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Perfluorooctane sulfonate and perfluorobutane sulfonate removal from water by nanofiltration membrane: The roles of solute concentration, ionic strength, and macromolecular organic foulants

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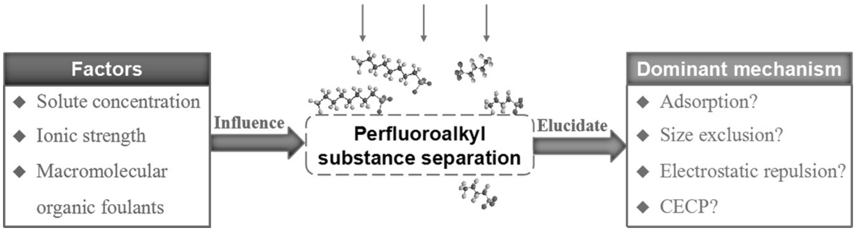
GRAPHICAL ABSTRACT



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ABSTRACT

The influence of solute concentration, ionic strength, and macromolecular organic matter on the rejection of perfluorooctane sulfonate (PFOS) and perfluorobutane sulfonate (PFBS) via nanofiltration (NF) was investigated using poly(piperazineamide) membranes. The results showed that compared with PFBS (steady-state rejection < 69%), PFOS with the larger molecular size and stronger hydrophobicity displayed higher retention (steady-state rejection > 88%) in all water matrices. Rejection of PFOS and PFBS increased with higher solute concentrations, attributable to enhanced size exclusion resulting from pore blockage. As ionic strength increased from 0 to 100 mM, PFOS retention increased from 89.6% to 91.9%; conversely, PFBS rejection declined from 48.9% to 20.5%. These phenomena, in conjunction with the decrease in membrane flux and charge with increasing ionic strength, suggest that the retention of PFOS and PFBS was dominated by size exclusion and electrostatic repulsion, respectively. In addition, model macromolecular organic foulants—bovine serum albumin (BSA) and sodium alginate (SA)—influenced the rejection of PFOS and PFBS significantly. The presence of BSA and SA caused improved PFOS rejection, while adsorption dominated PFOS retention before the formation of an organic fouling layer and size exclusion was dominant after formation of the layer. As for PFBS feed systems, SA facilitated PFBS rejection, while BSA only contributed to PFBS removal temporarily and thereafter led to decreased PFBS rejection. From further consideration of the characteristics of membrane surface charge variation and organic fouling, it is concluded that electrostatic repulsion was the preponderant retention mechanism for PFBS during the entire organic fouling process.

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1. Introduction

Polyfluoroalkyl and perfluoroalkyl substances (PFASs, C_nF_{2n+1}-R) are widely used in industrial manufacturing and consumer products because of their excellent thermal and chemical stability as well as high surface activity [1]. PFASs are a growing concern because they are recalcitrant in the environment and in humans, bioaccumulative, toxic, and are detected in water bodies globally [2,3]. Perfluorooctane sulfonate (PFOS) is one of the most widely used PFASs [4]. In 2009, PFOS was categorized as one of the new and emerging persistent organic pollutants [5]. The US and many European countries have proposed legislation or regulations to limit the use of PFOS. Nevertheless, PFOS is still being used in some important applications because of the lack of available appropriate alternatives [6]. Although PFOS usage has decreased sharply, PFOS is still ubiquitous in waters at relatively high concentrations [5] because of its heavy use over several decades and difficult degradation characteristics. In recent years, perfluorobutane sulfonate (PFBS), which includes a four-carbon backbone, has generally been used as a substitute for PFOS and its usage is increasing. Even though its toxicity is not as pronounced as that of PFOS, PFBS presents a potential threat to humans [7].

Increasingly severe water pollution and stringent water quality standards encourage the development of cost-effective water production technologies for high-quality water. PFOS and PFBS in drinking water sources directly affect human health. Conventional water treatment processes such as coagulation, sedimentation, conventional filtration, and chlorination have limited ability to remove PFASs from water [2,8]. Although some advanced technologies such as sonochemical decomposition [9] and ultraviolet-mediated photodegradation [10,11] can decompose PFASs, these methods need long reaction time, high energy consumption, and complicated and specific operational conditions [3]. Nanofiltration (NF), an economically attractive membrane separation technology, has been proved effective and reliable in removing organic micropollutants including PFASs from various water sources [4,12–16].

Generally, feedwaters from different sources vary in water quality, which influences the retention of micromolecular trace organic compounds (TOrCs) [17,18]. For instance, the effects of solute concentration on the rejection of TOrCs varied depending on the specifics of the NF membrane as well as those of the TOrCs [17,19]. An increment in ionic strength probably results in electrostatic shielding of some charges from charged TOrCs and the NF membrane, leading to a decrease in retention of TOrCs [20]. Moreover, membrane pores are likely to shrink under relatively high ionic strengths, thus, is increased because of enhanced size exclusion [21]; whereas membrane pores may swell at excessive ionic strengths, resulting in a decrease in TOrC rejection [22]. Not only the solution chemistry (e.g., concentration and ionic environment), but also the TOrC's physicochemical properties (e.g., molecular size, charge, and hydrophobicity) determine TOrC rejection by NF membranes [20]. Hence, the retention behaviors and dominant rejection mechanisms of different TOrCs are likely diverse. Consequently, it is imperative to evaluate how solute concentration as well as ionic strength influences PFAS separation by NF membranes.

When the feedwater contains macromolecular organic matters, the organic fouling of NF membranes is unavoidable and is a step-by-step process [23]. The surface properties of the NF membrane, which influence the rejection of micromolecular TOrCs [24], change continually until a stable adhered organic fouling layer has formed. Furthermore, the membrane fouling behaviors of different macromolecular organic matters are not identical [25]. Accordingly, organic fouling probably becomes a complex issue for the actual application of NF technology in TOrC removal. Therefore, gaining insight into the correlation between the removal behaviors of micromolecular PFASs and the characteristics of macromolecular organic matters in different organic fouling stages is crucial.

Studies available in the literature to date have mainly focused on the influence of operating pressure, pH, Ca^{2+}, and NF membrane properties on PFOS retention [4,16,26,27]. Several investigations reported the effects of Mg^{2+} [28], humic acid (HA) [28] on PFOS removal. Only Steinle-Darling and Reinhard [14] evaluated the effect of ionic strength on PFOS rejection and found the influence was much less pronounced, while it should be stressed that other coexisting perfluorochemicals may have interfered with the intrinsic PFOS separation ability of NF membranes. Besides, they observed that after a SA fouling layer formed, average rejections for PFASs decreased significantly from 99.3% (virgin NF membrane condition) to 95.3% [14]. However, Appleman et al. [13] found that when a HA fouling layer was present on the NF membrane, rejection for some PFASs (e.g., PFOS) was maintained, whereas for certain PFASs (e.g., PFBS), it was greater than the virgin membrane condition. Although the two studies investigated the influence of organic fouling layers on PFOS rejection, there is no information available regarding the removal characteristics or related rejection mechanisms of PFOS during the entire organic fouling process. Furthermore, these studies only considered one kind of macromolecular organic foulant. It is still unclear whether the effects of diverse macromolecular organic matters on PFOS retention are the same.

To date, few studies have considered removing PFBS by NF membranes and most of them simply focused on PFBS removal efficiency. The mechanisms for the influence of various factors and the predominant rejection mechanism of PFBS under different conditions have not been analyzed deeply [13,14,26]. Although PFOS and PFBS have similarities, their molecular sizes and hydrophobicities are different, which probably leads to differences in their rejection mechanisms, such as size exclusion and adsorption. Consequently, it is necessary to study the retention characteristics of PFBS by NF membrane and make a comprehensive comparison with PFOS. However, to our knowledge, no related work has been reported.

This study selected PFOS and PFBS as the typical PFASs according to the current pollution status of worldwide water bodies. Bovine serum albumin (BSA) and sodium alginate (SA) were used as the representative protein and polysaccharide, respectively. The influence of solute concentration and ionic strength on the rejection of the target PFASs (i.e., PFOS and PFBS) by NF membrane was evaluated systematically. The retention behaviors of the target PFASs during different organic fouling stages were also investigated. The rejection rate and adsorption amounts of target PFASs, flux decline, and membrane surface charge were combined to determine the mechanisms for the influence of each factor and the predominant rejection mechanisms of PFOS and PFBS in different conditions. The ultimate objective is to provide a theoretical basis for the selection of appropriate feedwater pretreatment processes and NF membranes according to primary target PFASs and feed conditions to maximize NF efficiency in removing PFOS and PFBS from water.

2. Materials and methods

2.1. Poly(piperazineamide) NF membrane

The poly(piperazineamide) composite NF membranes used in this study were manufactured in two steps. First, the polysulfone substrate was fabricated using phase inversion. Then, the poly(piperazineamide) ultrathin film was prepared via interfacial polymerization. The overall preparation process was described in detail in a previous study [25]. The average pure water flux (at an operating pressure of 0.6 MPa), molecular weight cut-off (MWCO), and pore size of the NF membrane were 48 L m^{-2} h^{-1}, 400 Da, and 0.912 nm, respectively.

2.2. Chemicals and reagents

2.2.1. Target PFASs

Potassium perfluorooctane sulfonate (PFOS, purity ≥99.99%) and potassium perfluorobutane sulfonate (PFBS, purity ≥99.99%) were