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Effect of filtration mode and backwash water on hydraulically irreversible fouling of ultrafiltration membrane

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Abstract

To investigate the effect of filtration mode and backwash water on ultrafiltration (UF) membrane performance, total fouling index (TFI) and hydraulic irreversible fouling index (HIFI) for constant pressure (CP) filtration and constant flux (CF) filtration were compared. Kaolin, humic acid (HA) and sodium alginate (SA) solutions were used as feed solutions, and then the fouled membranes were backwashed with UF permeate or ultrapure water. Results showed that when the kaolin solution was filtrated, the filtration mode had a limited effect on the membrane fouling, and low TFI and HIFI were observed. When HA and SA solutions were filtrated, the TFI of UF under CP mode was comparable to or slightly higher than that under CF mode. Higher TFI was observed at a hydrophobic membrane, a high filtration strength, a high feed concentration, a low pH, a high ionic strength, and a low Ca^{2+} concentration. When the UF permeate was used as the backwash water, the HIFI for the UF operated under CF mode was significantly less than that under CP mode. Low irreversible fouling was obtained when the ultrapure water was used for backwashing, and the HIFI for the UF under different filtration modes was almost identical.

Keywords: Ultrafiltration; Constant pressure; Constant flux; Membrane fouling; Backwash water

1 Introduction

The application of ultrafiltration (UF) membrane in potable water production has increased significantly in the past decades (Zheng et al., 2012; Ang et al., 2015) due to its good performance (Jacangelo et al., 1997). However, membrane fouling which results in deterioration in membrane permeability and increases the operating costs is a major obstacle for widespread application of UF (Shi et al., 2014). The extent of (irreversible) membrane fouling greatly correlates with membrane properties, feed characteristics, and operational conditions (Chang et al., 2015a). Regarding filtration modes of UF membranes, a great majority of bench-scale UF tests has been carried out under constant pressure (CP) mode (e.g., Katsoufidou et al., 2007; Jermann et al., 2008). Although many full-scale UF systems are also operated under CP mode, most of these applications are performed under constant flux (CF) mode. Obtaining the possible link between CP and CF operation during filtration and cleaning may be helpful for a better control of membrane fouling and an improvement of cleaning efficiency.

On one hand, there might be an intrinsic relation between CP and CF filtration since the fouling of both filtration modes could be described using a unified expression (Kanani and Ghosh, 2007; Huang et al., 2008; Sioutopoulos and Karabelas, 2012; Iritani et al., 2015). Iritani et al. (2015) successfully developed a combined mode which described well the flux decline behaviors in CP filtration and the pressure increase behaviors in CF filtration during filtration of very dilute colloids. Sioutopoulos et al. (2012) indicated that organic fouling behaviors of UF membranes

in terms of resistance versus pressure drop across the cake for constant deposited mass under CP and CF filtration modes were correlated very well in the early stage. Based on the relation between UF fouling under both filtration modes, the flux decline of protein solutions in CP filtration was predicted from a CF based mathematical model (Kanani and Ghosh, 2007). On the other hand, there was a difference in membrane performance between CP and CF filtration modes. Some reports indicated that it was preferable to filtrate at a CF mode than a CP mode in the initial stage of UF, because the CF filtration mode avoided overfouling (Defrance and Jaffrin, 1999). While published literature also demonstrated that the UF membrane resistance was much higher in CF mode than in CP mode tests at high fluxes (Miller et al., 2014). Results from Tarabara et al. (2002) indicated that an UF membrane operating under a CP mode yielded a higher permeability compared to a CF mode when polystyrene particles were filtrated. In addition, there was not a direct comparison between the UF fouling under CP filtration and under CF filtration, because of the different dependencies of modified fouling index under both filtration modes (Sim et al., 2011). Thus, the similarity and difference of UF fouling between CP filtration and CF filtration needs to be further explored.

In the well-documented researches mentioned before, the UF tests primarily focus on total membrane fouling rather than hydraulically irreversible fouling because a backwash step was not involved (Defrance and Jaffrin, 1999; Tarabara et al., 2002; Kanani and Ghosh, 2007; Sim et al., 2011; Sioutopoulos and Karabelas, 2012, 2016; Miller et al., 2014). As a key backwash parameter, backwash water quality greatly

influences backwash efficiency and hydraulically irreversible fouling (Resosudarmo et al., 2013; Chang et al., 2015b). In most bench-scale UF tests, ultrapure water (or deionized water) is employed as backwash water under CP filtration mode (Katsoufidou et al., 2007; Jermann et al., 2008), whereas UF permeates have been widely used for backwashing in pilot-scale and full-scale UF membrane systems. Recently, some research groups (Abrahamse et al., 2008; Li et al., 2009, 2010a, 2010b, 2011a, 2011b, 2012a, 2012b; Ma et al., 2013; Chang et al., 2015b, 2016) have investigated the roles of backwash water quality (UF permeate versus ultrapure water) in total or irreversible membrane fouling. The UF tests in these studies are operated in a CF filtration mode, but no information about the effects of backwash water quality on membrane fouling under different filtration modes could be obtained. Furthermore, inconsistent results about backwash behaviors may be obtained from different scale experiments, especially when different types of backwash water are employed.

In addition, different types of feed solutions may also attribute to inconsistent results of UF membranes operating under CP and CF filtration modes in different researches. In published studies, particles (Tarabara et al., 2002; Sim et al., 2011; Iritani et al., 2015) and organics (Kanani and Ghosh, 2007; Sioutopoulos and Karabelas, 2012, 2016; Miller et al., 2014) were usually employed as the feeds. Further, model foulants including kaolin (KL), humic acid (HA) and sodium alginate (SA) which were commonly used as representatives of inorganic particulate matter, humic substance and polysaccharide in natural water (Yuan and Zydney, 2000; Katsoufidou et al., 2005, 2007; Jermann et al., 2007; Tian et al., 2013) were employed

in this study. Therefore, in order to compare roles of filtration modes and backwash water in (irreversible) membrane fouling, UF tests using several membrane materials, filtration strengths, and feed solutions with different feed concentrations, pH values, ionic strengths and Ca^{2+} concentrations, were carried out. Specifically, this work was performed with twofold objectives: (a) to investigate the effect of filtration mode on the total fouling behaviors, and (b) to evaluate the effect of filtration mode and backwash water on hydraulically irreversible fouling of UF membranes.

2 Materials and Methods

2.1 Feed water and backwash water

Unless otherwise specified, all reagents and chemicals were analytical grade. Ultrapure water which was obtained from a water filtration system (EMD Millipore Corp, Billerica, USA) with a conductivity of 0.055 μS cm^{-1}, was used to prepare feed water. KL, HA and SA were purchased from Sigma-Aldrich Co., LLC (St. Louis, USA), and the primary characteristics of these model foulants could be found in Table S2 (Supporting Information). Fresh KL solutions were directly prepared and placed in an ultrasonic bath for 5 min before use (Jermann et al., 2008). The preparation of HA and SA stock solutions (2 g L^{-1}) could be found in our previous studies (Chang et al., 2015b, 2016), and the feed solutions were prepared by diluting the stock solutions with ultrapure water.

Unless otherwise stated, the pH of each solution was adjusted to 7.5 using 1 mol L^{-1} NaOH or HCl. KL with a concentration of 50 mg L^{-1} which resulted in a turbidity of about 50 NTU, was used as a typical particulate matter in surface water. The total

organic carbon (TOC) concentrations of surface waters often fall in the range of 1 to 20 mg L^{-1} (Crittenden et al., 2012). Typically, 5 mg L^{-1} of HA (TOC ~2.2 mg L^{-1}) and 2 mg L^{-1} of SA (TOC ~0.5 mg L^{-1}) were chosen to simulate the contents of humic substances and polysaccharide in natural water (Chang et al., 2015b, 2016). The concentrations of Ca^{2+} and ionic strengths for UF tests were usually 0-4 mmol L^{-1} and 0-20 mmol L^{-1}, respectively (Jermann et al., 2007; Katsoufidou et al., 2010; Tian et al., 2013; Chang et al., 2015b, 2016). Thus, the ionic strength (10 mmol L^{-1}) and Ca^{2+} concentration (0.5 mmol L^{-1}) were adjusted with NaCl and $CaCl_2$ stock solution, respectively. To investigate the effect of filtration mode on membrane fouling when feeding with different concentrations, pH, ionic strengths and Ca^{2+} concentrations, the feed solutions with different compositions were used, as summarized in Table S1 (Supporting Information). Ultrapure water and UF permeate were employed as the backwash water for cleaning the fouled membranes under CP filtration and under CF filtration.

2.2 Experimental setup and UF membranes

The setups used for the UF tests under CP filtration and under CF filtration are illustrated in Fig. S1 (Supporting Information). Under both filtration modes, UF tests were conducted in 400 mL unstirred UF cells (Amicon 8400, Millipore, USA). Each membrane was placed in the bottom of the cell with its glossy side towards the feed solution during filtration. Unless otherwise specified, a driven pressure of 40 kPa was employed during filtration and backwashing for CP mode, this value was chosen because it's a normal pressure for UF tests in drinking water treatment, and the same

pressure was used during filtration and backwashing as reported elsewhere (Jermann et al., 2007; Qu et al., 2014). A CF of 180 L m^{-2} h^{-1} (LMH) was used during filtration and backwashing to produce a similar fouling index under both CP and CF modes.

Unless otherwise stated, polyethersulfone (PES) flat-sheet membranes obtained from Pall Corp. (Pt. Washington, USA) were used. Besides, two other commercially available flat-sheet UF membranes, i.e., polyvinylidene fluoride (PVDF) and cellulose acetate (CA) membranes from Hangzhou Tianchuang Waterpure Equipment Co., Ltd (Hangzhou, China), and EMD Millipore Corp. (Billerica, USA), were also investigated. The effective filtration area of each membrane disk was 41.8 cm^2, with the same MWCO of 100 kDa for all the UF membranes. The primary characteristics of PVDF, PES and CA membranes were summarized in Table S3 (Supporting Information). Virgin membranes were rinsed carefully prior to use to remove preservatives. The membranes were soaked in ultrapure water for 24 h, and the water was replaced at least three times. Ultrapure water was then filtered through the membranes until the TOC content of the filtrate was zero.

2.3 Experimental protocol and backwash evaluation

The tests were performed at room temperature (21±2 °C). To eliminate differences in the throughput per filtration time due to differences in permeate fluxes (Field and Pearce, 2011; Chang et al., 2015a) or applied pressure under both filtration modes, the volume filtered per unit area of membrane (V_s, L m^{-2}) rather than the filtration time was used to measure the throughout. Each UF test consisted of the following steps: (1) filtration of ultrapure water for 50 mL, where the average flux or average TMP is

denoted as J_0 or P_0; (2) filtration of prepared feed solutions for 400 mL, where the flux decline (J_f) or TMP buildup (P_f) was recorded; (3) filtration of ultrapure water for 50 mL, with the average flux or average pressure as J_1 or P_1; (4) backwashing with the prepared backwash water solution for 50 mL by placing the reverse side of membrane upwards (Section S1, Supporting Information); and (5) filtration of ultrapure water for 50 mL, where the average flux or average pressure is denoted as J_2 or P_2. The filtration strengths for UF tests under CP and CF modes are also listed in Table S1 (Supporting Information). Each test was carried out three times, and the average value was reported. The flux decline under CP filtration and TMP buildup under CF filtration for all the UF tests are illustrated in Figs. S3-S8 (Supporting Information).

The performance of UF membrane during periodic filtration-backwash was evaluated via two indexes, i.e., total fouling index (TFI) and hydraulic irreversible fouling index (HIFI). The values of TFI were measured by linear regression method (Huang et al., 2008; Nguyen et al., 2011; Zupančič et al., 2014).

$$1/J_s'=1+(TFI)V_s \quad (1)$$

where J_s' is the normalized specific flux, under CP mode, $J_s'= (J_f/P_0)/(J_0/P_0)=J_f/J_0$, J_0 and J_f (LMH) are the fluxes of virgin membrane and the fluxes during filtration, respectively; under CF mode, $J_s'= (J/P_f)/(J/P_0)=P_0/P_f$, P_0 and P_f (kPa) are the TMPs of virgin membrane and the TMPs during filtration, respectively, and V_s (L m^{-2}) is the volume filtered per unit area of membrane. HIFI was calculated from the fouling curve via a "two-point" method, as described in previous literature (Huang et al., 2008;

Nguyen et al., 2011).

2.4 Analytical method

The HA concentrations were determined by UV absorbance measurements at the wavelength of 254 nm (UV_{254}) using a UV/Vis spectrophotometer (T6, Beijing Purkinje General Instrument, Beijing, China). UV_{254} was calibrated for HA concentration over the range of 0-50 mg L^{-1} with R^2 more than 0.999. The SA concentrations were measured by a TOC analyzer (multi N/C 2100, Jena, Germany). The concentrations of Ca^{2+} in solutions were measured using an inductively coupled plasma optical emission spectroscopy (Optima 8300, Perkin-Elmer Inc., Waltham, USA). The zeta potential of the membrane surface was measured by a streaming-current electro-kinetic analyzer (Surpass, Anton Paar GmbH, Graz, Austria) with an electrolyte solution of 1 mmol L^{-1} KCl at a pH of 7.5. The zeta potentials of the KL, HA, and SA solutions and sizes of HA and SA solutions were determined using a Zetasizer (Nano ZS90, Malvern, USA). The particle size of KL solution was determined by the Malvern 2000 (Malvern, USA). The contact angles of UF membranes were measured using a contact angle goniometer (JYSP-360, Beijing United Test Co., Ltd., Beijing, China).

To statistically evaluate the effects of filtration mode on TFI and HIFI under different types of membrane materials, filtration strengths, feed concentrations, pH values, ionic strengths and Ca^{2+} concentrations, a two-way analysis of variance (ANOVA) was conducted using SPSS Statistics software (IBM Corp., Armonk, USA).

3 Results and discussion

3.1 Effect of filtration mode under different membrane materials

Fig. 1 presents the effect of filtration mode on TFI and HIFI when different types of UF membranes were employed. As shown in Fig. 1a, during the filtration of KL solution, there was no significant difference in TFI for PES membranes operating under CP and CF modes ($p>0.05$), but the TFI under CP mode was less than that under CF mode for both PVDF and CA membranes. When feeding with HA and SA solutions, the TFI for PES membranes was not significantly influenced by filtration mode ($p>0.05$). However, there was not a direct comparison for CP mode and CF mode in TFI during the filtration of SA solutions, as the TFI was higher under CF filtration for PVDF membrane, while it was smaller under CF filtration for CA membrane ($p<0.05$).

As presented in Fig. 1b, a low HIFI was observed for KL fouled membrane after UF permeate backwashing, and there was no significant difference in HIFI between CP filtration and CF filtration ($p>0.05$), regardless of membrane materials. When feeding with HA solutions, the HIFI under CF mode was much less than that under CP mode ($p<0.05$). As for SA feed, the HIFI values for PES and CA membranes operating in a CF mode was much smaller than that in a CP mode, while there was not a significant difference in HIFI between CP filtration and CF filtration for PVDF membrane possibly due to the higher TFI of PVDF under a CF mode compared to a CP mode (Fig. 1a). As shown in Fig. 1c, low HIFI values were found when ultrapure water was employed as backwash water, compared to UF permeate backwashing (Fig.

1b). During filtration of KL solutions, the *p* values for PVDF, PES and CA membranes were 0.310, 0.507 and 0.130, respectively, suggesting identical HIFI values between CP filtration and CF filtration modes statistically. During the filtration of HA or SA solutions, UF membranes operating under CP filtration and CF filtration resulted in similar HIFI ($p>0.05$), irrespective of membrane materials. Although some researchers stated that it was preferable to filtrate at a CF mode than a CP mode (Field et al., 1995; Defrance and Jaffrin, 1999) based on the total fouling of UF (or microfiltration) membrane, the irreversible part has not been reported yet. When UF permeate was used as backwash water, CF filtration mode outperformed CP filtration mode in alleviation of irreversible fouling by organics, but the HIFI was not significantly influenced by filtration mode when the UF membrane was backwashed with ultrapure water.

Regarding membrane materials, the PVDF membrane sustained the most severe fouling, while the values of TFI and HIFI for CA membranes were the least, irrespective of filtration modes. In comparison, a moderate fouling occurred for PES membrane among the three types of UF membranes during filtration of all the feed solutions tested under CP and CF filtration modes (Figs. 1 and S3). This phenomenon was probably explained by the cohesive free energy of UF membranes, with the values of -58.17, -34.51 and 20.94 mJ m^{-2} for the PVDF, PES and CA membranes, respectively (Table S3, Supporting Information). Considering the intrinsic difference in characteristics of UF membranes (Chang et al., 2015b), different fouling behaviors under both filtration modes were observed for PVDF and CA membranes when the

filtration pressure (40 kPa) under CP mode and flux (180 LMH) under CF mode were chosen based on PES membrane. Therefore, the PES membrane was used as the typical UF membrane for the following sections.

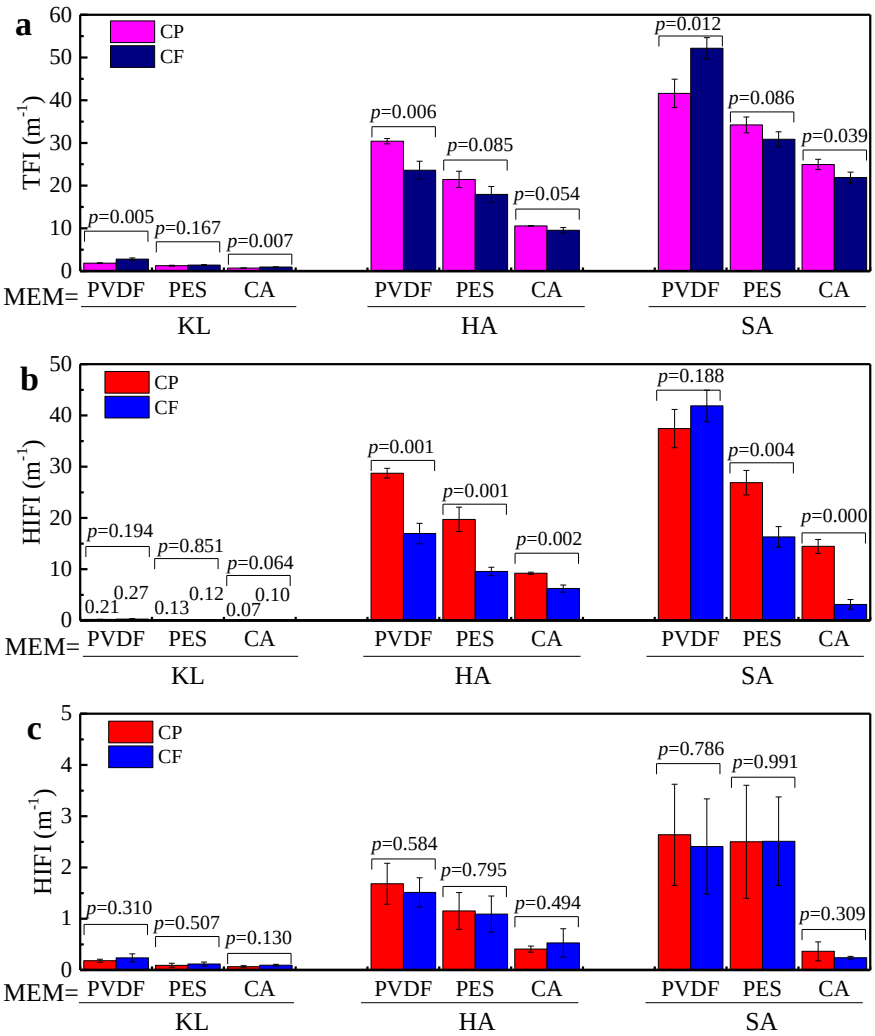

Fig. 1 Effect of filtration mode on membrane fouling under different types of membrane materials: (a) TFI, (b) HIFI using UF permeate backwashing and (c) HIFI using ultrapure water backwashing (error bars represent standard deviations; n=3). *p* values obtained from ANOVA (α=0.05) are shown in the figure. *p* values above each membrane indicate the difference in filtration mode.

3.2 Effect of filtration mode under different filtration strengths

Fig. 2 presents the effect of filtration mode on the TFI and HIFI when UF

membranes were operated under different filtration strengths. Seen from Fig. 2a, the TFI of UF membranes during the filtration of KL solutions was low, and the TFI under CP filtration was comparable to or less than that under CF filtration. During filtration of HA solutions, the TFI under different filtration strengths was not significantly influenced by filtration mode (p>0.05). The average TFI under both filtration modes ranged from 15.63 to 23.58 m^{-1} as the filtration strengths increased from 0.5 to 1.5. When feeding with SA solutions, the TFI of UF membrane operating under CP filtration at the least filtration strength (Lp/Lp_0=0.5) was higher than that under CF filtration. In comparison, there was not an obvious difference in TFI for UF membrane operating under both filtration modes (p>0.05), indicating that the total fouling of UF membrane operating under CF filtration was comparable to or slightly less than that under CP filtration. Moreover, the TFI increased almost linearly when filtration strengths increased from 0.5 to 1.0 and 1.5 (Fig. 2a), no over-fouling obtained was attributed to the filtration strengths investigated didn't exceed the critical values (Field and Pearce, 2011).

As illustrated in Fig. 2b, during the filtration of KL solutions, there was no significant difference in HIFI after UF permeate backwashing between UF membrane operating under CP filtration and under CF filtration (p>0.05) at different filtration strengths. The average HIFI increased from 0.09 to 0.18 m^{-1} with increasing in relative filtration strengths from 0.5 to 1.5. As for HA fouled membrane after UF permeate backwashing, the HIFI under CP filtration was much larger than that under CF filtration (p<0.05), with the HIFI ranging from 15.19 to 21.47 m^{-1} and from 6.42

to 16.27 m^{-1}, respectively. When the SA fouled membrane was backwashed with UF permeate, the HIFI values under CP filtration mode were 12.30, 26.86 and 29.76 m^{-1} as the filtration strengths increased from 0.5 to 1.0 and 1.5, respectively. In comparison, lower HIFI values were observed under CF filtration mode, with the average values ranging from 3.47 to 18.10 m^{-1}. Using ultrapure water as backwash water, much lower HIFI values were obtained as compared to UF membranes backwashed with UF permeate during filtration of HA or SA solutions (Figs. 2b-2c), the priority of ultrapure water backwashing has been reported in previous studies (Resosudarmo et al., 2013; Chang et al., 2015b, 2016). The HIFI of UF membranes cleaned by ultrapure water was hardly influenced by filtration mode for the three types of feed solutions (p>0.05), as shown in Fig. 3c. Meanwhile, the HIFI increased with the increase in filtration strength, the average values were 0.06-0.16, 0.83-2.27 and 1.57-4.68 m^{-1} for KL, HA and SA solutions, respectively (Fig. 2c). Increasing filtration strength, the obvious increase in HIFI after ultrapure water backwashing could be possibly due to the existence of a smaller critical filtration volume at a higher filtration strength (Bessiere et al., 2005).

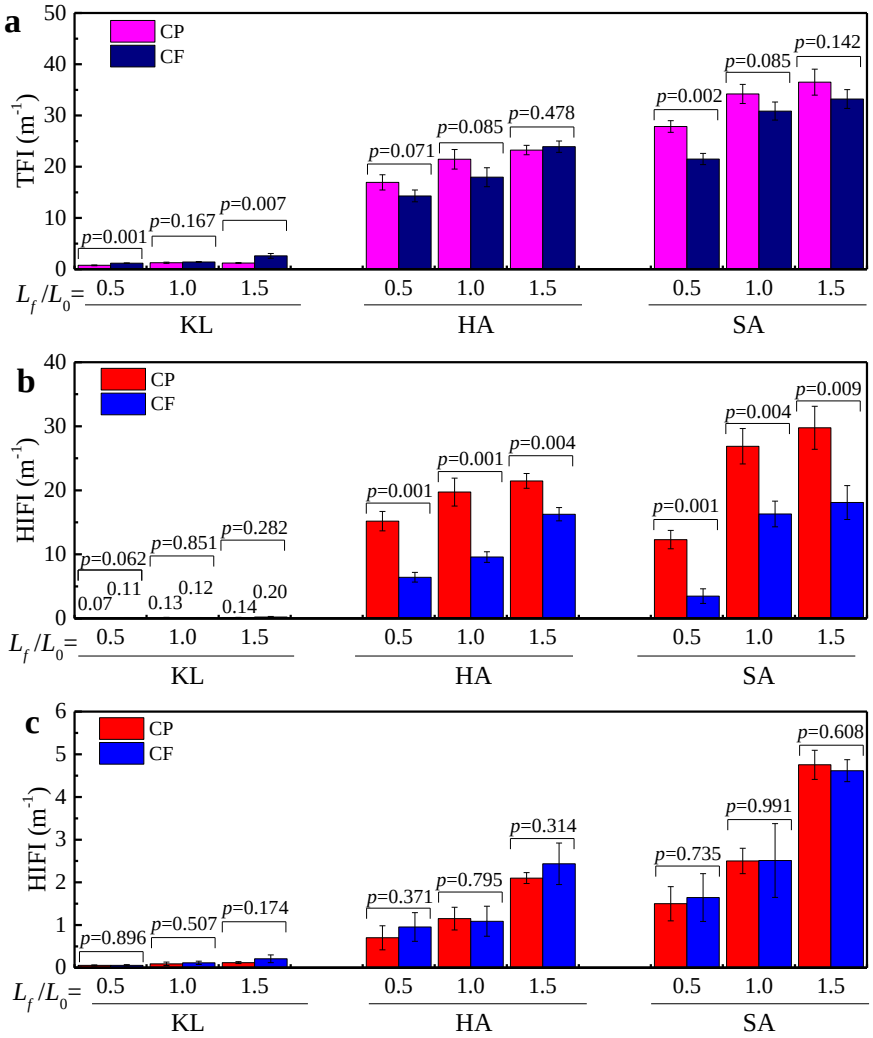

Fig. 2 Effect of filtration mode on membrane fouling under different filtration strengths: (a) TFI, (b) HIFI using UF permeate backwashing and (c) HIFI using ultrapure water backwashing

3.3 Effect of filtration mode under different feed concentrations

Based on the flux decline and TMP buildup under both CP and CF modes (Fig. S5, Supporting Information), the effect of filtration mode on the TFI and HIFI of UF membranes during filtration of KL, HA and SA solutions with different feed concentrations is elaborated in Fig. 3. As for UF membranes during filtration of KL solutions, a low TFI was observed under CP filtration for the least-concentration KL

solution (10 mg L^{-1}), while the TFI under CP filtration was similar to that under CF filtration at a feed concentration of 50 or 100 mg L^{-1}. When feeding with 1 mg L^{-1} HA solution, a higher TFI under CP filtration was observed compared to that under CF filtration, while the TFI was hardly affected by filtration mode for HA solutions at concentrations of 5 and 10 mg L^{-1}. Regarding the SA feed at concentrations of 1 and 2 mg L^{-1}, there was no significant difference in TFI between UF membrane operating under CP filtration and under CF filtration, while much larger TFI under CP filtration was observed than that under CF filtration for a high-concentration SA solution (5 mg L^{-1}).

As illustrated in Fig. 3b, during the filtration of KL solutions, the HIFI of UF permeate backwashing was hardly affected by filtration mode (p>0.05), with the average values ranging from 0.11 to 0.17 m^{-1}. As for HA fouled membranes, the HIFI after backwashing with UF permeate under CP filtration was much larger than that under CF filtration (p<0.05). Increasing HA concentrations from 1 to 5 mg L^{-1}, the HIFI increased from 8.62 to 29.04 m^{-1} and from 1.58 to 16.25 m^{-1} under CP and CF filtration modes, respectively. When the SA fouled membrane was backwashed with UF permeate, the HIFI values under both filtration modes were comparable at a concentration of 1 mg L^{-1}, probably due to the low and similar fouling during filtration (see Fig. 3a). Compared to CP filtration mode, the HIFI values under CF filtration mode during filtration of SA solutions with concentrations of 2 or 5 mg L^{-1} were much smaller. Using ultrapure water as backwash water (Fig. 3c), the HIFI under CF filtration mode was larger than that under CP mode at the KL concentration

of 10 mg L^{-1}, while the HIFI was not significantly affected by filtration mode (p>0.05) when KL concentrations were 50 and 100 mg L^{-1}. When the HA fouled membrane was backwashed by ultrapure water, comparable HIFI values were observed for CP and CF filtration modes (p>0.05). As for SA solution, the HIFI of UF membrane backwashed with ultrapure water was hardly affected by filtration mode when the concentrations were 1 and 2 mg L^{-1}, but the HIFI under CP filtration was much larger compared to that under CF filtration when the largest concentration (5 mg L^{-1}) was investigated.

Regarding the large TFI or HIFI during filtration of 5 mg L^{-1} SA under CP mode, when feed concentrations increased, a critical concentration reached in the membrane boundary layer, a slow aggregation was expected to occur within a boundary layer on an UF membrane during filtration (Aimar and Bacchin, 2010). Compared to CP filtration with high-concentration SA, the CF filtration mode provided the possibility of avoiding over-fouling in the first few minutes, reducing the severity of membrane fouling, as reported in previous literature (Field et al., 1995). The high-concentration SA solution led to severe membrane fouling under CP filtration, making membrane fouling transferred from reversible fouling at a low concentration to irreversible fouling at the high concentration. In addition, large TFI values were found when fed with high-concentration KL, HA and SA solutions, regardless of filtration modes (Fig. 3a). Moreover, increasing the concentrations of KL, HA or SA solutions, the HIFI increased not only for UF membranes operating under CP filtration but also for CF filtration, whatever the types of backwash water (Figs. 3b-3c).

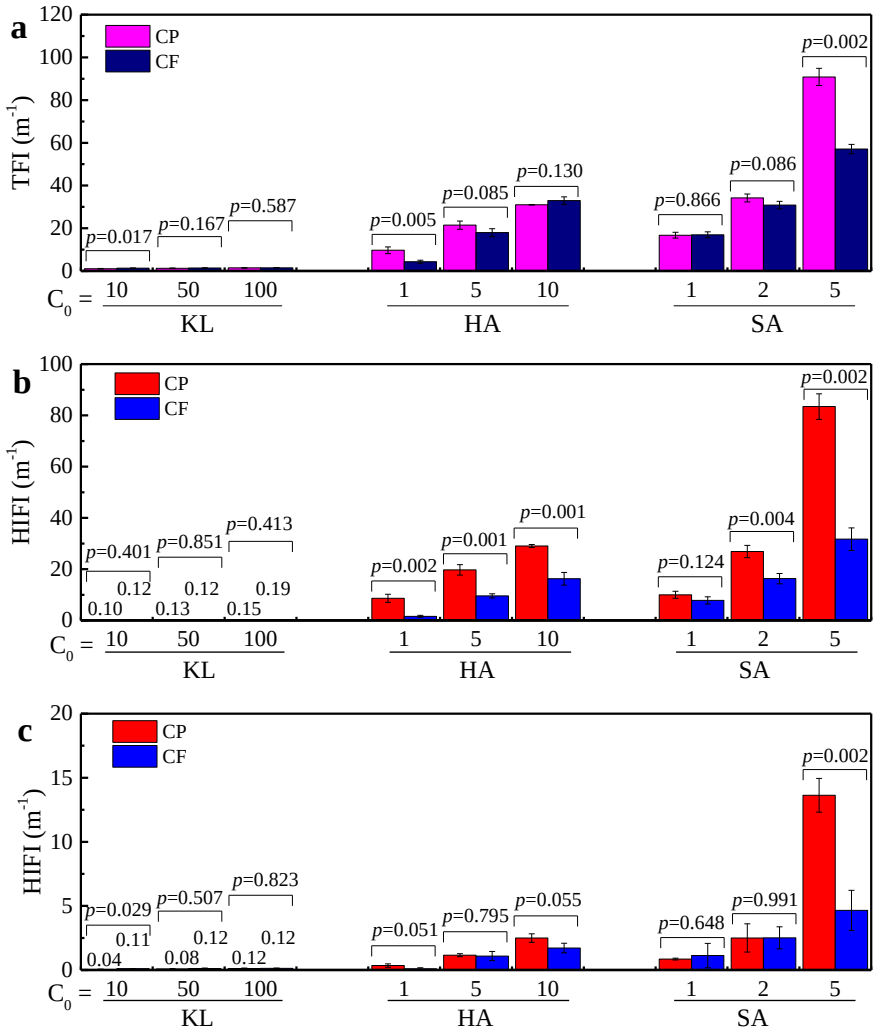

Fig. 3 Effect of filtration mode on membrane fouling under different concentrations of feed solutions: (a) TFI, (b) HIFI using UF permeate backwashing and (c) HIFI using ultrapure water backwashing

3.4 Effect of filtration mode under different pH

The effect of filtration mode on the TFI and HIFI of UF membranes during filtration of KL, HA and SA solutions with different pH is illustrated in Fig. 4. As presented in Fig. 4a, the TFI for UF membranes during filtration of KL solutions was hardly affected by filtration mode (p>0.05), considering the similar fouling behaviors under both filtration modes (Fig. S6, Supporting Information). Regarding the HA feed

solutions, the TFI of UF membrane operating under CP filtration mode was higher than that under CF one when the pH of HA solution was 6.0 or 9.0, though there was no significant difference between both filtration modes at the pH of 7.5. When fed with SA solution at a pH value of 6.0, a larger TFI was found for UF membrane operating under CP filtration mode compared to that under CF filtration mode. In comparison, the TFI was not significantly affected by filtration mode as the pH value was 7.5 or 9.0. Using UF permeate as backwash water (Fig. 4b), the HIFI values for UF membrane operating under CP and under CF filtration modes were identical statistically during filtration of KL solutions (p>0.05), with the average ranging from 0.16 to 0.13 m^{-1}. As also presented in Fig. 4b, during the filtration of HA or SA solutions with different pH, the irreversible fouling was much smaller for UF membrane operating under CF filtration mode than that under CP mode (p<0.05). As shown in Fig. 4c, when the fouled UF membranes were backwashed with ultrapure water, the HIFI was not significantly affected by filtration mode for KL, HA and SA solutions at all pH tested (p>0.05). Moreover, the TFI and HIFI values for KL solutions at different pH were statistically identical (p>0.05) not only for CP filtration mode but also for CF filtration mode. Regarding HA or SA solutions, both the total and irreversible fouling were alleviated when the pH values increased from 6.0 to 9.0 (also see Figs. S6c-S6f, Supporting Information), and the more severe fouling of HA solution at lower pH has been reported (Yuan and Zydney, 2000).

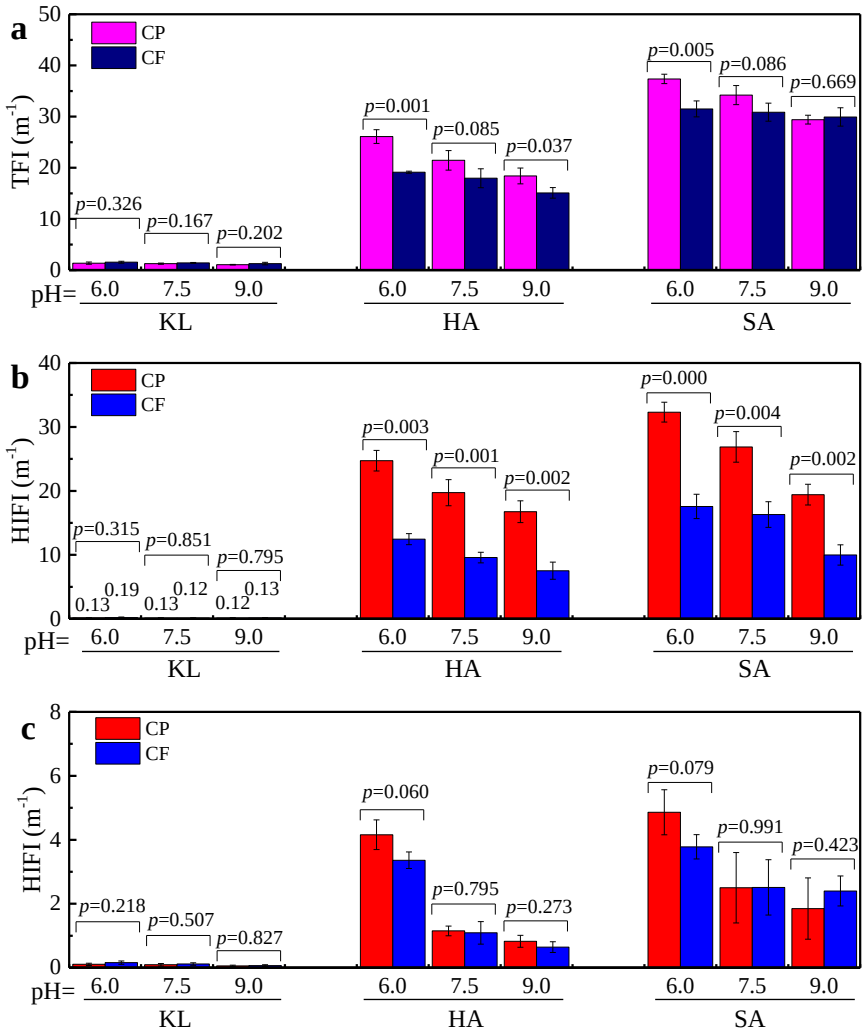

Fig. 4 Effect of filtration mode on membrane fouling under different pH values of feed solutions: (a) TFI, (b) HIFI using UF permeate backwashing and (c) HIFI using ultrapure water backwashing

3.5 Effect of filtration mode under different ionic strengths

Fig. 5 shows the effect of filtration mode on the TFI and HIFI of UF membranes during filtration of KL, HA and SA solutions with different ionic strengths. As presented in Fig. 5a, the TFI for UF membranes during filtration of KL solutions under CP filtration and under CF filtration were identical statistically (p>0.05). Using HA solutions as the feeds, there was no significant difference in TFI between both filtration modes at the ionic strength of 10 mmol L^{-1}, but for HA solutions with ionic

strengths of 2, 20, 50 and 100 mmol L^{-1}, the TFI of UF membrane operating under CP filtration mode was higher than that under CF filtration mode. Similar to HA solution, for SA solutions with all ionic strengths expect 10 mmol L^{-1}, a larger TFI was found for UF membrane operating under CP filtration mode compared to that under CF filtration mode. Moreover, the TFI values for KL solutions were hardly affected by ionic strengths. As for HA and SA solutions, larger TFI values were observed not only for UF membranes operating under CP mode but also for CF mode when the ionic strengths of organic solutions increased from 2 to 100 mmol L^{-1}, as shown in Fig. 5a. At a high ionic strength, the electrostatic repulsion between membrane and HA or SA decreased due to compaction of the electric double layers, the fouling layer might be dense with small permeable to water, resulting in a rapid TMP increase during UF of HA or SA solution, as reported in previous studies (Yuan and Zydney, 2000; van de Ven et al., 2008).

Using UF permeate as backwash water (Fig. 5b), comparable HIFI values were found for UF membrane operating under CP mode and under CF mode during filtration of KL solutions (p>0.05), with the average ranging from 0.12 to 0.16 m^{-1}. For the UF membranes fouled by HA or SA solutions, after backwashing with UF permeate, the HIFI was much smaller for UF membrane operating under CF filtration mode than that under CP mode (p<0.05). As presented in Fig. 5c, when the fouled UF membranes were backwashed with ultrapure water, the HIFI was not significantly affected by filtration mode for KL solutions at all ionic strengths tested (p>0.05). Regarding HA solutions, the HIFI values after ultrapure water backwashing were

equal statistically for UF membranes operating under CP and CF filtration modes at all ionic strengths (p>0.05), although the TFI values under CP mode were higher than that under CF mode (Fig. 5a). In comparison, the HIFI values were comparable for UF membranes operating under both filtration modes during filtration of SA solutions with an ionic strength of 10 or 20 mmol L^{-1}, while a much smaller HIFI was observed for UF membranes operating under CF mode than that under CP mode when ionic strengths were 2, 50 and 100 mmol L^{-1}. As also presented in Fig. 5c, the largest HIFI was obtained at the lowest ionic strength (2 mmol L^{-1}) when ultrapure water was used as backwash water. As reported in previous studies, for organic-fouled UF membrane, the effect of electric double layer release was involved in ultrapure water backwashing (Chang et al., 2015b, 2016). For HA or SA solutions with a high ionic strength (10-100 mmol L^{-1}), the forming cake or gel layer during filtration contained a small amount of sodium ions, which enhanced the removal of foulant during ultrapure water backwashing due to ion exchange between monovalent ion and complexed (with HA or SA) divalent ion (Fig. 5c). In comparison, the rigid cake or gel layer during filtration of HA or SA solutions at a low ionic strength could not be removed by ultrapure water backwashing (Chang et al., 2015b). As for SA solution with an ionic strength of 100 mmol L^{-1} under CP filtration, the large HIFI after backwashing with ultrapure water was probably due to the most severe fouling during filtration (Figs. S7e-S7f, Supporting Information).

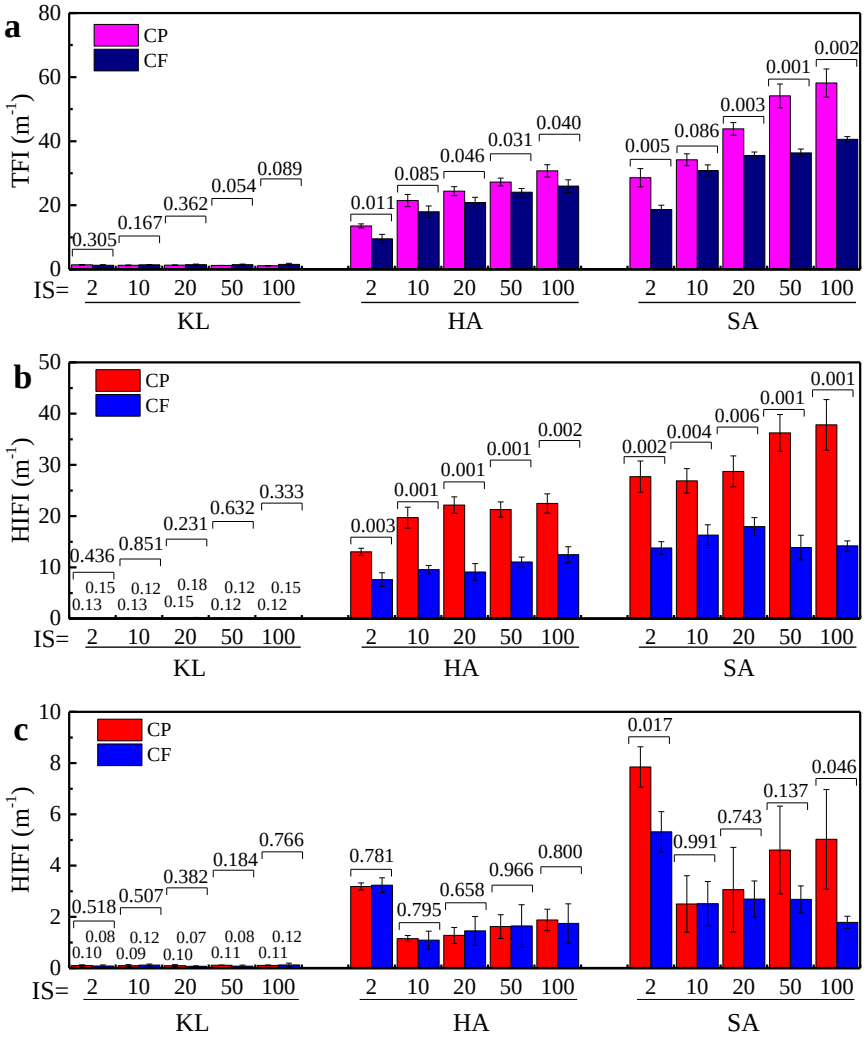

Fig. 5 Effect of filtration mode on membrane fouling under different ionic strengths of feed solutions: (a) TFI, (b) HIFI using UF permeate backwashing and (c) HIFI using ultrapure water backwashing

3.6 Effect of filtration mode under different Ca^{2+} concentrations

Fig. 6 illustrates the effect of filtration mode on the TFI and HIFI of UF membranes during filtration of KL, HA and SA solutions with different Ca^{2+} concentrations. As presented in Fig. 6a, during filtration of KL solutions, the TFI values for UF membranes operating under CP mode and under CF mode were identical statistically (p>0.05). When HA solution was filtrated, there was no significant difference between

both filtration modes at Ca^{2+} concentrations of 0.10-0.50 mmol L^{-1}. In comparison, the TFI of UF membrane operating under CP filtration mode was larger than that under CF one at high Ca^{2+} concentrations (0.75 and 1.00 mmol L^{-1}), while a less TFI was found under CP filtration when compared to CF filtration using HA solution without Ca^{2+} (0 mmol L^{-1}). When SA solution was filtrated, a larger TFI was observed for UF membrane operating under CP filtration mode compared to that under CF filtration mode for low Ca^{2+} concentrations (0.00-0.25 mmol L^{-1}), while the TFI values under both filtration modes were equal statistically for high Ca^{2+} concentrations (0.50-1.00 mmol L^{-1}). Moreover, the TFI varied with Ca^{2+} concentrations differently for HA and SA solutions. During the filtration of HA solutions, the TFI decreased after reaching the peak at Ca^{2+} concentration of ~0.25 mmol L^{-1} for both filtration modes. According to the report about the fouling behaviors of HA solutions (10 mg L^{-1}) under CP mode, more severe HA fouling was found as Ca^{2+} increased from 0 to 2 mmol L^{-1}, and then the trend was reversed at 4 mmol L^{-1} (Katsoufidou et al., 2005). The results obtained in this study (Figs. 6 and S8) was consistent with this phenomenon, considering the content of background ionic strength with 20 mmol L^{-1} NaCl in 10 mg L^{-1} HA. Regarding SA solutions, the TFI decreased with increasing Ca^{2+} concentrations for both filtration modes, as shown in Fig. 6a. Katsoufidou et al. (2007) also stated that the SA fouling under CP filtration tended to be reduced as Ca^{2+} concentrations increased due to the formation of SA aggregation with larger size.

Using UF permeate as backwash water (Fig. 6b), the HIFI values for UF membrane

operating under CP mode and under CF mode during filtration of KL solutions were identical statistically (p>0.05), with the average ranging from 1.48 to 1.11 m^{-1}. For the UF membranes fouled by HA or SA solutions, after backwashing with UF permeate, the role of filtration mode in HIFI was still great, with the values under CF filtration mode much smaller than that under CP mode (p<0.05). Moreover, when HA or SA solution was filtrated, larger HIFI under CF filtration mode was obtained with the increase in Ca^{2+} concentrations. As presented in Fig. 6c, when the fouled UF membranes were backwashed with ultrapure water, the HIFI was not significantly affected by filtration mode for KL solutions with all Ca^{2+} concentrations tested (p>0.05). When HA solution was filtrated, the HIFI values after ultrapure water backwashing were equal statistically for UF membranes operating under CP and CF filtration modes, regardless of Ca^{2+} concentrations (p>0.05). Regarding SA solutions, the HIFI values were comparable for UF membranes operating under both filtration modes. In addition, the trend of HIFI with Ca^{2+} concentrations (Fig. 6c) was consistent with the TFI during filtration of HA solution (Fig. 6a). Specifically, the HIFI using ultrapure water backwashing decreased after a peak value at ~0.25 mmol L^{-1} with the increase in Ca^{2+} concentrations, this phenomenon was similar to the result obtained in previous literature (Katsoufidou et al., 2008).

Overall, the comparisons of total membrane fouling and hydraulically irreversible fouling of UF membranes operating under CP mode and CF mode are summarized in Table. S4.

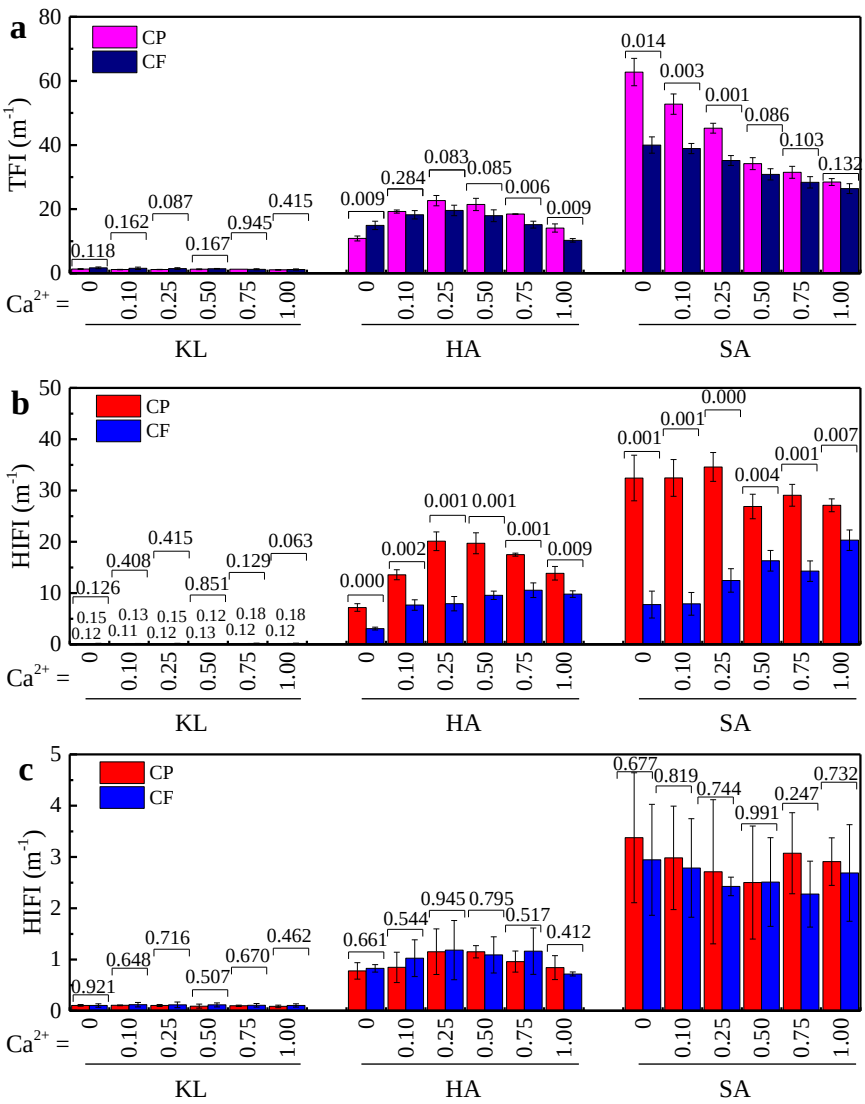

Fig. 6 Effect of filtration mode on membrane fouling under different Ca^{2+} concentrations of feed solutions: (a) TFI, (b) HIFI using UF permeate backwashing and (c) HIFI using ultrapure water backwashing

4 Conclusions

The TFI and HIFI of UF membranes operating under CP mode and CF mode were compared during filtration of KL, HA and SA solutions with different test conditions and backwash water. The following conclusions can be drawn:

(1) During filtration of KL solutions, low TFI and HIFI were found for all tested membranes, filtration strengths, feed solutions, pH values, ionic strengths and Ca^{2+}

concentrations. The TFI and both HIFI for ultrapure water backwashing and UF permeate backwashing were hardly affected by filtration mode.

(2) When HA and SA solutions were filtrated, similar TFI of UF membranes operating under CP mode and under CF mode were obtained. Higher TFI was observed at a hydrophobic membrane, a high filtration strength, a high feed concentration, a low pH, a high ionic strength, and a low Ca^{2+} concentration.

(3) As for the organic-fouled UF membranes, when the UF permeate was used as the backwash water, the HIFI for the UF operated under CF mode was significantly less than that under CP mode. Less irreversible fouling was obtained for ultrapure water backwashing compared to UF permeate backwashing, and the HIFI for the UF under different filtration mode was almost identical.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version.

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Figure captions:

Fig. 1 Effect of filtration mode on membrane fouling under different types of membrane materials: (a) TFI, (b) HIFI using UF permeate backwashing and (c) HIFI using ultrapure water backwashing

Fig. 2 Effect of filtration mode on membrane fouling under different filtration strengths: (a) TFI, (b) HIFI using UF permeate backwashing and (c) HIFI using ultrapure water backwashing

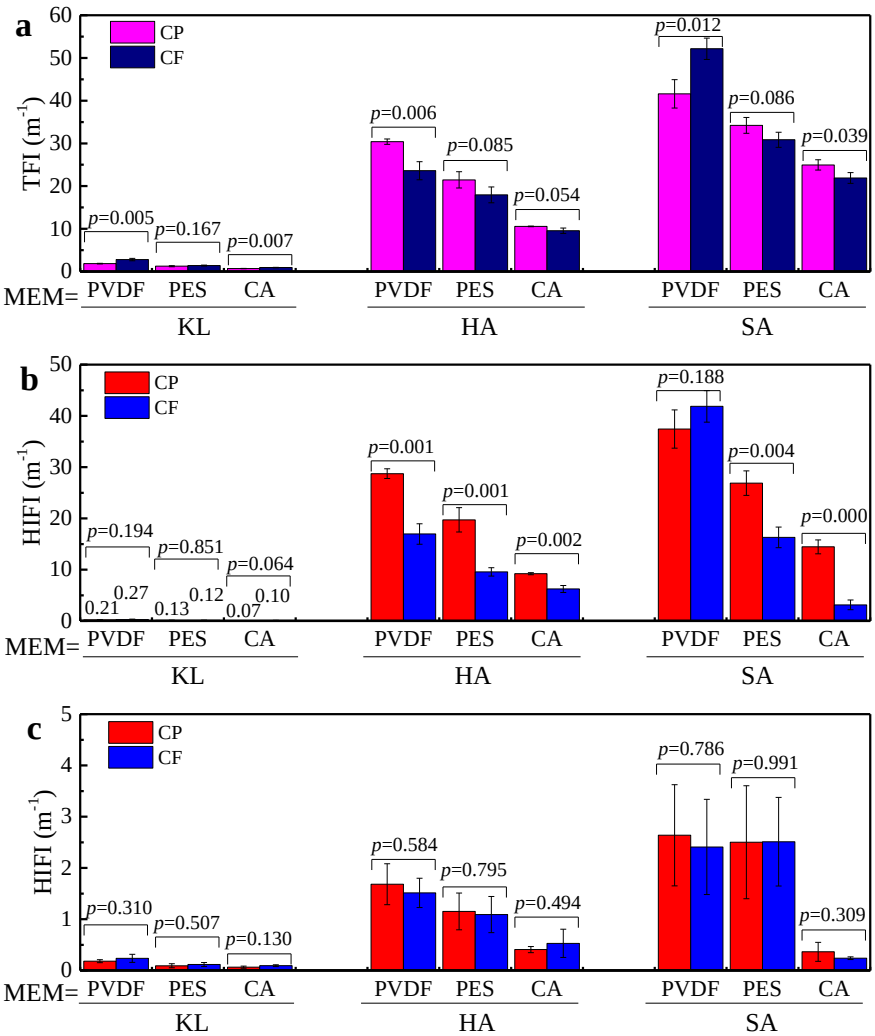
Fig. 3 Effect of filtration mode on membrane fouling under different concentrations of feed solutions: (a) TFI, (b) HIFI using UF permeate backwashing and (c) HIFI using ultrapure water backwashing

Fig. 4 Effect of filtration mode on membrane fouling under different pH values of feed solutions: (a) TFI, (b) HIFI using UF permeate backwashing and (c) HIFI using ultrapure water backwashing

Fig. 5 Effect of filtration mode on membrane fouling under different ionic strengths of feed solutions: (a) TFI, (b) HIFI using UF permeate backwashing and (c) HIFI using ultrapure water backwashing

Fig. 6 Effect of filtration mode on membrane fouling under different Ca^{2+} concentrations of feed solutions: (a) TFI, (b) HIFI using UF permeate backwashing and (c) HIFI using ultrapure water backwashing

Fig. 1 Effect of filtration mode on membrane fouling under different types of membrane materials: (a) TFI, (b) HIFI using UF permeate backwashing and (c) HIFI using ultrapure water backwashing (error bars represent standard deviations; n=3). *p* values obtained from ANOVA (α=0.05) are shown in the figure. *p* values above each membrane indicate the difference in filtration mode.



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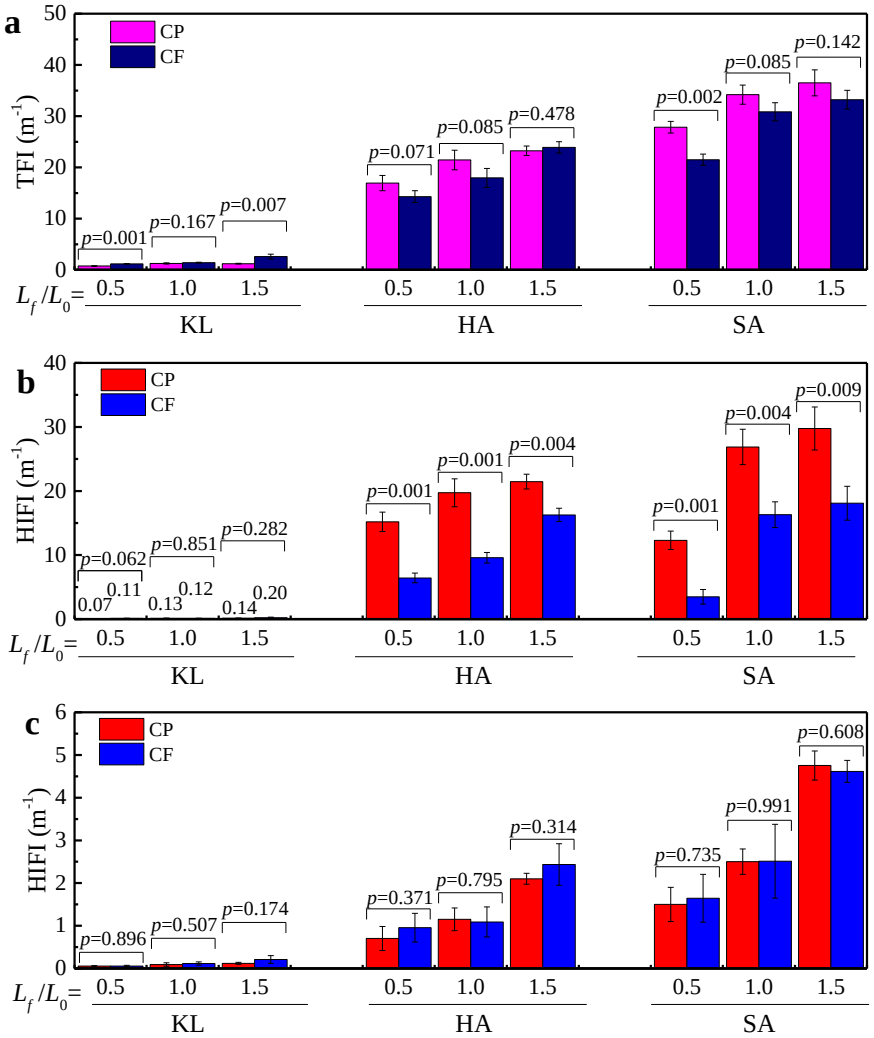

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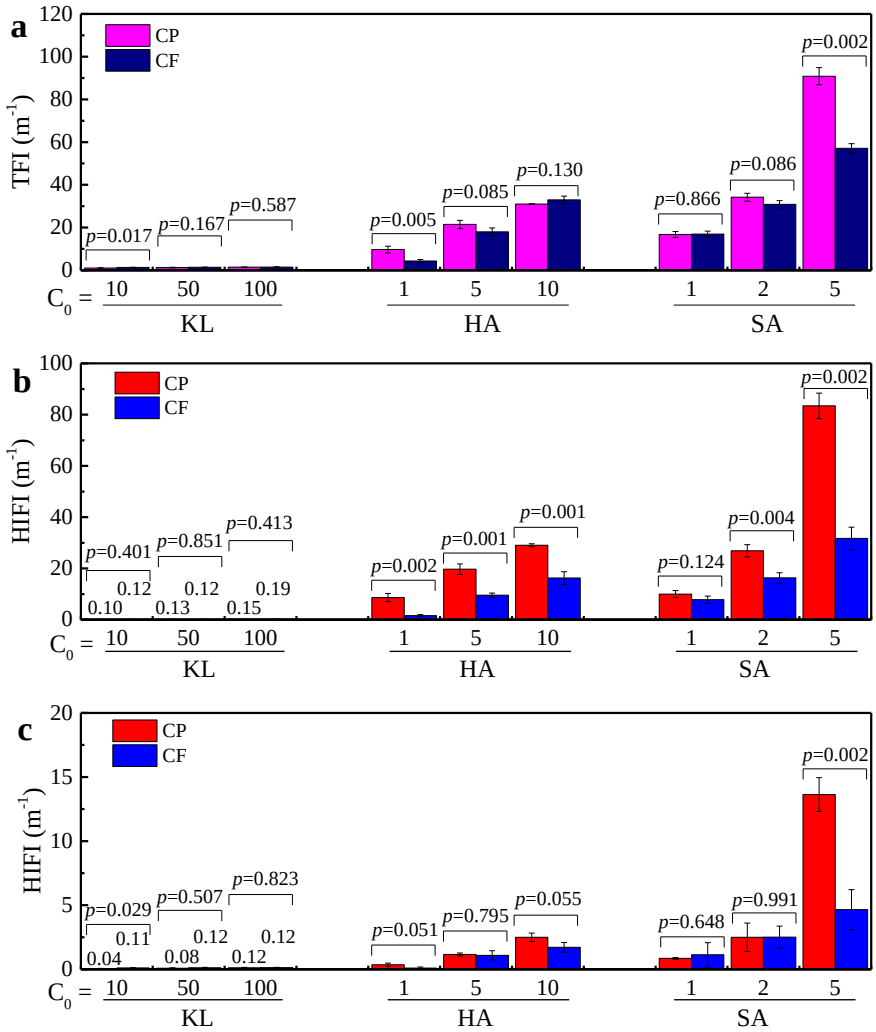

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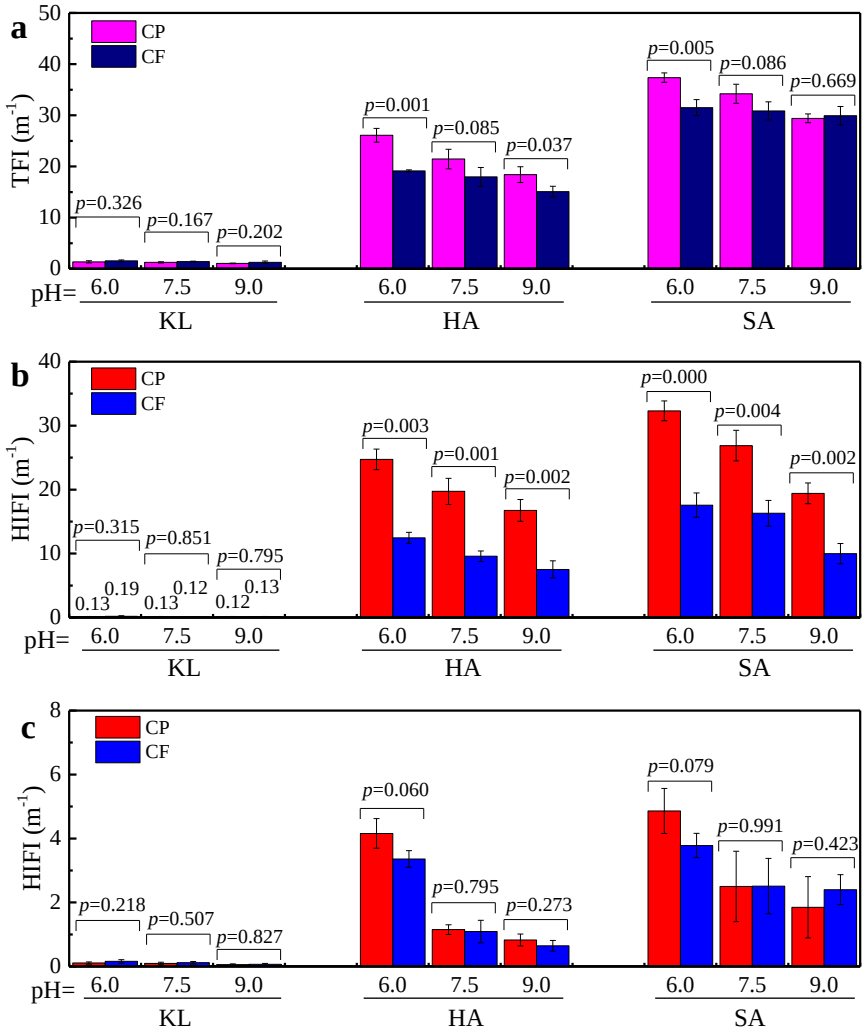


Fig. 5 Effect of filtration mode on membrane fouling under different ionic strengths of feed solutions: (a) TFI, (b) HIFI using UF permeate backwashing and (c) HIFI using ultrapure water backwashing

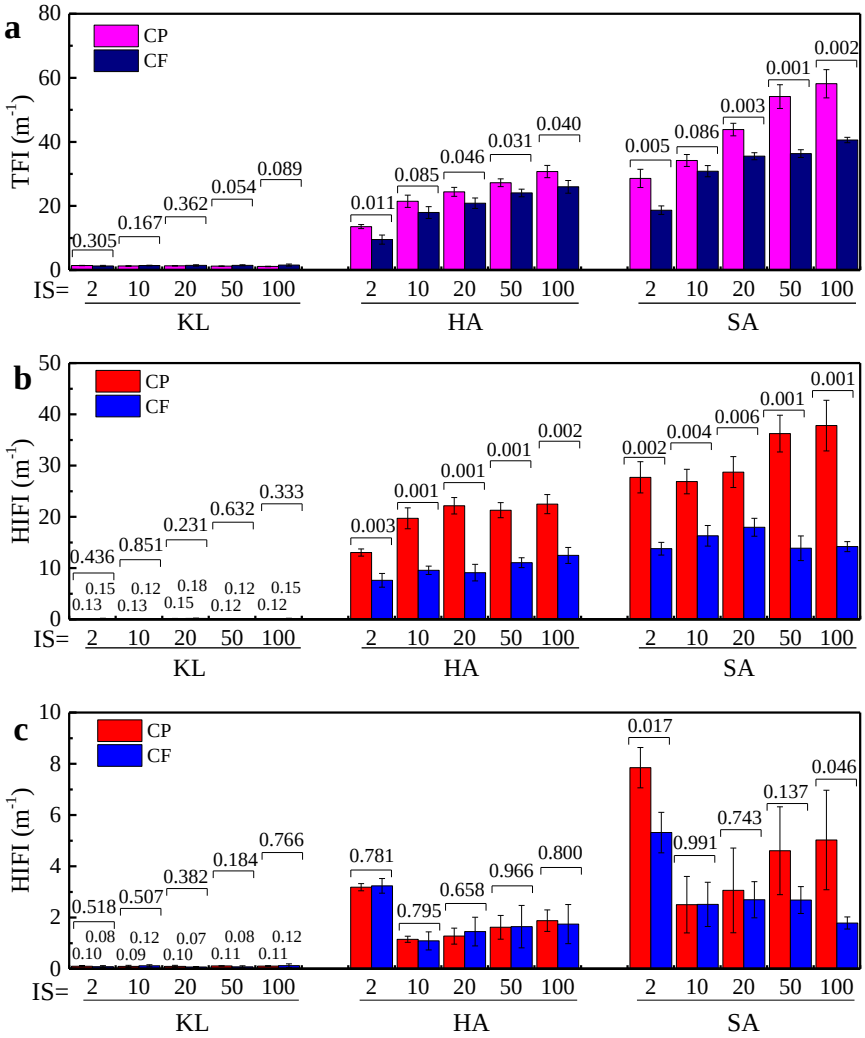
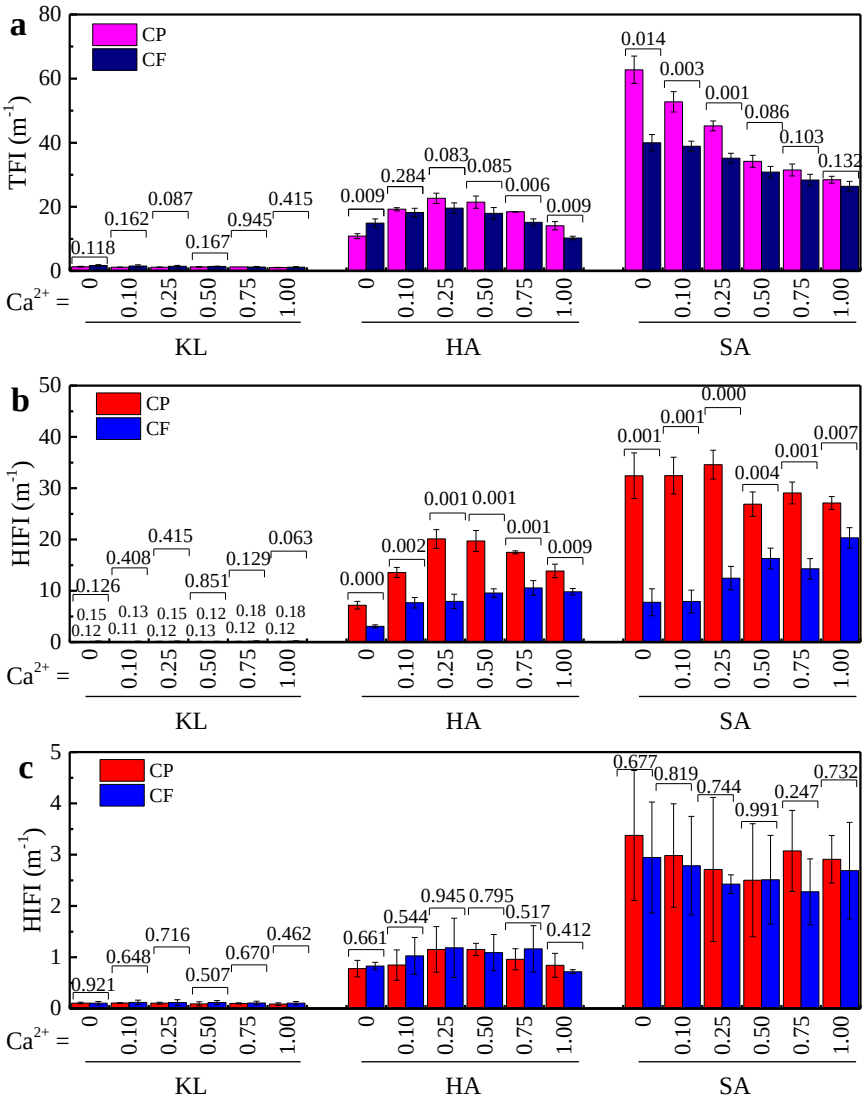
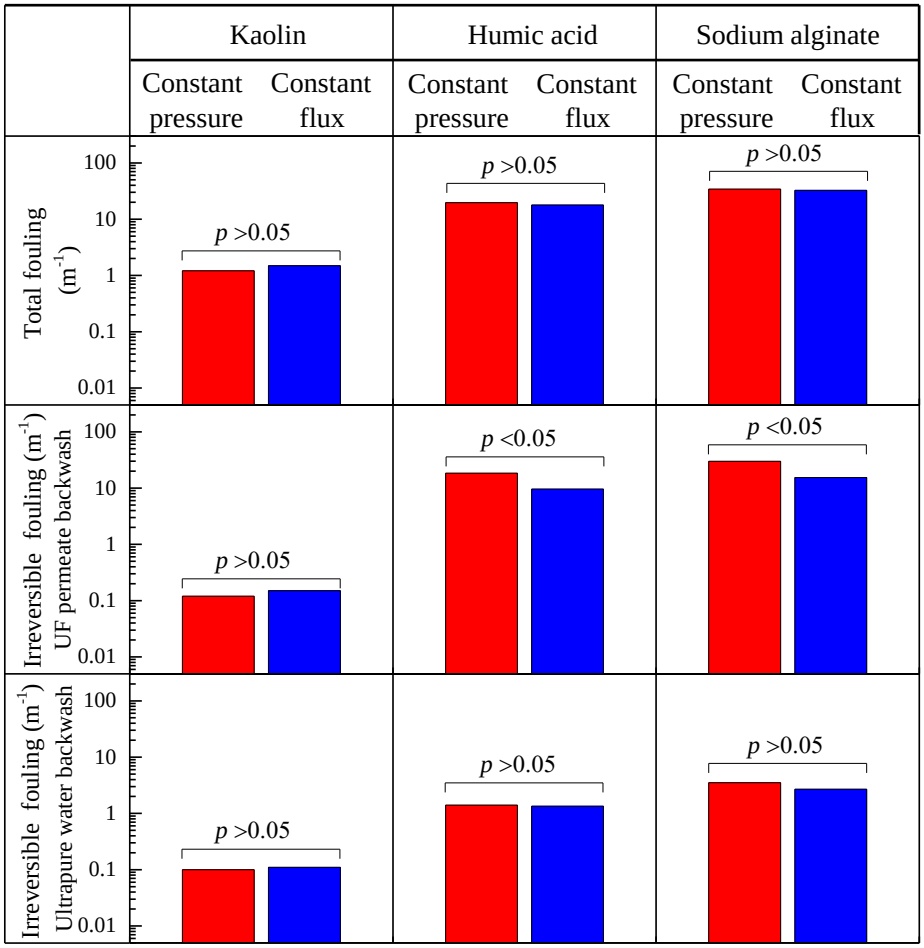


Fig. 6 Effect of filtration mode on membrane fouling under different Ca^{2+} concentrations of feed solutions: (a) TFI, (b) HIFI using UF permeate backwashing and (c) HIFI using ultrapure water backwashing



Graphic abstract