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Impact of operation conditions, foulant adsorption, and chemical cleaning on the nanomechanical properties of ultrafiltration hollow fiber membranes

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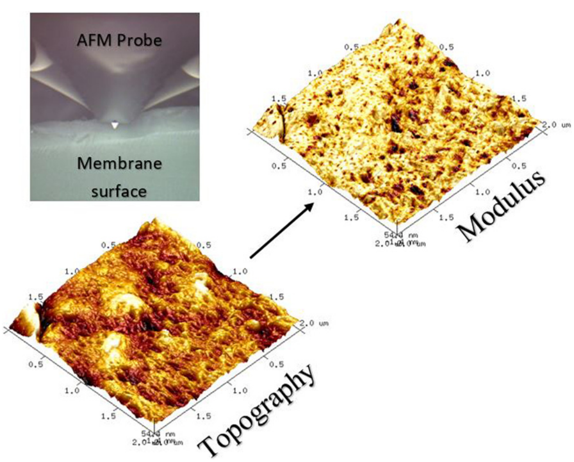
GRAPHICAL ABSTRACT



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ABSTRACT

This study analyzed the change in nanomechanical properties of ultrafiltration hollow fiber membranes harvested from pilot-scale units after twelve months of operation. Quantitative Nanomechanical Mapping technique was used to distinguish between adhesion, dissipation, deformation, and modulus while simultaneously generating a topographic image of membranes. Nanomechanical maps of virgin membranes evidenced surfaces of heterogeneous properties and were described by probability density functions. Operating conditions and feed quality exerted an impact on membranes. Clean harvested membranes showed a higher mean modulus and dissipation, and a lower deformation than virgin membranes, indicating stiffer membranes of lower elastic deformation. A significant fraction of these measurements displayed peak values deviating from the distribution; which represents regions of the membrane with properties highly differing from the probability density function. The membrane polymeric material experienced severe physicochemical changes by foulant adsorption and

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reaction with cleaning agents. Foulant adsorption on membranes was heterogeneous in both morphology and mechanical properties and could not be statistically described. Foulants, i.e., mainly consisting of polysaccharides and proteinaceous structures, displayed low elastic deformation and high roughness and adhesion. The presence of foulants after chemical cleaning and their high adhesion would be a direct nanoscale evidence of irreversible fouling. By the end of the operation, the Trans-Membrane Pressure experienced a 40% increase. The cleaning process was not able to fully recover the initial TMP, indicating irreversible fouling, i.e., permanent change in membrane characteristics and decrease in performance. These results suggest a link between the macroscopic properties and nanomechanical characteristics of membranes. This study advances our nanoscale understanding of the impact of fouling and operating conditions on membranes characteristics.

1. Introduction

The Atomic Force Microscope (AFM) is a versatile tool widely used for the investigation of surfaces at the nanoscale [1]. Briefly, topographic analyses are typically conducted in non-contact mode, where a stiff cantilever oscillates close to the surface in the attractive regime. Also, the AFM in contact mode can measure specific and non-specific interacting forces at the very interface between surfaces across a medium [1–3]. The non-destructive and non-invasive nature of this technique allows it to explore different types of samples (e.g., polymers, metal oxides, organics, bacteria) and their surface characteristics [4–7]. This latter AFM capability has been exploited in previous studies as a semi-quantitative scanning technique, i.e., phase imaging and force modulation [8]. However, the development of pulse-force AFM mode has provided a significant advantage in the quantitative calculation of surface characteristics, e.g., stiffness, adhesion, and Young's modulus [9,10]. Remarkably, the recent introduction of PeakForce™ Quantitative Nanomechanical Mapping (QNM™) technique (Bruker, USA) has offered enhanced benefits for the nanoscale characterization of materials [11]. Specifically, QNM technique quantitatively distinguishes between adhesion, dissipation, deformation, and modulus (i.e., recorded in different channels) while simultaneously generating a topographic image of a surface. The deformation channel measures the maximum deformation (nm) of materials caused by the AFM probe during approaching regime, while the adhesion channel measures the maximum adhesion force (nN) between surface of the sample and AFM probe during retracting regime. The modulus channel records the tensile elasticity of the structures of sample, while the dissipation channel describes the mechanical energy lost per approaching-retracting cycle; for instance, pure elastic deformation of the sample corresponds to very low dissipation.

At present, QNM technique has been used in several fields of research. Briefly, the nanomechanical properties of amyloid fibrils of the human α-synuclein protein were determined by QNM. The elastic moduli of the α-synuclein fibrils obtained was consistent to those determined by single-point nanoindentation and harmonic force microscopy [12]. In a similar study, the modulus values of 12 different polymeric surfaces (i.e., most of them commonly used in filtration membranes: polycarbonate, polyethersulfone, polyvinylidene fluoride, polystyrene, etc.) obtained by PeakForce™ QNM™ using diamond and silicon sharp probes were in reasonable agreement with those measured by instrumented indentation testing (IIT) [13]. Furthermore, other previous studies have reported consistent Young's modulus values between QNM and indirect evaluation of β-lactoglobulin amyloid fibrils stiffness obtained by combining polymer physics and topological statistical analysis on fibrils' structural conformations [14]. In cement research, different phases in the cement paste microstructure that could not be distinguished from back-scattered electron images, were discriminated by the quantitative mapping of the local elastic modulus [15]. QNM has also been used to characterize deformation, adhesion, and modulus gradient of the interphase region in poly(vinyl alcohol)–poly(acrylic acid)–cellulose nanocrystal composites [16]. The mechanical properties of modified, virgin, and industrially fouled membranes have been studied by AFM colloidal probe technique and nanoindentation [17,18]. Also, the introduction of chemical force microscopy (CFM) has significantly advanced our understanding of organics/membranes interactions leading to fouling. For instance, hydrogen has been suggested as the main mechanism inducing strong adhesion forces between polyvinylidene membranes and hydroxyl-modified AFM probes (i.e., simulating polysaccharides) [19]. Also, coating of AFM colloidal probes with model organics (e.g., bovine serum albumin or alginate) or natural organic matter (NOM) fractions and has also been a key approach to study organic fouling [6,20]. Nevertheless, the analytical advantages of QNM have not been majorly exploited in the field of membrane science and technology.

Membrane treatment-based technologies (e.g., desalination, membrane bio-reactor, ceramic membranes) have become suitable alternatives to face the current challenges of water scarcity [21]. This technology has quickly evolved and expanded worldwide as an attempt to reduce pressure on local natural water resources. Nevertheless, the performance of membranes is still severely affected by inorganic/organic/bio fouling. Specifically, the interfacial interactions between membrane and foulants (i.e., leading to adsorption) changes the surface properties of the membrane, thus influencing subsequent fouling behavior [6]. This adsorption of foulants on membranes may be reversible or irreversible. The latter type of association causes a permanent change in membrane characteristics and performance [22]. Different procedures and techniques for membrane cleaning (e.g., by chemical, biochemical, or physical means) are currently used for removing these non-integral substances (foulants) from the membrane [23]. Remarkably, the cleaning process itself (e.g., chemical cleaning) may have an impact on the physicochemical characteristics of the membranes. Different advanced autopsy techniques have been used to study this complex phenomena taking place at the membrane surface [24]. Despite extensive research, the adsorption of foulants, cleaning processes, and their effects on the (mechanical) properties of membranes are still poorly understood and have not yet been quantitatively measured at a nanoscale resolution.

The target of this investigation was to analyze the change in surface characteristics (i.e., nanomechanical properties) of ultrafiltration (UF) hollow fiber membranes harvested from pilot scale units after twelve months of continuous operation. The impact of the cleaning procedure on membrane surface characteristics received a special emphasis. PeakForce™ QNM technique was used to systematically investigate the nanomechanical properties (i.e., deformation, dissipation, modulus, adhesion) of UF hollow fiber membrane samples harvested from modules tested at pilot scale, recalcitrant foulants adsorbed on membranes (i.e., providing quantitative nanoscale evidence of irreversible fouling), and virgin hollow fiber membranes subjected to chemical cleaning at bench scale. Additionally, surface imaging by Scanning Electron Microscopy (SEM) coupled with Energy-dispersive X-ray Spectroscopy (EDS) and foulant characterization by Pyrolysis Gas Chromatography/Mass Spectrometry (GC/MS) were used as complementary tools. The methodology detailed in this study can be extended to numerous applications within the membrane science and technology field. The merit of this research is to provide a link between nanomechanical characteristics and macroscopic properties of membranes (e.g., transmembrane pressure) and to advance our nanoscale understanding of the