Monovalent ion-mediated fouling propensity of model proteins during low-pressure membrane filtration

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Xiang He [a,b], Fangang Meng [a,b,*], Anli Lin [a,b], Zhongbo Zhou [a,b], Yiwei Chen [a,b], Chuyang Y. Tang [c,*]

[a] SYSU-HKUST Research Center for Innovative Environmental Technology, School of Environmental Science and Engineering, Sun Yat-sen University, Guangzhou 510275, PR China
[b] Guangdong Provincial Key Laboratory of Environmental Pollution Control and Remediation Technology (Sun Yat-sen University), Guangzhou 510275, PR China
[c] Department of Civil Engineering, The University of Hong Kong, Pokfulam, Hong Kong, China

A B S T R A C T

In this study, we explored the response of membrane filtration behavior of bovine serum albumin (BSA) to various monovalent salts (i.e., NaCl, KCl, CsCl, NaBr, NaI) at 15 mM and 150 mM ionic strengths. The results demonstrated that the charge of BSA tended to be less negative with an increase in ionic strength. The presence of monovalent ions also resulted in the increased size of BSA. However, little change was observed in the viscosity of BSA with the involvement of monovalent ions (with the exception of 150 mM CsCl). The changes in the characteristics of BSA were primarily caused by their interaction with cations, and the greater specific interaction between Cs^+ and BSA led to a significant increase in the size and viscosity of BSA. In spite of the substantial dependence of the characteristics of BSA (i.e., size, zeta potential) on cations, the fouling behaviors of BSA were primarily determined by anion identity. Specifically, the order of the ability of anion identity to reduce the flux decline rate seemed to be $I^- > Br^- \sim$ or $> Cl^-$, which seemed to be ascribed to the changes in electrostatic repulsion between BSA and the membranes caused by anions.

1. Introduction

Membrane technology has been widely employed for water and wastewater treatment [1,2]. However, membrane fouling remains a major obstacle for application of membrane processes [3]. In particular, biopolymers, such as polysaccharides and proteins, have generally been considered as primary foulants because of their strong tendency to deposit on membranes [4]. Fouling depends on various factors such as membrane characteristics [5], biopolymer properties [6], pre-treatment processes [7] and solution chemistry [8], which can either accelerate or mitigate membrane fouling [9]. To date, understanding of the organic fouling behavior and the related factors are still of essential significance to membrane filtration of natural water or biologically treated wastewater.

Solution chemistry has been demonstrated to have significant influence on the characteristics of organic matter in the solution [10,11]. A number of investigations have shown that the interaction between, and thus the fouling potentials of proteins [12] and polysaccharides [13,14] are strongly governed by solution chemistry. For example, coagulation of humic substances was found to increase with increasing salt concentration, cationic charge and cationic charge density for a given charged cation [15]. Similarly, Wang et al. [16] found that the coagulation kinetics of humic substances were dependent on both pH and the added ions, and they also found that Mg^{2+} was more effective at enhancing coagulation than Na^+. Moreover, the presence of monovalent and divalent ions was found to cause changes in the viscosity of alginate [14]. In addition, the presence of monovalent salts could lead to the changes in hydrodynamic radius of organic matter, such as soluble microbial product (SMP) because of the increased repulsion between colloids [17].

Because of their significant role in modifying the characteristics of organic matter, solution chemistry is expected to impact the fouling propensity of organic matter. For instance, studies have shown that solution pH had strong effects on organic foulant adsorption [18], the compactness of the foulant cake layer [19], fouling resistance [20] and filtration flux [21,22]. Normally, organic matter fouling was more severe in the presence of the calcium ion [8,23,24]. Moreover, the combination effects of solution chemistry are very complicated. For example, membrane fouling by BSA was promoted by increasing ionic strength at pH 3.0, while the fouling was insensitive to ion concentration at pH 4.7 [25]. Specially, both effects of pH and calcium concentration on membrane fouling

were observed to be different at 10 mM from that at 600 mM ionic strength [26]. A study also demonstrated that reverse osmosis (RO) membrane fouling by octanoic acid was unaffected by calcium ions at pH below the pKa, whereas higher calcium ion concentrations could decrease the rate of flux decline at elevated pH [27]. Thus, the role of solution chemistry in the development of membrane fouling could be far more complex than we have known. Note that previous efforts mostly focused on the role of pH and multivalent ions in membrane fouling. However, one should also note that the multivalent ions are always present along with monovalent ions, and monovalent ions in some water bodies, such as saline water, contribute significantly to the ionic strength. Nevertheless, the published investigations are inadequate to determine whether monovalent ions play any roles in the organic fouling of membranes. If so, to what extent? And how? These issues are the main focus of the current study.

In this study, five different monovalent salts (i.e., NaCl, KCl, CsCl, NaBr, and NaI) were used to investigate the effects of ion species and ionic strength on organic fouling of membranes by BSA. The characteristics of BSA in the presence of monovalent ions were analyzed in terms of Zeta potentials, size and viscosity. The fouling behavior of BSA in the presence of monovalent salts was explored in a stirred dead-end filtration cell using polyethersulfone (PES) membranes. Moreover, bivariate Pearson correlation analysis was used to assess the relationship between the properties and fouling behavior of BSA.

2. Materials and methods

2.1. Organic foulants and monovalent ions

In this study, bovine serum albumin (BSA, J&KCHEMICA®) was selected as the model organic foulant. BSA was received in a powder form. Stock solutions (200 mg/L) were prepared by dissolving BSA powder in ultrapure water without further purification. AR-grade monovalent salts (i.e., NaCl, KCl, CsCl, NaBr, NaI) were purchased from ALADIN® and dissolved in ultrapure water to prepare stock solutions (300 mM). All stock solutions were stored in a refrigerator at 4 °C. All of the glassware or vessels were sterilized to avoid bacteria growth during the experiments.

Before membrane filtration tests, stock solutions were equilibrated to 25 °C in a water bath. Then, samples were prepared with care, and salt stock solutions were dosed to the desired ionic composition. In this study, all model solutions contained 50 mg/L BSA with desired amounts of background electrolytes (NaCl, KCl, CsCl, NaBr, or NaI). The concentration of BSA used in this study (i.e., 50 mg/L) was referred to a previous study of membrane fouling [28]. No pH adjustment was performed. The pH of all the prepared samples was ca. 6.0.

In the present study, the measurement of pH, Zeta potential, size and rheological properties were also controlled at the same experimental conditions (e.g., temperature) as those applied in the filtration tests.

2.2. Membrane filtration tests

Membrane filtration was performed as described by Shen et al. [29], with some modifications. In this study, membrane filtration was carried out using a stirred dead-end cell (MSC300, Mosu, China) with an effective membrane filtration area of 35 cm^2. All tests were conducted at a constant temperature of 25 °C (maintained by a water bath) and at a stirring speed of 200 rpm. All filtration experiments were performed under a constant trans-membrane pressure of 10 kPa using nitrogen gas, and the constant pressure was maintained using a pressure regulator (Type

10, Bellofram Corp, USA). For each test, a new PES membrane (Φ90 mm × 100 kDa, Shanghai Youyu Instrument & Meter Co., China) was used. The contact angle of the PES membranes was measured for three times using a contact angle meter (OCA15Plus, Dataphysics, Germany), and it was determined to be 55.5 ± 2.0°. Each membrane was soaked in pure water for over 24 h to remove residual organics, and then washed several times with ultrapure water. Subsequently, pure water was filtered in the filtration test unit to reach stable permeate flux, which was defined as the pure water permeability of the clean membrane. Then, 200 mL samples prepared by BSA with varying monovalent ions were supplied to the cell for the membrane filtration test. During the entire filtration process, the permeate flux was continuously recorded by weighing permeate samples with an electronic balance (FA2204B, Shanghai Precision & Scientific Instrument Co., Ltd, China) connected to a computer. Once the filtration test was completed, the fouled membrane was flushed with tap water [30] and soaked in 300 ppm NaClO solution for 1 min which was found to be an optimal cleaning duration based on performed preliminary experiments. Then, the pure water flux of washed membranes was measured under the same conditions. The pure water flux of the chemically washed membranes compared to the corresponding value of new membranes was denoted as the reversibility of the membrane permeability, which reflects the recovery capability of the fouled membrane by physical and chemical cleaning [31].

2.3. Analytical methods

Zeta potentials and size distribution of the samples were measured using a Zetasizer Nano-ZS90 instrument (Malvern instruments co., UK) at 25 °C. The Zeta potential of each sample was measured for three replicates, and the data were presented as mean values and standard deviations.

Rheological measurements were conducted using a rotational meter (DV-III Ultra, Brookfield, USA) connected to a circulator bath at a constant temperature (25 °C). Due to the non-Newtonian nature of model foulant solutions, the viscosity was measured at 16 different speeds in the range of 70–220 rpm with equal intervals. Experimental values show that the rheological behavior of BSA solution was closely approximated by the Herschel–Bulkley model.

$$\tau = k\gamma^n \tag{1}$$

where τ is the shear stress, k is the consistency index, γ is the shear rate and n is the flow index. In this study, the coefficients k and n were obtained by fitting the experimental data with the Herschel–Bulkley equation. The rheological property of each sample was also measured for three replicates.

Recently, the concept of unified membrane fouling index (UMFI) was introduced to evaluate membrane fouling under low pressure regardless of filtration scale or mode [32]. UMFI is defined based on Eq. (2), with some modifications after the Hermia model [32].

$$1/J'_s = 1 + (UMFI)V_s \tag{2}$$

where $1/J'_s$ is the inverse of normalized flux and V_s (L/m^2) is the unit permeate volume. Thus, UMFI has units of m^{-1} or m^2/L. Both J'_s and V_s can be determined experimentally. Herein, the values of UMFI can be obtained based on Eq. (2) using the linear regression approach. Depending on the selected data of $1/J'_s$ and V_s, UMFI can be indicative of total fouling, or hydraulically irreversible or chemically irreversible fouling rates. A higher UMFI value indicates a greater decline in normalized flux (i.e., higher rates of membrane fouling).

Because of the linear relationship between the concentration of BSA and the absorbance at 280 nm, a UV spectrophotometer