



A comparison of the roles of Ca^{2+} and Mg^{2+} on membrane fouling with humic acid: Are there any differences or similarities?



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ARTICLE INFO

Keywords:

Ultrafiltration membrane fouling
Humic acid
 Ca^{2+}
 Mg^{2+}
Comparative study

ABSTRACT

To further unravel the differences and similarities of the effect mechanisms of Mg^{2+} and Ca^{2+} on ultrafiltration membrane fouling with humic acid (HA), under a wide range of Mg^{2+} and Ca^{2+} contents, the adhesion forces of HA with both HA and membrane, HA cake layer structure, and fouling experiments were compared systematically. The results indicate that at lower Ca^{2+} or Mg^{2+} concentrations, membrane fouling is enhanced by the presence of Ca^{2+} or Mg^{2+} , in agreement with the Derjaguin–Landau–Verwey–Overbeek theory. However, membrane fouling in the presence of Ca^{2+} was more serious than with Mg^{2+} , mainly because the interaction of HA with the membrane and other HA molecules was much stronger in the Ca^{2+} environment. The stronger interaction promoted the accumulation of HA on the membrane surface and resulted in a denser fouling layer, which caused a more serious membrane fouling. In contrast, at much higher Ca^{2+} or Mg^{2+} concentrations, membrane fouling was mitigated significantly, but the mitigation mechanisms for both ions were different. For Ca^{2+} , the aggregation of HA molecules was responsible for the decrease in membrane fouling, whereas for Mg^{2+} , hydration repulsion forces prevented membrane fouling. Moreover, the aggregated HA in a Ca^{2+} environment seemed to mitigate membrane fouling to a greater extent, compared to the hydration forces with Mg^{2+} present.

1. Introduction

To meet the stringent requirements of water quality, in the field of wastewater reclamation and water treatment, the ultrafiltration (UF) technology has been used broadly to remove particles, turbidity, microorganisms, and organic matter [1,2]. However, humic substances (HS), which are a common membrane fouling species in municipal wastewater, seawater, surface water, and other wastewater, are a critical problem in UF membrane filtration processes [3–5].

Membrane fouling with HS is a complex process controlled by several factors, such as the operating conditions (permeate flux and crossflow velocity), membrane characteristics (hydrophilicity, charge, etc.), and the feedwater solution chemistry (pH and ionic conditions) [6,7]. Among these, the divalent, Ca^{2+} and Mg^{2+} , which are the two most abundant cations in wastewater, have been identified as key factors that can significantly affect membrane fouling with HS [8,9]. This is primarily due to their effects on HS cake layer structure and the deposition rate of HS foulants onto the surface of membranes, both of which are closely related to HS membrane fouling behavior [10,11]. Therefore, unraveling the influencing mechanisms of Ca^{2+} and Mg^{2+} in

membrane fouling by HS is critical to the control and prediction of membrane fouling.

Previous studies mostly chose Ca^{2+} as a representative divalent cation to investigate the effects of divalent cations on membrane fouling with HS, whereas research on the difference between the influencing mechanisms of Mg^{2+} and Ca^{2+} on the HS fouling of membranes is limited [11,12]. In recent years, a number of studies found that although Ca^{2+} and Mg^{2+} have the same positive charge, they have different effects on the membrane fouling with HS and some contradictory phenomena were reported [13].

In general, it has been shown that the HS fouling rate and fouling extent caused by Ca^{2+} were greater than those caused by Mg^{2+} at the same concentration [13–16]. Based on the flux decline rates of membranes, some reports speculated that the binding affinity of Ca^{2+} with the negatively charged HS molecules is stronger than that of Mg^{2+} , which may result in a highly resistant and very dense HS cake layer, thus contributing to greater membrane fouling in the Ca^{2+} environment. However, regarding the HS cake layer structure, the membrane–HS and HS–HS interactions in the presence of Ca^{2+} and Mg^{2+} have not been investigated at a molecular level [13].

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In contrast, some controversial observations have been made in recent years [10,17,18]. For example, Tang's group carried out UF of HS solutions at a CaCl_2 and MgCl_2 concentration of 10 mM, respectively, and found that the membrane exhibited significantly slower flux decline rates and extent in the Ca^{2+} environment than in the Mg^{2+} environment [18]. Similarly, Wang's research group systematically studied the effects of Ca^{2+} and Mg^{2+} (2, 5, and 10 mM) on membrane fouling by HS during dead-end UF with polyether sulfone and cellulose membranes, respectively. The results revealed that in the first filtration cycle (J_1/J_0), the flux decline rate of the cellulose membrane with 2 or 5 mM Mg^{2+} is more severe than that with 2 or 5 mM Ca^{2+} . The same phenomenon was observed for the polyether sulfone membranes at Ca^{2+} and Mg^{2+} concentrations of 10 mM [17]. One of the more interesting findings from Abrahamse's group is that the effect of Mg^{2+} is comparable to that of Ca^{2+} [10]. Obviously, in these cases, the membrane fouling rate and extent caused by Mg^{2+} were more severe or identical with those caused by Ca^{2+} . However, few or no studies explained the more serious or identical HS fouling of membranes in the Mg^{2+} environment than in the Ca^{2+} environment.

The studies mentioned above indicate that the impact of Ca^{2+} on membrane fouling is different from that of Mg^{2+} , and there have been contradictory phenomena published on the influences of Ca^{2+} and Mg^{2+} on membrane fouling. However, until now, few studies have focused on the above contradictory phenomena, and no systematic research or in-deep discussion has investigated the different contributions of Ca^{2+} and Mg^{2+} on HS fouling. Therefore, a systematic study is required to clarify the influential mechanisms of Ca^{2+} and Mg^{2+} on membrane fouling, which may be helpful in elucidating the above issues.

In the present study, a polyvinylidene fluoride (PVDF) membrane and humic acid (HA) were selected as the UF membrane and model HS foulant, respectively. HA filtration experiments with PVDF membranes and the HA removal rate were carried out under a wide range of Ca^{2+} and Mg^{2+} concentrations. Atomic force microscopy (AFM), associated with the HA and PVDF colloidal probes, was used to measure the microinteraction forces of HA with other HA molecules and the PVDF membrane. These results were measured in conjunction with the investigation of the HA cake layer structures, which were measured by a quartz crystal microbalance with dissipation monitoring (QCM-D), to compare the effect mechanisms of Mg^{2+} and Ca^{2+} on the UF membrane fouling with HA. The aim, ultimately, is to unravel the differences and similarities of the effect mechanisms of Mg^{2+} and Ca^{2+} on HS fouling.

2. Experimental

2.1. Materials and membranes

2.1.1. Materials

In this study, unless otherwise indicated, all the chemicals were analytical reagents with a purity exceeding 99%. HA with 98% purity was provided by Sigma-Aldrich (USA). Stock HA (1 g/L) solution was prepared as follows: first, 1 g of HA was dissolved in a 100 mM NaOH solution to ensure complete dissolution. This solution was later diluted to 1 L by deionized (DI) water. Then, the particulates and insoluble matter in the HA stock solution were removed by 0.45 μm micro-filtration membranes. The HA stock solution was obtained and stored at 4 °C.

Before each filtration experiment, a fresh HA working solution was prepared, whose pH and dissolved organic carbon (DOC) concentration were kept at 7.0 and 10 mg/L, respectively. A 0.01 mol/L NaOH or HCl solution was used to adjust the pH of the HA working solutions as needed. In all experiments, 0.5 mol/L MgCl_2 or CaCl_2 was used to adjust the desired Mg^{2+} or Ca^{2+} concentration of the HA working solutions.

2.1.2. Membrane preparation

In current study, the PVDF UF membranes were synthesized in the

laboratory by the phase inversion method [19]. PVDF and N,N-dimethylacetamide were the major materials used during PVDF UF preparation, and were supplied by Solvay Advanced Polymers Co (Solef 1015; USA) and Tianjin Fuchen Chemical Reagent Co. (China), respectively. The preparation conditions and the characteristics of PVDF UF membranes are described in detail elsewhere [19].

2.2. UF tests

A laboratory-scale dead-end filtration setup, which has been described in detail in our previous study, was used in all the HA filtration tests with PVDF membranes at various Ca^{2+} and Mg^{2+} concentrations, without any modification to the previous procedure [19]. Each fouling experiment consisted of three steps: compaction, conditioning and fouling. At pressures of 0.15 MPa, a clean PVDF membrane was compacted until the permeate flux stabilized. Then, the pure water flux (J_0) of the membrane was determined at a pressure of 0.10 MPa. Finally, at pressures of 0.10 MPa, the HA feed solution (pH = 7.0, DOC = 10 mg/L) with specific Ca^{2+} and Mg^{2+} concentration was filtered for 2 h, and the permeate flux (J) of membrane was monitored continuously by a computer. For convenient comparison, J/J_0 was used to evaluate the flux decline behavior of the PVDF membranes.

The HA removal rate (R) of the PVDF membranes was determined at various Ca^{2+} or Mg^{2+} concentrations by the following equation:

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

where C_p and C_f are the DOC concentrations of the HA permeate and the feed solution, respectively. It should be noted that, all HA removal rates were determined at the same filtration time.

Each HA filtration or HA removal rate test was repeated at least 6 times to ensure reproducibility.

2.3. Measurements of the HA fouling layer structure

The HA cake layer structure, formed under various of Ca^{2+} or Mg^{2+} concentrations, was investigated with a QCM-D (E1; Qsense, Sweden) system. As in our previous work, a PVDF-coated sensor crystal was developed and thoroughly cleaned before each QCM-D experiment [20].

For the QCM-D experiments, first, the flow modules of the QCM-D system were equipped with a new PVDF-coated sensor crystal. Then the system was pre-equilibrated with ultrapure water to achieve a stable baseline. Finally, the HA feed solution at the pH and Ca^{2+} or Mg^{2+} dosage of interest was pumped into the system for 25 min. Throughout this stage, the increase in dissipation (ΔD) and decrease in frequency (Δf) from the baseline were monitored continuously.

The $|\Delta D/\Delta f|$ ratio, which is the measure of energy dissipation in the adsorbed mass per unit, provides information on the HA fouling layer structure for the corresponding Ca^{2+} or Mg^{2+} concentration; that is, a higher $|\Delta D/\Delta f|$ ratio suggests the formation of a relatively loose HA fouling layer, while a low $|\Delta D/\Delta f|$ ratio indicates a much denser HA fouling layer [21,22].

For all QCM-D experiments, the flow rate through the measurement chamber and the temperature were kept at 0.1 mL/min and 23 °C, respectively. Both the Δf and ΔD at the third overtone were used and each QCM-D measurement was performed in triplicate.

2.4. AFM force measurements

A MultiMode 8.0 AFM (Bruker, Germany) equipped with PVDF- and HA-coated colloidal probes, which were developed by our research group, was used to determine the adhesion forces between the HA and the PVDF membrane or between the HA molecules at different CaCl_2 or MgCl_2 ionic strengths, respectively [23]. The HA samples were the HA-

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