Perfluorooctane sulfonate removal by nanofiltration membrane—the effect and interaction of magnesium ion / humic acid

Changwei Zhao [a,b,*], Chuyang Y. Tang [c], Pei Li [d], Pegoraro Adrian [b], Guangshuo Hu [a]

[a] State Key Laboratory of Environmental Aquatic Chemistry, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China
[b] School of Engineering and Applied Sciences, Harvard University, 29 Oxford St., Cambridge, MA 02138, USA
[c] Department of Civil Engineering, University of Hong Kong, Pokfulam, Hong Kong
[d] College of Materials Science and Engineering, Beijing University of Chemical Technology, No.15 Beisanhuandong Road, Chaoyang District, Beijing 100029, China

A B S T R A C T

Although the presence of perfluorooctane sulfonate (PFOS) in environmental systems has generated widespread interest, little information is available on PFOS removal from surface water by membrane technology. Herein, a novel nanofiltration membrane (NF270) was investigated so as to remove PFOS. More specifically, the interaction and effect of Mg^{2+} ion and/or humic acid (HA) in the feed solution on PFOS removal efficiency and total permeate flux were examined. Under 0.8 MPa, an improvement in PFOS rejection efficiency from 94.3% to 99.5% was observed when the concentration of Mg^{2+} ion was increased from 0–2 mM in the feed solution. This enhancement is attributed to enhanced size exclusion because PFOS molecules are linked together by Mg^{2+} ion, as shown by Density Functional Theory (DFT) calculation. The result shows that Mg^{2+} ion can more easily neutralize two PFOS anion than one PFOS anion on the basis of the Gibbs free energy changes. Conversely, the presence of HA had minimal improvement on PFOS rejection because HA had much weaker ability to bind with PFOS comparing to Mg^{2+}. Consequently, The further interaction between Mg^{2+} and the carboxylic groups of HA molecule, carboxylic group or amino group of NF270 membrane was also calculated via DFT theory. Corresponding DFT structures and calculation parameters of Mg^{2+} with different groups were obtained. These findings indicate that the size exclusion mechanism primarily governs PFOS removal by the NF270 membrane. Flux results showed that the co-presence of Mg^{2+} ion and HA in the feed solution resulted in the most flux reduction, by 70%, that was associated with the thickest fouled layer.

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1. Introduction

Perfluorooctane sulfonate (PFOS) has been widely used as ingredients surfactants, firefighting foams, lubricants and insecticides additives for many industrial, commercial, and consumer practices during the last five decades [1,2]. PFOS is an ubiquitous pollutant in rainwater, surface water, groundwater, and even tap water [3,4]. Its global presence, extreme persistence, bioaccumulative nature and strong toxicity have caused widespread concerns, prompting many environmental agencies around the world to restrict the use of PFOS [5–7]. Nevertheless, its use in some selected consumer application (e.g., semiconductor industry) has been exempted due to the lack of immediate replacement, and

industrial effluents from such activities will continue to be the main source of the PFOS entering into the environment [8]. Available models predict a continuous PFOS concentration rise in remote areas in the next two decades despite a decline of its concentration in surface ocean water in response to the chemical's phase out [8]. The constant presence of PFOS in surface water presents a potential threat to the security of drinking water, thereby raising extensive interest in controlling its occurrence in the environment [9–12].

Nanofiltration (NF) is a pressure-driven membrane filtration process that has intermediate characteristics between reverse osmosis and ultrafiltration. Low operation pressures, environmental friendliness, high retention of multivalent anion, low-molecule-weight organic contaminants (200–1000 Da) etc. as its nature advantages makes NF a promising and attractive technology in the removal of PFOS with high rejection efficiencies of > 90% from water [13–17]. In previous work, Steinle–Darling found NF membrane could effectively remove PFOS [18]. Appleman et al. also

indicated NF is effective to remove PFOS more than 95% [19]. However, the above investigation seldom focused on environmental matrix co-existence effects such as cations and natural organic matter (NOM) on PFOS removal. For instance, divalent cations such as magnesium, calcium ion are commonly present in natural water [20]. Our previous individual calcium research indicated that Ca^{2+} can interact with PFOS molecule and improved PFOS rejection [21]. Meanwhile, Mg^{2+} has the potential to alter the interaction between PFOS molecules as well as their interaction with other compounds/materials [22]. Wang and Shih [23] systematically studied the effects of four types of cations (Na^+, K^+, Mg^{2+}, and Ca^{2+}) on the adsorption of PFOS on alumina. The experiment outcomes demonstrated that the PFOS adsorption capacities increased as the ionic strength of the cations increased. The adsorption capacity of PFOS on the alumina decreased as Ca^{2+} presented in the solution owing to the potential bridging effects of Ca^{2+} in solution. Subramanian et al. studies indicated Ca^{2+} and Mg^{2+} might form complexes with PFO- and the monovalent complexes (PFO-Ca^+) by matrix experimental analysis [24]. Cheng et al.'s research showed that the effect of cations on the sonochemical degradation rates of PFOX has no significant difference by observation [25]. Humic acid (HA) is the major component of NOM present in natural water and has been recognized as a significant precursor of disinfection by-products [26,27]. On the other hand, HA is also an important contaminants to NF membranes [28]. The presence of HA in the feed water therefore can affect PFOS removal either due to its interaction with PFOS molecules or as an indirect result of membrane fouling [29]. To the best of our knowledge, the effect of co-existing of Mg^{2+} and HA on PFOS removal performance from surface water has not yet been systematically investigated by the NF separation process.

Presumably, Mg^{2+} ion could strengthen the cross-linkage between the PFOS molecules, which will change the size,properties of the solutes and thus removal by NF. In addition, Mg^{2+} could interact with the –COOH groups of HA molecule as well as the –COOH and –NH_2 group of NF270 membrane material. In this regard, molecule simulation such as Density Functional Theory (DFT) calculation could provide valuable insights into the geometry and bonding of PFOS molecules [30,31]. To the best knowledge of the authors, there has not been any systematic report on the interaction of Mg^{2+} with PFOS, HA and membrane at the microscopic level. Therefore, extending DFT to analyze Mg^{2+}-PFOS, Mg^{2+}-membrane and Mg^{2+}-HA interaction could pave the road to the understanding of PFOS removal mechanism.

In this work, we examined the role of Mg^{2+} ion and HA on the efficiency of the removal of PFOS from surface water using a NF process. Variation in feed condition (e.g., Mg^{2+} ion, HA, co-existing of Mg^{2+} and HA) were used to determine the role of Mg^{2+} and HA in governing PFOS rejection and membrane fouling. Furthermore, from the perspective of quantum chemistry it is the first time to obtain the interaction between Mg^{2+} and PFOS, HA and membrane material by the DFT method. These results allow us to explain the matrix effect on the PFOS removal and membrane fouling behavior.

2. Experimental

2.1. Materials

Potassium perfluorooctane-sulfonate (PFOS, 99%) was purchased from AccuStandard, Inc. (USA). Methanol (HPLC grade), acetonitrile, sodium chloride, sodium bicarbonate and magnesium chloride (analytical grade, > 99%) were purchased from Fisher Scientific (Hampton, NH). Humic acid (HA, technical grade) obtained from Sigma–Aldrich (St. Louis, MO) was purified [32] and

used as a model NOM and organic contaminant. The feed solution were prepared by first dissolving a known amount of PFOS in deionized water, to which known quantities of aqueous magnesium chloride solution were added. The HA concentration of 10 mg/L is common in water, HA was added to the PFOS or the Mg^{2+}-containing PFOS feed solution to achieve a concentration of 10 mg/L. The resulting solution was stirred for 24 h to obtain a homogenous solution. The commercial NF filtration membrane (NF270) employed was supplied by DOW FilmTec (Minneapolis, MN). NF270 membrane is composed of an active semi-aromatic piperazine-based polyamide layer supported on a microporous polysulfone layer [33], and the membrane features a pore size of 0.34 nm [34].

2.2. PFOS quantification

A 0.22 μm membrane filter needle was used to filter each water sample (the initial 4 mL mixture was discarded to reduce the effect of membrane adsorption based on PFOS high recovery rate of 0.99.), an ultra-performance liquid chromatography-tandem mass spectrometer (UPLC-MS/MS) was used for analysis PFOS concentration using an UPLC system (Waters Corp., USA) equipped with a C18 column (BEH, particle size 1.7 μm, 2.1 × 50 mm i.d., Waters Corp., USA) and an MS system Quattro Premier XE tandem quadrupole mass spectrometer (Waters Corp., USA) with an electrospray ionization source. A binary mixture with ratio of 32% solvent A (10 mmol/L ammonium acetate in MilliQ water) and 68% B (100% acetonitrile) as the mobile phase were applied at a flow rate of 0.15 mL/min with 10 μL rejection. Selected ion monitoring (SIM, 499-> 80) mode was employed to quantify the analytes with 30 V cone voltage and 11 eV collision energy.

2.3. Membrane performance tests

The PFOS rejection and water flux were assessed on a custom-assembled setup consisting of CEPA CFII crossflow cells (active membrane area of 140 cm², GE Osmonics, Minnetonka, MN). The detailed testing procedures have been reported previously [19]. All tests were performed at 25 ± 1 °C, which was controlled by the circulating water bath. For each test, a PFOS feed solution was introduced into the feed tank. The cross flow rate of 1.5 L min^{-1} of the feed solutions was applied to minimize the effect of concentration polarization (Re > 4000). The permeate samples were collected for PFOS concentration measurement based on flow stability after 2 h under the each test condition. The PFOS rejection, R, was determined as follows:

$$R(\%) = (1 - \frac{C_p}{C_f}) \times 100 \tag{1}$$

where C_f and C_p are the PFOS solute concentration in the feed and permeate samples, respectively.

The water flux, J, was obtained by measuring the volume of permeate that passed through the membrane during a set time as follows:

$$J = \Delta V / A \Delta t \tag{2}$$

where ΔV is the volume change of permeate during the experiment, A is the membrane area and Δt denotes the measuring time change.

2.4. Membrane characterization

2.4.1. Scanning Electron Microscopy (SEM)

A Hitachi S-3000N scanning electron microscope (Hitachi Ltd., Japan) was used to observe the morphology of the virgin and