



## Evaluating the effects of sodium and magnesium on the interaction processes of humic acid and ultrafiltration membrane surfaces



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### ABSTRACT

In this study, the adsorption behaviors of humic acid (HA) on ultrafiltration membrane surfaces and the HA adsorbed-layer structure were determined in the presence of Na<sup>+</sup> and Mg<sup>2+</sup>, and the interaction forces of membrane–HA and HA–HA were measured. HA fouling experiments were performed to unravel the influence mechanisms of Na<sup>+</sup> and Mg<sup>2+</sup> on HA fouling. Our results show that the cations mostly affect HA fouling by controlling the electrostatic forces and hydration forces of membrane–HA and HA–HA. For Na<sup>+</sup>, HA fouling was mainly dominated by electrostatic forces. With increasing Na<sup>+</sup> concentrations, the membrane–HA and HA–HA interaction forces increased because of the shielding effect, resulting in a higher deposition rate of HA onto the membrane surface and a more compact HA layer, accompanied by more serious membrane fouling. Mg<sup>2+</sup> affected HA fouling in two stages. Lower Mg<sup>2+</sup> concentrations acted similarly to Na<sup>+</sup>, with membrane fouling dominated by the electrostatic interaction forces. However, when the Mg<sup>2+</sup> concentration exceeded a critical value, hydration repulsion forces caused a decrease in the deposition rate and the extent of HA on the membrane surface, and a less rigid HA layer was formed; membrane fouling was therefore mitigated.

### 1. Introduction

Ultrafiltration (UF) technology has emerged as a very promising process for wastewater treatment and reuse because of its distinct advantages, such as energy and space savings and better safety [1]. However, membrane fouling with its increased operating and maintenance costs remains a major drawback to the widespread use of UF technology [2].

Natural organic matter (NOM), which is widely found in surface water, municipal wastewater, industrial wastewater, and other wastewater or water to be treated, has often been reported as one of the major foulants responsible for UF fouling [3]. Humic substances (HS) form the main part of NOM, making up 50–80% of its components of NOM, and humic acid (HA) is the major constituent of the HS, which have been considered as one of the most severe membrane fouling substances. Therefore, membrane fouling processes and mechanisms induced by HA have been of continuing interest in wastewater treatment and reuse [4].

HA fouling of a membrane is a very complicated process. It is closely related to water quality, type of membrane material, and operating conditions, among other factors [5]. Cations, such as Ca<sup>2+</sup>, Mg<sup>2+</sup>, K<sup>+</sup>, and Na<sup>+</sup>, which are commonly present in wastewater in a

wide range of concentrations, have been recognized as key factors affecting HA fouling of membranes [6]. This is because the interaction forces between membrane and HA and between HA and HA can be significantly affected by cations through complexation, neutralization, or electrical double layer formation, which primarily control the membrane fouling rate and fouling extent [7]. Therefore, an in-depth insight into the mechanisms by which cations influence HA fouling of membranes will be crucially important for controlling membrane fouling during UF.

Most research indicates that HA fouling rate and irreversible fouling of membranes are enhanced by increasing the amounts of cations (such as Ca<sup>2+</sup>, Mg<sup>2+</sup>, or Na<sup>+</sup>) [8–12]. This is well explained by the classical Derjaguin–Landau–Verwey–Overbeek (DLVO) theory. As the amounts of cations increases, charge screening, complexation, or bridging action would be strengthened, which weakens the electrostatic repulsion forces of membrane–HA and HA–HA. As a result, there is an increase in the deposition rate of the organic foulants on the membrane surface or in the membrane pores, leading to a significant increase in the fouling rate and the fouling extent of membranes.

In contrast with these results, other studies indicate that HA fouling was not enhanced by increasing the concentrations of cations. Li's group reported that different Na<sup>+</sup> concentrations resulted in essentially

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the same flux decline rate. They considered that there was no significant effect of  $\text{Na}^+$  on HA fouling behavior, and also speculated that charge screening by  $\text{Na}^+$  does not play a major role in HA fouling [13]. More interestingly, other studies investigated HA fouling at different  $\text{Ca}^{2+}$  concentrations, and found that the HA fouling rate and fouling extent of a membrane first increased and then decreased as  $\text{Ca}^{2+}$  concentrations increased [14–16]. They speculated that one possible explanation is that at high calcium concentrations, there were much stronger complexation and bridging interactions of HA with both HA and the membrane, forming larger HA aggregates and a looser cake layer with relatively high permeability on the membrane surface. Consequently, at high  $\text{Ca}^{2+}$  concentrations, the flux decline rates of membrane decreased.

It is not difficult to find that there were some contradictory results have been published on the effect of cations on HA fouling. Under some conditions, the presence of cations will enhance membrane fouling while in other conditions, the membrane fouling will be decreased by cations. However, there appears to be no systematic research or consistent explanation for why HA fouling of membranes exhibits different characteristics under different cation conditions. To date, there appears to be no consistent theoretical knowledge available on the main reasons for the contradictory results mentioned above. In particular, for the variations in the characteristics of membrane–HA and HA–HA interaction forces under different cation conditions, their relationship with the deposition and adsorption behavior of HA on the membrane surface, and the structure of the HA adsorption layers, most studies were based on experimental observations and visual comparison of the normalized permeate flux decline curves during the filtration process, and offered some simple descriptions or speculation [17]. Thus, it is essential to unravel the above issues because it may be helpful in identifying why HA fouling of membranes was enhanced or mitigated under different cation conditions. These findings would be crucially important for controlling and mitigating HA fouling during filtration.

In this study, one of the most extensively applied membrane materials in UF systems, polyvinylidene fluoride (PVDF), was chosen as the membrane material to prepare flat sheet UF membranes, the two most abundant cations in wastewater or water to be treated,  $\text{Na}^+$  and  $\text{Mg}^{2+}$ , were used. For a range of  $\text{Na}^+$  and  $\text{Mg}^{2+}$  concentrations, membrane–HA and HA–HA interaction forces were determined directly. A quartz crystal microbalance with dissipation monitoring (QCM-D) combined with a PVDF-coated sensor crystal was used to investigate the deposition and adsorption behavior of HA on the PVDF membrane surface and the adsorbed HA layer structure in the corresponding ionic environment. These results were combined with those of HA fouling experiments to unravel the mechanisms influencing HA fouling of UF membranes for  $\text{Na}^+$  and  $\text{Mg}^{2+}$ . The ultimate goal is to provide theoretical support for the prevention and control of HA fouling of UF membranes.

## 2. Materials and methods

### 2.1. Chemicals and UF membrane

#### 2.1.1. Chemicals

Commercial humic acid (HA; Sigma-Aldrich, St. Louis, Mo) was received in powder form. An HA stock solution (1 g/L) was prepared by dissolving 1 g HA in 0.1 mol/L (100 mL) sodium hydroxide solution and bringing to volume with deionized (DI) water. Then, HA stock solutions were filtered using 0.45  $\mu\text{m}$  microfiltration membranes to remove particulate and insoluble matter, and then stored in sterilized glass bottles at 4 °C prior to use. For each fouling experiment, fresh HA working solution at a dissolved organic carbon (DOC) concentration of 10 mg/L and pH 7.0 was prepared.

The concentrations of  $\text{Na}^+$  or  $\text{Mg}^{2+}$  of HA working solutions were adjusted with either 1 mol/L NaCl or 0.5 mol/L  $\text{MgCl}_2$  solutions.

Unless specified otherwise, all working solutions were prepared with ultrapure water (resistivity of 18.2 Mohm-cm, TOC < 0.001 mg/L), supplied by an Elga Purelab Ultra water purification system (Elga, UK). All reagents and chemicals were analytical grade, with purity > 99%.

#### 2.1.2. Preparation of PVDF UF membranes

PVDF UF membranes were used in the current study, which were prepared via a nonsolvent-induced phase separation method as follows [18]. PVDF (Solef 1015; Solvay Advanced Polymers Co., America) was mixed with N,N-dimethylacetamide (DMAc; Tianjin Fucheng Chemical Reagent Co., China) and stirred vigorously for 16 h at 60 °C to obtain a homogeneous solution. The polymer solution was then allowed to stand for 12 h to allow air bubbles to escape. The resulting homogeneous polymer solution was uniformly spread onto a glass plate using a casting knife, and the glass plate was then immersed immediately into a DI water bath set at a temperature of 40 °C. The membrane precipitated on the glass plate, which was thoroughly rinsed to remove residual solvent and then immersed in DI water for 5–7 days before use. The pure water flux of these PVDF UF membranes was  $300 \pm 20 \text{ L m}^{-2} \cdot \text{h}^{-1}$ , while their contact angle and surface roughness were  $75 \pm 2^\circ$  and 17.5 nm, respectively.

### 2.2. UF membrane fouling experiments

The HA fouling experiments with PVDF UF membranes were performed using a dead-end filtration setup as previously described [19]. The core component is a stirred cell that holds the HA working solution, and the test membrane was placed in the bottom of the stirred cell. The stirred cell was connected to a pressure control device that could apply constant pressure to the test membrane. The permeate flux data were continuously recorded using an electronic balance connected to a computer.

The protocol for the HA fouling experiments was as follows. First, a new PVDF UF membrane was compacted at 0.15 MPa with DI water until the membrane flux reached a stable value. Then, the transmembrane pressure was lowered to 0.10 MPa, and the membrane was stabilized with DI water to establish a stable permeate flux, which is referred to as the pure-water flux ( $J_0$ ). Finally, the HA solution with the desired  $\text{Na}^+$  or  $\text{Mg}^{2+}$  concentration (DOC = 10 mg/L) was filtered through the membrane under 0.1 MPa for 2 h; changes in the membrane flux ( $J$ ) were monitored online and it was normalized to the pure water flux ( $J/J_0$ ). The fouled membrane was removed from the filtration setup and immediately soaked in a solution identical to that used in the corresponding fouling experiment that was used for atomic force microscope (AFM) force measurements. All HA fouling experiments were conducted at 20 °C. At least six replicates of the fouling experiments were carried out for each chemical condition.

### 2.3. QCM-D experiments

A quartz crystal microbalance with dissipation monitoring (QCM-D, E1, Qsense, Sweden) was used to determine the adsorption behavior of HA on the PVDF membrane surface and the structure of the HA adsorption layer in different  $\text{Na}^+$  and  $\text{Mg}^{2+}$  environments.

A PVDF-coated sensor crystal was prepared as follows. First, some PVDF was dissolved in DMAc to form a homogeneous PVDF solution. Next, a gold-coated sensor crystal (QSX301 Au; Qsense) was treated for 10 min in a UV chamber, and soaked in a mixture of ultrapure water, ammonia (25% v/v), and hydrogen peroxide (30% v/v) at 75 °C for 10 min, rinsed thoroughly with ultrapure water and dried under pure nitrogen gas. The cleaned gold-coated sensor crystal was then fixed on the rotary platform of a spin coater (KW-4A; Institute of Microelectronics of the Chinese Academy of Sciences, China), 5  $\mu\text{L}$  of PVDF solution was dropped onto the sensor crystal surface, followed by rotation for 15 s at 1200 r/min. The sensor crystal was then heated to 60 °C and the rotation speed was increased to 6000 r/min for 40 s. A

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