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Mechanism Analysis of PFHxS Purification in Water Using Nanofiltration under the Coexistence of Sodium Alginate and Ca²⁺ Based on DFT

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Abstract: Perfluorohexanesulfonic acid (PFHxS) is considered a persistent and harmful substance to ecosystems and human health and should thus be necessarily removed. In this paper, the influence of working pressure, temperature, pH value, initial concentration, and the coexistence of sodium alginate (SA) and calcium ions on removing PFHxS using nanofiltration were hereby studied through a selfmade hyaluronic acid-interlayered thin-film composite nanofiltration membrane (HA-TFCiNFM). When the substances SA or/and calcium ions (Ca²⁺) co-existed, the retention rate of the HA-TFC_iNFM to PFHxS exceeded that in the single PFHxS system and increased with SA and Ca²⁺ concentrations. By filtering a single PFHxS, PFHxS/SA, and PFHxS/SA/ Ca^{2+} water sample system, it was observed that the HA-TFC_iNFM had the highest membrane fouling degree in the PFHxS/SA/Ca²⁺ system. The mechanisms of membrane separation and fouling when SA and Ca²⁺ co-existed were explored based on density functional theory (DFT). Building on DFT, the PFHxS structure was constructed, and when Ca^{2+} co-existed, Ca^{2+} complexed two PFHxS molecules to increase the complex compound size, making the sieving effect notable. When SA co-existed, although PFHxS and SA could not react with each other, the presence of SA would block the membrane pore and enhance the negative charge on the membrane surface, thereby strengthening the sieving and Donnan effects. When the substances Ca²⁺ and SA co-existed, Ca²⁺ complexed a PFHxS molecule and a SA molecule to form a larger complex compound so that the sieving effect could be enhanced. From the molecular perspective, the intermolecular interaction relationship between pollutants and the HA-TFC_iNFM was explored based on DFT, and weak interactions, such as hydrogen bonding and van der Waals interactions, were clarified as the main mechanisms to control the membrane fouling. These results provide insight into the purification mechanism of PFHxS in water using nanofiltration and highlight the usefulness of DFT in exploring membrane separation and fouling mechanisms.

Keywords: water treatment; PFHxS; nanofiltration membrane; membrane fouling; DFT

1. Introduction

As the industry advances, numerous synthetic organic micropollutants are discharged into water sources, and the safety of drinking water is threatened. Per- and poly-fluoroalkyl substances (PFASs) are an artificial organic with an alkyl chain as the skeleton, in which the hydrogen atoms on the carbon skeleton are replaced in whole or in part by fluorine atoms, and the ends contain a hydrophilic functional group (such as carboxyl and sulfonic acid groups) [1]. As the C-F bond (536 kJ/mol) has strong energy, PFASs feature unique physicochemical properties such as thermal stability, chemical stability, hydrophobicity, and lipophobicity [2–4]. Therefore, they are widely used in industries such as chrome plating, foam fire extinguishing agents, aviation hydraulic oil, and food packaging paper [3]. Due to large production and disorderly discharge, PFASs are prevalent in natural water. Such compounds are difficult to biodegrade or bio-transform in natural water, featuring



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Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). environmental persistence and bioaccumulation characteristics which threaten human health. Since 2002, some major manufacturers (such as 3M) have ceased manufacturing long-chain PFASs (C8~C14) such as perfluorooctane carboxylic acid (PFOA) and perfluorooctane sulfonic acid (PFOS). The short-chain PFASs (C4~C7) nevertheless began to be mass-produced as alternatives to long-chain PFASs. Among them, PFHxS is an alternative to long-chain PFOS and PFOA in the manufacture of fire foams, metal plating, textiles, leather, polishes, detergents, coatings, paper, electronics, and semiconductors. Due to the widespread use of PFHxS, it is enriched in some organisms, especially in humans [5,6]. The toxic potential of PFHxS is worrisome. Ramhoj et al. [7] studied and reported PFHxS to induce developmental toxicity in mice. Jiang et al. [8] discovered PFHxS induced liver damage in mice. PFHxS is characterized by small molecular weight, large C-F bond energy, and high polarity, making it hard to be removed by environmental adsorption and the water treatment process, so it has existed in the water cycle for a long time through the

cannot effectively remove PFHxS. Techniques such as adsorption [10,11], advanced oxidation [12,13], and nanofiltration [14–16] are reported to be efficient in removing PFASs from water and can somewhat remove PFASs. However, there are great differences in the treatment effect, operating conditions, and applicability. The adsorption effect on removing PFASs is general and exposed to problems such as long adsorption time, limited adsorption capacity, low regeneration efficiency, and secondary pollution of elution solvents [17]. The specific reaction conditions and additional catalysts, electrode materials, chemicals, etc., are required through advanced oxidation treatment. Secondary contamination and harmful chemical by-products can be generated [17]. Comparatively, nanofiltration technology has an excellent separation effect on PFASs, low operating pressure, low energy consumption, automatic operation, and without chemical by-products [14,15]. In conclusion, from the aspects of treatment effect, operating conditions, and applicability, nanofiltration technology is suitable for removing PFASs from water.

migration of surface water, groundwater, and natural and urban water systems [9]; this damages the quality of drinking water. Currently, conventional water treatment technology

Nanofiltration is a pressure-driven membrane process, and the pore size of the membrane is generally 0.5~2 nm so that the small molecule organic pollutants of PFASs can be removed. Tang et al. [18] utilized a hollow fiber nanofiltration membrane modified with SiO₂ and multi-walled carbon nanotubes (MWCNT) to remove PFOA. The retention rate of PFOA in the modified nanofiltration membrane increased from 97.2 to 98.6%. Zhao et al. [19] studied the effects of the coexistence of anions, cations, and humic acids on removing PFOS using nanofiltration membranes and found that the retention rate of PFOS increased from 92 to 99% when humic acid coexisted with both cations and anions. In the presence of cations, the sieving effect plays a vital role in the removal of PFOS. In the presence of anions, electrostatic repulsion remarkably removes PFOS. Zhao et al. [20] studied the effects and interactions of Mg²⁺ and humic acid on the PFOS removal rate and the total permeation flux in water and found that the retention rate of PFOS increased from 94.3 to 99.5% when the concentration of Mg^{2+} in water increased from 0 to 2 mM. It was also discovered that the retention rate increased with the enhancement of the sieving effect as the PFOS molecules became larger in size through Mg²⁺ complexation. According to the study, the coexistence of Mg²⁺ and humic acid in water decreased by 70% of flux, which is associated with a thicker membrane fouling layer. Currently, the research on the purification of PFASs using nanofiltration technology has focused on removing long-chain PFASs (PFOS and PFOA), and few studies investigated the purification efficiency and influencing factors of short-chain PFASs. There is a lack of exploration of the water purification mechanism of short-chain PFASs in water.

Membrane fouling is a bottleneck that restricts membrane selectivity and shortens membrane life [21]. It will notably decrease water flux, worsen product quality, and increase energy consumption. Moreover, frequent physical and chemical cleaning is needed to remove the membrane fouling, and the formation of membrane fouling can reduce the service life of the membrane and increase the treatment cost. Common pollutants in the water environment are natural organic matter (NOM) and inorganic ions that cause nanofiltration membrane fouling. According to relevant studies, the coexistence of NOM and inorganic ions affects the retention efficiency of PFASs and aggravates the membrane fouling process, thereby significantly reducing the membrane flux [20]. Sodium alginate (SA) is a component of NOM. It is ubiquitous in a variety of water systems [22,23]. Due to its abundant foulingrelevant functional groups (such as carboxyl and hydroxyl groups), high molecular weight (MW), and low biodegradation potential, it can cause severe membrane fouling in the water and wastewater treatment process [24–26]. Currently, SA has been widely used as a model pollutant in various types of membrane fouling studies, such as a membrane bioreactor (MBR), ultrafiltration [24,26,27], nanofiltration [28,29], reverse osmosis [30,31] and forward osmosis [25,32]. Calcium ions (Ca^{2+}), as cations in wastewater with an abundant content, can interact with other pollutants to exacerbate membrane fouling [33,34]. Ca²⁺ is often referred to as a "fouling promoter" that aggravates organic contamination by promoting the crosslinking of SA. It is predicted that the removal rate of PFHxS using nanofiltration and the nanofiltration membrane fouling process is associated with the interaction of SA and Ca^{2+} as well as the characteristics of the membrane. Nevertheless, few studies investigated the removal of short-chain PFHxS from water using a nanofiltration membrane and the effect of the coexistence of SA with Ca^{2+} on nanofiltration performance. Furthermore, the study of the membrane fouling mechanism is mostly focused on the macroscopic level and seldom focused on in-depth analysis at the molecular level. Therefore, it is vital to understand the mechanism of nanofiltration membrane separation and membrane fouling at the molecular level.

Considering that short-chain PFAS pollution is steadily worsening, in this study, a self-made hyaluronic acid-interlayered thin film composite nanofiltration membrane (HA-TFC_iNFM) was adopted with PFHxS selected as a model pollutant, and a water purification system was constructed using nanofiltration to remove PFHxS. The effects of working pressure, temperature, pH, initial concentration, and coexisting substances (SA and Ca²⁺) on the purification of PFHxS in the system were correspondingly investigated. Density functional theory (DFT) was used to understand the structure and existence form of PFHxS and elaborate on the mechanism of its separation using nanofiltration under the presence of SA and/or Ca²⁺. The influence of SA and Ca²⁺ on membrane fouling behavior was also studied, and the interaction between the nanofiltration membrane and pollutants was explored from a molecular perspective based on DFT. Based on the experimental results and DFT simulations, a mechanism for PFHxS purification in water using a nanofiltration membrane was proposed in the presence of Ca²⁺ and SA. The study demonstrated that DFT is a useful tool for investigating the mechanisms of membrane separation and fouling.

2. Materials and Methods

2.1. Materials and Reagents

Herein, the HA-TFC_iNFM was developed in two steps. First, a hyaluronic acid (HA) intermediate layer was introduced onto a polyethersulfone (PES) microfiltration substrate. Then, the HA-TFC_iNFM was developed using interfacial polymerization of piperazine (PIP) and trimesoyl chloride (TMC) on the substrate. The entire preparation process and analysis have been detailed in our previous studies [14]. The main parameters of the HA-TFC_iNFM are indicated in Table 1, and the change of Zeta potential with pH on the surface of HA-TFC_iNFM is depicted in Figure S1. The equipotential point of HA-TFC_iNFM reaches 3.57, and the crosslinking degree is 86.38%.

Table 1. Main parameters of HA-TFC_iNFM.

MWCO	Zeta Potential	Water Contact	Pure Water Flux	Rejection of Na ₂ SO ₄
(Da)	(mV)	Angle (°)	(L m ⁻² h ⁻¹ bar ⁻¹)	
345.35	29.53	28.45	29.53	94.9%

The chromatographic-grade acetonitrile used in the tests was purchased from Sigma-Aldrich Co., Ltd. (Shanghai, China), while the analytically pure SA, PFHxS, CaCl₂, and ammonium acetate were purchased from Sinopharm Chemical Reagent Co., Ltd. (Beijing, China). Ultrapure water (resistivity 18.1 M Ω ·cm) was used in all tests. The physicochemical properties of PFHxS are indicated in Table S1.

2.2. Membrane Performance Evaluation

The separation performance of HA-TFC_iNFM was tested using a self-made crossflow nanofiltration device with an effective membrane area of 34.65 cm². The schematic diagrams of the homemade cross-flow nanofiltration system are depicted in Figure S2. Before starting the test, the pressure was adjusted to 5 bar and pre-pressed for 30 min, and the membrane was compacted to obtain a stable water flux with deionized water as the influent water. After pre-pressurization, the deionized water can be replaced with a PFHxS-containing water sample and operated at 4 bar. The permeate mass was recorded in real time using the electronic balance software, and the pollutant concentration of the influent and permeated water was determined. In addition, the water permeability and retention rate of the membrane are calculated as follows:

$$I = \frac{V}{A \times t \times P} \tag{1}$$

where:

J—water permeability (L m⁻² h⁻¹ bar⁻¹)

V—permeated water volume (L)

A—effective filtration area (m^2)

t—filtration time (h)

P—transmembrane pressure difference (bar)

$$R = \frac{1 - C_p}{C_0} \tag{2}$$

where:

R—retention rate (%)

 $C_{\rm p}$ —concentration of contaminants in the permeated water

 C_0 —the concentration of contaminants in the influent water

In order to investigate the membrane fouling and antifouling performance of HA-TFC_iNFM during PFHxS purification, tests were conducted using a single PFHxS water sample, PFHxS/SA mixed water sample, and PFHxS/SA/CaCl₂ mixed water sample as the contaminated water samples. The specific steps are as follows:

- 1. Precompression: the membrane was preloaded at 5 bar for 30 min with deionized water as the influent water, stabilizing the membrane effluent.
- 2. Pure water permeability test: after conducting the above precompression process, adjust the pressure to 4 bar, test for 30 min, and record the effluent data to calculate the permeability of pure water, which is recorded as J_{w1} .
- 3. Membrane fouling test: the deionized water was replaced with the above contaminant water sample and operated at 4 bar for 16 h. The water quality data were recorded in real time through the electronic balance software. The final water permeability was calculated and recorded as *J*_p.
- 4. Hydraulic cleaning: after the above test, the pollutant water sample was replaced with deionized water, the inlet water pressure was adjusted to 2 bar, and the membrane was hydrologically cleaned for 2 h.
- 5. Repeated pure water permeability test: after hydraulic cleaning, increase the inlet pressure to 4 bar, run for 30 min, and determine the permeability of pure water at this time, which is recorded as J_{w2} .

6. Repeated membrane fouling test: the deionized water was replaced with a contaminant water sample, the inlet pressure was increased to 4 bar, and the water permeability was calculated by running the test again for another 16 h and recording the water quality in real time using the electronic balance software.

To quantitatively evaluate the antifouling performance of nanofiltration membranes, parameters, including the flux recovery rate (*FRR*), total pollution rate (R_t), reversible pollution rate (R_r), and irreversible pollution rate (R_{ir}), were introduced and calculated using the following formulas:

$$FRR = \frac{J_{w2}}{J_{w1}} \times 100\% \tag{3}$$

$$R_t = \left(1 - \frac{J_p}{J_{w1}}\right) \times 100\% \tag{4}$$

$$R_r = \frac{J_{w2} - J_p}{J_{w1}} \times 100\%$$
(5)

$$R_{ir} = \left(1 - \frac{J_{w2}}{J_{w1}}\right) \times 100\% \tag{6}$$

wherein the total pollution rate is the sum of the reversible pollution rate and irreversible pollution rate:

$$R_t = R_r + R_{ir} \tag{7}$$

2.3. PFHxS Analysis

Herein, the concentration of PFHxS was determined using ultra-high performance liquid chromatography–mass spectrometry under the following chromatographic conditions: the mobile phase is a mixture of acetonitrile and 2 mM ammonium acetate solution for the C18 column, with a volume ratio reaching 70:30. The column temperature achieved 30 °C, the flow rate was 0.15 mL/min, and the injection volume was 10 μ L. Mass spectrum condition: ionization was conducted in the electrospray negative ion scanning (ESI-) mode. The cone voltage and collision voltage were 45 and 11 V, respectively, and the *m*/*z* of PFHxS was selected as 398.8.

2.4. DFT Calculation

In order to explore the mechanism of membrane fouling from the molecular level, the structure of pollutants and membranes was built on Gauss View, and all carboxyl groups on the SA chain and PFHxS were deprotonated. DFT calculations were conducted on Gaussian16 software. First, the compound structure was geometrically optimized under the level of Becke three-parameter non-local exchange function and Lee–Yang–Parr correlation function B3LYP/6-311G(d,p), and the obtained structure was finally generated without imaginary frequency. After obtaining the optimized structure, the improved single-point mode was used to calculate the single-point energy at the B3LYP/6-311G(d,p) level, and the relevant water environment was simulated with the implicit solvent model SCRF. Herein, the single point energy obtained was calculated as the energy corrected for solvation effects. Finally, the binding energy (E_{ads}) was calculated $\Delta E_{ads} = \sum E(\text{ product }) - \sum E(\text{ reactant })$, where $\sum E(\text{ product })$ and $\sum E(\text{ reactant })$ are the total energy after and before the reaction, respectively. The electrostatic potential on the molecular surface passed through the Multiwfn program [35], and the electrostatic potential of van der Waals surface molecules obtained was calculated using the IGM independent gradient model.

3. Results and Discussion

3.1. Study on the Influencing Factors of PFHxS Removal by HA-TFC_iNFM

3.1.1. Effect of Operating Pressure

PFHxS water samples with a concentration of 100 μ g/L were selected as the target water samples to explore the changes of the HA-TFC_iNFM on the retention performance

of PFASs under pressures of 3 to 7 bar. As indicated by Figure 1a, the retention rate of the HA-TFC_iNFM to PFHxS decreases as the working pressure increases. As it increased from 3 to 7 bar, the PFHxS retention rate decreased from 94.25 to 61.94%. Ma et al. [16] also observed a similar phenomenon in removing PFHxA using a self-made nanofiltration membrane. There are two possible reasons for this. First, the small molecular weight of PFASs is close to the molecular weight cut-off (MWCO) of nanofiltration membranes, and when higher pressure is applied, they easily cross the polyamide (PA) separation layer into the permeate water [36]. Second, the organic solute (PFHxS) interacts strongly with the polyamide nanofiltration membrane, and the retention rate may decrease with the increase in pressure [37].



Figure 1. Effect of (**a**) pressure, (**b**) temperature, (**c**) concentration, and (**d**) PH on the removal of PFHxS by HA-TFC_iNFM.

3.1.2. Effect of Temperature

Herein, to study the influence of water sample temperature on the retention performance of the HA-TFC_iNFM, the water temperature was set at 5 °C~35 °C using a thermostatic bath, and the results are shown in Figure 1b. During the temperatures from 5 to 35 °C, the retention rate of the HA-TFC_iNFM to PFHxS decreased from 95.36 to 92.13%, presenting a slight decrease. This may be because the membrane undergoes thermal expansion at higher temperatures, while PFHxS in the permeate has a higher diffusion coefficient at high temperatures, making it easier for PFHxS to pass through the membrane pores into the permeate [38].

3.1.3. Effect of PFHxS Concentration

Single PFHxS water samples with concentrations of 10, 50, 100, and 200 μ g/L were prepared as target water samples to study the effect of initial PFHxS concentration on the HA-TFC_iNFM removal efficiency, and the test results are shown in Figure 1c. As the PFHxS concentration increased from 10 to 200 μ g/L, the HA-TFC_iNFM retention rate for PFHxS increased by 8.12% from the initial 88.16 to 96.28%. During the nanofiltration process, a part of PFHxS would be deposited on the surface of the nanofiltration membrane to form a filter cake layer. With the increase in the concentration of PFHxS in the target water sample, there was increasingly more PFHxS deposited on the surface of the nanofiltration membrane. The filter cake layer was also thickened, enhancing the sieving effect of the HA-TFC_iNFM and leading to the increase in the retention rate of PFHxS with the initial concentration [39].

3.1.4. Effect of pH

The pH value can affect the removal efficiency by altering the electrostatic interaction between PFHxS and the membrane surface through different functional groups [40]. Herein, HCl solution and NaOH solution with a concentration of 0.1 M were adopted to adjust the initial pH range of the water samples to 2~10, and the effect of pH value on the removal of PFHxS by the HA-TFC_iNFM was studied; the test results are indicated in Figure 1d. As the initial pH increased, the retention rate of the HA-TFC_iNFM on PFHxS increased from 48.85% at pH = 2 to 95.26% at pH = 10. The isoelectric point of the HA-TFC_iNFM is 3.57. The nanofiltration membrane is positively charged when the pH value is lower than this value. The positive charge decreases as the PH increases. When the pH value exceeded this value, the nanofiltration membrane exhibited negative electricity, and the negative electricity increased with the pH value. According to Table 1, the dissociation constant of PFHxS was less than 1 in a dissociated state in the pH range of 2~10 and existed in the form of negatively charged ions in water. According to the Donnan effect, when the HA-TFC_iNFM was positively charged or not strongly charged in the early stage, the electrostatic repulsion was weak, lowering the retention rate for PFHxS. When the positive or negative electricity of the nanofiltration membrane decreased or increased in the later stage, the retention rate of PFHxS went up. Given that the negative enhancement of the HA-TFC_iNFM surface with increasing pH was not as obvious as before, the rise in the retention rate of PFHxS was stabilized after pH = 7 (see Figure S1).

3.1.5. Effect of Coexisting Substances

In order to study the effect of Ca^{2+} coexistence on the removal effect of PFHxS, a certain amount of $CaCl_2$ solid was added to a water sample containing 100 µg/L PFHxS. As indicated by Figure 2a, after adding calcium ions, the retention rate of PFHxS by the HA-TFC_iNFM was enhanced. As the Ca^{2+} concentration in water samples increased from 0 to 3 mM, the retention rate of PFHxS increased by 5.49%, from 93.4 to 98.89%. The reasons for Ca^{2+} enhancing the PFHxS retention performance might involve the following three aspects: first, Ca^{2+} complexed with PFHxS to form complex compounds with larger molecular sizes; second, Ca^{2+} can undergo surface bridging on the HA-TFC_iNFM surface rich in -NH₂ and -COOH with PFHxS [41]; and third, part of the PFHxS was deposited on the surface of the HA-TFC_iNFM, which increased the thickness of the filter cake layer and advanced the retention rate of the target contaminant. After adding Ca^{2+} , although the surface negativity of the HA-TFC_iNFM decreased, the retention rate of PFHxS increased, indicating that the sieving effect had replaced the Donnan effect as the main mechanism for the HA-TFC_iNFM to intercept PFHxS when Ca^{2+} coexisted.



Figure 2. Effect of (**a**) the concentration of Ca^{2+} , (**b**) the concentration of SA, and (**c**) the coexistence of Ca^{2+} and SA on the removal of PFHxS by HA-TFC_iNFM.

In order to study the effect of SA coexistence on the removal of PFHxS, a certain amount of SA was added to the water sample containing 100 μ g/L PFHxS. As indicated by Figure 2b, when the SA concentration was in the range of 0~20 mg/L, the retention rate of the HA-TFC_iNFM on PFHxS increased from 93.4 to 97.07% for the following two reasons: first, a part of the SA in the water sample would block the membrane pores or be deposited on the membrane surface, reducing the membrane pore size and increasing the sieving effect; and second, the SA molecules were rich in carboxyl groups, so the SA deposited on the nanofiltration membrane surface enhanced the electronegativity of the membrane surface, thereby enhancing the Donnan effect.

To explore the effect of the coexistence of Ca^{2+} and SA on the removal effect of PFHxS, a certain amount of $CaCl_2$ solid and SA was added to the water sample containing 100 µg/L PFHxS so that the Ca^{2+} concentration in the water sample was 2 mM and the SA concentration was 5 mg/L. According to Figure 2c, compared with the single PFHxS water sample, in the presence of Ca^{2+} and SA in the water sample, the retention rate of the HA-TFC_iNFM to PFHxS increased, and the PFHxS retention rate increased from 93.48% of the single PFHxS system to 99.02%, which was attributed to the following two reasons: first, after adding Ca^{2+} and SA, the filter cake layer on the surface of the nanofiltration membrane became thicker due to the surface bridging effect, and the screening effect was thus strengthened; and second, Ca^{2+} complexed PFHxS and SA to form a complex compound, which increased the size of the contaminant and made it more difficult to pass through the PA separation layer, thereby improving the retention rate.

3.2. Membrane Fouling Behavior under the Coexistence of Ca²⁺ and SA

In order to study the effect of the coexistence of SA and Ca²⁺ on membrane fouling behavior, the single PFHxS water sample (100 μ g/L of PFHxS), PFHxS/SA mixed water sample (100 μ g/L of PFHxS and 5 mg/L of SA), and PFHxS/SA/Ca²⁺ mixed water sample (100 μ g/L of PFHxS, 5 mg/L of SA, and 2 mM of CaCl₂) were selected as contaminated water samples for membrane fouling tests.

The change in the HA-TFC_iNFM normalized flux over time under the single PFHxS, PFHxS/SA, and PFHxS/SA/Ca²⁺ systems is shown in Figure S3. Under the single PFHxS system, although the specific flux somewhat decreased, the decline degree remained low. The decline in membrane flux is due to the adsorption and deposition of small molecule PFHxS on the membrane surface and within the membrane pores, forming a cake layer or blocking the membrane pores, which increases the resistance to water passing through the membrane and gradually leads to a decrease in flux. The degree of flux decline was lower due to the lower concentration of PFHxS and weaker membrane fouling. Compared with the single PFHxS system, the specific flux notably decreased under the PFHxS/SA system, which was mainly attributed to the dense gel layer formed by adding SA, thus worsening membrane fouling and decreasing membrane flux. The specific flux of the PFHxS/SA/Ca²⁺ system decreased more than that of the PFHxS/SA system without Ca²⁺ for the following reasons: (1) the addition of Ca^{2+} neutralized the negative charge of the HA-TFC_iNFM surface and SA, thereby decreasing the charge repulsion between the membrane and SA, and SA was easier to adsorb and settle on the membrane surface; (2) Ca²⁺ could be complexed with SA to form larger pollutants settling on the membrane surface, thus forming a dense gel layer and enhancing the membrane resistance; and (3) Ca^{2+} could also bridge the negatively charged HA-TFC_iNFM and SA to form a stable gel layer.

In order to quantify membrane fouling, the contamination index was adopted to study the effects of the single PFHxS, PFHxS/SA, and PFHxS/SA/Ca²⁺ systems on HA-TFC_iNFM fouling (see Figure 3). The total pollution rates R_t of the three systems were 4, 48.1, and 62.4%, respectively, which was consistent with the normalized flux decay trend. The reversible pollution rates of the three systems were 3.3, 46.4, and 58.1%, respectively, indicating that the membrane fouling was mainly reversible fouling. After hydraulic flushing, the flux recovery rates (FRRs) of the three systems reached 99.3, 98.3, and 95.7%, respectively, and the membrane flux was highly restored, suggesting the high hydrophilicity of the HA-TFC_iNFM and the existence of a hydration layer on the membrane surface, which could reduce the interaction between the membrane and pollutants.



Figure 3. The relative antifouling indexes for HA-TFC_iNFM under PFHxS/SA/Ca²⁺ system.

3.3. HA-TFC_iNFM Purification Mechanism of PFHxS

3.3.1. Structural Optimization of PFHxS and SA Theoretical Models

As per Table S1, the dissociation constant pKa of PFHxS was 0.14, and PFHxS existed as an anion in water. SA has numerous carboxyl groups on the molecular chain and exists in the form of anions in water. Therefore, the above structures were hereby calculated with one negative charge and a spin multiplicity of 1. As the filtration test was implemented in the water environment to simulate the real environment as far as possible, an implicit solvent model was adopted to simulate the water environment and avoid the problem of system height caused by directly filling the system with water molecules. The implicit solvent model considered the influence of solvent molecules on the potential energy change of the system solute, and the final energy result was the energy after correction by the solvent effect (see Figure 4 for the schematic diagram of the optimized structure of PFHxS and SA).



Figure 4. Structure optimization diagram of (a) PFHxS and (b) SA.

3.3.2. Active Sites of PFHxS and SA

The electrostatic potential of the molecular surface refers to the potential energy of a unit of positive charge at a certain position around the molecule, and the electrostatic potential map of the molecular van der Waals surface can intuitively represent the electrostatic potential distribution. Besides, the active site of the pollutant can be predicted by combining it with the electrostatic potential map. Hence, the Multiwfn program was hereby utilized to plot the stereoscopic distribution of electrostatic potential on a 0.001 a.u electron density isosurface for PFHxS. According to Figure 5, the surfaces of both PFHxS and SA pollutants were negatively charged, with the red area representing a large electrostatic potential value and the blue area indicating a small electrostatic potential value. The -SO₃ part of PFHxS presented more negative electrical properties, and a minimum point appeared near the -SO₃ group, suggesting an electron-rich environment that facilitates complexation with inorganic salt ions at this site. For SA, regions with a small electrostatic potential appeared near the -COOH group on the SA chain, demonstrating that this was an active site. Compared to PFHxS, the molecular surface electrostatic potential of SA carried more negative charge.



Figure 5. The van der Waals surface electrostatic potential of (a) PFHxS and (b) SA.

3.3.3. Mechanism of HA-TFC_iNFM Purification of PFHxS

In the PFHxS/Ca²⁺ system, PFHxS carried a unit of negative charge in water, and when Ca²⁺ existed in solution, both of them tended to complex two PFHxS molecules to form a stable structure and release more energy, indicating that the reaction of Ca²⁺ complexing PFHxS could be implemented spontaneously. As indicated by Figure 6a,b, the PFHxS-Ca-PFHxS binding form had a larger size and lower binding energy than the PFHxS-Ca²⁺ binding form, suggesting the general existence of Ca²⁺ in the form of complexing two PFHxS molecules in water. This binding form had a large size, and the size of the PFHxS monomer was significantly increased compared with the single PFHxS system, enhancing the sieving effect and removal of PFHxS, and consistent with the experimental phenomenon that the addition of Ca²⁺ increased the removal rate of PFHxS.



Figure 6. The configuration and interaction energy of PFHxS combined with Ca^{2+} or/and SA. (a) a Ca^{2+} ion bound to one PFHxS molecule, (b) a Ca^{2+} ion bound to two PFHxS molecules, (c) a SA bound to one PFHxS molecule, (d) a Ca^{2+} ion bound to one PFHxS molecule and one SA molecule, (e) a Ca^{2+} ion bound to two SA molecules.

In the PFHxS/SA system, as indicated by Figure 6c, in the absence of Ca^{2+} , the interaction between PFHxS and SA was weak, and the adsorption energy was low because of the loss of Ca^{2+} bridging, so these two had their respective impact on the membrane filtration process. As PFHxS and SA could not mutually react, SA present in the solution would form a filter cake layer on the membrane surface, increasing the membrane screening effect and retention rate of PFHxS. Moreover, the large electronegativity of SA enhanced the electronegativity of the membrane surface when the filter cake layer was formed on the membrane surface, thereby enhancing the electrostatic repulsion between PFHxS and the membrane.

In the PFHxS/SA/Ca²⁺ system, when PFHxS, SA, and Ca²⁺ simultaneously existed in the solution, the strong complexing ability of Ca²⁺ would complex PFHxS and SA to form three different complexing structures, namely, PFHxS-Ca-PFHxS, SA-Ca-PFHxS, and SA-Ca-SA. According to the binding energy of Figure 6b,d,e, one PFHxS molecule and one SA molecule bound to Ca²⁺ in the most stable way, so this structure was the main form of the presence of the complex compound. Compared with PFHxS-Ca-PFHxS, PFHxS-Ca-SA had lower binding energy and larger size, so it helped remove PFHxS. In the PFHxS/SA/Ca²⁺ system, as mentioned above, the presence of SA would improve the surface electronegativity of the HA-TFC_iNFM and enhance the electrostatic interaction between the nanofiltration membrane and PFHxS. Moreover, Ca²⁺ complexed PFHxS and SA to form complex compounds, further increasing the size of pollutants. Compared with the PFHxS/Ca²⁺ system, the pollutants in the PFHxS/SA/Ca²⁺ system had a larger molecular size, so the retention rate of the PFHxS/SA/Ca²⁺ system was higher, indicating that the sieving effect might dominate the removal of PFHxS by the HA-TFC_iNFM.

3.4. HA-TFC_iNFM Fouling Mechanism

3.4.1. Construction and Simulation Optimization of the Membrane Fouling Model

The PA separation layer on the surface of the nanofiltration membrane is a semiaromatic polyamide polymer formed by the interfacial polymerization of PIP and TMC, and the reaction mechanism of PIP and TMC interfacial polymerization is shown in Figure S4. The structure of the membrane surface is associated with the degree of cross-linking of the membrane. The cross-linking degree of the membrane surface reached 86.38%, and the membrane surface was thus considered a highly cross-linking polymer. In order to simplify the calculation, the groups at both ends of the membrane surface were protonated to preserve the number of charge conservation. The membrane surface was optimized under the B3LYP/6-311G(d,p) level, and the optimized structure shown in Figure S5 was finally obtained. According to the optimized structure, the membrane surface was still in a highly cross-linking state, while the optimized structure was in the lowest energy state.

3.4.2. Analysis of Membrane–Contaminant Interactions

When no Ca²⁺ was present in the water, the contaminants were individually bound to the membrane surface in the form of monomers. Explorations on the interaction between contaminants and membranes could help elaborate membrane fouling mechanisms. The independent gradient model (IGM) was hereby used to identify the type of interaction between membranes and contaminants [42]. Weak interactions between membranes and contaminants [42]. Weak interactions between membranes and contaminants included hydrogen bonding, steric hindrance effects, and van der Waals interactions. As indicated by Figure 7a, PFHxS interacted with the membrane primarily through hydrogen bonding and van der Waals interactions. When SA is present in the solution, as PFHxS does not react with SA, they interact with the membrane surface, respectively. As indicated by Figure 7b, there were also hydrogen bond interactions between SA and the membrane surface. SA generated large and loose flocs on the membrane surface, thereby creating a smooth gel layer on the membrane surface. Therefore, in the presence of natural organic pollutants in the system, the flux decay of the system increases.



Figure 7. The schematic diagram of the interaction between contaminants and the membrane surface: (a) PFHxS, (b) SA, (c) PFHxS-Ca-SA, and (d) SA-Ca-SA.

In the presence of Ca^{2+} in water, Ca^{2+} complexed a PFHxS molecule and a SA molecule to form a large-sized complex compound, which was intercepted by the membrane to interact with the membrane surface. Moreover, as the concentration of SA exceeded that of PFHxS, complex compounds of SA-Ca-SA were also present in the solution. As indicated by Figure 7c,d, compared with the interaction between the pollutant monomer and membrane, the hydrogen bonding between the complex compound of Ca²⁺ and the pollutants, as well as the membrane, was weakened, indicating that the complexation between Ca^{2+} and the pollutants produced a charge neutralization effect, which decreased the hydrogen bonding between the complex and membrane surface. As hydrogen bonding weakened, the tightness of the hydrogen bond network formed between the complex compound and the membrane surface decreased. The reason for the flux decay after adding Ca^{2+} was that the powerful electrical neutralization capacity of Ca²⁺ neutralized the negative charge on the membrane surface, reduced the electrostatic repulsion between SA and the membrane surface, and enhanced the adsorption capacity of SA on the membrane surface, thus forming a thicker gel layer. Moreover, given that the concentration of SA in the solution exceeded that of PFHxS, the effect on the fouling layer on the membrane surface was still much smaller than that formed by SA due to the small number of PFHxS complexes, although the tightness of the bond between the PFHxS complex compound and the membrane surface was reduced. Thus, the flux attenuation degree decreased notably.

4. Conclusions

In this study, the effects of pressure, temperature, pH, solute concentration, and coexisting substances on the removal of PFHxS in water by the HA-TFC_iNFM were investigated. The influence of the coexistence of SA and Ca^{2+} on membrane fouling behavior was also studied. The mechanism of PFHxS purification by the nanofiltration membrane was analyzed using DFT. The study results are as follows:

- 1. It was found that the retention rate of the HA-TFC_iNFM on PFHxS decreased as the operating pressure (or temperature) improved but increased with the increase in the initial pH (or concentration) of the water sample. When the coexisting substances SA and Ca²⁺ were present, the retention rate of the HA-TFC_iNFM on PFHxS was higher compared to the single PFHxS system and increased with the concentration of SA and Ca²⁺. The results showed that the membrane fouling degree was greatest when SA and Ca²⁺ coexisted, as indicated by the water flux attenuation and anti-pollution index of the HA-TFC_iNFM in the PFHxS/SA/Ca²⁺ water sample system.
- 2. The active sites of PFHxS and SA were analyzed based on electrostatic potential, and the optimal configuration was determined from the perspective of energy and the product structure. The presence of Ca^{2+} increases the size of the complex compound by complexing two PFHxS molecules, thereby enhancing the sieving effect. The presence of SA, although unable to react with PFHxS, blocks membrane pores and increases the negative charge on the membrane surface, thus strengthening the size of the sieving and Donnan effects. When both Ca^{2+} and SA are present, they form a larger complex compound by complexing one PFHxS and one SA molecule, further enhancing the sieving effect. The removal mechanism of the HA-TFC_iNFM on PFHxS in the coexistence system is mainly based on the sieving effect, with the Donnan effect playing a supporting role.
- 3. During the removal of PFHxS pollutants with the HA-TFC_iNFM, weak interactions, such as hydrogen bonding and van der Waals, became crucial for binding between the membranes and pollutants. The addition of Ca²⁺ impacted the membrane fouling process by influencing the hydrogen bonding interaction between the HA-TFC_iNFM and pollutants.

Supplementary Materials: The following supplementary materials can be downloaded at: https: //www.mdpi.com/article/10.3390/w15040792/s1, Figure S1: Zeta potential of HA-TFC_iNFM; Figure S2: Schematic diagrams of the homemade cross-flow nanofiltration system; Figure S3: Changes in normalized flux with filtration time for HA-TFC_iNFM under PFHxS/SA/Ca²⁺ system; Figure S4: IP mechanism of PIP and TMC; Figure S5: Three-dimensional structure of the membrane surface; Table S1: The physical and chemical properties of PFHxS.

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