Natural organic matter interactions with polyamide and polysulfone membranes: Formation of conditioning film

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HIGHLIGHTS

- Humic NOM solely displayed repulsive forces to polyamide and polysulfone membranes.
- Biopolymer NOM randomly displayed short-ranged attractive forces to membranes.
- Ca^{2+} ions influenced adhesion of humic NOM to polyamide and polysulfone membranes.
- Hydrogen bonding was a biopolymer NOM dominant interacting mechanism with membranes.
- Hydrophilicity of polyamide membrane was fundamental during NOM interactions.

GRAPHICAL ABSTRACT
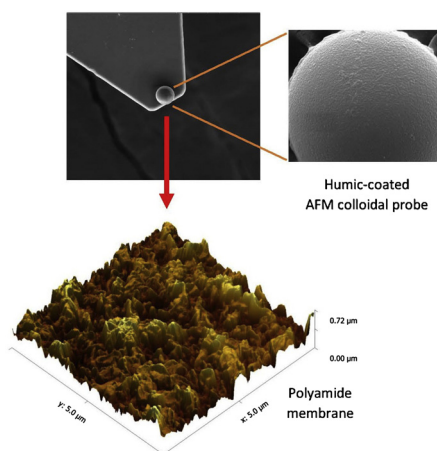
Humic-coated AFM colloidal probe

Polyamide membrane

ARTICLE INFO

ABSTRACT

A conditioning film changes the physicochemical properties of the membrane surface and strongly affects subsequent fouling behavior. Results from this Atomic Force Microscopy study indicate that natural organic matter (NOM) characteristics, membrane surface properties, and solution chemistry are fundamental during conditioning film formation. Repulsive forces were observed between HUM (humic-NOM) and polyamide (pa) or polysulfone (PS) membranes during approach in Na^+ and Ca^{2+} solutions. However, repulsive and attractive forces were randomly recorded during BIOP (biopolymer-NOM) approach to both membranes, possibly caused by low electrostatic repulsion, hydrogen bonding, and presence of chemically/physically heterogeneous regions on membrane surfaces. During retracting, Ca^{2+} ions increased HUM adhesion to PA and PS membrane, indicating cation bridging/complexation as dominant interacting mechanism for this isolate. BIOP adsorption on PS and PA membrane was stronger than HUM under similar solution conditions, where hydrogen bonding would play an important role. Additionally,

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irrespective of solution conditions, higher adhesion energy was recorded on PS than on PA membrane for both NOM isolates, indicating membrane hydrophobicity as an important interacting factor. Results from this research will advance our understanding of conditioning film formation for NOM isolates and membranes of different physicochemical characteristics.

1. Introduction

Water quality and quantity are essential for the sustainability of every ecosystem. People rely on water for diverse activities (e.g., industrial applications, household consumption, etc.). However, many regions in the world are experiencing shortcomings in water supply because of extensive water demand, consequently exacerbating environmental problems [1]. Membrane treatment-based technology (e.g., membrane bio-reactor, desalination) has quickly evolved and expanded worldwide in an attempt to face the current challenges of water scarcity, becoming a suitable alternative to reduce pressure on natural water resources and to improve water quality [2].

Despite extensive research and recent breakthrough, membranes performance is still severely affected by fouling, resulting in increased energy consumption, operation costs, and short membrane life. A major foulant in membrane systems is natural organic matter (NOM) [3]. NOM (e.g., biopolymers, fulvic/humic compounds) is the complex and heterogeneous product of biological/chemical decay of living organisms. Although ubiquitous in aquatic environments, NOM characteristics can considerably vary from one water source to another [4,5]. Previous research has provided a deep insight on NOM-fouling phenomena (e.g., membrane cross-flow systems, morphological analysis, membrane autopsy), suggesting that NOM characteristics, feed water, and membrane surface properties are influential during fouling [6–8]. However, the introduction of atomic force microscopy (AFM), colloidal probe technique, and chemical force microscopy (CFM) has signified a crucial advance in our understanding of a key aspect of fouling: conditioning film formation (i.e., interfacial NOM–membrane interactions). This conditioning film changes the physicochemical properties of the membrane surface and affects subsequent fouling behavior.

Previous AFM studies have focused on investigating this initial foulant deposition. For instance, hydrogen bonding was suggested as the main mechanism causing strong adhesion forces between hydroxyl-modified AFM probes and polyvinylidene (PVDF) membranes (i.e., hydroxyl-modified and carboxyl-modified AFM probes have been widely used to simulate polysaccharides and humics, respectively) [9]. In a similar research, adhesion forces between carboxyl-modified latex (CML) probe and PVDF membrane decreased with increasing NaCl concentration [10], indicating influence of ionic strength on the interacting mechanisms. Likewise, adhesion forces between CML probe and polyamide (PA) membrane in Ca^{2+} solutions were statistically distributed in a wide range, possibly due to membrane surface heterogeneities [11]. In addition, coating of AFM colloidal probes with model organic foulants has also been an important approach to study NOM–membrane interactions. Recent studies suggested hydrophobic effects as a dominant mechanism responsible for bovine serum albumin (BSA) strong adhesion to PVDF film or PA membranes [12,13]. Interestingly, while bridging was the proposed mechanism between carboxyl groups on alginate and PA membranes in divalent cation solutions, low intermolecular and physicochemical interactions were observed between Suwannee River NOM and PA membranes [13]. Despite these recent research efforts, a comprehensive and comparative study of interactions between aquatic NOM isolates of different physicochemical characteristics and membranes as a function of solution chemistry has not been conducted and represents a key gap in knowledge.

In this investigation, a detailed methodology to study surface interactions between aquatic NOM and membranes is described. Gartempe River NOM and Brittany River NOM, both rigorously characterized in previous studies, were selected as model humic and biopolymer aquatic NOM isolates, respectively. Two manufactured membranes (PA and PS) were selected due to their different properties. AFM was used as a sensitive technique that allows the study of specific and non-specific interactions at the interface [14]. Moreover, AFM can be adapted to closely mimic engineered water systems or aquatic environments by the measurement of interacting forces in solution of varied but controlled chemistry. The dominant mechanisms that govern NOM–membrane interactions as a function of their physicochemical characteristics and solution chemistry were proposed and correlated to the results of previous studies. The merit of this research is to advance our fundamental understanding of conditioning film formation during NOM-fouling, which would aid in the design and optimization of membrane coatings.

2. Material and methods

2.1. Origin and characteristics of NOM isolates

The NOM isolates used in this investigation were collected from two surface water sources (Gartempe River and Brittany River, France) and then isolated following the protocol previously described [15]. Both fractions have been rigorously characterized in earlier studies [7,16]. Gartempe River NOM (HUM) has been defined as a typical humic-like substance with a significant content of aromatic and phenolic carbon and high C/O, C/H, and C/N ratios. Fulvic structures and carboxyl groups are predominant. Conversely, Brittany River NOM (BIOP) is characterized by high nitrogen content and low content of aromatic/phenolic carbon. Amino sugars, proteins, and polysaccharides are found incorporated in BIOP structure, conferring it considerable hydrophilic properties. Although present, carboxyl groups are not the dominant functional group in BIOP. Also, BIOP is significantly less negatively charged than HUM [17].

2.2. Preparation of electrolyte solutions and NOM stocks

Analytical grade $NaHCO_3$, NaCl, and $CaCl_2$, and double-deionized water (DDI, 18 MΩ cm resistivity, Millipore, USA) were used to prepare all the electrolyte solutions. These solutions were filtered through a 0.22 μm sterile cellulose acetate membrane and stored at 4 °C. NOM stocks were prepared by following the procedure described elsewhere [18]. Briefly, 20 mg of HUM or BIOP was dissolved in 100 mL of 1 mM $NaHCO_3$ solution, stirred overnight, and filtered through a 0.22 μm sterile CA membrane. The NOM stocks were then stored at 4 °C in the dark. The total organic carbon (TOC) concentrations of the NOM stocks were measured with a TOC-V CPH total organic carbon analyzer (Shimadzu, Japan). Before