Supporting Information

New insights into the organic fouling mechanism of in-situ Ca^{2+} modified thin film composite forward osmosis membrane

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S1. Membrane performance

The real water flux and reverse solute diffusion of origin membranes were shown in Figure S1. A slight reduction in flux was attributed to the dilution of draw solution. The higher concentration of reverse solute on TFC-control membrane was due to the lower permeability property of the membrane, which needed higher draw solution concentration to achieve the same initial permeate flux with the TFC-Ca membrane. Compared with the concentration of draw solution, reverse solute diffusion has little effect.

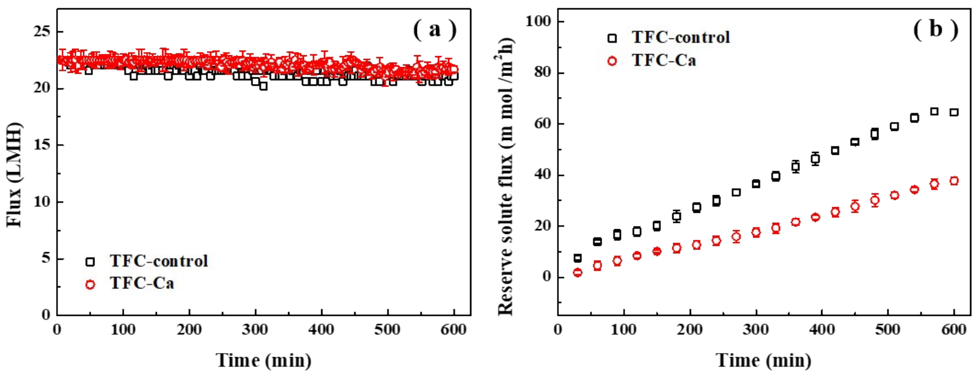

Fig. S1. The real water and reserve solute flux curves of TFC-control and TFC-Ca membranes without the addition of organic foulant.

S2. Characterization of the fouled TFC membranes

In this study, we tried to analyze the functional groups on the fouled membrane surface by FTIR-ATR spectroscopy (Figure S2). The results showed that the intensity of the fouled TFC-control membranes was significantly higher than the fouled TFC-Ca membranes. In addition, a major peak was found in the clean TFC-Ca membrane at a wave number of 1728 cm^{-1}. This peak is associated with carboxylic groups, representing a typical characteristic of Ca^{2+}-carboxylic group interactions. The FTIR-ATR spectra of fouled TFC-Control membranes also showed weak peaks at wave numbers of 1728 cm^{-1}.

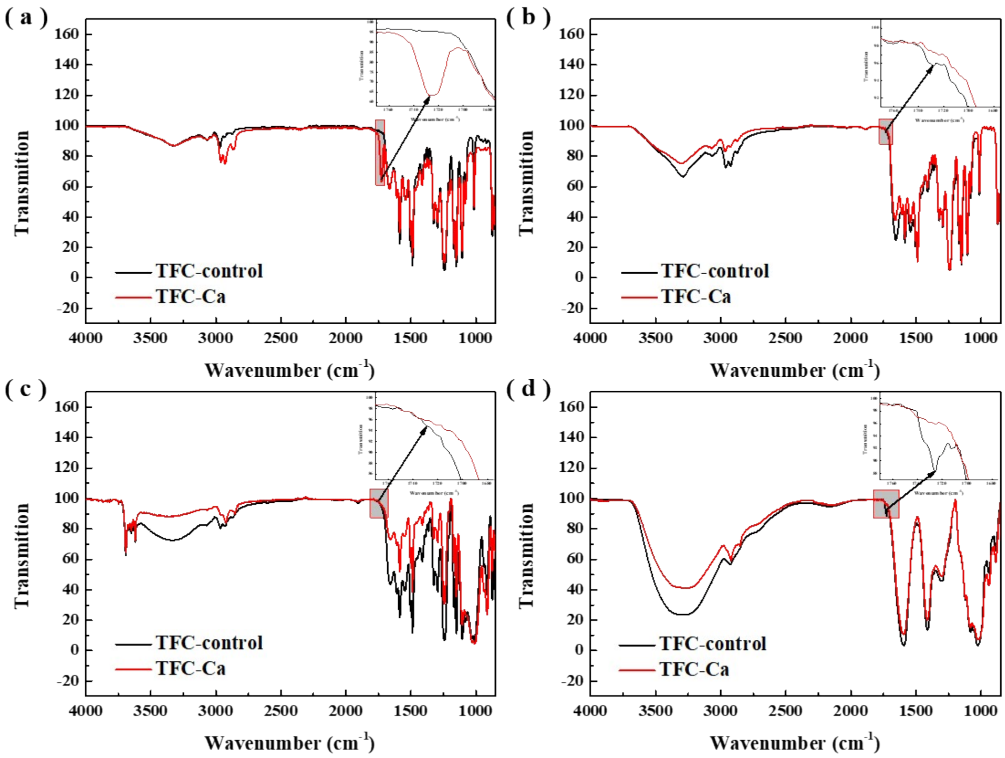

Fig. S2. Surface characterization of the fouled TFC-control and TFC-Ca membranes by FTIR-ATR spectra: (a) clean TFC-control and TFC-Ca membranes, (b) BSA as simulated foulant, (c) HA as simulated foulant, (d) SA as simulated foulant.

S3. The evaluation of membrane fouling performances using surface water as medium

Based on the existing research, we further study the antifouling performance of the TFC-Ca membrane that employed surface water samples as medium, sodium alginate was used as simulated foulant. Surface water samples were taken from the Songhuajiang River in Harbin, China. Water quality indexes for the raw water can be found in Table S1. The experimental process followed the same protocol as described for the fouling experiment. As shown in Figure S3, there was no significant difference on the fouling performance between TFC-control membrane and TFC-Ca membrane in the absence of SA in the feed solution, which was attributed to the low concentration of foulant in surface water and the short running time. Obviously, with the addition of 200 mg/L SA in the feed solution, TFC-Ca membrane remained good antifouling performance than TFC-control membrane as shown in Figure S3. It is fully proved that the proposed Ca^{2+} intra-bridging strategy plays an important role in the antifouling of polyamide layer.

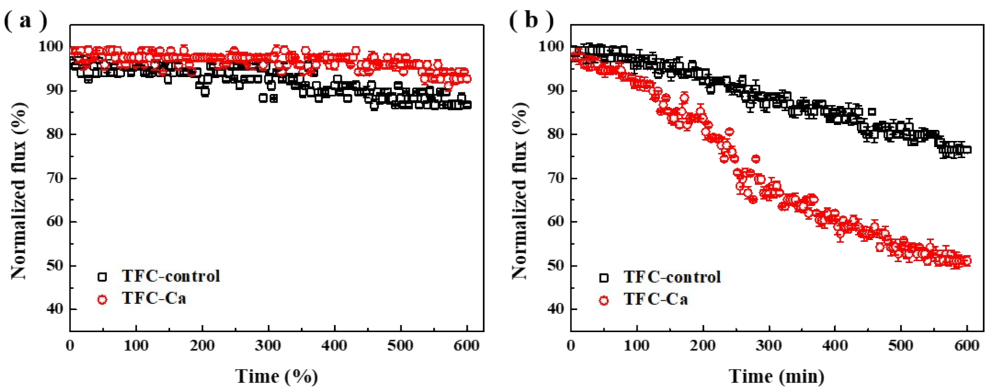

Fig. S3. Representative membrane fouling curves of the TFC-control and the TFC-Ca membranes as a function of operation time using surface water sample as medium. Sodium alginate (SA, 200 mg/L) was used as model foulant with 1 mM Ca^{2+} and 50 Mm NaCl in the simulated feed solution, (a) without SA in the simulated feed solution, (b) with 200 mg/L SA in the simulated feed solution.

Table S1 Quality of water in Songhuajiang river

Indexes	Ranges
pH	7.40
Turbidity (NTU)	6.6
DOC (mg L^{-1})	5.8
UV_{254} (cm^{-1})	0.098
K^+ (mg L^{-1})	3.02
Na^+ (mg L^{-1})	14.28
Ca^{2+} (mg L^{-1})	26.15

Mg^{2+} (mg L^{-1})	3.68
Al^{2+} (mg L^{-1})	1.11
Cl^{-} (mg L^{-1})	8.68
SO_4^{2-} (mg L^{-1})	16.25
NO_3^{-} (mg L^{-1})	4.22

S4. The effect of Na^+ or Mg^{2+} in the feed solution on TFC-Ca membrane fouling

The fouling performances of the TFC-Ca membranes were evaluated as Na^+ or Mg^{2+} presented in the feed solutions as shown in Figure S3. The results showed that flux decline was generally mild for all the membranes when the feed solution contained Na^+ (Figure S4a). While the divalent cations in the simulated feed solution turn to Mg^{2+}, the TFC-control membrane suffered more severe membrane fouling than that of TFC-Ca membrane (Figure S4). However, both TFC-control membrane and TFC-Ca membrane did not have a significant flux decline in comparison with the presence of Ca^{2+} in the feed solutions. Previous studies also demonstrated that Mg^{2+} had the weaker affinity than that Ca^{2+}.[1] Thus, the anti-fouling mechanism of TFC-Ca membrane can be clarified by analyzing the interaction between Ca^{2+} and different organic matters.

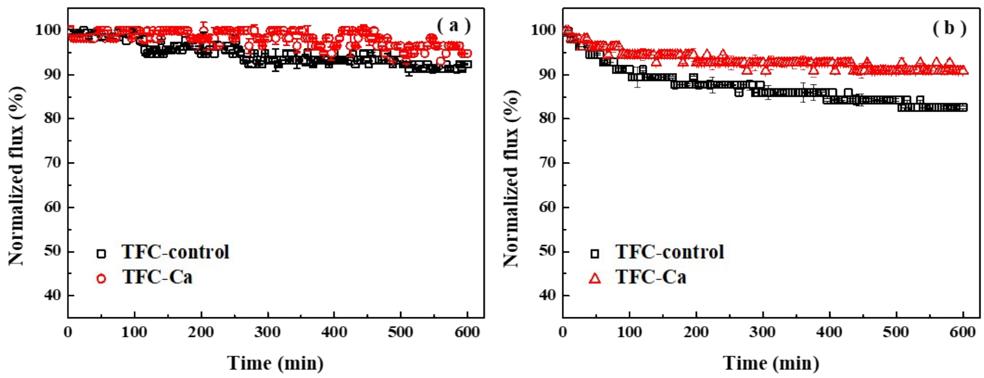

Fig. S4. Representative membrane fouling curves of the TFC-control and the TFC-Ca membranes as a function of operation time. Sodium alginate (SA, 200 mg/L) was used as model foulant, (a) with 50 mM NaCl in the simulated feed solution, (b) with 1 mM Mg^{2+} and 50 Mm NaCl in the simulated feed solution SA.

References:

1 M. M. Motsa, B. B. Mamba, A. D'Haese, Organic fouling in forward osmosis membranes: The role of feed solution chemistry and membrane structural properties, *J. Membr. Sci.,* 460 (2014) 99-109.