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Towards a better hydraulic cleaning strategy for ultrafiltration membrane fouling by humic acid: Effect of backwash water composition

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ABSTRACT

As a routine measurement to alleviate membrane fouling, hydraulic cleaning is of great significance for the steady operation of ultrafiltration (UF) systems in water treatment processes. In this work, a comparative study was performed to investigate the effects of the composition of backwash water on the hydraulic cleaning performance of UF membranes fouled by humic acid (HA). Various types of backwash water, including UF permeate, Milli-Q water, NaCl solution, CaCl₂ solution and HA solution, were compared in terms of hydraulically irreversible fouling index, total surface tension and residual HA. The results indicated that Milli-Q water backwash was superior to UF permeate backwash in cleaning HA-fouled membranes, and the backwash water containing Na⁺ or HA outperformed Milli-Q water in alleviating HA fouling. On the contrary, the presence of Ca²⁺ in backwash water significantly decreased the backwash efficiency. Moreover, Ca²⁺ played an important role in foulant removal, and the residual HA content closely related to the residual Ca²⁺ content. Mechanism analysis suggested that the backwash process may involve fouling layer swelling, ion exchange, electric double layer release and competitive complexation. Ion exchange and competitive complexation played significant roles in the efficient hydraulic cleaning associated with Na⁺ and HA, respectively.

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Introduction

Worldwide water pollution has boosted the problem of water scarcity, especially for safe drinking water. Under this circumstance, more effective water treatment processes are required in potable water production. With pore sizes less than 20 nm, the ultrafiltration (UF) membrane, which can totally retain the pollutants such as colloids, protozoa, bacteria and virus (Jacangelo et al., 1997), has been one of the most attractive alternatives to the conventional water treatment process. However, the retained pollutants may

accumulate on the membrane surface, inevitably leading to severe membrane fouling. Membrane fouling would definitely boost energy demand and operating cost, making the membrane technology less cost-effective.

To address the problem of membrane fouling, a variety of measures have been taken, including membrane modification (Rana and Matsuura, 2010), pretreatment (Gao et al., 2011; Huang et al., 2009), hydraulic cleaning and chemical cleaning (Porcelli and Judd, 2010; Shi et al., 2014). However, membrane modification and pretreatment, which may retard the accumulation of foulants by improving the anti-fouling ability of

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membranes and the quality of feed water, respectively, cannot completely eradicate the fouling. Therefore, the cleaning of membranes is indispensable for the sustainable application of UF systems. As strong acids and alkalis are involved, the widely employed chemical cleaning is not only unfriendly to surrounding environment but also harmful to membrane life-span (Crozes et al., 1997). Therefore, it is essential to explore the hydraulic cleaning so as to minimize the frequency of chemical cleaning.

The hydraulic cleaning consists of two aspects, i.e. a backward hydrodynamic force related to backwash intensity and a dispersion potential associated with solution chemistry of backwash water. A variety of studies have been performed to optimize backwash conditions, and the cleaning performance proved to be improved at a higher backwash strength (Crozes et al., 1997; Kennedy et al., 1998). Nonetheless, the gains in membrane permeability by applying the stronger backwash intensity may be easily offset by the increase in water/energy consumption (Akhondi et al., 2014; Crozes et al., 1997; Kennedy et al., 1998). Thus, backwash water composition is still a fertile area to explore. To date, several types of backwash water have been investigated, including tap water (Chen et al., 2003), UF permeate (Abrahamse et al., 2008; Li et al., 2009, 2012b), nanofiltration permeate (Li et al., 2010), reverse osmosis (RO) permeate (Chen et al., 2003; Li et al., 2012a), deionized (DI) water (Abrahamse et al., 2008; Li et al., 2009, 2010, 2012a, 2012b; Resosudarmo et al., 2013) and some other types of water with different ions. In consideration of convenience, UF permeates have been widely used for backwashing in full-scale applications, but this approach is limited by the low backwash efficiency (Abrahamse et al., 2008; Li et al., 2009, 2012b). Previous studies have demonstrated that backwashing with UF permeate treated by dialysis resulted in a high backwash efficiency (Li et al., 2009). Compared with UF permeate, RO permeate exhibited much greater capacities in cleaning the membranes fouled during filtration of sea water or surface water (Li et al., 2012a; Ma et al., 2013). Moreover, Li et al. (2009, 2012a) verified the effectiveness of backwashing with DI water in fouling control via both pilot- and bench-scale UF experiments treating canal water as well as brackish water. However, as reported by Resosudarmo et al. (2013), backwashing with DI water was ineffective for removing fouling caused by humic acid (HA).

Obviously, the differences among the mentioned backwash water lie in the composition. So it is reasonable to propose a question about the backwashing of fouled membranes. Is more purer water necessarily better for backwashing? By investigating the effects of monovalent and divalent cations on the backwash performance, Li et al. (2011) found that the cleaning efficiency was impaired to some extent perhaps due to the charge screen effects. However, for UF membranes fouled by hydrophilic organic matter, Lee et al. (2001) demonstrated that NaCl (0.1 mol/L) was much more effective than DI water, with a cleaning efficiency even greater than that achieved by chemical agents (e.g., NaOH or citric acid). Moreover, by determining the intermolecular foulant–foulant adhesion, the exposure of fouled membranes upon salt solution could induce a structural breakup of cross-like gel layer by ion exchange (Lee and Elimelech, 2007). Apparently, the reported results in the previous literature are not always consistent, leaving a huge room for debate.

Existing studies involving the composition of backwash water mainly focused on controlling membrane fouling to treat specific natural water, and controversial results were typically related to the complexity and diversity of natural surface waters. Because the effects and mechanisms of various components (such as organics and cations) in removing the retained foulants during backwash have been unknown, the design of backwash water composition for specified target foulants has been under debate. There are more uncertainties regarding the case of a complex foulant matrix in natural water. Therefore, the effect of backwash composition on the alleviation of UF membrane fouling by HA was investigated. Overall, the objectives of this study were to find a better backwash water composition for effective membrane cleaning. Several types of backwash water, including UF permeate, Milli-Q water, NaCl solution, CaCl₂ solution and low-concentration HA solution, were used in hydraulic cleaning, and the effects of the compositions were discussed.

1. Methods and materials

1.1. Feed water and backwash water

Unless otherwise specified, all reagents and chemicals were analytical grade, and prepared by diluting with Milli-Q water. NaCl, CaCl₂·2H₂O, HCl and NaOH were purchased from Tianjin Benchmark Chemical Reagent Co., Ltd (Tianjin, China). Milli-Q water (18.2 MΩ·cm) was obtained from a Millipore water system (EMD Millipore Corp, Billerica, MA, USA). To better understand the relevant mechanisms involved in the backwashing process, HA, which was purchased from Sigma-Aldrich Co., LLC (St. Louis, MO, USA), was used as a model foulant to represent natural organic matter (NOM), following previous studies (Jermann et al., 2007; Yuan and Zydney, 2000). A stock HA solution (2 g/L) was prepared as follows. First of all, 2 g of HA was dissolved in 1000 mL of NaOH solution (pH = 12). Next, the solution was stirred for 24 hr, and the pH of the solution was adjusted to 7.0 using 1 mol/L HCl. Then, the stock solution was stored at 4°C in the dark. A HA concentration of 5 mg/L was chosen to simulate the organic matter content in surface water (Suttkover-Gutman et al., 2010; Tian et al., 2013) and was prepared by diluting the stock solution with Milli-Q water.

Two types of HA solutions with different types of cations were used as feed water, as listed in Table 1. To ensure a sufficient amount of deposited HA for the backwashing tests, feed solutions containing Ca²⁺ (0.5 mmol/L) were employed. The typical concentrations of Ca²⁺ and Na⁺ were chosen following previous literature (Tian et al., 2013). The pH of feed water was adjusted to 7.5 using 1 mol/L NaOH or HCl. Meanwhile, backwash water samples containing different compounds that were in the UF permeate were prepared and used. The compositions of the various types of backwash water are also summarized in Table 1. The abbreviations MQBW, NaBW, HABW, CaBW and UFPBW represent backwashing with Milli-Q water, NaCl solution, HA solution, CaCl₂ solution and UF permeate, respectively. The NaCl and CaCl₂ solutions were prepared by adding the appropriate

Table 1 – Water quality of the feed water and backwash water.

Types		Ca ²⁺ (mmol/L)	Na ⁺ (mmol/L)	HA (mg/L)
Feed water	HA + Ca ²⁺	0.5	0	5.00
	HA + Na ⁺ +Ca ²⁺	0.5	10.0	5.00
Backwash water	MQBW	0	0	0
	NaBW	0	10	0
	HABW	0	0	0.71/0.81
	CaBW	0.50	0	0
	UFPBW	~0.49	10	0.71/0.81

The abbreviations MQBW, NaBW, HABW, CaBW and UFPBW represent backwashing with Milli-Q water, NaCl solution, HA solution, CaCl₂ solution and UF permeate, respectively. HA: humic acid.

amounts of NaCl and CaCl₂·2H₂O, respectively, to Milli-Q water. In the preparation of the HA solution used for backwashing, the HA concentrations in the feed water were chosen to ensure that the HA content in the permeate was equal to that in the permeates of each corresponding UF test.

1.2. Experimental setup and UF membranes

The setup used for the UF tests is presented in Appendix A Fig. S1. The setup consisted of a self-made unstirred filtration cell, a high-level tank, a peristaltic pump, a pressure transducer and a programmable logic controller. The filtration cell had an inner diameter of 23 mm and an effective volume of 20 mL and was connected to a glass reservoir in which up to 1 L of feed water could be stored. The peristaltic pump (BT100-2 J, Longer Precision Pump Co., Ltd., Baoding, China) was used to maintain a constant flux during filtration or backwashing. The pressure transducer (PTP708, Tuopo Electric, Foshan, China) was located between the filtration cell and the suction pump to monitor the trans-membrane pressure (TMP); the transducer was connected to a computer, and the pressure data were automatically logged every 30 sec.

Flat sheet polyethersulfone (PES) (Pall Corp., USA) UF membranes with a molecular weight cut-off of 100 kDa were used. The effective filtration area of the membrane disk was 4.15 cm². The membranes were negatively charged, with a zeta potential of −21.7 mV (pH 7.5, 1 mmol/L KCl), respectively. New membrane disks were used for each filtration run and a careful rinse was performed to remove preservatives prior to using. The membranes were soaked in Milli-Q water for 24 hr and the water was replaced at least three times. Subsequently, the membranes were filtered with Milli-Q until the total organic carbon (TOC) concentration of the filtrate was comparable to that of Milli-Q water.

1.3. Experimental protocol

Unless otherwise stated, multi-cycle UF tests with periodic hydraulic backwashing were performed under the constant flux (180 L/(m² · hr)) at room temperature (21 ± 2°C). Each cycle consisted of 4 steps as follows: (1) feeding approximately 100 L/m² (~42 mL) of a given feed solution; (2) filtration at the constant flux of 180 L/(m² · hr) for 29 min (90 L/m²); (3)

flushing the setup to clean the tubes with the given backwash water for 1 min (3 L/m²); and (4) backwashing with the prepared backwash water solution at the constant flux of 180 L/(m² · hr) for 2 min (6 L/m²). Each UF test was terminated after 10 full cycles or when TMP exceeded 80 kPa. The concentrate (10 L/m², ~4.5 mL) was collected after UF and the backwash waste was collected after the backwash procedure to further analyze its components.

Moreover, extra experiments, in which soaking was adopted instead of backwashing, were carried out to analyze the amounts of residual HA and Ca²⁺. Because this study primarily focused on the effect of the dispersion potential of different types of backwash water, it made sense to substitute soaking for backwashing. The results were presented in part of the correlation between residual HA and residual Ca²⁺ (i.e., Section 2.3.2). The operation parameters used for hydraulic cleaning focusing on dispersion potential are listed in Appendix A Table S2.

1.4. Analytical method

HA concentrations were determined by UV absorbance at a wavelength of 254 nm using a UV/Vis spectrophotometer (T6, Beijing Purkinje General Instrument, Beijing, China). The concentrations of Ca²⁺ in solutions were measured using inductively coupled plasma optical emission spectroscopy (Optima 8300, Perkin-Elmer Inc., Waltham, MA, USA). An energy dispersive spectrometer (EDS) (Quanta 200, FEI, Hillsboro, OR, USA) was employed to identify the weight percentage of elemental Ca in the fouling layer. Membrane samples were initially dried in a desiccator for 72 hr and then coated with gold using a precision etching coating system (Model 682, Gatan, USA) prior to EDS observation. Moreover, the membranes were characterized by an attenuated total reflectance Fourier transform infrared (ATR-FT-IR) spectroscope (Spectrum One B, Perkin Elmer Inc., Waltham, MA, USA). For each membrane sample, ten scans were taken between 4000 and 650 cm^{−1} with a resolution of 4 cm^{−1}.

In this study, the efficiency of hydraulic cleaning was evaluated via two indexes, irreversible fouling rate and surface tension, representing accumulative fouling and fouling potential after cleaning, respectively. By monitoring the development of TMP, the hydraulically irreversible fouling index (HIFI, m^{−1}), which indicated the fouling degree of UF membranes after hydraulic cleaning, was calculated via Eq. (1) (Huang et al., 2008; Nguyen et al., 2011).

$$1/J'_s = 1 + (HIFI)V_s \quad (1)$$

where $J'_s = (J/P_{irr})/(J/P_0) = P_0/P_{irr}$, P_0 (kPa) and P_{irr} (kPa) are the TMPs of virgin membrane and the initial TMPs after backwashing, respectively, and V_s (L/m²) is the volume filtered per unit area of membrane.

The surface tensions were determined using contact angle data of new, fouled and cleaned membranes. The contact angles were measured using a contact angle goniometer (JYSP-360, Beijing United Test Co., Ltd., Beijing, China) and the standard sessile drop method, and the membrane samples were vacuum-dried in an oven (45°C) for at least 72 hr. At least eight measurements were taken for each sample, and the highest and lowest values were discarded

before calculating the average. The probe liquid was placed on the membrane surface using a 2- μ L microsyringe. By performing contact angle analyses on membrane surface with at least three types of probe liquids with known surface tension (γ_l), the surface tension compositions of the membrane (γ_s^{LW} , γ_s^+ and γ_s^-) could be calculated from Eqs. (2) to (4).

$$\gamma_s^{Tot} = \gamma_s^{LW} + \gamma_s^{AB} \quad (2)$$

$$\gamma_s^{AB} = 2\sqrt{\gamma_s^+ \gamma_s^-} \quad (3)$$

$$(1 + \cos\theta)\gamma_l = 2\left(\sqrt{\gamma_s^{LW}\gamma_l^{LW}} + \sqrt{\gamma_s^+\gamma_l^+} + \sqrt{\gamma_s^-\gamma_l^-}\right) \quad (4)$$

where γ^{Tot} (mJ/m^2), γ^{LW} (mJ/m^2), γ^{AB} (mJ/m^2), γ^+ (mJ/m^2) and γ^- (mJ/m^2) are the total, Lifshitz–van der Waals (LW) component, Lewis acid–base (AB) component, electron acceptor component and electron donor component of surface free energy, respectively; the subscripts s and l denote membrane and probe liquids, respectively; θ ($^\circ$) is contact angle. The definitions of surface tension components were described elsewhere (Van Oss, 1993). The selection criterion for probe liquids and the procedure for calculating the surface tension components can be found in previous literature (Hwang et al., 2011). In this study, diiodomethane, Milli-Q water and glycerol (or formamide) were selected as the probe liquids.

A mass balance analysis, of which the eligibility was confirmed for the filtration of particles (Remize et al., 2010), was employed to calculate the amount of HA and Ca^{2+} in fouling layer during UF and backwashing. Here, the permeate, concentrate and deposit refer to foulants in the permeate, those remaining in the bulk solution and those deposited on membrane, respectively. In addition, the foulants deposited on membrane were further divided into two portions, i.e., the removable and residual, which refer to the HA removed by backwashing and the residual foulant after backwashing, respectively. The deposited foulants on membrane during filtration and residual foulants were calculated from Eqs. (5) and (6), respectively.

$$C_0V_0 = C_pV_p + C_cV_c + m_d \quad (5)$$

$$m_d = C_{rem}V_{rem} + m_{res} \quad (6)$$

where, C (mg/L) is the concentration, V (mL) is the volume; the subscripts 0, p, c, d and rem denote feed water, permeate, concentrate, deposit and removal, respectively; m_d (μg) and m_{res} (μg) are the mass of deposited foulants on membrane during filtration and the residual foulants, respectively.

2. Results and discussion

2.1. Effects of compositions of backwash water on TMP buildup during UF

The buildup of TMP and corresponding HIFI during the filtration of HA + Ca^{2+} and HA + Na^+ + Ca^{2+} are illustrated in Fig. 1. Note the fouling caused by HA in the presence of Ca^{2+} was primarily the formation of a cake layer (Appendix A Figs. S2 and S3). Generally, the development of TMP varied with the

compositions of backwash water used. For HA + Ca^{2+} (Fig. 1a), the fastest TMP increase occurred as CaCl_2 solution was used as the backwash water, with the TMP of 58 kPa at the V_s of 1000 L/m^2 . UFPBW ranked in the second place with the final TMP of 53 kPa. The HIFI of CaBW and UFPBW were 3.15 and 2.62 m^{-1} , respectively. By contrast, the fouling alleviation effect was much better when Milli-Q water was used to backwash the fouled membrane, with the HIFI of 1.26 m^{-1} . When the monovalent cations (Na^+) or organic compounds (HA) were present in the backwash water, a fouling alleviation efficiency comparable to (or superior) to that of MQBW was accessed with the HIFI of 0.35 and 0.73 m^{-1} , respectively. For HA + Na^+ + Ca^{2+} , UFPBW led in the largest TMP increase, followed by CaBW, indicating the low backwash efficiencies by hydraulic cleaning with both types of backwash water, with the HIFI of 7.55 and 6.97 m^{-1} , respectively. In the case of NaBW, HABW and MQBW, the TMP buildups were substantially retarded, with the HIFI of 0.34, 1.58 and 1.61 m^{-1} , respectively. Compared with the HA + Ca^{2+} feed, HA + Na^+ + Ca^{2+} caused more severe fouling, irrespective of the compositions of backwash water, probably due to the strengthened charge screening associated with the presence of Na^+ (Pinheiro et al., 1996), as demonstrated by the less net charge and smaller particle diameter (Appendix A Fig. S4), increasing the possibility for organics to adhere to membrane surface. NaCl solution was the best for membrane fouling alleviation, probably due to the difference in mechanisms involving in backwashing (Section 2.4).

2.2. Characteristics of membranes when using different types of backwash water

2.2.1. Variation in γ^{Tot}

γ^{Tot} , which is related to the surface hydrophobicity of a membrane, is a good indicator for fouling potential (Brant and Childress, 2002; Subhi et al., 2012). Firstly, the relations between γ^{Tot} and HIFI were investigated. Striking correlation between γ^{Tot} and the HIFI were found with R^2 values of 0.929 ($p = 3.545 \times 10^{-4}$) and 0.989 ($p = 1.372 \times 10^{-6}$) for the filtration of HA + Ca^{2+} and HA + Na^+ + Ca^{2+} , respectively (Appendix A Fig. S5a). Moreover, a positive linear relationship was also observed between γ^{Tot} and fouling (the reversible part) during the UF of wastewater by Subhi et al. (2012). Accordingly, γ^{Tot} could serve as an indicator of membrane fouling so as to distinguish the effects of compositions of backwash water (Van Oss, 1993).

The new membranes had an average γ^{Tot} value of $41.22 \pm 0.80 \text{ mJ}/\text{m}^2$. As presented in Fig. 2, the largest γ^{Tot} was observed for the fouled membranes without backwashing (w/o BW) with values of 45.90 ± 0.51 and $45.10 \pm 0.35 \text{ mJ}/\text{m}^2$ after filtering HA + Ca^{2+} and HA + Na^+ + Ca^{2+} , respectively. These results indicated that the deposit of foulants could boost the surface characteristic (i.e., free energy parameter) of UF membrane shifted to that of foulant (i.e., HA). As presented in Fig. 2a, when backwashing with CaCl_2 solution and UF permeate were performed, the values of γ^{Tot} were only slightly reduced, suggesting the low cleaning efficiencies of CaBW and UFPBW. By contrast, smaller γ^{Tot} values were observed for NaBW, MQBW and HABW, implying further reductions in fouling potentials of cleaned membranes. These results are well

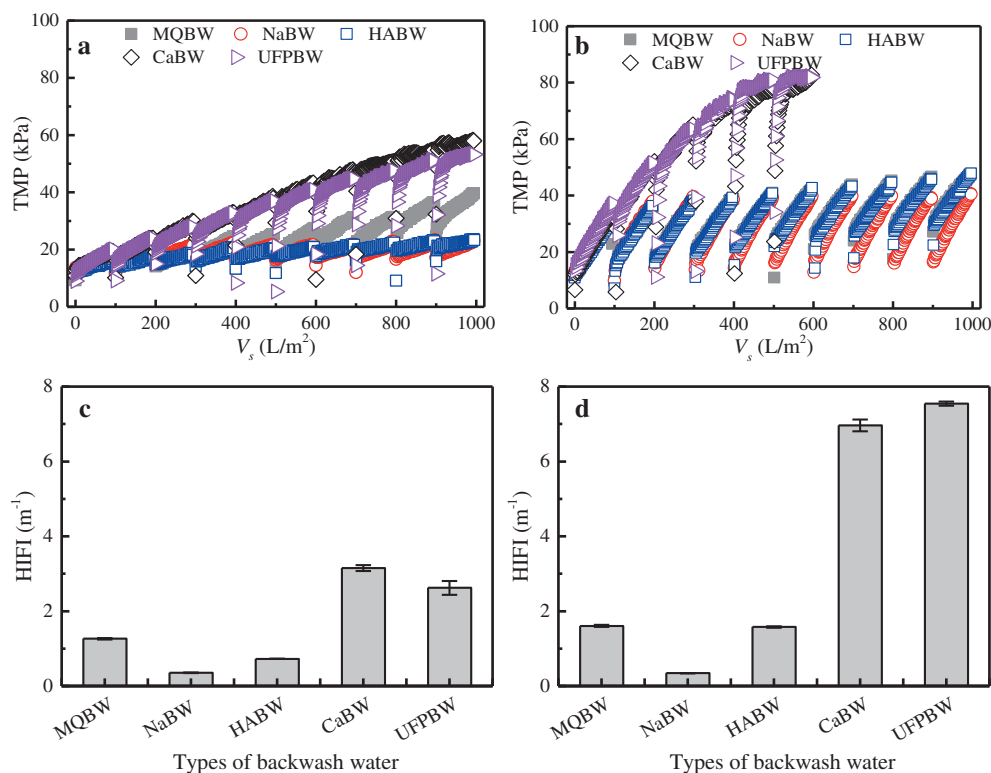


Fig. 1 – Trans-membrane pressure (TMP) buildup (a)(b) and corresponding hydraulically irreversible fouling index (HIFI) (c)(d) during UF with hydraulic cleaning using different types of backwash water: (a) (c) HA + Ca²⁺ and (b) (d) HA + Na⁺ + Ca²⁺.

consistent with the TMP buildup and the HIFI obtained in this study (Fig. 1). Similarly, regarding HA + Na⁺ + Ca²⁺ (Fig. 2b), in terms of γ^{Tot} , the priority of backwash water types in the hydraulic cleaning performance was in the order of NaBW > MQBW > HABW > CaBW \approx UFPBW.

2.2.2. Fourier transform infrared analysis

The ATR-FT-IR spectra of fouled and hydraulically cleaned membranes are provided in Fig. 3. For the new membrane, a variety of small absorbance peaks were observed within a wavenumber range between 1800 and 650 cm⁻¹. When the

membrane was fouled by HA + Ca²⁺ (Fig. 3a), the characteristic absorbance peaks of HA (Appendix A Fig. S7) occurred at the wavenumbers of 3400, 1630 and 1420 cm⁻¹. When backwashing with UF permeate or CaCl₂ solution was engaged, few changes in location and intensity of the peaks were observed, suggesting the inefficacy of UFPBW or CaBW in cleaning performance. In comparison, the intensity of the FT-IR spectra of membrane cleaned with Milli-Q water weakened. Further, the FT-IR spectra of cleaned membranes backwashed by the NaCl solution or HA solution were nearly identical to that of a new membrane, implying the total detachments of foulants from membrane

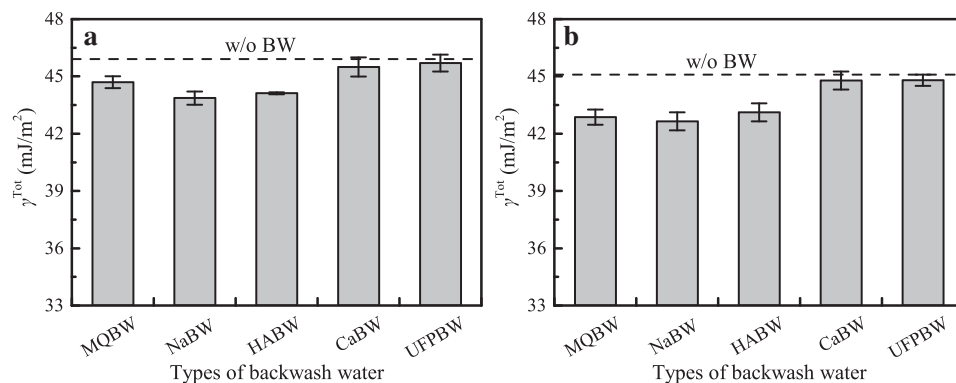


Fig. 2 – Variations in the γ^{Tot} of fouled membranes after filtration with different types of backwash water: (a) HA + Ca²⁺ and (b) HA + Na⁺ + Ca²⁺ ($n = 3$).

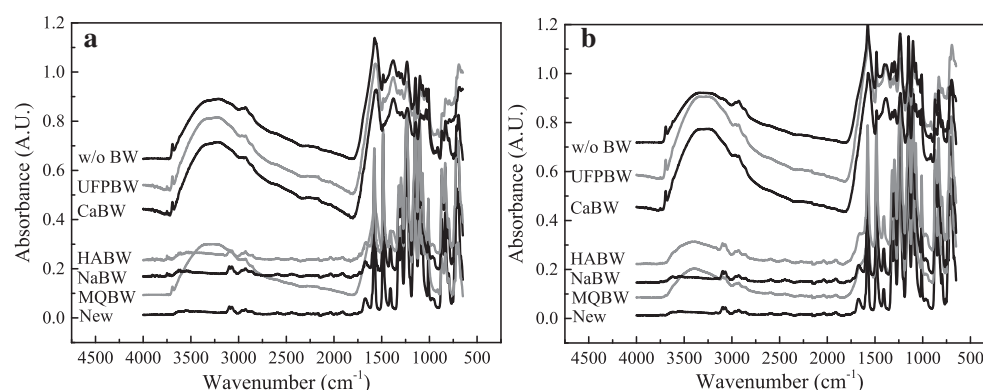


Fig. 3 – Fourier transform infrared spectra of membranes when using different types of backwash water: (a) HA + Ca²⁺ and (b) HA + Na⁺ + Ca²⁺.

surface during backwashing. These results further confirmed the superb fouling alleviation effects of backwashing with NaCl solution and HA solution.

When the feed water switched to HA + Na⁺ + Ca²⁺ (Fig. 3b), the FT-IR spectra of fouled membranes were generally similar to those with HA + Ca²⁺ as feed water, allowing some minor variations in the intensities of the characteristic peaks. For UFPBW and CaBW, the cleaning efficiencies were impaired to some extent as illustrating by the higher intensities of the characteristic peaks. Overall, the FT-IR results verified that the effect of the compositions of backwash water on fouling alleviation was significant. NaCl solution and HA solutions outperformed other types of backwash water independent on feed water, and Milli-Q water worked better under the circumstances with higher ionic strength.

2.2.3. Residual amounts of HA and its relations with fouling indicators

The net amounts of deposited HA were 37.69 ± 0.77 and 35.43 ± 0.92 $\mu\text{g}/\text{cm}^2$ (per unit area of membrane) in each cycle during filtration of HA + Ca²⁺ and HA + Na⁺ + Ca²⁺, respectively. Fig. 4 shows the detached and residual HA amounts after backwashing using various types of backwash water. As shown in Fig. 4a, UFPBW or CaBW exhibited a poor backwashing performance, with the ratios of residual HA exceeding 97.0%. A moderate hydraulic cleaning performance

was obtained when Milli-Q water was used as the backwash water, with approximately 44.6% of the deposited HA washed away. When NaBW or HABW was applied, a superb performance was observed with the ratios of the residual HA less than 2.1%. When the feed water switched to HA + Na⁺ + Ca²⁺, the performance of different types of backwash water was generally similar to that using HA + Ca²⁺ as feed water. The ratios of residual HA were 94.6% and 95.8% (Fig. 4b) using UF permeate and CaCl₂ solution, respectively, as the backwash water, indicating the poor cleaning performance. When the backwash water containing monovalent cation (Na⁺) or organic compound (HA) was adopted for hydraulic cleaning, a majority of deposited HA was washed away, with the ratios of residual HA as low as 1.6% and 5.4% (Fig. 4b), respectively, suggesting the positive role of NaCl solution and HA solution in hydraulic cleaning. For MQBW, only 2.9% of the residual HA remained attaching to the membrane surface, much less than that in the case of HA + Ca²⁺.

Moreover, the relations between the fouling indicators (i.e. HIFI and γ^{Tot}) and the residual HA amounts were investigated. The amount of residual HA related well to the HIFI with R^2 values of 0.915 ($p = 5.929 \times 10^{-4}$) and 0.978 ($p = 1.120 \times 10^{-5}$) (Appendix A Fig. S5b) during filtration of HA + Ca²⁺ and HA + Na⁺ + Ca²⁺, respectively. Meanwhile, striking correlations between the γ^{Tot} and the amount of residual HA were also found, with R^2 values of 0.963 ($p = 5.039 \times 10^{-5}$) and

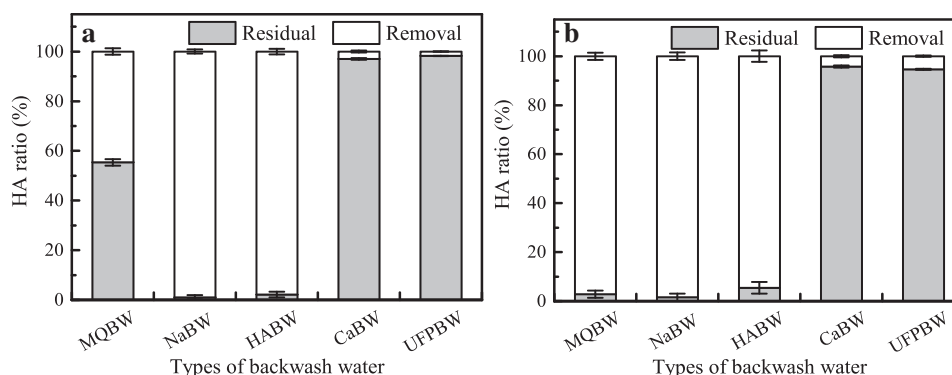


Fig. 4 – Transport of deposited HA during backwashing using different types of backwash water: (a) HA + Ca²⁺ and (b) HA + Na⁺ + Ca²⁺ ($n = 3$).

0.983 ($p = 4.815 \times 10^{-6}$) (Appendix A Fig. S5c) for filtering HA + Ca²⁺ and HA + Na⁺+Ca²⁺, respectively.

2.3. Release of Ca²⁺ from fouling layer during backwashing

2.3.1. Residual amounts of Ca²⁺ in the fouling layer

Ca²⁺ plays an important role in the formation of HA-Ca aggregations in fouling layer by binding and complexing with carboxylic groups of HA (Li and Elimelech, 2004). The existence of Ca²⁺ in HA fouling layer was identified through EDS measurements (the EDS spectra of fouled membranes w/o BW are shown in Appendix A Fig. S6). The average amounts of deposited Ca²⁺ in each filtration cycle were 2.15 and 1.72 µg/cm² (per unit area of membrane) during UF of HA + Ca²⁺ and HA + Na⁺+Ca²⁺, respectively. In the presence of Ca²⁺, the HA layer may be compacted and strongly adhere to the membrane surface. Therefore, breaking HA-Ca aggregations is indispensable to achieve effective hydraulic cleaning.

Fig. 5 shows the detached and residual Ca²⁺ amounts after backwashing using various types of backwash water. When HA + Ca²⁺ was used as the feed water (Fig. 5a), backwashing with NaCl or HA solution could obtain a high release of Ca²⁺ from the fouling layer with residual ratios of Ca²⁺ less than 16.2%. MQBW could also achieve a considerable release of Ca²⁺ with 55.7% of total Ca²⁺ dissolved in the backwash waste. However, when UF permeate and CaCl₂ solution were used as the backwash water, a minor release of Ca²⁺ from the cake layer was observed. When the feed water switched to HA + Na⁺+Ca²⁺ (Fig. 5b), the release of Ca²⁺ was generally similar to that during filtration of HA + Ca²⁺. A high release of Ca²⁺ was achieved using NaBW, HABW, and MQBW, with the ratios of residual Ca²⁺ of 10.1%, 8.5% and 11.8%, respectively. By contrast, the CaBW and UFPBW showed limited abilities for releasing Ca²⁺ from the fouling layer, with the residual Ca²⁺ content of 86%–90% for both types of backwash water. To verify the mass balance results of Ca²⁺, the contents of elemental Ca in fouling layer of fouled membranes cleaned by various types of backwash water were identified through EDS measurement, with the results listed in Table 2. As shown in Table 2, the relative contents of elemental Ca were consistent with the amounts of residual Ca²⁺ which were calculated in the mass balance analysis (Fig. 5).

Table 2 – Elemental Ca contents on the surfaces of the fouled membranes under different types of backwash water identified by an energy dispersive spectrometer (EDS).

Backwash type	HA + Ca ²⁺		HA + Na ⁺ + Ca ²⁺	
	wt.%	at.%	wt.%	at.%
MQBW	2.79	1.01	1.27	0.47
NaBW	0.51	0.18	0.86	0.32
HABW	0.49	0.18	0.79	0.28
CaBW	5.83	2.08	5.73	2.03
UFPBW	9.95	3.57	7.41	2.69

wt.%, weight percentage; at.%, atom percentage.

Similar to the case of residual HA (Fig. 4), a significant difference in residual Ca²⁺ for MQBW between HA + Ca²⁺ and HA + Na⁺+Ca²⁺ was also observed. This was likely attributed to the difference in fouling layer forming by HA + Ca²⁺ and HA + Na⁺+Ca²⁺. As stated above, the amounts of deposited HA for both feeds during each cycle were comparable, while the total Ca²⁺ amount in fouling layer formed by HA + Na⁺+Ca²⁺ was approximately 80% of that by HA + Ca²⁺. Meanwhile, there was a certain amount of Na⁺ in the fouling layer during UF of HA + Na⁺+Ca²⁺ solution, as identified through the EDS spectra (Appendix A Fig. S6).

2.3.2. Correlations between Ca²⁺ and HA by hydraulic cleaning

The relations between residual HA and residual Ca²⁺ after hydraulic cleaning were analyzed, with the results illustrated in Fig. 6. Striking linear relationships were observed with R² ranging from 0.808 to 0.977, irrespective of the types of backwash water and feed water, indicating the simultaneous release of HA and Ca²⁺ during hydraulic cleaning. These observations are well consistent with the general recognition that Ca²⁺ plays a significant role in agglomerating HA molecules and bridging HA to membrane surface. Meanwhile, the slopes of the fitting curves for the NaCl solution cleaning were the largest, followed by HABW, and then MQBW. In other words, compared with MQ water cleaning, the ratio of the residual HA and residual Ca²⁺ in fouling layer (i.e., HA/Ca²⁺ in the fouling layer after backwashing) decreased when NaCl

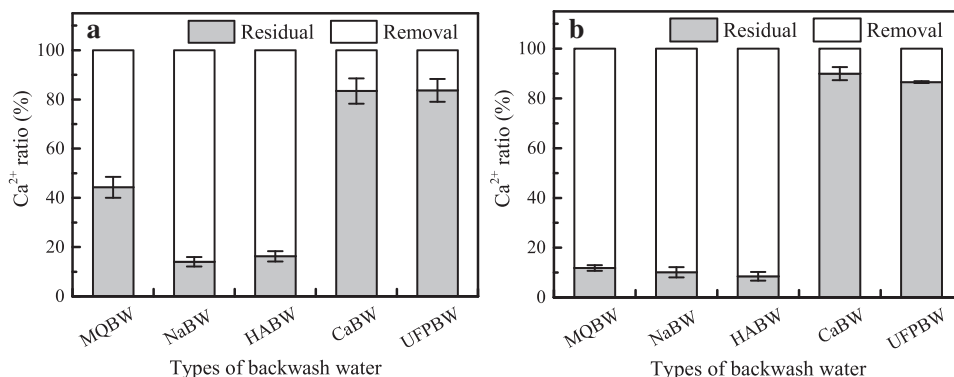


Fig. 5 – Mass balance of deposited Ca²⁺ during backwashing with different types of backwash water: (a) HA + Ca²⁺ and (b) HA + Na⁺ + Ca²⁺ (n = 3).

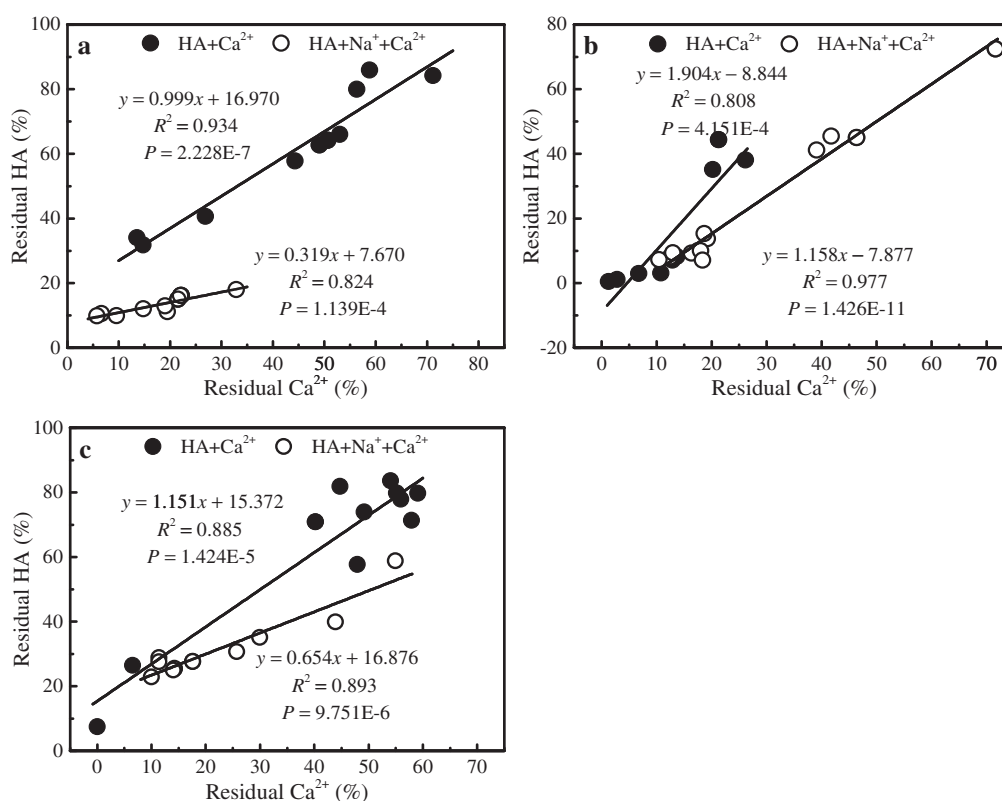


Fig. 6 – Correlations between residual HA and residual Ca^{2+} under different types of cleaning solutions: (a) Milli-Q water, (b) NaCl solution and (c) HA solution.

solution or HA solution cleaning was performed. This was probably attributed to the partial replacement of Ca^{2+} by Na^{+} in the intermolecular complexes, and the competing complexation of Ca^{2+} in fouling layer with negative-charged groups in PES membranes and these in HA molecules, respectively. The detailed mechanism analysis was discussed in Section 2.4.

2.4. Mechanisms involving in backwashing with different types of backwash water

2.4.1. Double layer release

During periodical backwash with UF permeate, high salt concentrations in the backwash water prevented effective fouling layer dispersion (Li et al., 2009; Resosudarmo et al., 2013), and the primarily mechanism involved in UFPBW was the backward hydrodynamic force. By comparison, MQBW significantly improved the dispersion of the fouling layer since Milli-Q water is nearly free of any ions and organics. This is primarily attributed to release of the compressed electric double layer (Li et al., 2009; Resosudarmo et al., 2013), loosening the compact fouling layer and making foulant mobile. Then, the swelled fouling layer is transported away from the membrane surface by the backward hydrodynamic force. However, only part of the HA can be removed by MQBW, likely because the bonds between the HA and the membrane with Ca^{2+} bridging are strong enough to resist the hydrodynamic forces. The dispersion potential of Milli-Q water is not sufficient large to break up the Ca-HA bonds. Similar behavior

was reported during the hydraulic cleaning of membranes fouled with NOM (Li et al., 2012b) or model seawater (Resosudarmo et al., 2013) using backwashing with DI water.

2.4.2. Ion exchange

By comparing the cleaning behaviors of NaBW, CaBW and MQBW, the existence of ion exchange reaction can be verified. Specifically, the superior cleaning efficiency of NaBW to MQBW is attributed to ion exchange between Na^{+} and bound Ca^{2+} in fouling layer, as illustrated by the existence of Ca^{2+} in backwash waste and the larger slopes of the fitting curves (the residual HA vs. residual Ca^{2+}) in case of NaBW (Figs. 6a and b) than that of MQBW. Meanwhile, the higher cleaning efficiency of MQBW for feeding with HA + Na^{+} + Ca^{2+} than that for HA + Ca^{2+} may also result from the ion exchange reaction due to the presence of a certain amount of Na^{+} in the fouling layer, as identified through EDS measurement (Appendix A Fig. S6). In addition, the significant differences in the cleaning performance between NaBW and CaBW may also provide additional support for ion exchange, since cations with different valences (Na^{+} and Ca^{2+}) were included in both types of backwash water. Therefore, during backwashing with NaCl solution, the substitute (i.e., Na^{+}) breaks down the cross-linked HA-Ca-HA and HA-Ca-membrane, making the foulants easier to detach from membrane surface. The ion exchange between Na^{+} and bound Ca^{2+} has been reported for cleaning gel fouled membranes using NaCl solution (Lee and Elimelech, 2007).

Table 3 – Comparison of cleaning performance for different types of backwash water.

Backwash type	Mechanisms involved	Residual HA	Residual Ca^{2+}	HIFI
MQBW	Double layer release Fouling layer swelling	55.4%/2.9%	44.3%/11.8%	1.26/1.61
NaBW	Ion exchange Fouling layer swelling	1.0%/1.6%	14.1%/10.1%	0.35/0.34
HABW	Double layer release Competitive complexation Fouling layer swelling	2.1%/5.4%	16.2%/8.5%	0.73/1.58
CaBW	×	97.0%/95.8%	83.4%/90.0%	3.15/6.97
UFPBW	×	98.2%/94.6%	83.6%/86.6%	2.62/7.54

HIFI: hydraulically irreversible fouling index.

2.4.3. Competitive complexation

Since cations are not included in Milli-Q water and HA solution, the only difference between Milli-Q water and HA solution resulted from the organic compound (HA). By comparing the hydraulic cleaning behaviors of MQBW and HABW, the competitive complexation involved in HABW was verified. To be specific, HABW outperforms MQBW in alleviating membrane fouling. It may be assumed that HA molecules in the backwash water take effect by competing complexation of Ca^{2+} in fouling layer with charged groups of PES membranes, because the bond between the Ca^{2+} and the carboxyl groups in the HA was relatively stronger than that between the Ca^{2+} and the sulfonyl groups in the PES membrane (Ahn et al., 2008). This was identified by the existence of Ca^{2+} in backwash waste and the greater slopes of the fitting curves (the residual HA vs. residual Ca^{2+}) in the case of HABW (Appendix A Fig. 6a and c). Therefore, when the HA solution was used as the backwash water, some of the Ca^{2+} were potentially removed from the fouling layer by bonding with the substantial amount of HA in the backwash solution, resulting in a better backwash performance.

Moreover, the swelling of fouling layer occurred usually accompanying with other foulant removal mechanisms. Regarding the CaBW, the release of the electric double layer and swelling of the fouling layer would not occur due to the high ionic strength of the backwash water. Meanwhile, ion exchange and competitive complexation did not occur due to the absence of Na^+ and HA, respectively. Therefore, the CaBW showed the worst cleaning performance in removing HA fouling. Regarding the UFPBW, although Na^+ was present in the backwash water, little ion exchange occurred due to the simultaneous existence of substantial amount of Ca^{2+} . Although competitive complexation may play a role, the Ca^{2+} could consume HA and decrease the free HA concentration. Thus, the backwash performance of the UFPBW was limited. According to the proposed mechanisms involved in the backwash processes with Milli-Q water, NaCl solution and HA solution, the amount of residual foulant, extent of irreversible fouling, and the efficiency of each backwash water composition are summarized in Table 3 and Fig. 7.

3. Conclusions

- (1) The backwash water compositions had significantly affected the alleviation of membrane fouling by hydraulic cleaning. Milli-Q water backwashing controlled membrane fouling to some extent. The existence of monovalent cations (Na^+) and organic compounds (HA) in the backwash water could enhance the alleviation of HA fouling, whereas divalent cations (Ca^{2+}) significantly decreased the backwash efficiency.
- (2) Variations in total surface tension and FT-IR spectra analysis confirmed that the superior backwash performance of the NaCl and HA solutions compared with the other backwash water compositions and the negative impacts associated with the presence of Ca^{2+} .
- (3) In the backwashing process, the release of HA and Ca^{2+} from the fouling layer was simultaneous, and the hydraulic irreversible fouling was strongly correlated with the residual amount of HA which was closely related to the amount of residual Ca^{2+} .
- (4) The alleviation of membrane fouling by backwashing was governed by various mechanisms, and ion exchange and competitive complexation resulted in better

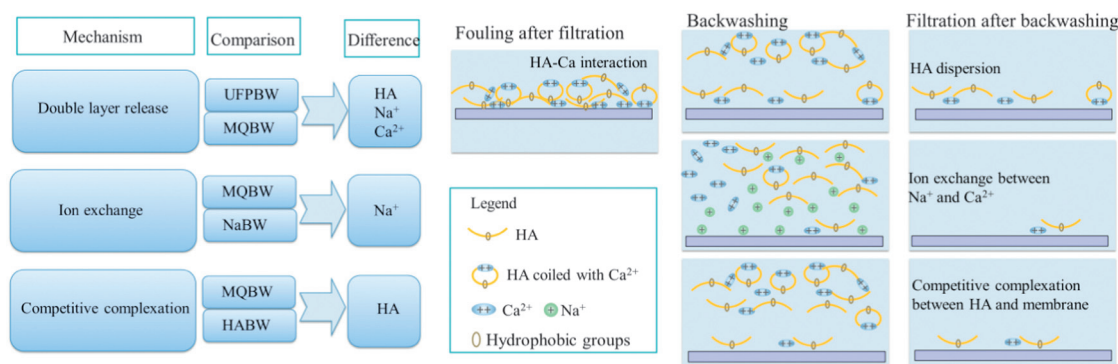


Fig. 7 – Proposed mechanisms for UF membrane fouling alleviation involving in backwashing.

backwash performance when Na⁺ and HA, respectively, were involved.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.jes.2015.09.005>.

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