



# *In situ* extracting organic-bound calcium: A novel approach to mitigating organic fouling in forward osmosis treating wastewater via gradient diffusion thin-films

Ling Li <sup>a</sup>, Xinhua Wang <sup>a,\*</sup>, Ming Xie <sup>b</sup>, Zhiwei Wang <sup>c</sup>, Xiufen Li <sup>a,\*\*</sup>, Yueping Ren <sup>a</sup>

<sup>a</sup> Jiangsu Key Laboratory of Anaerobic Biotechnology, School of Environmental and Civil Engineering, Jiangnan University, Wuxi, PR China

<sup>b</sup> Institute for Sustainability and Innovation, College of Engineering and Science, Victoria University, Melbourne, Australia

<sup>c</sup> State Key Laboratory of Pollution Control and Resource Reuse, School of Environmental Science and Engineering, Tongji University, Shanghai, PR China

## ARTICLE INFO

### Article history:

Received 17 October 2018

Received in revised form

13 March 2019

Accepted 14 March 2019

Available online 19 March 2019

### Keywords:

Forward osmosis

Membrane fouling

Organic foulants

Calcium

Gradient diffusion thin-films

Wastewater treatment

## ABSTRACT

Forward osmosis (FO) has gained increasing interests in wastewater treatment and reclamation. However, membrane fouling has become one major obstacle hindering FO application. A novel mitigation approach for FO membrane fouling via *in situ* extracting  $\text{Ca}^{2+}$  binding with the organic foulants using the gradient diffusion thin-films (DGT) was proposed in this study. The DGT could effectively adsorb the  $\text{Ca}^{2+}$  binding with the sodium alginate via the chelation of the Chelex functional groups, and its adsorption amount of  $\text{Ca}^{2+}$  correspondingly increased as a function of the  $\text{Ca}^{2+}$  concentration in the feed solution. Owing to the extraction of  $\text{Ca}^{2+}$  from the fouling layer by the DGT, the FO membrane fouling was effectively mitigated evident by significant enhancement of water flux, and at the same time, foulants became easily removed by physical cleaning. The alleviation of FO membrane fouling by the DGT could be attributed to the fact that the structure of the fouling layer became more porous and looser after *in situ* removing  $\text{Ca}^{2+}$  from the alginate- $\text{Ca}^{2+}$  gel networks. The feasibility of fouling control strategy via *in situ* removing  $\text{Ca}^{2+}$  binding with the foulants in the fouling layer was demonstrated, which provides new insights into fouling control mechanisms during FO treating wastewater.

© 2019 Elsevier Ltd. All rights reserved.

## 1. Introduction

Forward osmosis (FO) process has raised increasing attentions as a promising technology for wastewater treatment and reclamation (Liu and Mi, 2012; Zhao et al., 2012; Lutchmiah et al., 2014). FO process utilizes osmotic pressure gradient as driving force to extract water molecule from the feed solution (FS) through the FO membrane to the draw solution (DS). Compared to the pressure-driven membrane processes including reverse osmosis (RO) and nanofiltration (NF), the osmotic pressure-driven FO process has several advantages such as lower energy consumption (if no need to regenerate the draw solution), higher water recovery, and superior water flux stability against fouling (McGinnis and Elimelech, 2007; Mi and Elimelech, 2010; Gu et al., 2013; McGovern and

Lienhard, 2014; Shaffer et al., 2015; Tow and Lienhard, 2016; Siddiqui et al., 2018). Nevertheless, similar to other membrane processes, membrane fouling remains a major obstacle hindering a wider application of FO to complex waste streams, and its combined bioreactor (e.g., osmotic membrane bioreactor (OMBR) and anaerobic membrane bioreactor (AnOMBR)) in wastewater treatment and reclamation (Mi and Elimelech, 2010; She et al., 2016; Wang et al., 2016a, 2017; 2018a, 2019; Luo et al., 2017).

Fouling occurs when solutes or particles in the feed deposit onto surfaces or into pores of the FO membrane (Liu and Mi, 2012), which not only enhances the resistance of FO membrane but also increases the external concentration polarization (ECP) (Wang et al., 2014; Motsa et al., 2015). FO membrane fouling can be classified as organic, inorganic, microbial (biofouling) and colloidal fouling (Liu and Mi, 2012; Wang et al., 2014; Sun et al., 2016). Abundant and ubiquitous organic substances in the feed water such as, natural organic matters, alginates, and proteins, induce severe fouling on FO membrane surface (Mi and Elimelech, 2008, 2010; Xie et al., 2013). In addition, inorganic species not only tend to directly precipitate onto the FO membrane surface but also interact

\* Corresponding author.

\*\* Corresponding author.

E-mail addresses: [xhwang@jiangnan.edu.cn](mailto:xhwang@jiangnan.edu.cn) (X. Wang), [xfli@jiangnan.edu.cn](mailto:xfli@jiangnan.edu.cn) (X. Li).

with the organic foulants by bridging negatively charged functional groups (Sobeck and Higgins, 2002; Boo et al., 2012). Moreover, microorganisms especially bacteria can adhere to the FO membrane and subsequently form a biofilm (Yoon et al., 2013; Kwan et al., 2015), and colloidal fouling is owing to the deposition of colloidal particles (Liu and Mi, 2012). Correspondingly, FO membrane fouling has been extensively investigated using single model foulant such as alginate, bovine serum albumin (BSA), gypsum and *Pseudomonas aeruginosa* (Mi and Elimelech, 2008; Arkhangelsky et al., 2012; Kwan et al., 2015). Compared with other fouling types, organic fouling is more complicated, not only because specific interactions between chemical functional groups on the FO membrane surface and those of the organic foulants may occur, but it was also found to be affected by the ionic composition of the feed solution (Li and Elimelech, 2006). As a result, previous studies on FO membrane fouling are focused on organic fouling (Li and Elimelech, 2006; Mi and Elimelech, 2010; Liu and Mi, 2012; Motsa et al., 2015; Zheng et al., 2018). In these studies, it has been demonstrated that organic fouling of FO membrane is enhanced by divalent cations, i.e., forming a dense, cross-linked organic fouling layer, and consequently resulting in a rapid flux decline (Li and Elimelech, 2006). It is hypothesized that if the divalent cations can be extracted from the foulants on the FO membrane surface, the organic fouling layer might become loose and subsequently easily remove by a simply physical cleaning.

Diffusive gradients in thin-films (DGT) has become an attractive technology with a wide range of applications, including water quality monitoring, dynamic processes and bioavailability in waters and soils (Perez et al., 2009; Town et al., 2009; Schintu et al., 2010). The DGT technology can be used to adsorb most metals (e.g., Al, Zn, Cu) in water and soil based on Fick's first law of diffusion (Zhang and Davison, 1995; Degryse et al., 2009; Guan et al., 2015). It consists of the innermost resin layer, a specific thickness of the diffusion gel, and a membrane filter (Zhang et al., 1998; Guan et al., 2015). The diffusive gel provides a controlled medium through which ions migrate before being adsorbed on the resin, and the resin layer is used to absorb the enriched target ions (Sherwood et al., 2009). The adsorbent material in the resin layer has a strong binding ability to metal (metalloid) ions, and its target in the solution is adsorbed immediately after passing through the diffusion gel to the resin layer (Davison and Zhang, 2012). The DGT technology has the advantages of simplicity, *in situ* and quantitative concentration of metals and non-metallic elements, as well as morphological analysis by simulating the absorption process of organisms (Zhang and Davison, 2015).

We are inspired by the successful extraction of metal ions from soils/sediments using DGT, where the metal ions in soils/sediments are effectively transferred to the DGT and subsequently to the liquid phase. In this study, applying the DGT technology for *in situ* adsorbing the divalent cations binding with the organic foulants from the FO membrane surface was attempted, thereby for mitigating membrane fouling and facilitating the subsequent membrane cleaning. Studies on applying the DGT technology for controlling organic fouling of FO membrane were rare in current literature. The objective of this study is to evaluate the feasibility of alleviating the FO membrane fouling through *in situ* removing the  $\text{Ca}^{2+}$  combined with the organic foulants by the DGT technology.

## 2. Materials and methods

### 2.1. Experimental set-up

Fouling profile of the FO membrane was evaluated in a bench-scale filtration system, as schematically shown in Fig. S1, Supporting Information. This test system included a cross-flow membrane

cell with two symmetric flow channels (each of 85 mm × 39 mm × 2 mm in dimension). Membrane coupons were placed in the membrane cell between the two channels for the DS and FS, respectively. Two peristaltic pumps (Longer Precision Pump, China) were used to pump the DS and FS into the separate closed loops. The cross-flow velocity in both channels of the membrane cell was constant at 1.3 mm/s. Both DS and FS were kept at room temperature ( $25 \pm 2^\circ\text{C}$ ). Change in the weight of FS was monitored by a digital balance (Mettler Toledo, China) and recorded in a computer by a data acquisition software (Mettler Toledo, China), which was converted into changes in water flux of FO membrane.

### 2.2. Operating conditions

Thin film composite (TFC) polyamide FO membrane (supplied by Hydration Technology Innovations) was used in this study. The TFC membrane has an asymmetric structure including a dense active layer (AL) and a porous support layer (SL) embedded with a polyester mesh. The water permeability coefficients ( $A$ ) and salt permeability coefficients ( $B$ ) of the TFC FO membrane were  $4.9 \times 10^{12} \text{ m/(s Pa)}$  and  $0.95 \times 10^{-7} \text{ m/s}$ , respectively. Membrane samples were stored in deionized (DI) water at  $4^\circ\text{C}$  and soaked in DI water at room temperature for 24 h before each test.

A 4 M NaCl solution was used as the DS in both fouling and baseline experiments. Sodium alginate (75–100 kDa) was selected as the model organic foulant. The baseline experiment was conducted before the fouling experiment with the DI water as the FS and the 4 M NaCl as the DS. In order to evaluate the adsorption efficiency of DGT for  $\text{Ca}^{2+}$  binding with the sodium alginate, the FO membrane was fouled by the sodium alginate and  $\text{CaCl}_2$  in sequence, which was different from the previous fouling protocol (Liu and Mi, 2012; Motsa et al., 2015). The procedure of the FO membrane fouling tests was conducted as follows (see for Fig. S2, Supporting Information). Firstly, a new FO membrane coupon was sealed in the FO cell with active layer facing FS, and then a baseline experiment was performed for 4 h to obtain the initial flux of the FO membrane. After that, the fouling tests were started with 2 L of FS and DS. With regard to the single organic fouling, the fouling filtration was operated for 48 h; while the enhanced organic fouling filtration was conducted with a  $\text{CaCl}_2$  solution for 24 h after the single organic fouling experiments operated for 24 h. As for the single organic fouling, the FS consisted of 200 mg/L sodium alginate, 20 mM NaCl, 20 mM  $\text{Na}_2\text{SO}_4$  and 1 mM  $\text{NaHCO}_3$ , while the FS was changed into the  $\text{CaCl}_2$  solution with three concentration levels of 1, 15 and 35 mM, respectively, for the tests of enhanced organic fouling by the  $\text{Ca}^{2+}$ . All the chemicals were obtained from Sigma-Aldrich (Shanghai, China).

### 2.3. DGT adsorption and evaluation

The DGT adsorption experiments were conducted after the fouling tests. As schematically shown in Fig. 1, the DGT device

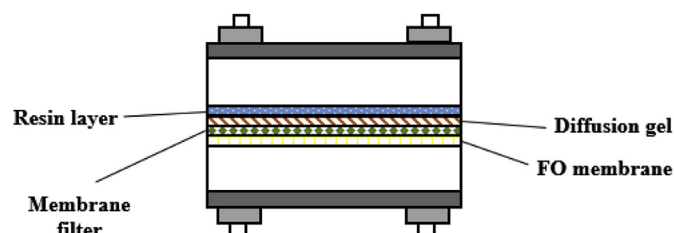


Fig. 1. Schematic view of the DGT adsorption device for the fouled FO membranes.

included the membrane filter, the diffusive gel strip and the resin layer (DGT Research Ltd., UK). During the adsorption experiments, the fouled FO membranes were attached to the membrane filter for 48 h. After that, the resin layer made of Chelex-100 strip (a commonly used chelating resin) was removed into the 1 M HNO<sub>3</sub> eluent for 24 h. Meanwhile, the remaining foulants were removed from the FO membrane surface by ultrasound (35 Hz, 15 min) (Pendashteh et al., 2011). The extracted and ultrasound-extractable remaining Ca<sup>2+</sup> concentrations were measured by an Atomic Absorption Spectrometer (Shimadzu Tokyo, Japan).

In order to evaluate the adsorption efficiency of the DGT, the extracted Ca<sup>2+</sup> concentration was converted into the adsorption amount on the Chelex gel strip according to the below equation.

$$M = C_e V_e / f_e \quad (1)$$

where  $M$  is the amount of Ca<sup>2+</sup> absorbed on the Chelex gel strip,  $C_e$  is the concentration of Ca<sup>2+</sup> in the eluent,  $V_e$  is the volume of the eluent (50 mL in this study), and  $f_e$  is the elution efficiency (0.8 for Ca<sup>2+</sup>) (Zhang and Davison, 1995; Warnken et al., 2006; Montero et al., 2012).

The ultrasound-extractable remaining Ca<sup>2+</sup> amount on the fouled FO membrane was correspondingly converted by the following equation.

$$M_R = C_R V_R \quad (2)$$

where  $M_R$  is the amount of Ca<sup>2+</sup> remained on the fouled membrane surface,  $C_R$  is the concentration of the ultrasound-extractable remaining Ca<sup>2+</sup>, and  $V_R$  is the volume of the dissolved residual foulants (100 mL in this study).

Based on the calculation of  $M$  and  $M_R$ , the adsorption efficiency ( $\eta$ ) was obtained according to the below equation.

$$\eta (\%) = M / (M + M_R) \times 100\% \quad (3)$$

#### 2.4. Analytical method

Water flux through the FO membrane was obtained based on the weight change of the FS. After the fouling tests and the DGT adsorption experiments, the water flux of the fouled and adsorbed FO membranes were determined by the FO cell for 4 h with the DI water as the FS and the 4 M NaCl as the DS. In order to eliminate the impacts of initial water flux (also measured by the FO cell) for different FO membranes, a normalized water flux was used for characterizing the fouled and adsorbed FO membranes. It was obtained through the determining flux dividing by the initial flux before fouling tests.

The conductivity of the FS was monitored and recorded by a conductivity meter (EC300A, YSI, USA). The FO membrane samples were obtained by randomly cutting from the fouled FO membranes removed from the FO cell. An energy diffusive X-ray (EDX) analyzer (Su-8020, Hitachi, Japan) and a field-emission scanning electron microscopy (FE-SEM) (Su-8020, Hitachi, Japan) were applied for capturing the element compositions and surface images of the fouled and adsorbed FO membrane samples, respectively. Prior to SEM and EDX observations, all FO membrane samples were prepared by freezing the membrane at  $-80^\circ\text{C}$  in a chiller for 2 h followed by freeze drying at  $-48^\circ\text{C}$  for 6 h using a freeze dryer (FreeZone 25, Labconco, Czech Republic). The distributions of polysaccharides on the fouled and adsorbed FO membrane samples were analyzed by the confocal laser scanning microscopy (CLSM) (LSM 710, ZEISS, Germany). The probe of Calcofluor white (CW) (0.3 g/L) was used to stain the polysaccharides on the FO membrane

samples. After the labeling process, the samples were incubated for 30 min at room temperature in the dark, and then were washed twice with phosphate buffered saline (PBS) solution to remove the extra probes. The stained FO membrane samples were characterized by the CLSM at the excitation/emission wavelengths of 405 nm/410–480 nm. Three-dimensional reconstructions were obtained with ZEISS confocal software, and the images were analyzed by softwares of PHILIP (Version 0.7) and Image J (NIH, Bethesda, MD, USA) to calculate the quantitative parameters including average amount of polysaccharide, mean thickness and porosity (Mueller et al., 2006; Yu et al., 2011; Yuan et al., 2015; Wang et al., 2016b).

All experiments are repeated at least three times for statistics. The data shown in tables and figures is expressed as means with standard deviations.

### 3. Results and discussion

#### 3.1. Water flux profile

Water flux profiles of FO membranes at different fouling conditions are shown in Fig. 2. Water flux of FO membrane decreased with the extension of the operating time regardless of the composition of the FS. However, the profile for FO membrane water flux decline was highly dependent on the foulants composition in the FS. Compared with the single organic fouling only induced by the sodium alginate, the flux decline became severer when the Ca<sup>2+</sup> was added into the FS. In addition, the rate for water flux decline was accelerated with an increase of the Ca<sup>2+</sup> concentration. Moreover, the cleaning experiments on the fouled FO membranes at different fouling conditions were conducted by the backwashing in the FO cell for 0.5 h with the 0.5 M NaCl as the FS and the DI water as the DS according to previous literature (Mi and Elimelech, 2010; Motsa et al., 2017). The results indicated that the alginate fouling became difficult to clean when Ca<sup>2+</sup> was present in the influent, e.g., the increasing rate of the normalized water flux was about 20% for the single organic fouling only induced by the sodium alginate while it became less than 5% for the organic fouling induced by the sodium alginate and 35 mM Ca<sup>2+</sup>. These facts clearly showed that Ca<sup>2+</sup> aggravated the organic fouling of FO membrane, which was consistent with previous literature (Liu and Mi, 2012; Motsa et al., 2015; Charfi et al., 2017). This phenomenon could be attributed to the fact that Ca<sup>2+</sup> and alginate form complexes with unique structure, thereby leading to a high density gel network

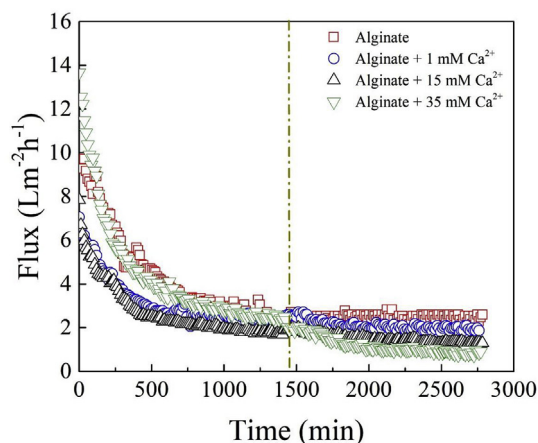


Fig. 2. Water flux profile of FO membranes during fouling filtration. FO fouling filtration was conducted with feed solution containing 200 mg/L sodium alginate, 20 mM NaCl, 20 mM Na<sub>2</sub>SO<sub>4</sub> and 1 mM NaHCO<sub>3</sub>, with varying calcium concentration from 1 to 35 mM. Draw solution was 4 M NaCl. The filtration was operated for 24 h.

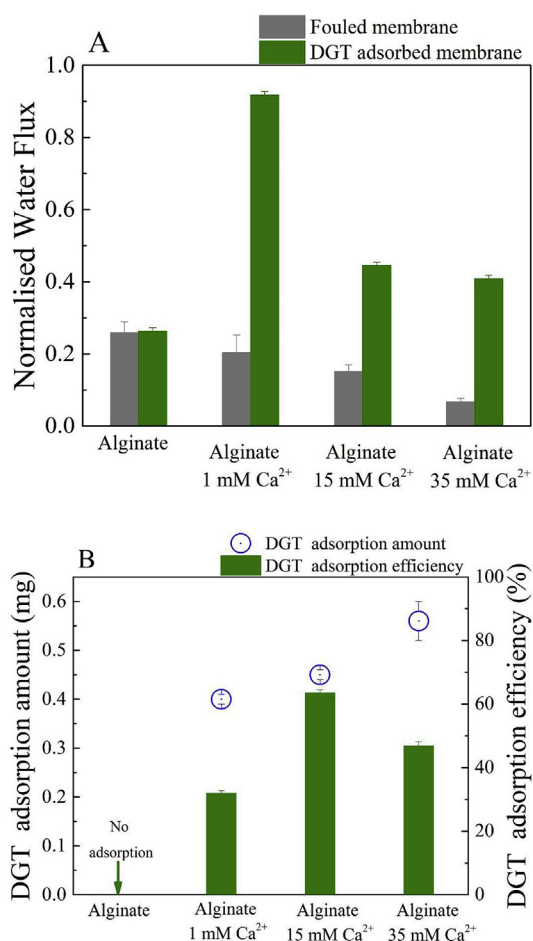


(Van den Brink et al., 2009; Wang and Waite, 2009).

### 3.2. DGT approach effectively extracted calcium from fouling layer

After the fouling tests of the FO membranes,  $\text{Ca}^{2+}$  was extracted from the fouled FO membranes by the DGT technology. The normalized membrane flux of the fouled FO membranes before and after DGT adsorptions are summarized in Fig. 3 (a). Specifically, there were no changes in the normalized water flux of the fouled FO membrane with only alginate sodium before and after the DGT adsorption, indicating that the DGT had no impacts on the single organic fouling of FO membrane. By contrast, the normalized water flux had a significant increase after the DGT adsorption for the organic fouling enhanced by  $\text{Ca}^{2+}$ , suggesting an effective mitigation of FO membrane fouling. Variations of the normalized water flux for different fouling conditions were consistent with the DGT adsorption efficiency (see for Fig. 3 (b)): indeed, there was no  $\text{Ca}^{2+}$  adsorption for the single organic fouling while the DGT adsorption efficiency was ranged from 32.6% to 62.8% for the enhanced organic fouling with different concentrations of  $\text{Ca}^{2+}$ . These results implied that the DGT could effectively adsorb  $\text{Ca}^{2+}$  from the alginate bound foulants. As a result, organic fouling of the FO membrane could be alleviated via the extraction of  $\text{Ca}^{2+}$  from the fouling layer.

Although the DGT could adsorb the  $\text{Ca}^{2+}$  from the fouling layer



**Fig. 3.** DGT performance in fouling mitigation: (A) Normalized water flux and (B) DGT adsorption amount and efficiency at different fouling conditions. The FO fouling filtration conditions were described in Fig. 2. DGT adsorption was performed using a DGT device with Chelex-100 strip, 1 M  $\text{HNO}_3$  as the eluent. The error bar represents the standard deviation from three repeated experiments.

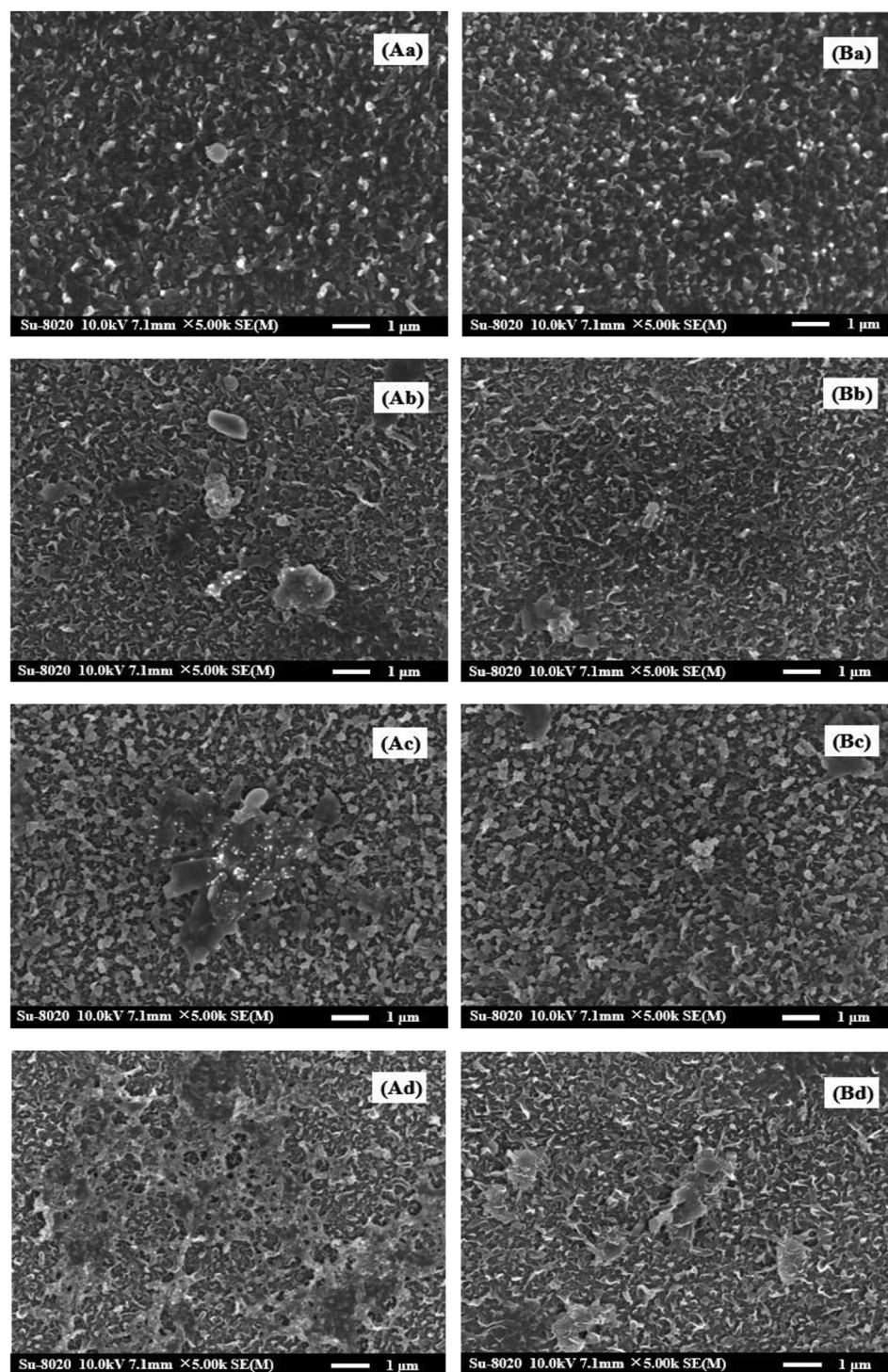
of the FO membrane, the adsorption amount and efficiency were significantly influenced by adding concentration of  $\text{Ca}^{2+}$ . DGT adsorption amount of  $\text{Ca}^{2+}$  correspondingly increased with the feed  $\text{Ca}^{2+}$  concentration (Fig. 3 (b)), which was driven by more  $\text{Ca}^{2+}$  binding with the alginate at a higher addition of  $\text{Ca}^{2+}$ . However, the adsorption efficiency was enhanced from 1 to 15 mM  $\text{Ca}^{2+}$ , and started to decrease when  $\text{Ca}^{2+}$  concentration reached 35 mM. Given that the DGT was constrained by adsorption capacity, the decrease of adsorption efficiency at  $\text{Ca}^{2+}$  concentration of 35 mM could be attributed to the saturation of DGT adsorption ( $0.59 \pm 0.01$  mg). Indeed, it was interesting that the DGT adsorption efficiency was not correlated with the increase of the normalized water flux after the DGT adsorption (Fig. 3 (a)), suggesting that the different structure and composition of the fouling layer on the FO membrane surface at different fouling conditions might strongly affect the mitigation of membrane fouling by the DGT adsorption. Thus, it is very necessary to further investigate the changes in structure and composition of the fouling layer before and after the DGT adsorption.

### 3.3. DGT adsorption altered fouling layer structure and improved cleaning efficiency

In order to evaluate the structure of fouling layer before and after DGT adsorption, the morphology, element composition and structure of fouled and DGT adsorbed FO membranes were analyzed by SEM, EDX and CLSM, respectively. The SEM images of the fouled FO membranes before and after the DGT adsorption are shown in Fig. 4. Compared with the SEM image of the virgin FO membrane (Fig. S3), a fouling layer was formed on the FO membrane surface when only sodium alginate was used. However, except for the fouling layer, some macromolecular biopolymers were appeared on the FO membrane surface in all scenarios with  $\text{Ca}^{2+}$  addition into the feed. More importantly, more macromolecular biopolymers deposited on the membrane surface with the increase of  $\text{Ca}^{2+}$  concentration. This result further demonstrated that  $\text{Ca}^{2+}$  enhanced the organic fouling and induced a severer FO membrane fouling. Noting that the high density “egg-box-shaped” gel networks were observed on the FO membrane surface when  $\text{Ca}^{2+}$  concentration increased to 35 mM. Correlation of foulant deposition amount on the FO membrane surface and the  $\text{Ca}^{2+}$  concentration observed from SEM images were consistent with the variations of the flux decline (Fig. 2). After the DGT adsorption, except for the single organic fouling induced by the sodium alginate (Fig. 4 (Aa) and Fig. 4 (Ba)), the deposition of alginate fouling layer on the FO membrane surface minimized regardless of the  $\text{Ca}^{2+}$  concentration, indicating the effective adsorption of  $\text{Ca}^{2+}$  from the fouling layer of the FO membrane by the DGT technology.

From the EDX analyses, various elements including C, O, Na, S, Cl and Ca could be detected on the fouled FO membranes (Fig. S4 and Table S1). It was notable that the relative weight percentage of Ca on the fouled FO membranes correspondingly increased with the increase of the adding  $\text{Ca}^{2+}$  concentration, further indicating the occurrence of more severe “egg-box-shaped” gel networks on the FO membrane surfaces. After the DGT adsorptions, the relative weight percentage of Ca significantly reduced (Fig. S5 and Table S2). This result strongly proved the effective adsorption of  $\text{Ca}^{2+}$  from the fouling layer of the FO membrane by the DGT technology.

For further understanding the impacts of the DGT adsorption on the fouling structure of the FO membrane, the fouled FO membranes before and after the DGT adsorption were analyzed by the CLSM observations. From Fig. S6, all the fouled FO membrane surfaces were covered by polysaccharides, and these formed fouling layers were thick. The deposited polysaccharides slightly decreased for the fouling by both sodium alginate and  $\text{Ca}^{2+}$  after the DGT



**Fig. 4.** SEM images of the fouled (A) and DGT adsorbed (B) FO membranes: (a) single organic fouling; (b) organic fouling + 1 mM  $\text{Ca}^{2+}$ ; (c) organic fouling + 15 mM  $\text{Ca}^{2+}$ ; (d) organic fouling + 35 mM  $\text{Ca}^{2+}$ .

adsorption (Fig. S6 and Table 1). In addition, the porosity of the fouling layers induced by both the sodium alginate and  $\text{Ca}^{2+}$  significantly increased after the DGT adsorption (see for Table 1). It has been demonstrated that the porosity significantly affects membrane fouling, i.e., less porosity results in a severe membrane fouling (Wu et al., 2009; Wang et al., 2018b). Thus, the mitigation of the fouling owing to both the alginate and  $\text{Ca}^{2+}$  by the DGT technology was mainly attributed to the fact that the structure of the

fouling layer became more porous after the extraction of the organic-bound  $\text{Ca}^{2+}$ .

In order to further investigate whether DGT adsorption could enhance the physical cleaning, the fouled and DGT adsorbed FO membranes at the FS condition of sodium alginate and 35 mM  $\text{Ca}^{2+}$  were backwashed according to previous literature (Mi and Elimelech, 2010; Motsa et al., 2017). There was no significant variation of the normalized water flux for the fouled FO membrane

**Table 1**  
Structural parameters of fouling layer before and after DGT adsorption obtained from CLSM images via PHILIP<sup>a</sup>.

	Fouling layer	Average amount of polysaccharide ( $\mu\text{m}^3 \mu\text{m}^{-2}$ )	Porosity (%)	Mean thickness ( $\mu\text{m}$ )
Before DGT adsorption	single organic fouling	$12.25 \pm 0.41$	$32.10 \pm 4.70$	$24.85 \pm 1.32$
	organic fouling + 1 mM $\text{Ca}^{2+}$	$13.00 \pm 1.08$	$22.78 \pm 7.54$	$24.81 \pm 3.69$
	organic fouling + 15 mM $\text{Ca}^{2+}$	$14.06 \pm 0.93$	$18.26 \pm 9.46$	$26.26 \pm 1.44$
	organic fouling + 35 mM $\text{Ca}^{2+}$	$14.13 \pm 0.87$	$16.27 \pm 0.80$	$25.56 \pm 3.38$
After DGT adsorption	single organic fouling	$12.45 \pm 0.05$	$35.06 \pm 2.51$	$24.68 \pm 3.26$
	organic fouling + 1 mM $\text{Ca}^{2+}$	$12.40 \pm 0.09$	$33.49 \pm 2.90$	$22.31 \pm 0.95$
	organic fouling + 15 mM $\text{Ca}^{2+}$	$13.00 \pm 0.19$	$28.14 \pm 8.81$	$23.46 \pm 0.29$
	organic fouling + 35 mM $\text{Ca}^{2+}$	$13.14 \pm 0.26$	$20.86 \pm 3.62$	$24.78 \pm 0.49$

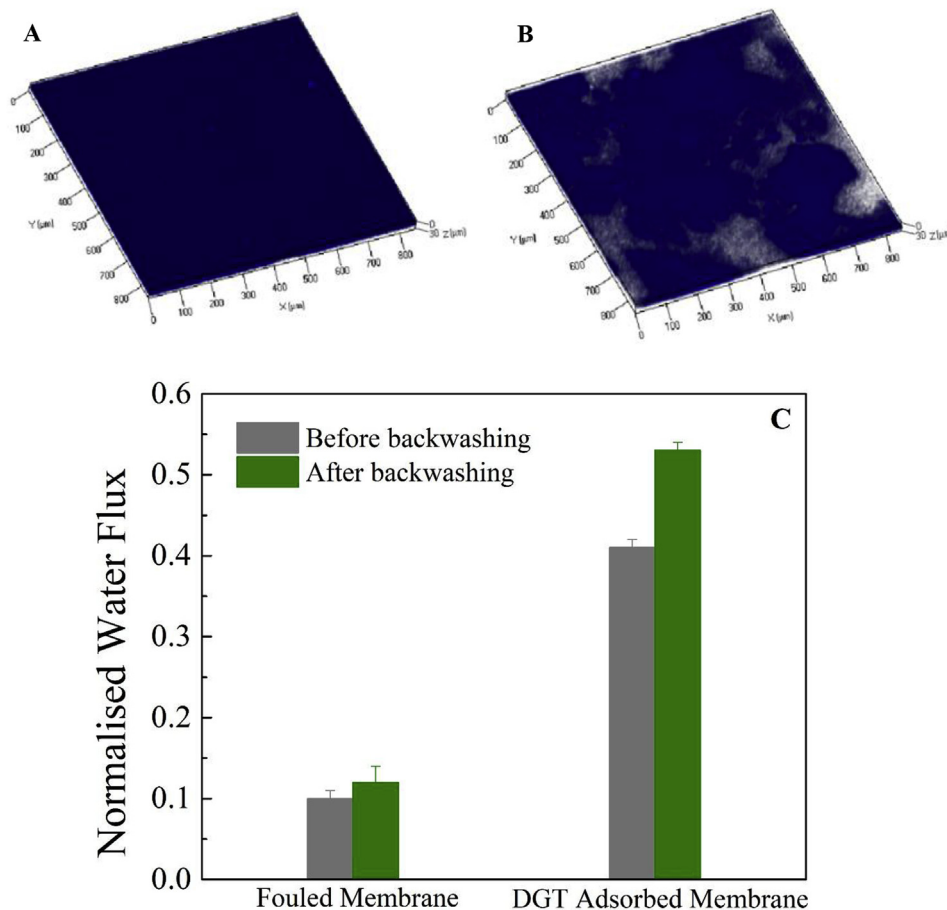
<sup>a</sup> Values are given as mean values  $\pm$  standard deviation (number of measurements:  $n = 3$ ). The scanning area was  $850 \times 850 \mu\text{m}^2$  in size.

after the backwashing; by contrast, it significantly increased from 0.41 to 0.53 for the DGT adsorbed FO membrane after backwashing (Fig. 5). It suggested that the DGT adsorption could enhance the physical cleaning of the fouled FO membranes. Such evidence strongly suggested that the DGT adsorption not only mitigated the FO membrane fouling but also enhanced the membrane cleaning via changing the structure of the fouling layer.

### 3.4. Implications

We demonstrated that the DGT technology can effectively alleviate organic fouling of FO membranes via directly adsorbing  $\text{Ca}^{2+}$  from the fouling layer. The mechanisms on the *in situ* mitigating FO membrane fouling are conceptualized in Fig. 6. With regard to a thick fouling layer with alginate- $\text{Ca}^{2+}$  gel networks, the Chelex

resin in the DGT device can directly remove the alginate-bound  $\text{Ca}^{2+}$  via the chelation of the Chelex functional groups. Due to the extraction of the alginate-bound  $\text{Ca}^{2+}$  from the organic fouling layer, the structure of the fouling layer became more porous and looser, which mitigated the FO membrane fouling and further enhanced the cleaning efficiency. Moreover, the DGT device can be reused for adsorbing  $\text{Ca}^{2+}$  after the resin layer was regenerated by  $\text{HNO}_3$  based on the results that the reused DGT device had a similar  $\text{Ca}^{2+}$  adsorption amount compared with the new one. The success in alleviating organic fouling of the FO membrane demonstrated the feasibility of fouling control strategy via directly extracting  $\text{Ca}^{2+}$  from the fouling layer. Extracting the calcium from fouling layer played a critical role in altering membrane fouling layer structure, which shed light on novel fouling control and management. However, applying such DGT-based technique in controlling real FO



**Fig. 5.** CLSM images of the fouled (A) and DGT adsorbed (B) FO membranes with alginate and 35 mM  $\text{Ca}^{2+}$  and normalized water flux before and after backwashing (C). Experimental condition for FO filtration was described in Fig. 2, and DGT adsorption protocol was described in Fig. 3.



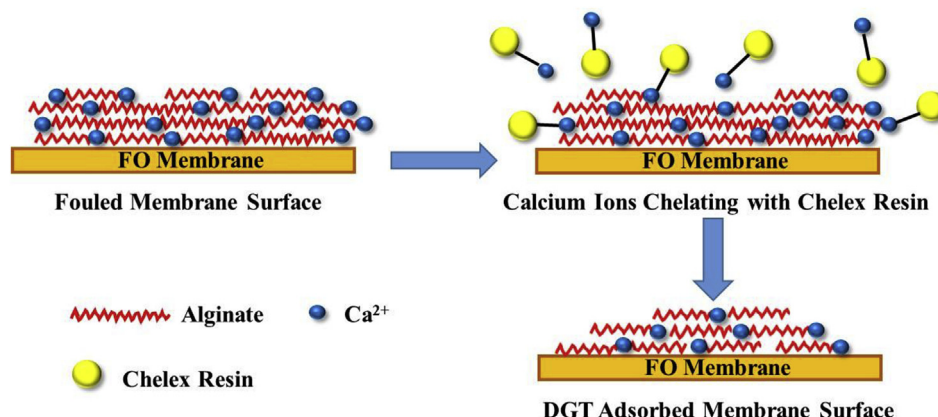


Fig. 6. Mechanisms of  $\text{Ca}^{2+}$  adsorption from the fouling layer by the DGT technology.

membrane fouling still has limitations. On one hand, the real FO fouling is composed of many other constituents such as precipitates, microorganisms, and humic substances, which might disrupt the extraction of  $\text{Ca}^{2+}$  from the fouling layer. On the other hand, although the DGT technology was suitable for the flat-sheet FO membrane module applied in this study, it is difficult to directly apply in the spiral-wound or other tightly-packed membrane configurations. Thus, further studies should be focused on evaluating the DGT technology in real fouling scenarios where the co-existence of sparingly soluble inorganic minerals and organic foulants leads to a more complicated membrane fouling, and emphasized on developing other chelating agent or resin to replace with the DGT technology for *in situ* adsorbing calcium from the fouling layer in order to adapt to different foulants composition and membrane configurations.

#### 4. Conclusions

This study proposes a novel approach to mitigating the FO membrane fouling via the DGT for *in situ* removing  $\text{Ca}^{2+}$  binding with organic foulants. With regard to a thick fouling layer with alginate- $\text{Ca}^{2+}$  gel networks, the Chelex resin in the DGT equipment can directly remove the organic-bound  $\text{Ca}^{2+}$  via the chelation. Owing to the extraction of the organic-bound  $\text{Ca}^{2+}$  from the membrane surface, the structure of the fouling layer became more porous and looser. The changes in the fouling structure alleviated the FO membrane fouling and further enhanced the cleaning effect. The success in mitigating the FO membrane fouling induced by the sodium alginate and  $\text{Ca}^{2+}$  demonstrated the feasibility of fouling controlling strategy via directly extracting  $\text{Ca}^{2+}$  from the fouling layer.

#### Declaration of interests

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

#### Acknowledgements

This work was supported by the National Natural Science Foundation of China [grant number 51578265]; the Six Major Talent Peaks of Jiangsu Province [grant number 2018-JNHB-014]; the Major Science and Technology Innovation Projects of Shandong Province [grant number 2018CXGC1006]; the Fundamental Research Funds for the Central Universities [grant number JUSRP

51728A]; and Jiangsu Cooperative Innovation Center of Technology and Material of Water Treatment.

#### Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.watres.2019.03.018>.

#### References

- Arkhangelsky, E., Wicaksana, F., Tang, C.Y., Al-Rabiah, A.A., 2012. Combined organic-inorganic fouling of forward osmosis hollow fiber membranes. *Water Res.* 46 (19), 6329–6338.
- Boo, C., Lee, S., Elimelech, M., Meng, Z.Y., Hong, S., 2012. Colloidal fouling in forward osmosis: role of reverse salt diffusion. *J. Membr. Sci.* 390–391, 277–284.
- Charfi, A., Jang, H., Kim, J., 2017. Membrane fouling by sodium alginate in high salinity conditions to simulate biofouling during seawater desalination. *Bioresour. Technol.* 240, 106–114.
- Davison, W., Zhang, H., 2012. Progress in understanding the use of diffusive gradients in thin films (DGT) - back to basics. *Environ. Chem.* 9 (1), 1–13.
- Degryse, F., Smolders, E., Zhang, H., Davison, W., 2009. Predicting availability of mineral elements to plants with the DGT technique: a review of experimental data and interpretation by modelling. *Environ. Chem.* 6 (3), 198–218.
- Gu, Y.S., Wang, Y.N., Wei, J., Tang, C.Y., 2013. Organic fouling of thin-film composite polyamide and cellulose triacetate forward osmosis membranes by oppositely charged macromolecules. *Water Res.* 47, 1687–1874.
- Guan, D.X., Williams, P.N., Luo, J., Zheng, J.L., Xu, H.C., Cai, C., Ma, L.N.Q., 2015. Novel precipitated zirconia-based DGT technique for high-resolution imaging of oxyanions in waters and sediments. *Environ. Sci. Technol.* 49 (6), 3653–3661.
- Kwan, S.E., Bar-Zeev, E., Elimelech, M., 2015. Biofouling in forward osmosis and reverse osmosis: measurements and mechanisms. *J. Membr. Sci.* 493, 703–708.
- Li, Q.L., Elimelech, M., 2006. Synergistic effects in combined fouling of a loose nanofiltration membrane by colloidal materials and natural organic matter. *J. Membr. Sci.* 278 (1), 72–82.
- Liu, Y.L., Mi, B.X., 2012. Combined fouling of forward osmosis membranes: synergistic foulant interaction and direct observation of fouling layer formation. *J. Membr. Sci.* 407–408, 136–144.
- Luo, W.H., Phan, H.V., Xie, M., Hai, F.L., Price, W.E., Elimelech, M., Nghiem, L.D., 2017. Osmotic versus conventional membrane bioreactors integrated with reverse osmosis for water reuse: biological stability, membrane fouling, and contaminant removal. *Water Res.* 109, 122–134.
- Lutchmiah, K., Verliefe, A.R.D., Roest, K., Rietveld, L.C., Cornelissen, E.R., 2014. Forward osmosis for application in wastewater treatment: a review. *Water Res.* 58, 179–197.
- Mi, B.X., Elimelech, M., 2008. Chemical and physical aspects of organic fouling of forward osmosis membranes. *J. Membr. Sci.* 320, 292–302.
- Mi, B.X., Elimelech, M., 2010. Organic fouling of forward osmosis membranes: fouling reversibility and cleaning without chemical reagents. *J. Membr. Sci.* 348 (1), 337–345.
- McGinnis, R.L., Elimelech, M., 2007. Energy requirements of ammonia-carbon dioxide forward osmosis desalination. *Desalination* 207 (1), 370–382.
- McGovern, R.K., Lienhard, J.H., 2014. On the potential of forward osmosis to energetically outperform reverse osmosis desalination. *J. Membr. Sci.* 469, 245–250.
- Montero, N., Belzunce-Segarra, M.J., Gonzalez, J.L., Larreta, J., Franco, J., 2012. Evaluation of diffusive gradients in thin-films (DGTs) as a monitoring tool for the assessment of the chemical status of transitional waters within the Water Framework Directive. *Mar. Pollut. Bull.* 64 (1), 31–39.

- Motsa, M.M., Mamba, B.B., Verliefde, A.R.D., 2015. Combined colloidal and organic fouling of FO membranes: the influence of foulant-foulant interactions and ionic strength. *J. Membr. Sci.* 493, 539–548.
- Motsa, M.M., Mamba, B.B., Thwala, J.M., Verliefde, A.R.D., 2017. Osmotic backwash of fouled FO membranes: cleaning mechanisms and membrane surface properties after cleaning. *Desalination* 402, 62–71.
- Mueller, L.N., de Brouwer, J.F.C., Almeida, J.S., Stal, L.J., Xavier, J.B., 2006. Analysis of a marine phototrophic biofilm by confocal laser scanning microscopy using the new image quantification software PHILIP. *BMC Ecol.* 6, 1–15.
- Pendashteh, A.R., Fakhru'l-Razi, A., Madaeni, S.S., Abdullah, L.C., Abidin, Z.Z., Biak, D.R.A., 2011. Membrane foulants characterization in a membrane bioreactor (MBR) treating hypersaline oily wastewater. *Chem. Eng. J.* 168 (1), 140–150.
- Perez, A.L., Anderson, K.A., 2009. DGT estimates cadmium accumulation in wheat and potato from phosphate fertilizer applications. *Sci. Total Environ.* 407 (18), 5096–5103.
- Schintu, M., Marras, B., Durante, L., Meloni, P., Contu, A., 2010. Macroalgae and DGT as indicators of available trace metals in marine coastal waters near a lead-zinc smelter. *Environ. Monit. Assess.* 167 (1), 653–661.
- Shaffer, D.L., Werber, J.R., Jaramillo, H., Lin, S.H., Elimelech, M., 2015. Forward osmosis: where are we now? *Desalination* 356, 271–284.
- She, Q.H., Wang, R., Fane, A.G., Tang, C.Y., 2016. Membrane fouling in osmotically driven membrane processes: a review. *J. Membr. Sci.* 499, 201–233.
- Sherwood, J.E., Barnett, D., Barnett, N.W., Dover, K., Howitt, J., Li, H., Kew, P., Mondon, J., 2009. Deployment of DGT units in marine waters to assess the environmental risk from a deep sea tailings outfall. *Anal. Chim. Acta* 652 (1–2), 215–223.
- Siddiqui, F.A., She, Q.H., Fane, A.G., Field, R.W., 2018. Exploring the differences between forward osmosis and reverse osmosis fouling. *J. Membr. Sci.* 565, 241–253.
- Sobeck, D.C., Higgins, M.J., 2002. Examination of three theories for mechanisms of cation-induced biofouling. *Water Res.* 36, 527–538.
- Sun, Y., Tian, J.Y., Zhao, Z.W., Shi, W.X., Liu, D.M., Cui, F.Y., 2016. Membrane fouling of forward osmosis (FO) membrane for municipal wastewater treatment: a comparison between direct FO and OMBR. *Water Res.* 104, 330–339.
- Tow, E.W., Lienhard, J.H., 2016. Quantifying osmotic membrane fouling to enable comparisons across diverse processes. *J. Membr. Sci.* 511, 92–107.
- Town, R.M., Chakraborty, P., Van Leeuwen, H.P., 2009. Dynamic DGT speciation analysis and applicability to natural heterogeneous complexes. *Environ. Chem.* 6 (2), 170–177.
- Van den Brink, P., Zwijnenburg, A., Smith, G., Temmink, H., Van Loosdrecht, M., 2009. Effect of free calcium concentration and ionic strength on alginate fouling in cross-flow membrane filtration. *J. Membr. Sci.* 345 (1), 207–216.
- Wang, X.M., Waite, T.D., 2009. Role of gelling soluble and colloidal microbial products in membrane fouling. *Environ. Sci. Technol.* 43 (24), 9341–9347.
- Wang, Z.W., Ma, J.X., Tang, C.Y., Kimura, K., Wang, Q.Y., Han, X.M., 2014. Membrane cleaning in membrane bioreactors: a review. *J. Membr. Sci.* 468, 276–307.
- Wang, X.H., Chang, V.W.C., Tang, C.Y., 2016a. Osmotic membrane bioreactor (OMBR) technology for wastewater treatment and reclamation: advances, challenges, and prospects for the future. *J. Membr. Sci.* 504, 113–132.
- Wang, X.H., Zhao, Y.X., Yuan, B., Wang, Z.W., Li, X.F., Ren, Y.P., 2016b. Comparison of biofouling mechanisms between cellulose triacetate (CTA) and thin-film composite (TFC) polyamide forward osmosis membranes in osmotic membrane bioreactors. *Bioresour. Technol.* 202, 50–58.
- Wang, X.H., Hu, T.Z., Wang, Z.W., Li, X.F., Ren, Y.P., 2017. Permeability recovery of fouled forward osmosis membranes by chemical cleaning during a long-term operation of anaerobic osmotic membrane bioreactors treating low-strength wastewater. *Water Res.* 123, 505–512.
- Wang, X.H., Zhang, J.F., Chang, V.W.C., She, Q.H., Tang, C.Y., 2018a. Removal of cytostatic drugs from wastewater by an anaerobic osmotic membrane bioreactor. *Chem. Eng. J.* 339, 153–161.
- Wang, W.Y., Yue, Q.Y., Li, R.H., Bu, F., Shen, X., Gao, B.Y., 2018b. Optimization of coagulation pre-treatment for alleviating ultrafiltration membrane fouling: the role of floc properties on Al species. *Chemosphere* 200, 86–92.
- Wang, H.L., Wang, X.H., Meng, F.G., Li, X.F., Ren, Y.P., She, Q.H., 2019. Effect of driving force on the performance of anaerobic osmotic membrane bioreactors: new insight into enhancing water flux of FO membrane via controlling driving force in a two-stage pattern. *J. Membr. Sci.* 569, 41–47.
- Warnken, K.W., Zhang, H., Davison, W., 2006. Accuracy of the Diffusive Gradients in Thin-Films Technique: Diffusive boundary layer and effective sampling area considerations. *Anal. Chem.* 78 (11), 3780–3787.
- Wu, B., An, Y.Y., Li, Y.Z., Wong, F.S., 2009. Effect of adsorption/coagulation on membrane fouling in microfiltration process post-treating anaerobic digestion effluent. *Desalination* 242 (1), 183–192.
- Xie, M., Nghiem, L.D., Price, W.E., Elimelech, M., 2013. Impact of humic acid fouling on membrane performance and transport of pharmaceutically active compounds in forward osmosis. *Water Res.* 47 (13), 4567–4575.
- Yoon, H., Baek, Y., Yu, J., Yoon, J., 2013. Biofouling occurrence process and its control in the forward osmosis. *Desalination* 325, 30–36.
- Yu, G.H., Tang, Z., Xu, Y.C., Shen, Q.R., 2011. Multiple fluorescence labeling and two dimensional FTIR-13C NMR heterospectral correlation spectroscopy to characterize extracellular polymeric substances in biofilms produced during composting. *Environ. Sci. Technol.* 45 (21), 9224–9231.
- Yuan, B., Wang, X.H., Tang, C.Y., Li, X.F., Yu, G.H., 2015. In situ observation of the growth of biofouling layer in osmotic membrane bioreactors by multiple fluorescence labeling and confocal laser scanning microscopy. *Water Res.* 75, 188–200.
- Zhang, H., Davison, W., 1995. Performance characteristics of diffusion gradients in thin films for the in situ measurement of trace metals in aqueous solution. *Anal. Chem.* 67 (19), 3391–3400.
- Zhang, H., Davison, W., Knight, B., McGrath, S., 1998. In situ measurements of solution concentrations and fluxes of trace metals in soils using DGT. *Environ. Sci. Technol.* 32 (5), 704–710.
- Zhang, H., Davison, W., 2015. Use of diffusive gradients in thin-films for studies of chemical speciation and bioavailability. *Environ. Chem.* 12 (2), 85–101.
- Zhao, S.F., Zou, L., Tang, C.Y., Mulcahy, D., 2012. Recent developments in forward osmosis: opportunities and challenges. *J. Membr. Sci.* 396, 1–21.
- Zheng, L., Price, W.E., Nghiem, L.D., 2018. Effects of fouling on separation performance by forward osmosis: the role of specific organic foulants. *Environ. Sci. Pollut. Res.* 1–12.