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Characterization of natural organic matters using flow field-flow fractionation and its implication to membrane fouling

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ABSTRACT

Transport and deposition characteristics of natural organic matter (NOM) are systematically investigated using flow field-flow fractionation (Fl-FFF) at various chemical and physical conditions. Humic acid (HA) was chosen as model organic foulants. Prior to Fl-FFF analysis, HA was fractionated by membranes with different molecular weight cut-offs. To elucidate physicochemical factors affecting the deposition and transport characteristics of organic foulants, various concentrations of NaCl (i.e. up to seawater level) and $CaCl_2$ were employed as carrier solutions in Fl-FFF. Each fractionated NOM showed different transport and deposition characteristics with respect to the chemical and physical conditions employed during Fl-FFF analysis. When the total dissolved solids (TDS) concentration increased, there was more significant variation in the retention time for large NOM fractions compared with small NOM fractions. This means that the transport and deposition tendency of the larger NOM fractions varied more significantly with the alteration of ionic strength in Fl-FFF channel than the smaller ones. However, the smaller NOM fractions showed more considerable variation in retention time with increasing cross-flow intensity (i.e. flow perpendicular to channel flow in Fl-FFF) in Fl-FFF channel. This also means that the variation of physical factor could affect the transport and deposition tendency of the smaller ones more influentially. Results also elucidated that the retention time and area of elution peak of fractionated NOM were directly related to the amount of organic foulants attached to the membrane in Fl-FFF channel. It has been demonstrated that the deposition tendency of organic foulants increased at the higher TDS concentration, calcium concentration, and cross-flow intensity. This has been quantitatively determined using fouling index, Q_f, derived from the data obtained from Fl-FFF. Based on this study, it is implied that Fl-FFF can be a useful tool to characterize the transport and deposition behavior of organic foulants in the solid–water interface and optimize pretreatment options for reducing membrane fouling.

Keywords: Flow field-flow fractionation (Fl-FFF); Natural organic matters (NOM); Total dissolved solids (TDS); Chemical and physical factors; Deposition and transport

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1. Introduction

Membrane desalination plants utilize seawater as feed water that contains various constituents such as natural organic matters (NOM), inorganic particles, salts, microorganisms, and so on. These constituents could cause membrane fouling with different manners. Among these potential foulants, NOM plays a defective role in desalination plant causing organic fouling, which results in high operation cost by inducing low permeability or high transmembrane-pressure drop [1]. Due to these adverse aspects of NOM, various pretreatment options are required to remove this recalcitrant foulant prior to reverse osmosis (RO) process. NOM has wide range of molecular weight distribution (i.e. 500–200,000 Da) so that having an exact composition is hardly available [2]. NOM also has various transport characteristics in the membrane desalination process. NOM property related to its aggregation and stability is significantly affected by water chemistry. Therefore, understanding NOM deposition and transport behaviors is of paramount importance in the efficient operation of desalination process.

Giddings first introduced the theory of flow field-flow fractionation (Fl-FFF) in 1970s [3]. Wahlund also introduced the asymmetrical type of the Fl-FFF in 1987 [4]. The Fl-FFF is one of the flow-based separation techniques with capability to separate colloids ranging in size from 1 nm to 50 μm [5–7]. The schematic principle of particle separation and analysis by Fl-FFF is illustrated in Fig. 1. The detailed principle of Fl-FFF can be found elsewhere [8,9]. Fl-FFF employs a horizontal laminar flow through a channel (i.e. channel flow) with a semipermeable membrane. The channel flow applied is composed of laminar flow conditions. Parabolic fluid velocity profile is applied in Fl-FFF channel, which has different channel flow velocity. Injected samples with carrier solution are transported along the Fl-FFF channel. The membrane retains samples in the channel while allowing the carrier liquid to penetrate the membrane channel and to exit the system via a porous frit. The separation force is induced by a field that is applied perpendicular to the channel flow. This force is so-called "cross-flow" which distinguishes it from the direction of the cross-flow of conventional cross-flow filtration process. In Fl-FFF, the cross-flow passes through a porous frit of fluid that is identical in terms of composition to that of the carrier solution, while channel flow flows parallel to the Fl-FFF channel. Channel flow and cross-flow separate solutes injected to the channel with respect to solute characteristics (i.e. solute size, shear-induced diffusion, inertial lift, hydrophobicity, charge distribution, etc.). For studying the hydrodynamic transport behavior of NOM, these features (i.e. involving both cross-flow and channel flow) represent the typical cross-flow filtration system and allow the determination of membrane–solute interaction, which is one of the important factors affecting fouling [10,11]. Since various types and concentrations of carrier solutions are available in Fl-FFF channel, physicochemical conditions of Fl-FFF channel can be controlled more practically than those of other common liquid

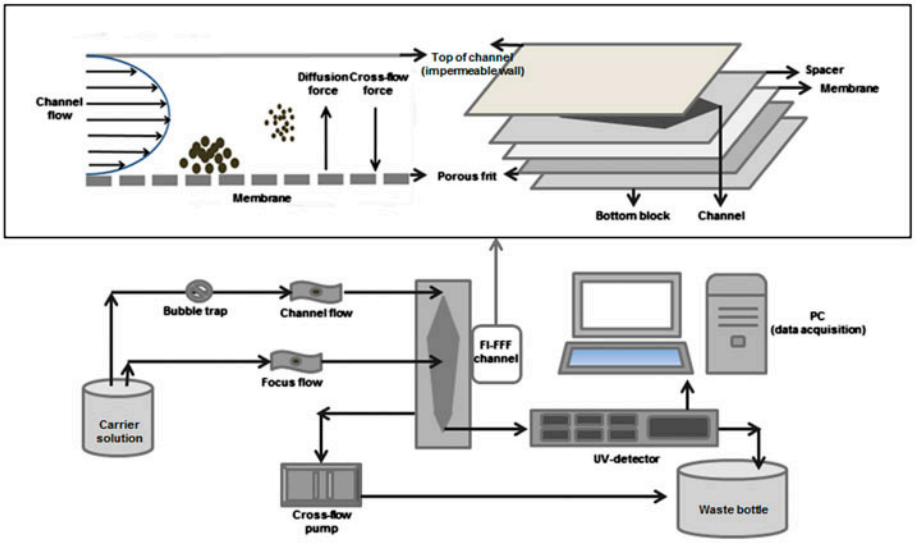

Fig. 1. Schematic description of flow field-flow fractionation.

chromatographic tools. In normal mode separation, smaller particles are located at the upper side where faster velocity streamlines of the laminar flow profile exits due to their high diffusion rates. These samples are eluted earlier than larger particles in the slower velocity streamlines near the membrane wall. Exceptionally, when the injected sample size in Fl-FFF channel is larger than approximately 1 μm, the elution order is reversed so that larger samples eluted earlier than smaller particles [5,6,12]. The separated samples from the channel were eluted within minutes and flowed into a UV detector which detects and records their passage. The measured retention time of samples could be used to calculate the theoretical sample hydrodynamic diameters and diffusion coefficients using relevant mathematical equations[10,13–16].

Recently, Fl-FFF has been widely applied to characterizing colloid and NOM, and transport and deposition behaviors in the solid–liquid interface. Several studies have been carried out for NOM characterization using Fl-FFF. Moon et al. [17] used the Fl-FFF to fractionate NOM in terms of its size and diffusivity and determined the hydrodynamic effective size with respect to solution ionic strength. Assemi et al. [8] also fractionated NOM using Fl-FFF. They separated the NOM into five nominal fractions in terms of size and determined molecular weight distribution. Results showed that the separation was influenced by molecular structure as well as molecular size; however, the influence of solution chemistry on the separation was not considered. Stolpe et al. [18] characterized colloidal organic matter and trace elements using Fl-FFF coupled with UV detector, fluorescence detector, and ICP MS. They fractionated the colloidal size spectra of organic samples and protein like matters. Fl-FFF has also been used to separate fractions of bio-polymers and bio-particles [5]. This study showed some similarities with the former studies in terms of fractionation and characterization of organic matter. However, this study also did not include the characteristic changes of bio-solutes with respect to chemical and physical conditions. Some research groups have studied the organic fouling behaviors using Fl-FFF by varying chemical conditions in Fl-FFF channel. Heartman et al. [19] used Fl-FFF to quantify and evaluate the organic fouling of RO and NF membranes. They found that organic fouling tendency was severe as the calcium ion concentrations increased. Also, they founded that ethylenediamine tetraacetic acid could reduce the amount of free calcium facilitating interactions between the membrane and organic samples. Neubauer et al. [20] investigated and compared the influences of ionic strength and sample load on the retention time and sample recovery of polysterene sulfonate and natural nanoparticles including NOM. They found that the minimum ionic strength in the carrier solution and the maximum injected sample were required for satisfactory separation depending on the nature of samples injected. Lim et al. [21] also evaluated the bio-fouling potential using Fl-FFF to predict bio-fouling potential with different ionic strength conditions and membrane properties. However, they applied the narrow range (0.1, 1.0, and 10 NaCl) of ionic strength in carrier solution which is somewhat unrealistic compared with practical applications of seawater and brackish water desalination. When referring the chemical conditions employed in the aforementioned Fl-FFF studies [8,21–24], it can be known that the range of ionic strength was varied from 0.001 to 0.1 M condition. This means that no recent study has been conducted under the condition of actual brackish water and seawater level ionic strengths. Studies investigating physical factors affecting solute deposition and transport in Fl-FFF channel are rather scarce. For example, Heartman et al. [19] varied cross-flow velocity during Fl-FFF analysis to quantify the membrane fouling, however, without any sample fractionations.

Fl-FFF was utilized to invent the membrane fouling index. Kim et al. [25] utilized the Fl-FFF as a method to characterize a membrane performance index. By calculating the amount of organic sample absorbed, detached, and penetrated to the membrane, they invented the fouling index that can represents the fouling resistibility and rejection capability. They utilized the integral area of the peak to quantify the amount of foulants absorbed to membrane. Phuntso et al. [19] also assessed the membrane fouling potential using Fl-FFF. They quantified the reversible and irreversible adsorption through the analysis of Fl-FFF fractogram using peak area. They performed the momentum analysis using retention time distribution considering the Fl-FFF system to behave as a nonideal reactor. However, physical factors such as cross-flow velocity were not considered. Lee et al. [22] evaluated the bio-fouling potential using Fl-FFF. Their experimental results showed that the bacterial size could influence the bio-fouling potential regardless of the membrane properties. They evaluated the fouling potential using the retention time of bacteria samples. Thus, as mentioned above, there are two ways to interpret the fouling potential using Fl-FFF. Using mean peak area is the basic way to quantify the amount of fouling based on mass balance. In addition, momentum analysis is another way to interpret the fouling potential. The first momentum analysis using mean Fl-FFF size distribution can represent the effective hydrodynamic size of each solute applied to

Fl-FFF channel with respect to the interactions between the membrane surface and the solute. In the third momentum analysis, the skewness value was applied, which can strongly depend on the shape of the peak, and it can manifest the mutual interactions between the membrane and the solute [23]. In this study, simple Fl-FFF analysis of sample recovery and retention time was applied to organic fouling measurements. Using the mass balance and retention time analysis similar to those of Heartman [19] and Lee [22], we evaluated the fouling potential of organic matters with different molecular sizes by fractionating NOM through UF treatment. The elution peaks and peak areas were related to actual fouling amount of each fractionated humic acid (HA) samples with the variations of chemical and physical conditions. As shown in the Eqs. (1) and (2), we considered the Q_f value as a fouling index using Fl-FFF.

In this study, the transport and deposition behaviors of fractionated NOM were analyzed by Fl-FFF under different chemical and physical conditions. The unique feature of this study from the previous studies is that the following investigations carried out simultaneously for more systematic and precise application of Fl-FFF as a tool to investigate the transport and deposition characteristics of organic foulants in solid–water interface; (1) NOM fractionation was carried out, (2) ionic strength (i.e. important chemical factor affecting NOM transport and deposition) varied up to concentrated seawater level, and (3) interplay between chemical and physical factors was investigated. In this research, broad range of ionic strength has been employed to imitate the conditions of brackish water, seawater, and concentrated seawater level ionic strengths (i.e. carrier solutions used are 0.152 M NaCl, 0.593 M NaCl, and 1.186 M NaCl). The results obtained in this study are expected to give useful information of using Fl-FFF to understand NOM transport and fouling behavior in real membrane practices.

2. Materials and methods

2.1. Organic foulants

2.1.1. Bulk organic foulants

HA (Sigma-Aldrich, USA) was used as model organic foulants. HA was dissolved in ternary deionized (DI) water to make 2 g/L stock solutions of bulk organic foulants. HA concentrations were determined in terms of dissolved organic carbon (DOC) measured using TOC-V CPH (Shimadzu, Japan). Based on the DOC concentrations (in mg/L), all HA sample's concentrations were adjusted to 200 and 300 mg DOC/L by dilution.

2.1.2. Fractionation of organic foulants

Fractionated organic sample was prepared to separate and fractionate the bulk organic sample. The fractionation procedure has been explained in earlier studies [5,8]. Fractionation process was equipped with 0.45 μm MF, 300, 100, 30, and 10 kDa UF membranes that represent the pore size of MF/UF pretreatment filter. Bulk organic sample was separated using air pump. By separating the bulk organic sample using MF/UF filters, the relative size distribution of organic sample could be represented as less than each pore size of MF/UF. All concentrations of fractionated HA samples were adjusted to 200 and 300 mg TOC/L also. HA samples have been named as HA < 0.45 μm, HA < 300 kDa, HA < 100 kDa, HA 30 < kDa, and HA 10 < kDa. For example, HA < 300 kDa represents 200 mg DOC/L humic acid filtered by UF membrane with molecular weight cutoff (MWCO) of 300 kDa.

2.2. Membranes for Fl-FFF analysis and NOM fractionation

A flat-sheet polyether sulfone (PES) membrane with nominal MWCO of 1 kDa was used for the Fl-FFF experiment. The pore size of this PES membrane could be represented as the pore size of NF membrane. The general properties, including the surface charge, roughness, material, and MWCO, are summarized in Table 1. By converting the unit of Dalton (Da) to length (of diameter), the pore size of 1 kDa PES membrane is considered to be about 2 nm. Before every experiment was begun, 1 kDa PES membranes were soaked in deionized water overnight and rinsed with ternary deionized water three times to remove the dehumidifying agent prior to do all experiments. MF/UF membranes that have different pore sizes (0.45 μm MF, 300, 100, 30, and 10 kDa, Millipore) were used for fractionating the bulk organic sample. The material of each membrane filter discs are composed of regenerated cellulose. Prior to use each filter disk, they were also soaked in deionized water for 1 h, and then, this procedure was repeated three times to

Table 1
General properties of PES membrane

Membrane	Postnova
Surface charge (mV) (@pH = 7.64 ± 0.01)	−6.17 ± 0.88
Roughness (nm)	34.08
Material	Polyether sulfone
Molecular weight cut off	1 kilodalton (kDa)

remove the dehumidifying agent absorbed. After each fouling experiment was performed, 0.1 N NaOH solution was injected to overall loop of Fl-FFF to remove the organic samples absorbed completely. Then, ternary deionized water was injected again for an hour to stabilize the membrane in Fl-FFF channel.

2.3. Specifications and operating conditions of Fl-FFF

The Fl-FFF consisted of an asymmetric channel, two HPLC pumps, and a UV detector (SPD 20A from Shimadzu, Japan). The channel dimensions are 2 cm in width, 27.5 cm in length, and a thickness of 0.02 cm. Samples were injected to the channel via 25 µm injection loop. The operating conditions are 4-min focusing time, 1-min transition time, 30-min total elution time, 0.2 ml/min injection flow, 1 ml/min detector flow, and 2.5 and 3 ml/min cross-flows. The detection of HA samples in the eluent from Fl-FFF channel was carried out by UV detector at a wavelength of 254 nm. Operating control and data acquisition were automated by the software AF2000 Control (Postnova Analytics, Germany) system.

2.4. Carrier solutions

The carrier solutions consisted of 0.152 M NaCl, 0.593 M NaCl, and 1.186 M NaCl prepared with reagent grade NaCl combined with 0.5 mM $CaCl_2$, 1 mM $CaCl_2$, and 1.5 mM $CaCl_2$ (Samchun chemical, Korea). All carrier solutions were also contained 0.1 mM NaN_3 (Junsei chemical, Japan) as bactericide. By diversifying total dissolved solids (TDS) concentration of the carrier solution, it can emulate different conditions such as brackish water (0.152 M NaCl), sea water (0.593 M NaCl), and concentrated seawater (1.186 M NaCl). Also, concentration of calcium ion was diversified at 0.5 mM $CaCl_2$, 1 mM $CaCl_2$, and 1.5 mM $CaCl_2$. Calcium chloride was used as model hardness causing material.

2.5. Elution peak analysis and mass balance calculation

Retention time (*X*-axis), detector signal (*Y*-axis), and peak area (signal integral area, min·V) can provide information about sample–membrane interactions and sample recoveries. The retention time is the basic parameter that represents the average residence time of the sample injected in Fl-FFF channel. Retention time values could provide the properties for fractionated ones directly related with diffusion coefficients and Stokes radii. By comparing the retention time results value obtained by Fl-FFF runs, we could know how long the organic foulants have been delayed in the channel.

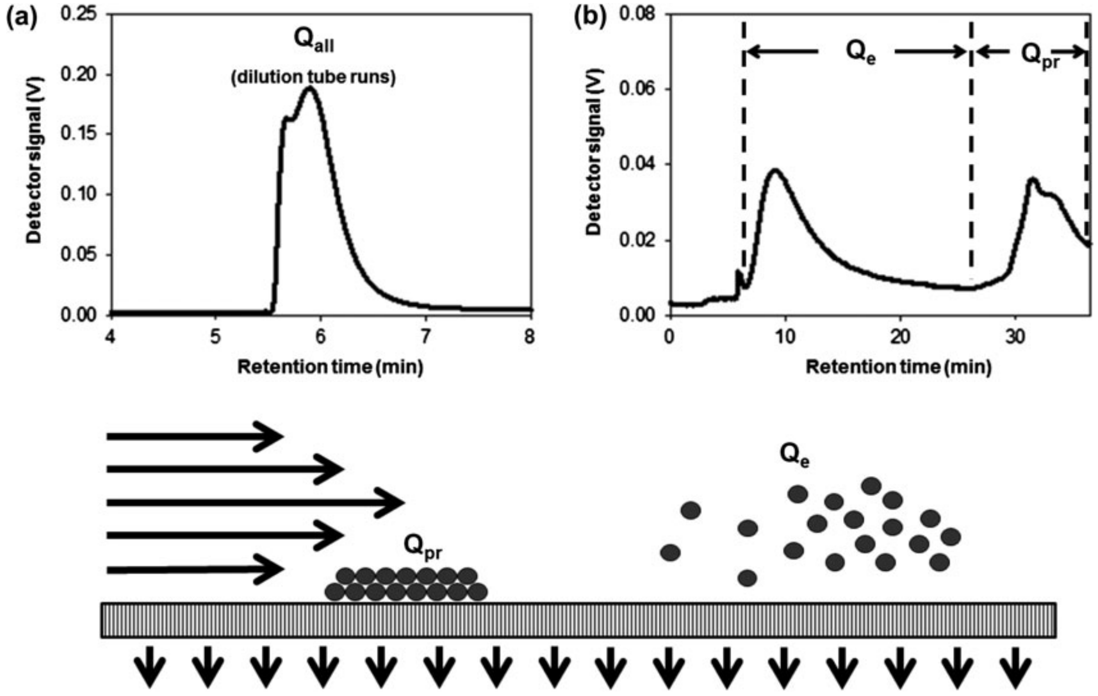

Fig. 2. Elution peak analysis and mass balance calculation: (a) elution peak of HA sample injected (b) all peaks used for calculating mass balance. Bottom diagram shows the foulants behavior in Fl-FFF channel corresponding to each peak.

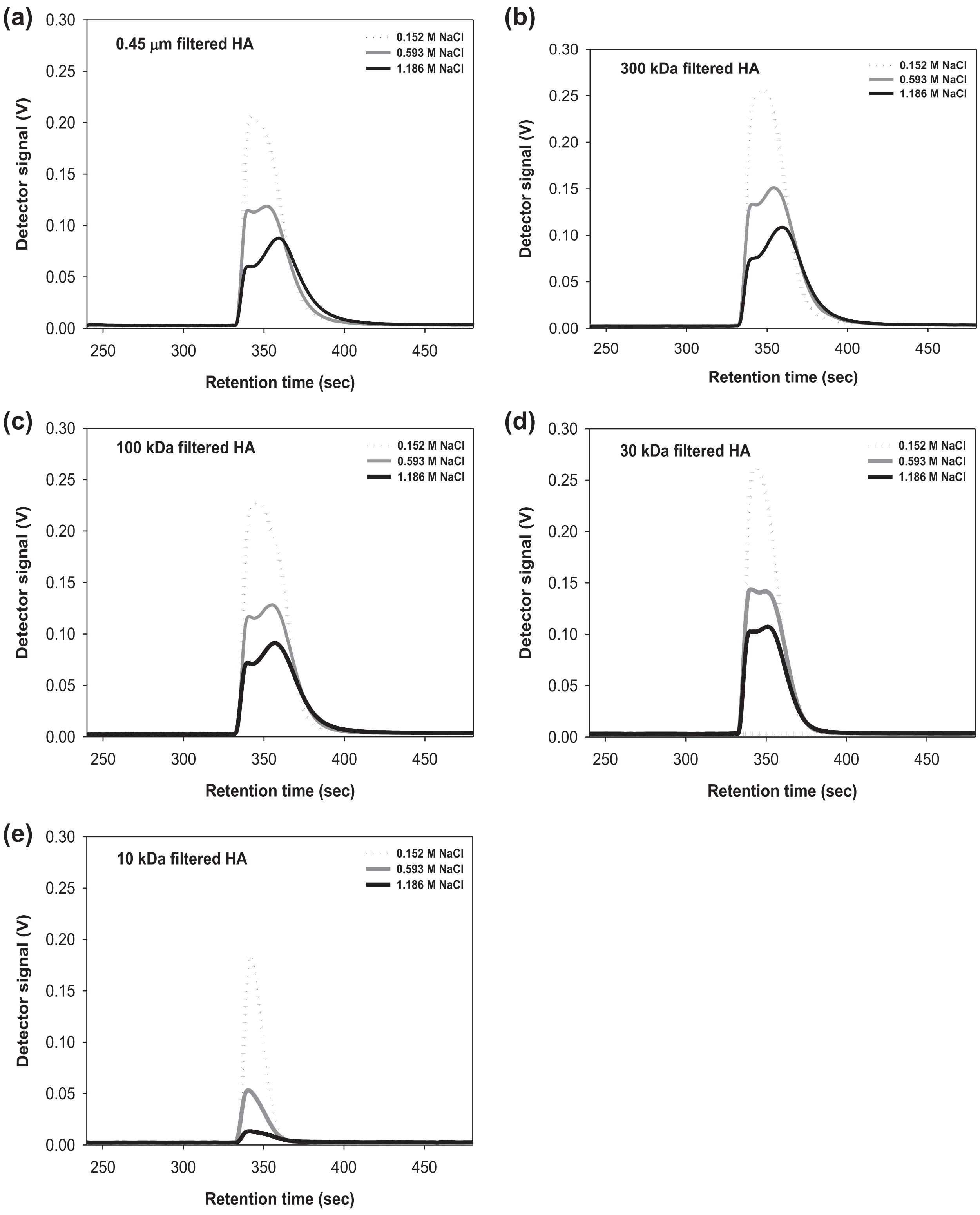

Fig. 3. Effect of TDS on elution peak of fractionated organic samples. The channel flow rate is 1 ml/min, and cross-flow rate is 3 ml/min, and the carrier solutions are 0.152 M NaCl, 0.593 M NaCl, and 1.186 M NaCl. The injected foulants are: (a) 0.45 μm filtered HA, (b) 300 kDa filtered HA, (c) 100 kDa filtered HA, (d) 30 kDa filtered HA, and (e) 10 kDa filtered HA samples of 200 mg TOC/L.

Peak areas provide various data as shown in Fig. 2 [24]. The eluted sample injected to channel membrane can be recorded by the detector in the form of area type of peak used in determining the quantity of sample adsorbed on the Fl-FFF membrane when normal mode runs. Fig. 2(a) shows the elution peak of HA sample which is associated with total amount of sample and is obtained by injection through a dilution tube run. Fig. 2(b) describes the all retained peak when a sample is injected in the Fl-FFF channel for normal mode separation including the peak of Q_e and Q_{pr}. While most injected samples are eluted (Q_e) from the channel caused by horizontal channel flow, some samples (Q_{pr}, Q_{ir}) remain absorbed to the membrane due to solute-membrane interactions by the action of cross-flow field. Q_{pr} indicates the amount of eluted sample from the Fl-FFF channel membrane when the cross-flow mode terminates. Q_{pr} also reflects that the amount of foulants can be removed at physical washing process. Q_{ir} (not presented in Fig. 2) is the amount of samples irreversibly absorbed to membrane, which can be only regained using chemical washing process and can be obtained using Eqs. (1) and (2). Fl-FFF is typically used to measure molecular weight and particle size distributions. Moreover, this quantitative capability of Fl-FFF offers a unique analytical perspective in the study of membrane fouling. It could efficiently represent the cross-flow filtration process as mentioned.

To analyze the quantity of samples eluted and absorbed to membrane in Fl-FFF channel, percent sample recovery (%) was determined by comparing the mean peak area of each sample recovery runs (Q_e, Q_{pr}) to the mean peak area without cross-flow (Dilution tube runs, Fig. 2(a), Q_{all}). Eqs. (1) and (2) were used to calculate sample recoveries throughout the course of this work. The amount of sample irreversibly adsorbed (Q_{ir}) to the membrane was determined via a mass balance [7]. As shown in Eqs. (1) and (2), Q_f indicates that the amount of sample adsorbed when system runs. So Q_f was calculated by subtracting the amount of eluted sample (Q_e) from the amount of total diluted sample (Q_{all}) (Eq. (2)). The amount of sample passed through the PES membrane of all experiments is calculated using total organic carbon (TOC) analyzer. This amount was not included to mass balance, since its quantity was not significant to detect.

$$Q_{all} = Q_e + Q_{pr} + Q_{ir} \tag{1}$$

$$Q_f = Q_{all} - Q_e = Q_{pr} + Q_{ir} \tag{2}$$

3. Results and discussion

3.1. Chemical aspects

The chemical aspects of elution peak (i.e. effect of TDS (NaCl) and calcium concentration) have been systemically investigated to find out the characteristics of fractionated HA behavior in Fl-FFF channel in terms of retention time. In addition, the sample recoveries were related to the amount of each fractionated HA samples eluted, transported, and deposited to membrane at different chemical conditions. Fouling experiments presented in this section were performed at fixed physical conditions (channel flow and cross-flow) so that only the chemical aspects of elution peak and sample recovery could be investigated.

3.1.1. Effect of NaCl on elution peak

It has been demonstrated that the NaCl concentration of solution affected the retention time and elution amount of injected sample. We suggested that the increase in NaCl concentration within Fl-FFF played an important role to increase the amount of HA deposited on membrane. In Fig. 3, the elution peaks of fractionated HA samples (200 mg TOC/L) from Fl-FFF channels equipped with 1 kDa PES membrane were obtained and compared. The injected sample volume was 20 µl. To analyze the effect of ionic strength, the carrier solutions were varied with compositions that are 0.152 M NaCl, 0.593 M NaCl, and 1.186 M NaCl solutions. A channel flow rate of 1 ml/min and a cross-flow rate of 3 ml/min were employed.

The results in Fig. 3 showed that the elution peak retention times were delayed, and the elution peak areas of all fractionated samples (Fig. 3a–e) decreased with the increase in ionic strength in carrier solution. These features are expressed in numerical value in Table 2. The longer retention time at the high ionic strength is resulted from the increase in the attractive

Table 2
Effect of TDS on elution peak retention time (sec) of fractionated organic samples

Size	0.152 M NaCl	0.593 M NaCl	1.186 M NaCl	Retention time difference (s)
HA < 0.45 µm	343.38	351.0	359.88	16.50
HA < 300 kDa	346.80	353.22	359.82	13.02
HA < 100 kDa	346.68	355.50	357.66	10.98
HA < 30 kDa	343.74	348.96	351.18	7.44
HA < 10 kDa	342.30	340.20	342.30	–

interaction between HA molecules and membrane wall. It is supposed that the electrostatic double-layer repulsion between HA and membrane in Fl-FFF diminishes as solution ionic strength increases [26]. Higher ionic strength of the carrier solution compresses the electric double layer of HA as well as membrane and, thus, allowing HA samples getting closer to the membrane surface where the hydraulic velocity of flow stream is slower as membrane is located to the wall of Fl-FFF channel. This implies that organic fouling in membrane process gets more severe with increasing NaCl concentration.

Regarding to TDS condition, there was more significant variation in retention time of the HA sample compared with the higher TDS condition. Retention time difference listed in Table 2 is the time difference between 0.152 M and 1.186 M NaCl carrier solutions. These results indicate that the elution peak retention times were also varied more significantly for HA of higher molecular weight range. This phenomenon is due to the organic fractions that have relatively large molecular distributions are located narrowly in lower position of channel flow stream. Thus, relatively larger organic fractions are affected by solution chemistry than that of smaller ones.

As shown in Table 2, there was a little variation in elution peak retention times of each fractionated samples at the same TDS concentration with the increase in molecular weight at 0.152 and 0.593 M NaCl condition, the retention time of each sample increased to some point and then decreased with the increase of molecular weight. Some research works [27] showed the results similar to these phenomena. To be specific, if the particle size range is less than 100 nm, the filtration process is determined only by the diffusion. While at the particle size is larger than 1 μm, the filtration is mainly controlled by the hydrodynamics. Results from Fl-FFF experiments also showed that the organic particles smaller than certain sizes were affected by interactions only by the diffusion and ionic

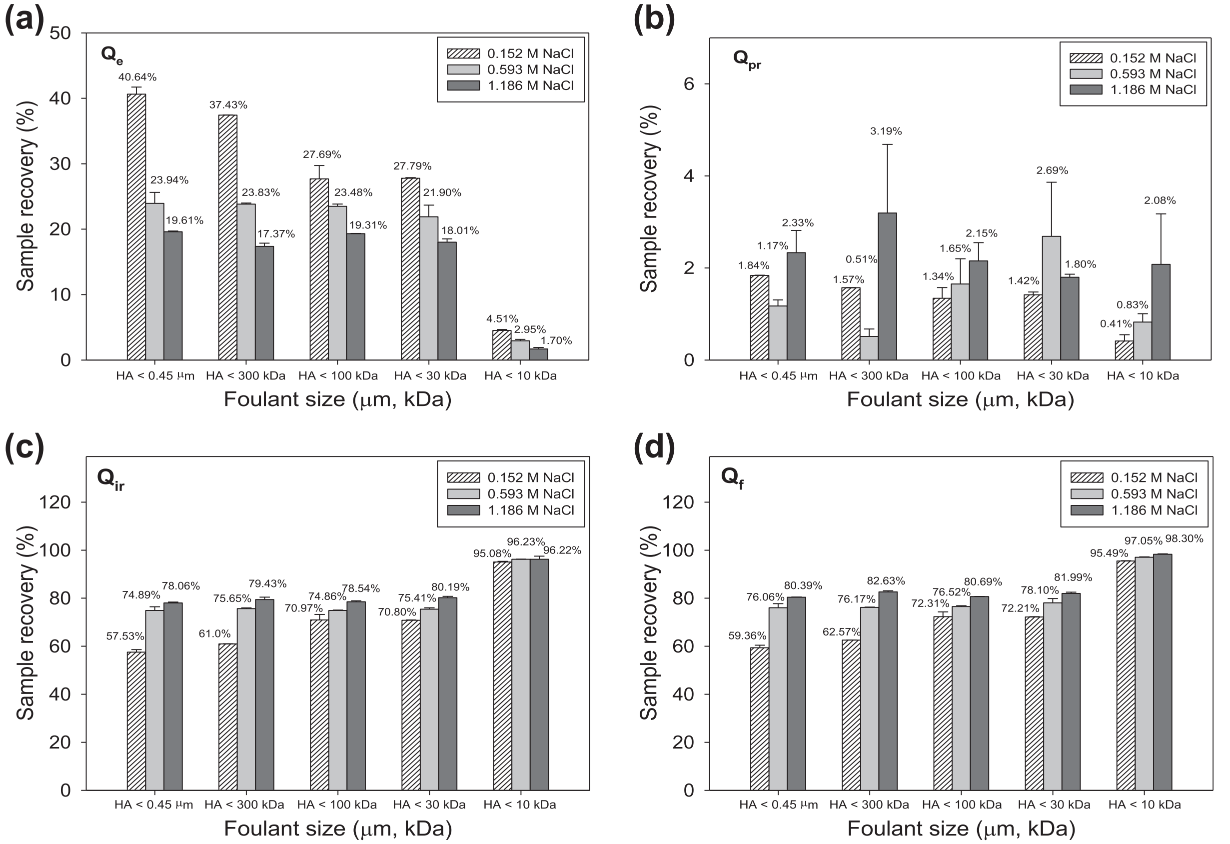

Fig. 4. Effect of TDS on sample recovery of fractionated organic samples. The channel flow rate is 1 ml/min and crossflow rate is 3 ml/min, and the carrier solutions are 0.152 M NaCl, 0.593 M NaCl, and 1.186 M NaCl. The injected foulants are 0.45 μm filtered HA, 300 kDa filtered HA, 100 kDa filtered HA, 30 kDa filtered HA and 10 kDa filtered HA samples of 200 mg TOC/L: (a) elution amount (Q_e) of each HA samples, (b) reversible fouling amount (Q_{pr}) of each HA samples, (c) irreversible fouling amount (Q_{ir}) of each HA samples, and (d) actual fouling amount (Q_f, $1-Q_e$) of each HA samples.

strength, while larger ones were mainly controlled by the hydrodynamics. Whereas, at the 1.186 M NaCl condition, the retention time decreased because the ionic strength was so strong that foulants were attracted by membrane surface due to charge screening effect. Thus, it drove the large samples to a slower velocity streamlines as the molecular weight of HA increased.

If we assume that the longer elution peak retention time means more severe organic fouling, in this manner, we could determine the HA samples causing the most severe fouling under given TDS conditions, as shown in Table 2. In 0.152 M NaCl condition, HA smaller than 300 kDa was found to be the most significant organic foulant among the fractionated HA samples tested based on Fl-FFF retention times compared with other fractionated HA samples. HA smaller than 100 kDa was the most significant foulant in 0.593 M NaCl condition and HA smaller than 0.45 μm was also shown most severe fouling in 1.186 M NaCl condition in terms of retention time.

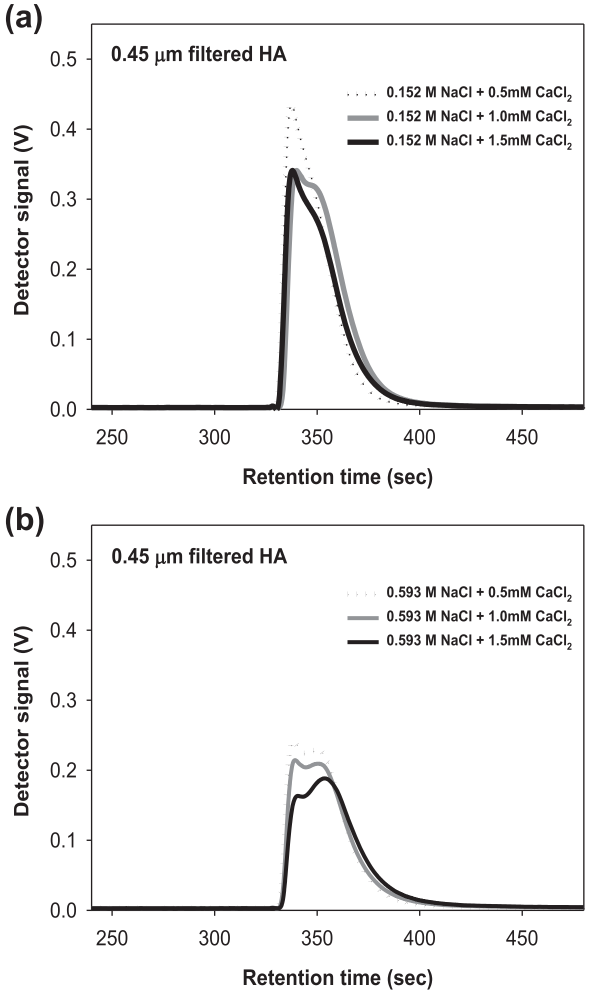

Fig. 5. Effect of calcium on elution peak of 0.45 μm filtered 300 mg TOC/L. The channel flow rate is 1 ml/min and cross-flow rate is 3 ml/min, and the carrier solution is: (a) 0.152 M NaCl combined with 0.5 mM $CaCl_2$, 1 mM $CaCl_2$ and 1.5 mM $CaCl_2$ and (b) 0.593 M NaCl combined with 0.5 mM $CaCl_2$, 1 mM $CaCl_2$ and 1.5 mM $CaCl_2$.

3.1.2. Effect of TDS on sample recovery

The elution peak retention time and peak areas were related to the amount of actual fouling with each fractionated HA samples at different TDS. Fig. 4 shows the percentage values of sample recovery of fractionated organic samples. The total value of sample recovery (100%) is corresponding to the total amount of each sample (200 mg TOC/L HA). Sample recoveries were measured using Fl-FFF software and calculated using Eqs. (1) and (2) with the results shown in Fig. 3. Fig. 4(a), by comparing the amount of sample eluted (Q_e), clearly showed that as the TDS concentration increased, the fouling amount of fractionated samples absorbed to membrane also increased. Fig. 4(b) exhibited that the amount of reversible fouling (Q_{pr}) had no distinct relation to TDS concentration. Results in Fig. 4(c) showed the increase in the amount of irreversible fouling. Fig. 4(d) represented the amount of samples absorbed to membrane when the Fl-FFF runs (Q_f). It can be also considered to the reverse value of Q_e (Fig. 4(a)). In direct opposition to the results of Fig. 4(a), sample absorbed (Q_f) clearly showed that as the TDS concentration increased, the actual fouling amount of fractionated samples absorbed to membrane also increase. As reported in the previous studies [21,26], as the TDS concentration of the solution increases, the electrical double layers around the humic acids decrease. As shown these fouling tendencies imply that the characteristics of NOM in Fl-FFF channel can be related to actual fouling behavior of membrane and specific size distribution of HA samples with variation of TDS can affect the fouling characteristics in Fl-FFF channel. Thus, cautions need to be exercised when designing the desalination plant concerning the TDS concentration and size of pretreatment filter (size distribution of HA foulants).

3.1.3. Effect of calcium on elution peak

It has been demonstrated that the calcium concentration of solution affected the elution peak retention time and elution peak area of injected sample at the presence of TDS. Similarly, the experiments were conducted to analyze the behavior of NOM mixed with calcium ions. The 20 of 0.45 μm filtered 300 mg TOC/L sample was injected through injection loop. To analyze the effect of calcium ions, the composition of carrier solutions were varied to be 0.5 mM $CaCl_2$, 1.0 mM $CaCl_2$, and 1.5 mM $CaCl_2$ combined with 0.152 M NaCl and 0.593 M NaCl. Fig. 5 indicates that as the calcium concentration increased at the same TDS condition, the retention time of HA samples slightly increased with little decreases in elution peak area except in the case of 1 mM $CaCl_2$ condition combined with 0.152 M NaCl solution. These features could be expressed in numerical value in Table 3. Although the calcium concentration was varied in very short range, the elution peak retention times increased and the elution peak areas decreased with increase in calcium ions. From the view point of retention time, organic fouling was most severe at 0.593 M NaCl combined with 1.5 mM $CaCl_2$ condition.

3.1.4. Effect of calcium on sample recovery

The elution peak retention times and peak areas were related to actual fouling amount of 0.45 μm filtered HA samples with the variations of calcium concentration. Fig. 6 shows the percentage values of sample recovery of 0.45 μm filtered organic samples injected to Fl-FFF channel. The results showed that the fouling amount of organic samples also increased when the calcium ion concentration increased. The amount of sample eluted (Q_e) clearly showed that as the calcium concentration increased, the amount of HA samples eluted from the membrane in Fl-FFF channel also decreased (Fig. 6(a)). However, the physically reversible fouling amount (Q_{pr}) of samples had no relationship with calcium concentration (not shown). The results described in Fig. 6(b) demonstrated the trend that the amount of irreversibly attached samples (Q_{ir}) increased with the increase in calcium ions. As shown in Fig. 6(c), the amount of HA (Q_f) actually absorbed increased gradually with the increase of calcium ions. Hong and Elimelech [26] reported that the presence of calcium ions in solution accelerated the fouling tendency of membranes by humic substances. When the calcium ion is present, the repulsion between the negatively charged groups of the humic acids also decreased causing the HA to become more coiled and compact. As the results obtained in Fig. 6, this also allows the HA to more

Table 3
Effect of calcium on elution peak retention time (sec) of 0.45 μm filtered 300 mg TOC/L samples

Carrier solution	0.5 mM $CaCl_2$	1.0 mM $CaCl_2$	1.5 mM $CaCl_2$
0.152 M NaCl	338.16	340.38	338.04
0.593 M NaCl	349.98	351.18	353.34

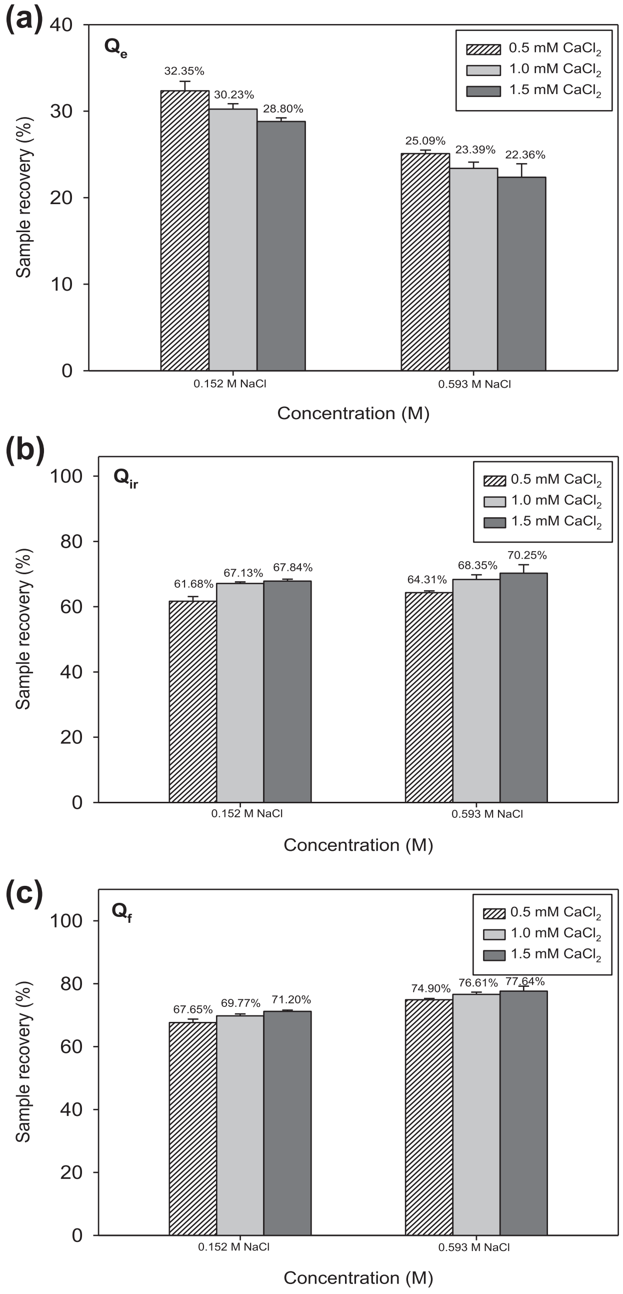

Fig. 6. Effect of calcium on sample recovery of 0.45 μm filtered 300 mg TOC/L samples. The channel flow rate is 1 ml/min and cross-flow rate is 3 ml/min, and the carrier solution are 0.152 M NaCl and 0.593 M NaCl combined with 0.5 mM $CaCl_2$, 1 mM $CaCl_2$ and 1.5 mM $CaCl_2$: (a) elution amount (Q_e) of HA sample, (b) irreversible fouling amount (Q_{ir}) of HA sample, and (c) actual fouling amount (Q_f, $1-Q_e$) of HA sample.

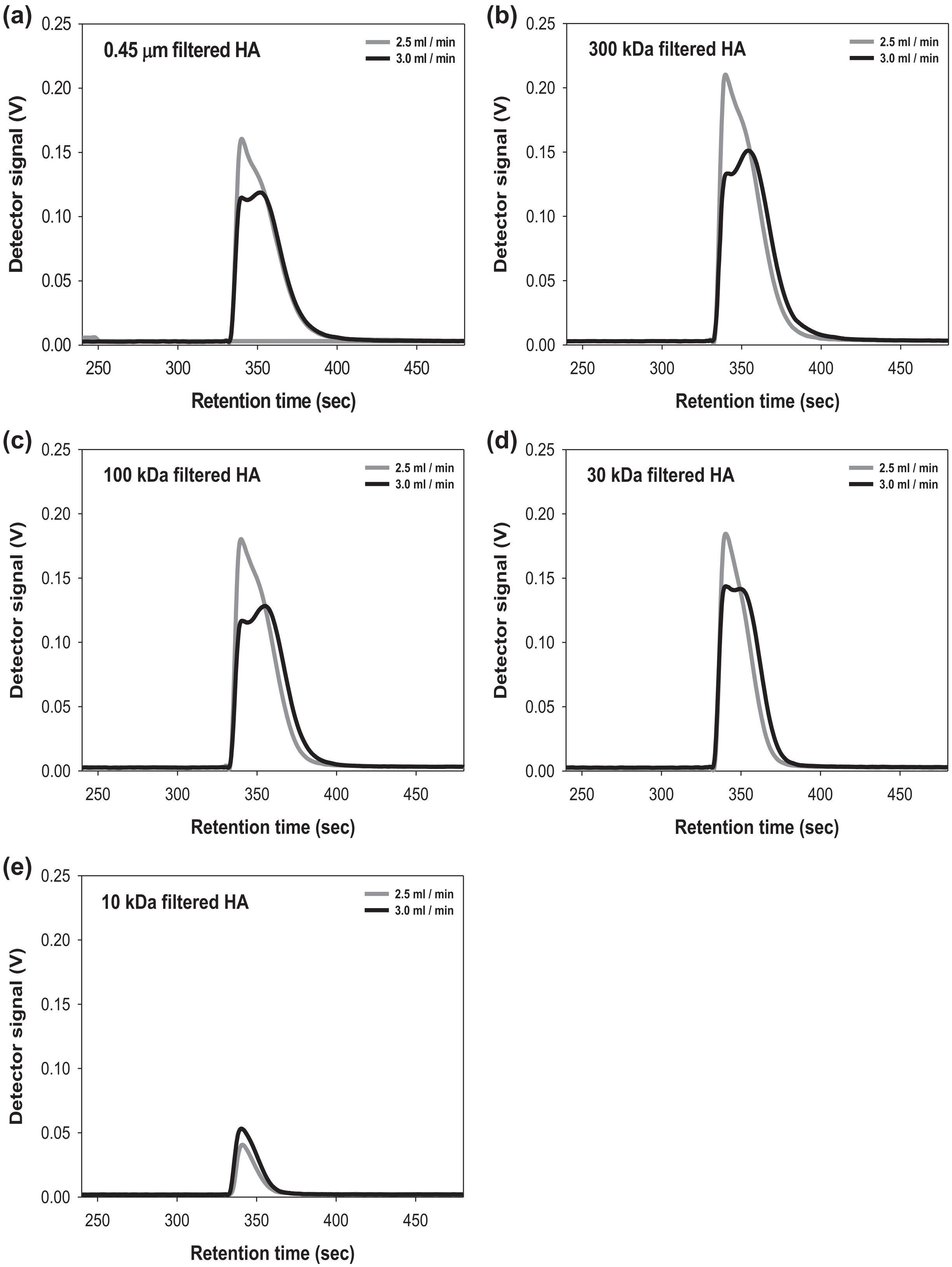

Fig. 7. Effect of cross-flow on elution peak of fractionated organic samples. The channel flow rate is 1 ml/min and cross-flow rate is 2.5 ml/min and 3 ml/min, and the carrier solution is 0.593 M NaCl. The injected foulants are: (a) 0.45 μm filtered HA, (b) 300 kDa filtered HA, (c) 100 kDa filtered HA, (d) 30 kDa filtered HA, and (e) 10 kDa filtered HA samples of 200 mg TOC/L.

closely approach to each other and the membrane. In addition, this smaller configuration allows the humic sample to form a more packed and dense adsorption layer on the membrane surface. Calcium ions also could connect negatively charged HA to each other and to the negatively charged membrane surface.

3.2. Physical aspects

In this section, we investigated the physical aspects of elution peak (i.e. effect of cross-flow intensity) to analyze the transport characteristics of fractionated HA with different physical conditions in terms of retention time. To relate the actual fouling amount of fractionated HA samples with various physical conditions, Fl-FFF experiments were also carried out under different cross-flow intensity. Fouling phenomenon was studied under fixed chemical conditions (ionic strength and divalent ions) so that only the physical aspects of elution peak and sample recovery could be investigated in this section.

3.2.1. Effect of cross-flow on elution peak

To analyze the physical effect, the cross-flow intensity was varied from 2.5 to 3.0 ml/min. The carrier solution consisted of 0.593 M NaCl to mimic the seawater condition. The results shown in Fig. 7 indicated that, when the cross-flow rate increased, the elution peak retention times increased and elution peak areas decreased, except for the case of 10 kDa filtered HA sample. The increase in the intensity of cross-flow narrowed the distance between the fractionated sample and the membrane surface. Former study [19] reported that the higher intensity of cross-flow drove the sample into slower velocity stream lines near the membrane surface increasing the probability of sample-membrane interactions and eluting the sample more late. These features could be verified in numerical value in Table 4.

Table 4 also indicated that the elution peak retention times were varied more significantly for HA of lower molecular weight range except for the cases of 30 and 10 kDa filtered HA samples. It was suggested that organic samples with relatively small molecular weights are more affected by physical hydrodynamics than larger ones. Specifically, HA samples larger than 100 kDa (i.e. HA < 0.45 μm, HA < 300 kDa, HA < 100 kDa) could be affected by physical factors dominantly in Fl-FFF channel. Lastly, the retention times presented in Table 4 also implied that the most severe fouling could be observed with HA smaller than 100 kDa in 0.593 M NaCl with 3 ml/min condition in Fl-FFF channel.

3.2.2. Effect of cross-flow on sample recovery

The intensity of cross-flow was related to actual fouling amount of each fractionated HA samples. The sample recoveries obtained using the results in Fig. 7 are expressed in Fig. 8. Fig. 8 shows that, as the intensity of cross-flow increased, the fouling amount of fractionated samples increased. This means that the increase of cross-flow intensity in the range investigated in this study could enhance the organic fouling of all HA samples in Fl-FFF channel as mentioned in section 3.2.1. However, the reversible fouling amount (Q_{pr}) and irreversibly attached amount (Q_{ir}) of samples showed no clear relationship with cross-flow

Table 4
Effect of cross-flow on elution peak retention time (sec) of fractionated organic samples

HA fractions	Cross-flow 2.5 ml/min	Cross-flow 3.0 ml/min	Retention time difference(sec)
HA < 0.45 μm	340.08	351.06	10.98
HA < 300 kDa	340.44	353.22	12.78
HA < 100 kDa	340.14	355.50	15.36
HA < 30 kDa	340.14	345.90	5.76
HA < 10 kDa	340.20	340.20	–

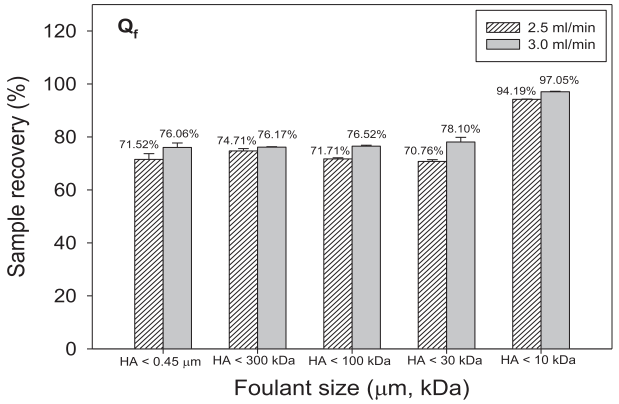

Fig. 8. Effect of cross-flow on sample recovery of fractionated organic samples: fouling amount (Q_f, $1-Q_e$) of each HA samples. The channel flow rate is 1 ml/min and cross-flow rate is 2.5 ml/min and 3 ml/min, and the carrier solution is 0.593 M NaCl. The injected foulants are 0.45 μm filtered HA, 300 kDa filtered HA, 100 kDa filtered HA, 30 kDa filtered HA and 10 kDa filtered HA samples of 200 mg TOC/L.

intensity (not shown). More profound research will be needed to further verify and elucidate organic fouling mechanisms under various hydrodynamic conditions.

4. Conclusion

The results shown in this study demonstrated that Fl-FFF analysis can be a useful tool to characterize NOM transport and fouling characteristics under various chemical and physical conditions corresponding to actual NF/RO processes. The molecular size and structure of fractionated HA samples can be influenced by the chemical (TDS, calcium ion concentration) and physical (cross-flow intensity) conditions due to interactions between Fl-FFF membrane wall and the HA samples. In particular, organic fouling tendency of HA < 300 kDa was the most severe at brackish water condition and HA < 100 kDa was most severe in seawater condition in terms of retention time. NOM with relatively large molecular weight was significantly influenced by chemical factors. It was found that there might be a critical size of organic foulants where both chemical and physical factors influence its transport and deposition behavior. This is an area we need to study in greater depth. In addition, it was observed that the elution peak and peak areas obtained from Fl-FFF analysis could be related to actual fouling amount of HA samples with variations of chemical and physical factors. It was found from Fl-FFF analysis that there was the obvious trend in the amount of sample eluted (Q_e) from membrane and absorbed (Q_f) to the membrane channel. However, no clear trends were observed in case of the physically reversible (Q_{pr}) amount of samples with variations of TDS, calcium concentration, and cross-flow intensity. By studying these characteristics of NOM under different chemical and physical conditions, it can be known that which NOM has to be separated at the pretreatment process of desalination or water treatment process. Specifically, by analyzing the data from Fl-FFF measurements, organic fouling is expected to be severe for HA with 100–300 kDa in brackish and seawater conditions and, thus, optimum pretreatment such as UF membrane with proper pore size and coagulation right doses should be designed and operated for minimizing organic fouling under seawater conditions.

Acknowledgments

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