iron(III), react with hydrogen peroxide which are known as a Fenton (Eqs. (4) and (5)) and a Fenton-like reaction (Eqs. (3) and (5)) [39,40].

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HOO^{\cdot} + H^+ \tag{3}$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^{\cdot} + OH^- \tag{4}$$

$$HO^{\cdot} + OM \rightarrow OM_{oxid} \tag{5}$$
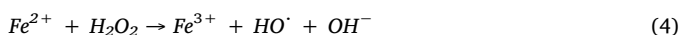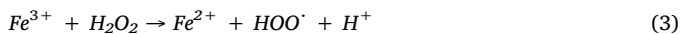
Iron(III) chloride 41% solution (Merck) was used for the precoating suspension. Iron(III) chloride was diluted in demineralised water to the required concentration. Various concentrations were tested: 40, 420, 2100, and 4200 mg·L^{-1}. Moreover, the pH was adjusted to 5, 7, and 8 to determine the most effective pH, since it affects iron floc sizes [41].

The precoating suspension was filtered on a clean ceramic NF membrane at laminar flow conditions with a cross-flow velocity of 0.4 m·s^{-1} at 5 bar with a duration of 10 min. Then, a fouling test was done using model sewage for 40 min as described before. Next, a hydrogen peroxide solution was dosed for 1, 5, or 10 min with a pH of around 2.5, since this is the optimal pH to initiate a Fenton or Fenton-like reaction [25]. Only iron(III) was dosed, however, iron(III) converts into iron(II) in the presence of hydrogen peroxide (Eq. (3)). Thus, during dosage of hydrogen peroxide, both iron(II) and Iron(III) were present on the membrane surface resulting in a Fenton and a Fenton-like reaction. Finally, forward flush was executed at a cross-flow velocity of 1.1 m·s^{-1} for 5 min without pressure using feed water to remove the loosened cake layer (see Fig. 2). This procedure of precoating and hydrogen peroxide dosing was repeated three times.

The amount of iron which deposited on the membrane surface during precoating was measured and analysed using a mass balance. The iron concentration of the feed, concentrate, and permeate stream was analysed using the total iron test cell test using the NOVA 60 Spectroquant® (Merck) (Table 1).

2.4.3.2. Reaction based precoat using calcium carbonate particles. Calcium carbonate particles were used as precoat, after filtration two kinds of acids were dosed to initiate the reaction between calcium carbonate and acid forming calcium carbonate bubbles (Fig. 3). For the reaction based precoat using calcium carbonate two different acids were tested to initiate carbon dioxide release: hydrochloric acid (Eq. (6)) or citric acid (Eqs. (7) and (8)).

$$CaCO_3(aq) + 2HCl(aq) \rightarrow CaCl_2(aq) + H_2O(aq) + CO_2(g) \tag{6}$$

$$3CaCO_3 + 2C_6H_8O_7 \rightarrow Ca_3(C_6H_5O_7)_2 + 6H^+ + 3CO_3^- \tag{7}$$

$$H_2CO_3(aq) \rightarrow H_2O(aq) + CO_2(g) \tag{8}$$

A calcium carbonate suspension used for precoating was prepared from CaCO$_3$ powder (Merck). The powder was carefully mixed with water in a concentration of 100, 200, or 400 mg·L^{-1} to make a colloid

Table 1
Deposition of iron membrane surface during precoating derived from mass balance.

Precoating suspension, concentration iron chloride	Net Iron deposited	Precoating suspension, concentration CaCO$_3$	Net calcium deposited
40 mg·L^{-1}	0.2 mg	100 mg·L^{-1}	104 mg
420 mg·L^{-1}	97 mg	200 mg·L^{-1}	239 mg
2100 mg·L^{-1}	406 mg	400 mg·L^{-1}	801 mg
4200 mg·L^{-1}	626 mg		

suspension. To avoid dissolution of Ca^{2+} and CO$_3^{2-}$ the suspension was kept at a pH of 10, and to ensure uniformly distributed CaCO$_3$ nanoparticles, the suspension was sonicated at 40% amplitude for three hours [42]. Then, the suspension was filtrated over the clean membranes for 10 min to create a precoat layer. After filtration with model sewage, the membrane was cleaned using citric acid or hydrochloric acid in a concentration of 400 mg·L^{-1} for a duration of 1, 5, or 15 min (see Fig. 3). This procedure of precoating and acid dosing was repeated three times.

The amount of calcium which was deposited on the membrane surface during precoating was measured and analysed using a mass balance. The calcium concentration of the feed, concentrate, and permeate stream was analysed using the calcium test cell test using the NOVA 60 Spectroquant® (Merck) (Table 1).

2.4.4. Chemical cleaning

After each experiment, the membranes were chemically cleaned to remove all fouling. The chemical cleaning was carried out by soaking the membranes in a 0.1% sodium hypochlorite solution for 1 h.

2.5. MWCO analysis

The MWCO of the ceramic NF membranes were measured before and after each experiment to monitor the quality of the membranes. Tam & Tremblay (1991) described a method to calculate the MWCO; this method is widely used for the determination of the pore size distribution of polymeric and ceramic membranes [43–47]. The MWCO was investigated by filtering a mixture of five different polyethylene glycol (PEG) molecules (200, 300, 400, 600, and 1000 Da) (Sigma-Aldrich) each in a concentration of 6 mg·L^{-1}. The same settings were used during filtration as described for the hydraulic permeability.

The feed and permeate samples were analysed using HPLC (Shimadzu) equipped with size exclusion chromatography columns (SEC, 5 μm 30 Å PSS SUPREMA) and a RID-20A refractive index detector. The carrier liquid in the HPLC was ultrapure water at a flow rate of 1 mL·min^{-1}. From the HPLC analyses, the molecular weight distribution curves of the dissolved PEG molecules in the feed and permeate were derived. These were transformed into retention curves by calculating the rejection percentage of a PEG with a certain molecular weight (R_i) using Eq. (4):

$$R_i(\%) = \left(\frac{c_{i,feed} - c_{i,permeate}}{c_{i,feed}} \right) \cdot 100\% \tag{9}$$

where $c_{i,\,feed}$ is the PEG concentration in the feed samples and $c_{i,\,permeate}$ in the permeate samples. Afterwards, the experimental retention curves were described by a log-normal model as function of molecular weight (*MW*) and MWCO using Eq. (5) [44,45,48]. Eq. (5) was used to model retention curve to be able to calculate the MWCO.

$$\sigma(MW_s)$$
$$= \int_0^{MW_s} \frac{1}{s_{MW}\sqrt{2\pi}} \cdot \frac{1}{MW} \cdot$$
$$exp\left[-\frac{(\ln(MW) - \ln(MWCO) + 0.56 \cdot s_{MW})^2}{2 \cdot s_{MW}^2} \right] \cdot dMW \tag{10}$$

where $\sigma(MW_s)$ is the reflection coefficient for a PEG with a molecular weight MW_s, s_{MW} is the standard deviation of the molecular weight distribution.

In this method, the separation of the PEG molecules is assumed to be only based on size exclusion with negligible solute diffusion. Therefore, the molecular size of the PEG solutes (d_s in nm) is correlated to their molecular weight (*MW* in Da) as shown in Eq. (6) [44,48].

$$d_s = 0.065 \cdot MW^{0.438} \tag{11}$$

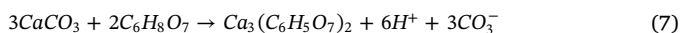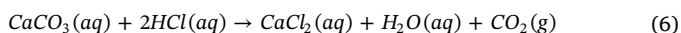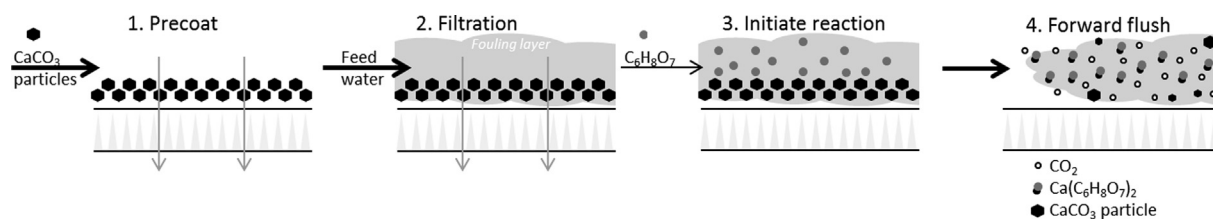Finally, the MWCO was estimated at 90% of the retention curve [36,45].

Fig. 3. Conceptual illustration of reaction based precoat method using the calcium carbonate particles. The precoat consisting of calcium carbonate particles was filtered on the membrane surface (step 1), followed by regular filtration of model sewage water (step 2). After filtration, citric acid was added to initiate the reaction between calcium carbonate and citric acid forming calcium carbonate bubbles (Eqs. (6)–(8)) (step 3). Finally, the precoat and calcium carbonate bubbles will enable the fouling layer to detach more easily from the membrane surface and will be removed by forward flush (step 4).

## 3. Results & discussion

3.1. Hydraulic backwash

First, the MWCO of the four large membranes was determined to ensure the right quality of the membranes. Then, the effect of hydraulic backwash was studied by comparing it with the permeability of the membrane and without cleaning. In the experiment without hydraulic backwash the permeability decreased from 22 to 4.5 L·(m^2·h·bar)$^{-1}$ within two hours (Fig. 4a). After hydraulic backwash was applied, an increase in permeability was shown; 43, 37, 31, and 25%, respectively, resulting in a higher permeability than without cleaning and thus postponing the chemical cleaning. However, the performed hydraulic backwash had a high relative production downtime (Table 2).

Afterwards, the effect of hydraulic backwash on the filtration layers was analysed by determining the MWCO of the membranes. The results showed that the MWCO of the membranes after the hydraulic backwash experiments was too high to measure. Therefore it was concluded that the ceramic NF membranes were damaged during the backwash operation. After opening the membrane modules, the damage on the edges of the membranes was clearly visible; resulting in the transport of feed water to the permeate via the support layer of the membranes (Fig. 4b). The experiments were repeated at lower pressures of 1 and 2 bar. However, this did not affect the permeability compared to the permeability without cleaning; apparently the cleaning back flux or hydraulic sheer force was too low to have an effect. This is in line with the finding of Chang et al. (2017) who studied hydraulic backwash parameters of

polymeric membranes treating surface water [49]. They found that the hydraulic backwash strength should be 2.1 times the filtration flow. The backwash strength was expressed as the ratio between the backwash flux to permeate flux under constant flux, or the ratio of backwash pressure to operating pressure under constant pressure. In our case, at a pressure of 1 and 2 bar, a backwash strength of 2.1 was not reached.

3.2. Forward flush cleaning

First, the MWCO of the small membranes, used for these experiments, were measured to be between 602 and 649 Da. The MWCO remained constant for the whole duration of this study. Next, interval forward flush cleaning was studied using feed water at 20 min intervals, since these intervals were found to be the most effective in removing reversible fouling (results not shown). Various cross-flow velocities, ranging from 0.4 to 4.3 m·s^{-1}, during forward flush were compared. At a cross-flow velocity of 0.4 m·s^{-1} the flow was laminar and at higher cross-flow velocities the flow was turbulent. The fouling experiment was performed with a cross-flow velocity of 1.1 m·s^{-1}. The results indicate that the effect of the forward flush was similar for all cross-flow velocities (Fig. 5a). This is in contrast with results obtained with polymeric UF, where forward flush is commonly applied, and where higher forward flush cross-flow velocities have resulted in higher fouling removals [16,19,50]. This could be explained by the weak attachment of the fouling layer on the ceramic NF membrane surface than polymeric NF membrane surface [8,9] which makes a low cross-flow sufficient to remove organic fouling. Moreover, similar results were
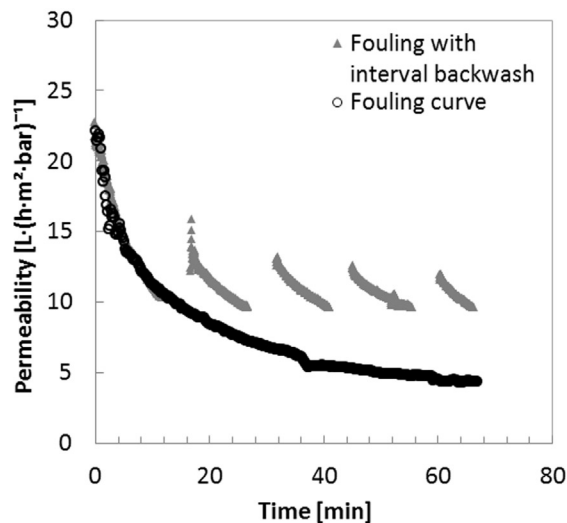
Fig. 4. (a) Permeability in time during ceramic NF using model sewage with and without interval hydraulic backwash performed with the configuration with large membranes. Hydraulic backwash was applied at 6 bar pressure for 5 min when the permeability had reached 10 L·(m^2·h·bar)$^{-1}$. (b) Pictures of damage of the ceramic NF membranes after hydraulic backwash was applied. The layer on the edges of the membrane were damaged. Therefore, the feed water can flow directly to the permeate via the support layer of the membrane.

Table 2
Summary of the cleaning protocol of different fouling control methods.

Cleaning method	Membrane configuration	Cleaning interval (min)	Cleaning time (min)	Precoat time (min)	Relative production downtime (min·h^{-1})
Forward flush	Small	20	3	NA	7.8
Reaction based precoat: Fenton	Small	40	1	10	16.1
Reaction based precoat: CaCO$_3$	Small	40	1	10	16.1

reported by Fujioka et al. using similar ceramic NF membranes while applying forward flush with clean water [21].

The decrease in permeability – meaning the accumulation of fouling – reduced with each forward flush cycle until a steady state was reached (Fig. 5b). The impact of the forward flush (the hydraulic removal) thus increased with each cycle, and fouling became more reversible. This can be explained by the fact that irreversible fouling stabilises in time [51].

3.3. Reaction based precoat

3.3.1. Reaction based precoat using a Fenton-reaction

In order to test the effectiveness of a Fenton (like) reaction, two preliminary tests were executed. Firstly, the fouling curve of a membrane with a precoat layer was compared with a fouling curve of a clean membrane; the shape of the curve was more or less similar and both curves ended at the same value after 130 min (Fig. 6a). Secondly, the effect of hydrogen peroxide dosing was tested on both the untreated and the precoated membranes. The permeability of the uncoated membrane increased with 8% after the first hydrogen peroxide cleaning, while the precoated membranes showed an increase of about 75% in permeability (Fig. 6b) which is a clear indication of the occurrence of Fenton (like) reactions.

Next, several experiments were executed to optimise the Fenton reactions. Firstly, the feed suspension, used for the precoating, of iron chloride was prepared at pH 5, 7, and 8 which affects the size and strength of the iron flocs [41]. The deposition of the flocs on the membrane surface was influenced by the size and strength of the flocs and, thus, determines the stability of the precoat layer [25]. The highest recovery was obtained when the reaction was realised at a pH of 7 (Fig. 6c). Thus, the deposition of the flocs was most stable with a feed suspension of pH 7. Secondly, the concentration of iron chloride in the feed suspension, used for precoating, was optimised. When comparing

feed concentrations of 42, 420, 2100, and 4200 mg·L^{-1} iron chloride, the concentration of 420 and 4200 mg·L^{-1} iron chloride performed the best (Fig. 6d). When precoating with a feed concentration of 420 mg·L^{-1} iron chloride, net 97 mg iron deposited on the membrane surface (Table 1). The rest of the suspension could be reused.

After the first reaction based precoat, the method was repeated a second time including precoating and hydrogen peroxide treatment. Since not all fouling was removed, probably the precoat was not deposited on the membrane surface itself, but on the fouling layer on the membrane surface. The results therefore showed that the second cleaning was less effective than the first cleaning (Fig. 6b-d). The increase in irreversible fouling was probably caused by the fact that the precoat layer was not evenly distributed on the membrane surface due to the presence of fouling on the membrane surface. Galjaard et al. (2001) also saw an increase in irreversible fouling after the first cycle because the membrane surface was not entirely covered with the dosed precoat material [25]. Causing the non-protected layer to foul and not being restored after hydraulic backwash.

3.3.2. Reaction based precoat using calcium carbonate

The effectiveness of a calcium carbonate reaction with acid was studied with a series of preliminary tests. Firstly, the fouling curves of an untreated and a precoated membrane were compared; the permeability drop of the precoated membrane in comparison with the uncoated membrane was slower but after 130 min the curves were at the same permeability value (Fig. 7a). Secondly, the effect of an acid cleaning, using either citric acid or HCl, on the permeability of an untreated fouled membrane was studied. The citric acid cleaning of the untreated membrane resulted in a permeability increase of 27%, whereas HCl was less effective with 11% permeability increase (Fig. 7b). Thirdly, the fouled precoated membranes were cleaned with HCl, causing an increase of 12% in permeability (Fig. 7c). However, the effect was much greater when cleaning the fouled precoated
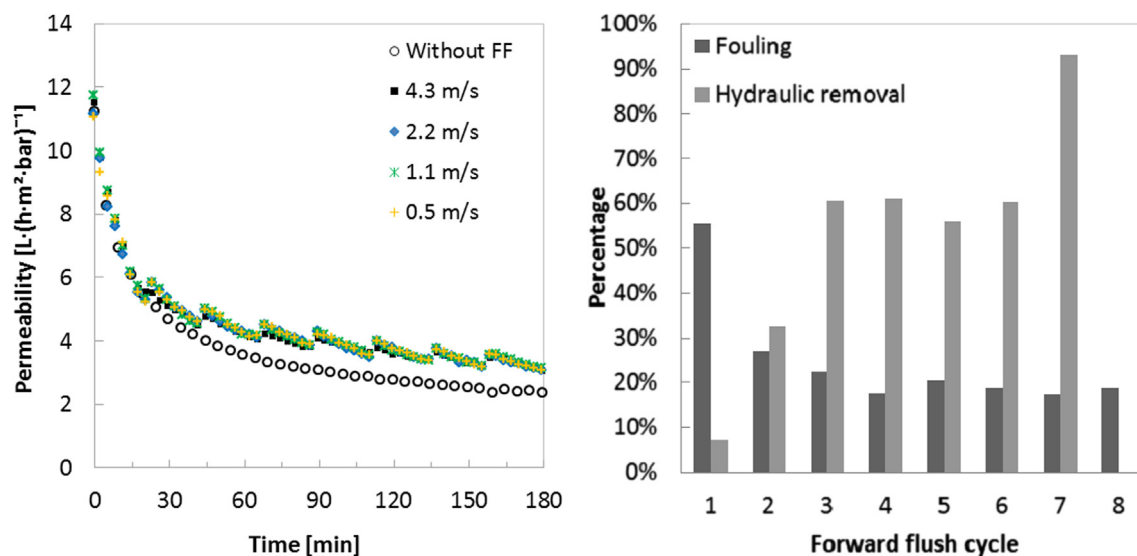
Fig. 5. (a) Permeability in time during ceramic NF using model sewage with and without interval forward flush (20 min). Different cross-flow velocities during forward flush were compared, ranging from 0.5 to 4.3 m·s^{-1}. (b)Fouling and hydraulic removal per forward flush cycle. Forward flush cycles of 20 min were executed.
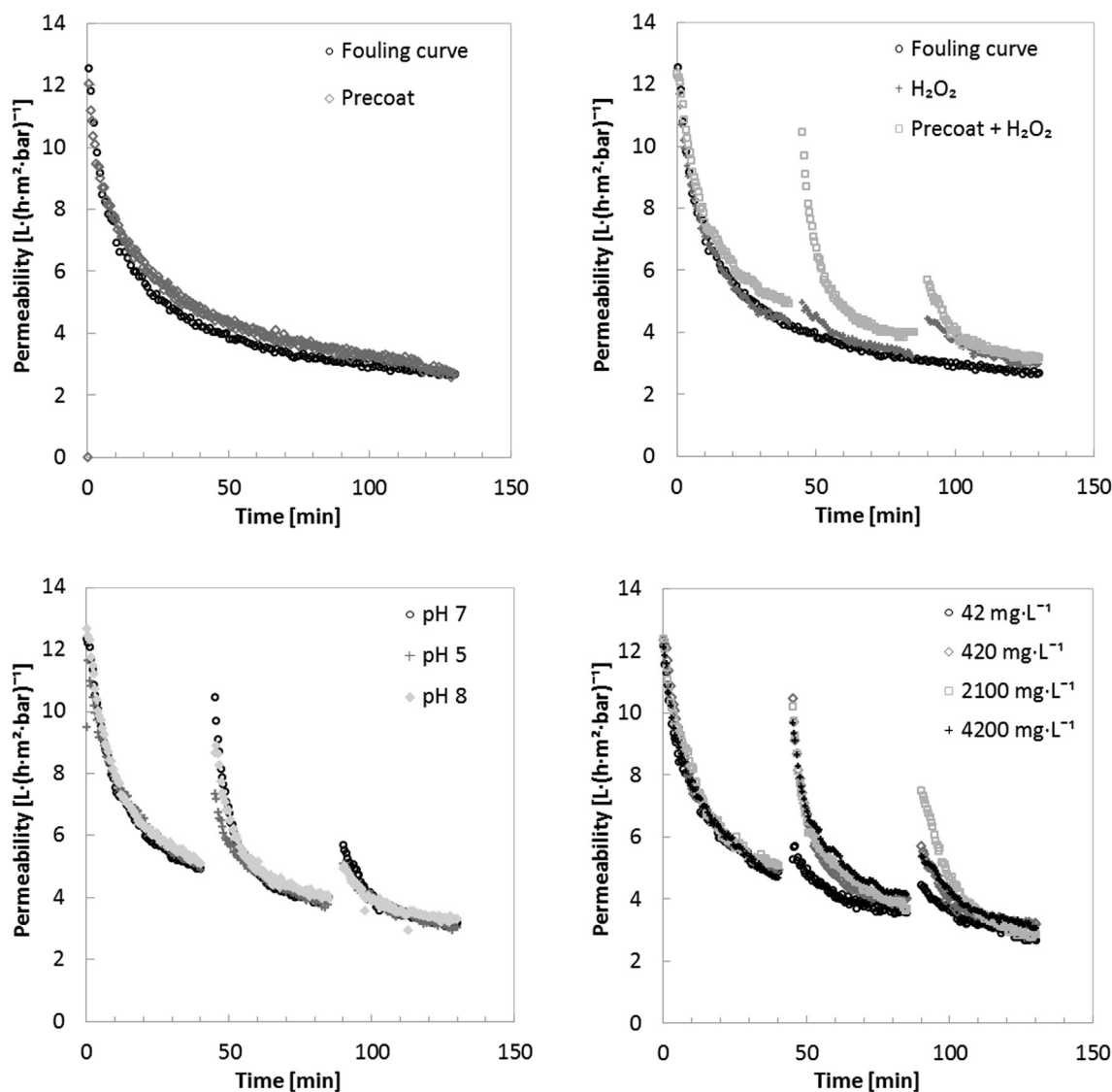
Fig. 6. A–d: Permeability in time during ceramic NF using model sewage using (a) untreated and iron chlorite precoated membranes. (b) Comparison of hydrogen peroxide cleaning on an untreated and precoated membrane. (c) Comparison of precoating suspensions of pH 5, 7, and 8. (d) Comparison of different precoating suspension concentrations.

membranes with citric acid: 76% permeability increase. This is probably due to the fact that citric acid is a weak acid whereas HCl is an strong acid. During the reaction of HCl with calcium carbonate, H^+ was converted which causes a pH increase which limits the reaction (Eq. (6)). However, the reaction of citric acid with calcium carbonate works does not affect the pH and keeps going (Eqs. (7) and (8)). Therefore, citric acid is probably more effective.

Then, the concentration of calcium carbonate in the feed suspension, used for precoating, was optimised. When comparing a feed concentration of 100, 200, and 400 mg·L^{-1} calcium carbonate, the concentration of 200 and 400 mg·L^{-1} calcium carbonate showed the highest permeability recovery after cleaning (Fig. 7d). This relates to a deposition of 239 and 801 mg calcium carbonate on the membrane surface during precoating (Table 1).

Again, the second cleaning of the reaction based precoat was less effective in permeability increase than the first one (Fig. 7c-d). Probably, a calcium carbonate deposition was less stable during the second interval, since not all fouling was removed during the first interval, similar results were observed by the reaction based precoat using the Fenton reaction (Fig. 6a–d).

3.4. Net water production

To compare the various fouling control methods, the net water production was calculated for all experiments and compared to a situation without fouling control with a duration of 130 min including downtime. The net water production was calculated as an accumulation of the hydraulic flux. The net water production was positively affected by two factors: (i) when a high hydraulic flux was maintained during filtration and (ii) with a low relative production downtime (Table 2). For none of the fouling control methods permeate water was used. The water production of membranes cleaned with forward flush and reaction based precoat, using the Fenton reactions, were more or less similar to the curve without the use of a fouling control method, resulting in a net water production of 51 L·m^{-2} for a duration of 130 min (Fig. 8). Reaction based precoat using calcium carbonate produced the most net water with 80 L·m^{-2} (58% more than without cleaning), even though this method requires a high relative production downtime of 16.1 min·h^{-1} (Table 2). Moreover, calcium carbonate and citric acid are biodegradable compounds and thus environmentally suitable for postponing chemical cleaning of ceramic NF membranes.
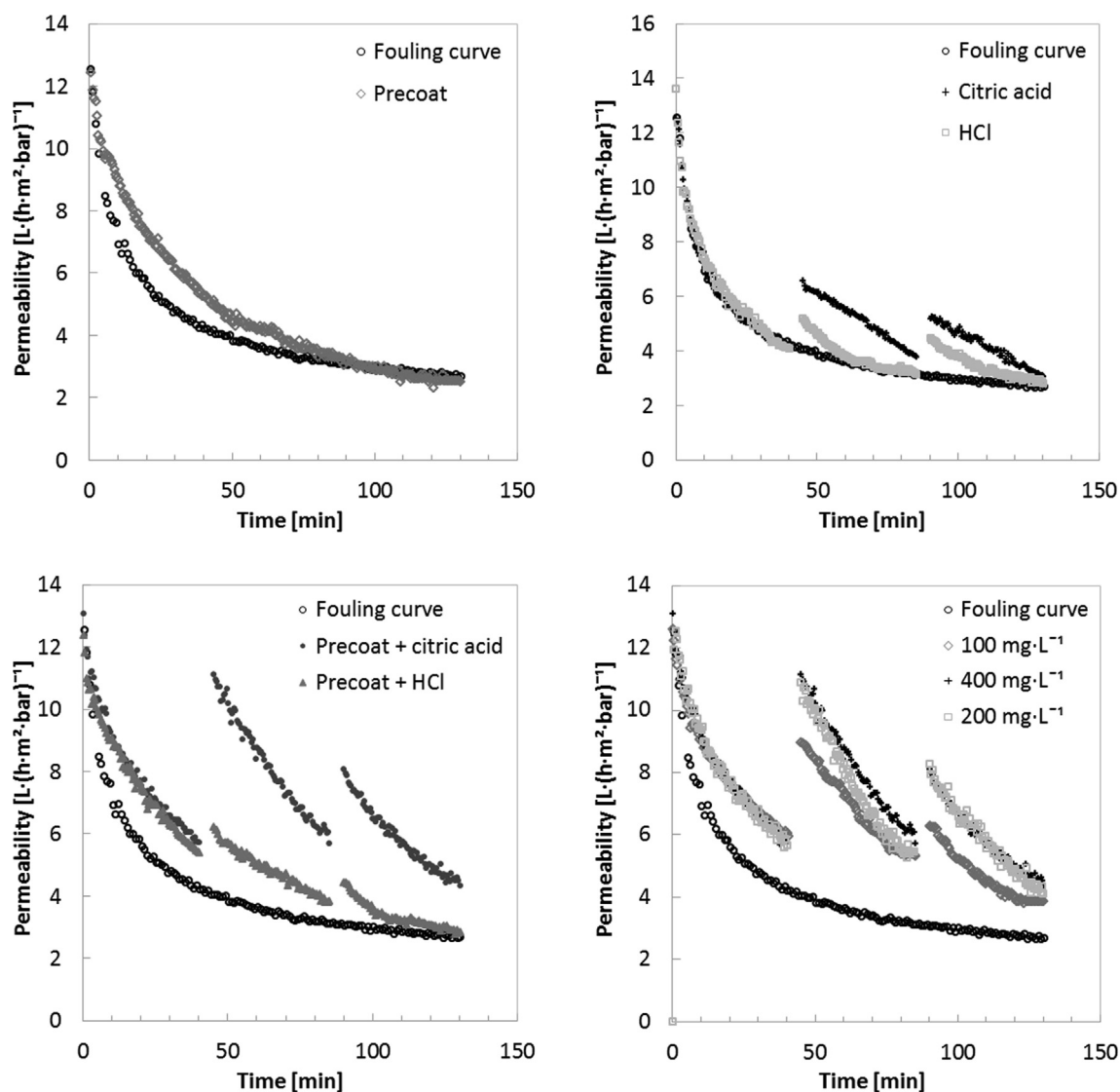
Fig. 7. Permeability in time during ceramic NF using model sewage using (a) untreated and calcium carbonate precoated membranes. (b) Comparison of hydrochloric acid and citric acid on an untreated membrane. (c) Comparison of hydrochloric acid and citric acid on an precoated membrane. (d) Comparison of different precoating suspension concentrations.

4. Conclusions

Various fouling control methods of ceramic NF membranes were studied, resulting in the following conclusions:

- Hydraulic backwash was not an appropriate cleaning method for ceramic NF membranes since the glass seal layer at the edges of the membranes was damaged due the hydraulic sheer force. At lower pressure hydraulic backwash the fouling was not removed.
- Interval forward flush increased the flux of the ceramic NF membranes. However, the water production was not higher than during fouling without forward flush, due to the high relative production downtime of 7.8 min·h^{-1}.
- During forward flush the cross-flow velocity had no effect on the efficiency.
- Reaction based precoat was tested with two different reactions. The calcium carbonate reaction was more effective in fouling removal than the Fenton based reactions.
- The net water production of using reaction based precoat with calcium carbonate was the highest of all fouling control methods.

CRediT authorship contribution statement

F.C. Kramer: Conceptualization, Methodology, Investigation, Writing - original draft and formal analysis. **R. Shang:** Writing - review & editing, Conceptualization. **L.C. Rietveld:** Writing - review & editing. **S.J.G. Heijman:** Conceptualization, Writing - review & editing, Supervision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.
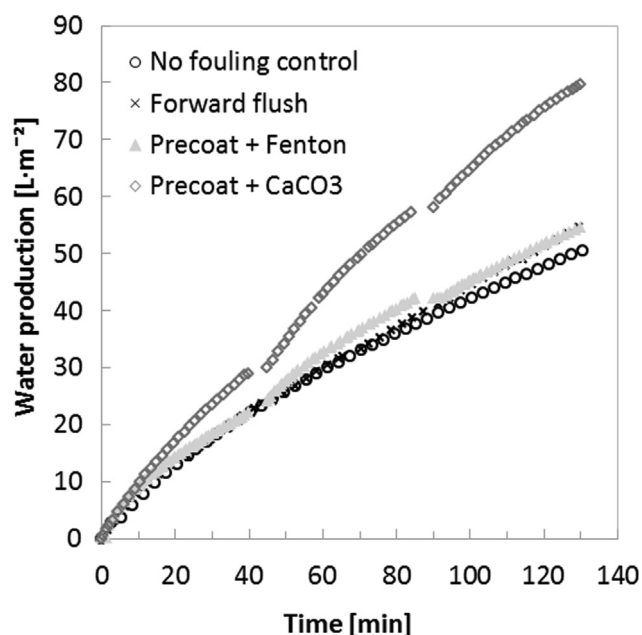
Acknowledgements

Fig. 8. Net water production in litre per membrane area during ceramic NF. Different fouling control methods compared with no fouling control (○): interval forward flush (x), reaction based precoat with Fenton reaction (Δ) and CaCO₃ reaction (◊).

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