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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

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 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 PeakForceTM QNMTM 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 impact of foulant adsorption, operation conditions, and chemical cleaning on the surface characteristics of membranes; thus, generating a new insight into the role of interfacial science in environmental engineering.

2. Materials and Methods

2.1. Membranes samples and ageing experiments

The raw water quality parameters, full-scale plant operation, pilot-scale plant operation, and sampling points for membrane autopsy were described in detail in the SI section. Briefly, the membrane samples were recovered from UF hollow fiber (inside-out) modules harvested after a final Chemically Enhanced Backwash (CEB) from a pilot plant (Kvarnagården water treatment plant, Varberg, Sweden) consisting of a primary UF unit (horizontal dead-end filtration) with two Pentair X-Flow Xiga membrane modules. This primary UF unit received a coagulated water consisting of 80% surface water and 20% ground water (turbidity: 0.3-2.0 NTU; DOC: 2.0-8.1 mg C/L; TOC: 2.3-8.3 mg C/L). The total filtration volume was 57,150 m³ operated in dead-end

(Table S1-S3). Membrane samples were collected at specific locations of this modules, and termed as: a) Xiga right, b) Xiga center, and c) Xiga left.

Ageing experiments (i.e., chemical cleaning of Xiga virgin membranes) were performed using the automated bench scale filtration system as previously described [25]. These experiments were conducted to assess the impact of chemical cleaning on the nanomechanical properties of membranes under controlled laboratory conditions. Two hollow fiber membranes of approximately 20 cm in length were potted in epoxy with one end cut open to allow inside out dead end filtration. The mini hollow fiber modules were soaked overnight in ultrapure water (resistivity: 18.2 M Ω ·cm, Millipore, USA). Prior to aging experiment, each module was flushed with ultrapure water and the pure water flux measured by the flux step method [26]. The chemical aging process was performed in inside-out filtration mode at: 2 ml/min, 250 ppm NaOCl, and pH 12 for 10 h; corresponding to a C.t exposition dose of 2500 mg.h.L⁻¹. The resulting membrane samples were termed as Xiga virgin-chemically cleaned.

2.2. Pyrolysis GC/MS, AR-FTIR, SEM, and EDS analysis of membrane samples

Harvested, virgin, and virgin-chemically cleaned UF hollow fiber membrane samples were dissected in halves with the assistance of an optic microscope under aseptic conditions to expose the inner-membrane surface. Virgin hollow fiber membranes were rinsed overnight in ultrapure water to remove any preservative/additive from their surfaces. All membrane samples were analyzed with a SEM Quanta 250 (FEI, Netherlands), working in environmental mode (ESEM). Pressure of water vapor was maintained at a constant value of 500 Pa allowing to remove any charging effect due to the non-conductive nature of the membranes. Chemical analyzes were conducted with an EDS detector from EDAX at the same condition as for ESEM imaging.

SEM high-resolution images of virgin membrane samples were acquired with a NovaNano SEM (FEI, Netherlands) working in immersion mode. First, membrane coupons were coated by

sputtering a 10 nm thick layer of Au/Pd on the sample (PECS 628, Gatan) to avoid any charging effect due to the non-conductive nature of the samples. The images were analyzed by ImageJ software (National Institute of Health, USA) to determine pore size distribution. A threshold filter was used to discriminate pores from the membrane surface. The data was statistically analyzed by probability density functions to extract the pore size distribution. Also, cross-sectioning of membrane coupons were conducted using a FIB Quanta 3D dual beam FIB (FEI, Netherlands). Prior sample etching, a 50 nm protective layer of Au/Pd was deposited on the sample surface to preserve it from any damage caused by the ion beam. During this process, samples were tilted 45° to enhance the coating of the cross-section. An additional protective layer was added on virgin coupon by depositing a 2.5 μm thick band (25 μm in length and 2.5 μm in width) on the Au/Pd layer using the gas injection system (GIS). Samples were then etched with FIB until a cross-section was observable. Finally, samples were coated with a 10 nm thick layer of Au/Pd to image the cross-section with high resolution SEM.

Foulant material recovered from Xiga virgin and Xiga center was subjected to Pyrolysis GC/MS analysis. Approximately 2.5 g of hollow fiber membranes dissected in halves were placed in 50 mL of ultrapure water and sonicated for 20 minutes. The aqueous phase was separated from the membrane fibers that easily settled and lyophilized. A small mass (few milligrams) of dry material was recovered from each sets of membrane. Approximately 0.5 mg of material was placed into the pyrolysis quartz tube and analyzed according to the flash pyrolysis protocol [27].

2.3. Quantitative nanomechanical mapping (QNM)

Electrolyte solutions were prepared immediately before QNM experiments with ultrapure water and analytical grade reagents, and then filtered through a 0.22 μm membrane. A Dimension FastScan AFM (Bruker, USA) with an Icon Head were used for QNM analysis in solution of the

following hollow fiber membrane samples: a) Xiga virgin, b) Xiga right, c) Xiga center, d) Xiga left, and e) Xiga virgin-chemically cleaned. Sharp Nitride Lever AFM probes (SNL-10 A, k: 0.35 N/m, silicon nitride cantilever, Bruker, USA) were used. This type of probe was selected as a function of the characteristics of the membrane samples themselves (i.e., soft polymeric surface); specifically, based on the capacity of probes to cause enough deformation without damaging the sample while still retaining sensitivity. The calibration of the AFM probes was conducted as follows. Briefly, the deflection sensitivity of the AFM probes was measured in air conditions and using mica as a control substrate. The spring constant (k) of the cantilevers were determined by the Thermal Tuning method, where deflection (V) was converted to force (nN) in accordance to Hooke's law [1]. The calculation of the radius of curvature of the probes was performed by scanning a titanium model surface (Bruker, USA) in air conditions via Tip Qualification function in the NanoScope Analysis Software V1.5 (Bruker, USA). Dissected membrane samples were immobilized concave up on a glass slide (i.e., to expose their inner-membrane surface) using double-sided tape. The glass slide was placed on the AFM stage and examined with the AFM high resolution camera to verify the correct position of the membrane sample and to locate a suitable area to scan at the center of the membrane. The QNM images of the membrane samples were acquired in 1 mM NaCl solution, at a scan rate of 0.5 kHz, over an area of $2 \times 2 \mu\text{m}$, and at 512 samples/line, while the ScanAssyst Auto Control was set ON (i.e., Peak Force Setpoint was automatically controlled by the software). Between 15 to 25 locations were randomly selected in every hollow fiber membrane sample for QNM analysis (i.e., the images shown in this study are considered as representative). The following parameters (channels) were generated: topography, Peak Force error, adhesion, deformation, dissipation, and LogDMT Modulus. Briefly, the deformation channel measures the maximum deformation (nm)

of the polymeric structures of the membrane caused by the AFM probe during approaching regime, while the adhesion channel measures the maximum adhesion force (nN) between the membrane surface and AFM probe during retraction regime. The LogDMT Modulus describes the tensile elasticity of the polymeric structures of the membrane sample. In PeakForce™ QNM™, Young's modulus is calculated using Derjaguin-Muller-Toporov (DMT) model (i.e., modified Hertzian model which considers adhesion forces between tip and surfaces) [28]. However, LogDMT Modulus (i.e., used in the current investigation) is calculated as the logarithm of the elastic modulus of the sample based on the DMT model. The Peak Force error channel generates a map of the peak force measured during the scan. Finally, the dissipation channel describes the mechanical energy lost per approaching-retracting cycle; for instance, pure elastic deformation of the membrane corresponds to very low dissipation. Every image of a specific characteristic (e.g., height, LogDMT Modulus, adhesion, dissipation, or deformation) was processed by Image Quadratic Mean (R_q) analysis and using NanoScope Software V1.5 (Bruker, USA). These values were statistically analyzed by probability density functions, where mean (μ) and variance (σ) were calculated. This statistical analysis provides the advantage of detecting peak values deviating from the distribution. These peak values would indicate regions of the membrane with properties differing from the probability density function (i.e., taking virgin membranes as a baseline). Every generated image was also inspected for the presence of foulants. Additionally, a topographic and phase analysis of the membrane samples by Soft-Tapping Mode™ (Bruker, USA) in air conditions using TESPA AFM probes (silicon tip, k: 42 N/m, f: 320 kHz, Bruker, USA) was conducted. Specifically, phase analysis provided supplementary information on the characteristics of membrane samples (i.e., phase imaging allows chemical mapping of surfaces based on these material differences).

3. Results and Discussion

3.1. Surface morphology of Xiga virgin membrane samples

As a first step, the morphology of Xiga virgin was studied. The pore size distribution was calculated from the SEM images (Figure S1a) using ImageJ software. A statistical analysis by probability density function was used due to the heterogeneity of the pore size. The mean pore size of Xiga virgin was calculated as 7.0 nm (i.e., σ : 0.65 and R^2 : 0.95). This value of pore size is smaller than that reported by the manufacturer (i.e., 20 nm nominal pore size) and previous studies [29]. Topography (3D-height sensor) images acquired in tapping mode in air revealed the physically heterogeneous nature of the surface of Xiga virgin, and a roughness (R_{RMS}) of 14.3 ± 3.7 nm ($n=5$). Phase images (i.e., chemical mapping of surfaces based on material differences) suggested a surface of heterogeneous characteristics (Figure S1b).

3.2. Quantitative nanomechanical mapping of hollow fiber membrane samples

3.2.1. Xiga virgin hollow fiber membranes

The surface of Xiga virgin was analyzed by QNM. The following properties were collected: 1) Height sensor, 2) Peak Force error, 3) LogDMT Modulus, 4) Adhesion, 5) Deformation, and 6) Dissipation (Figure 1). Briefly, Xiga virgin displayed a low roughness, i.e., μ :13.7 nm (σ :0.43) (Figure 2a, Table S4), which was consistent to that obtained by tapping mode in air during morphological analysis.

The surface morphology of Xiga virgin acquired by QNM-Height sensor (Figure 1a) was similar to that observed in high-resolution SEM (Figure S1a). This result confirmed the capability of QNM to image surface structures at a nanoscale. The nanomechanical characteristics of virgin membranes extracted from QNM were statistically processed by normal distributions (i.e., Gauss, Log-Normal). This data could not be processed by average and standard deviation due to

the heterogeneity at the nanoscale of these mechanical properties; thus, resulting in high standard deviation values. Membranes have been previously described as physically and chemically heterogeneous surfaces by chemical force spectroscopy analysis [30]. The mean adhesion, Peak Force error, dissipation, LogDMT Modulus, and deformation of Xiga virgin were 0.19 nN, 0.12 nN, 54.9 eV $\pm$, 0.12 Log[Pa] $\pm$, and 12.2 nm, respectively (Table S4, Figure 2a-f). No significant peak values deviating from the probability density fitting functions were observed. However, every nanomechanical map also evidenced surfaces of heterogeneous properties (Figure 1a-f).

3.2.2. *Harvested hollow fiber membranes showing no adsorbed foulants*

This section of the study focused on those harvested membrane samples that showed no adsorbed foulants (i.e., locations where the cleaning process seemed effective). The selection of these samples was conducted by a rigorous morphological analysis by QNM-height sensor (Figure 3a) and Soft-Tapping ModeTM, and supported by adhesion and modulus analysis (Figure 3c-d). Clean membrane surfaces (i.e., showing pores and a characteristic polymeric structure as seen in virgin membranes) were observed in the three types of membrane samples analyzed: Xiga right, Xiga center, and Xiga left (Figure 3a), suggesting the efficiency of the CEB procedure. Their properties were statistically processed and analyzed by probability density functions (Figure S2-S4, Table S4). Briefly, the mean roughness of the three Xiga samples were similar to that of Xiga virgin (i.e., Xiga left: 18.5 nm, Xiga center: 19.4 nm, and Xiga right: 14.9 nm), where no value significantly deviated from the fitting function (Figure S2a, S3a, and S4a). The morphology of these samples showed physically heterogeneous at the nanoscale. Except for Xiga right (mean adhesion: 0.10 nN), the AFM tip mean adhesion to Xiga center and Xiga left were similar to that of Xiga virgin (Figure S2b, S3b, and S4b). Nevertheless, 30% and 28% of the recorded adhesions forces from Xiga center and Xiga right deviated from the fitting functions, where

forces of up to 2.25 nN and 0.62 nN were observed, respectively (Figure S3b, S4b). These results indicate a change in surface characteristics in the samples displaying high adhesion forces (i.e., deviating from the probability density functions). Conversely, the mean LogDMT Modulus of Xiga center and Xiga right (i.e., 0.33 and 0.21 log[Pa] $\pm$, respectively) were higher than that of Xiga virgin (0.12 log[Pa] $\pm$). Besides, high LogDMT Modulus values of up to 0.7, 1.4, and 1.0 were recorded for Xiga left, Xiga right, and Xiga center, respectively (Figure S2e, S3e, and S4e); indicating that Xiga membranes displayed stiffer surfaces after fouling and chemical cleaning. Also, approximately 40% and 8% of the recorded LogDMT Modulus deviated from the fitting functions for Xiga left and Xiga Right, respectively. The mean deformation shown by chemically-cleaned membranes was lower than that of Xiga virgin (i.e., although 40% and 12% of the recorded values for Xiga left and Xiga right deviated from the fitting functions, respectively) (Figures S2f, S3f, and S4f). As an outcome of fouling and cleaning process, the stiffness of membranes increased and these surfaces would need more force to deform. This observation is also supported by the Peak Force values recorded (i.e., PeakForceTM QNM mode uses peak force as a feedback signal; essentially, as a peak force Setpoint plus the error). The Peak Force of Xiga center, Xiga right, and Xiga left were higher than that of Xiga virgin (i.e., 0.34 nN, 0.17 nN, 0.20 nN, and 0.12 nN, respectively) (Figure 2c, S2c, S3c, and S4c). Finally, the mean dissipation (i.e., dissipated energy calculated by integrating the area between approaching and retracting curves) of Xiga right and Xiga left were lower than that of Xiga center (i.e., 36.6, 39.5, and 74.6 eV $\pm$, respectively). However, a fraction of the dissipation values of the three membrane samples highly deviated from the fitting functions, i.e., 26.6%, 22%, and 28% for Xiga left, Xiga center, and Xiga right, respectively (Figure S2d, S3d, and S4d); indicating membranes of significantly lower elastic deformation.

Fouling and chemical cleaning exerted an impact on the surface characteristics of Xiga membranes, and was evidenced by a change in mean mechanical properties (i.e. considering virgin membrane characteristics as a baseline) and by peak values deviating from the probability density functions. Specifically, the membrane material of Xiga (PES/PVP) might undergo physicochemical changes by reacting with the cleaning agent and by the adsorption of foulant molecules; thus, resulting in a less elastic, more adhesive, and stiffer membrane. The operation conditions would play an important role in this phenomenon (SI). Xiga modules were extensively used for twelve months; filtering 57,150 m³ of feed water and backwashed 267 times using the CEB procedure (Table S1-S3).

3.2.3. *Harvested membrane samples showing foulant adsorption*

This section presents an overview of the morphology and nanomechanical characteristics of membrane samples showing the presence of foulants after operation and CEB. The three samples analyzed: Xiga center, Xiga right, and Xiga left showed adsorption of foulants. At a nanoscale, foulant adsorption was heterogeneous in both morphology and mechanical properties. Specifically, foulant partially coating a membrane surface (5×5 μm) (Figure 4), as well as foulant layers completely covering a scanning area (Figure 5, S6-S7) were observed. In both cases, the morphology and mechanical properties of foulants highly differed from membranes and could not be statistically described by probability density functions due to their high heterogeneity. Previous AFM studies have observed the heterogeneous physicochemical properties of foulant layers during a kinetic study of RO membrane fouling [31].

QNM technique also proved to be a powerful tool for discriminating foulant from membrane surface due to their different mechanical properties (Figure 4). Briefly, the roughness of an apparently clean area of Xiga right was 26.6 nm (Figure 4a). Nevertheless, in the adhesion

channel (Figure 4b) two small areas (yellow arrows) displaying high adhesion forces of up to 1.8 nN were evident. The values of Peak Force of the foulant were lower than those of the surrounding membrane (i.e., 0.151 nN vs. 0.241 nN) (Figure 4f). Also, the LogDMT Modulus (Figure 4e) of this foulant was lower than the surrounding membrane surface (i.e., 0.163 vs. 0.248 log[Pa] $\pm$, respectively), while the dissipation (605 eV $\pm$) was higher than the values typically observed for virgin membrane. These results indicate a soft foulant displaying high adhesion and low elastic properties. Previous studies have reported foulants of lower elastic modulus compared to virgin membranes [17]. Interestingly, the presence of this foulant after chemical cleaning and its high adhesion would be a direct nanoscale evidence of irreversible fouling. Specifically, the strength of the bond (i.e., adhesion forces) between foulants and membrane would be correlated to the reversibility of the adsorption, as suggested in previous studies [19, 32]. This current QNM analysis also indicates that the detection of foulants solely using height sensor or phase channels can be incomplete and misleading.

Foulant layers showed a different morphology compared to that of Xiga virgin, where no pores and polymeric structures were observed (Figure 5, S6). SEM images (Figure S7) supported AFM morphology results. The heterogeneity of the fouling layers was evidenced in each SEM image acquired, ranging from full fouling layers (Figure S7a, S7c, S7e) to foulants partially coating the membrane surface, where the membrane pores could be distinguished (Figure S7b, S7d). The mean roughness of the foulant layers, e.g., 51.3 nm (Figure 5a) or 76.1 nm (Figure S6a), were higher than those of Xiga virgin (13.7 nm). The mean LogDMT Modulus values were variable, ranging from 0.065 (Figure 5e) to 0.237 log[Pa] $\pm$ (Figure S6c). Remarkably, the magnitudes of the mean adhesion forces of these foulant layers were considerably higher (>1 order of magnitude) than those of Xiga virgin, e.g., 1.87 nN (Figure 5b), 1.20 nN (Figure S6d). The

dissipation energies also reached high values, e.g., $943 \text{ eV} \pm$ (Figure 5d) or $588 \text{ eV} \pm$ (Figure S6e). Although these results indicate foulant layers of variable modulus (i.e., from soft to stiff structures), they all display high roughness, low elasticity, and high adhesion forces. This latter characteristic and the very occurrence of foulant layers after extended operation, suggest irreversible fouling as above-discussed.

To better understand the observed fouling phenomena, the fouling layers were characterized as follows. Energy Dispersive X-ray spectroscopy (EDS) analysis of Xiga virgin revealed peaks of Carbon, Oxygen, and Sulfur present in the spectra (Figure S8a), and would originate from the membrane material. The generated spectra and elements (%) observed can be considered as representative of clean membrane surfaces. Conversely, the EDS spectra and elemental analysis of harvested membranes (e.g., Xiga center, Xiga Right) showed additional peaks of Si, Cl, Ca, and Fe (Figure S8b), suggesting the presence of foulants. Additionally, a pyrolysis GC/MS analysis was conducted on the material recovered from Xiga center (Figure S9a). A comparison with the pyrochromatogram recorded from Xiga virgin (Figure S9b) confirmed the presence of foulant material accumulated at the membrane surface. Pyrolysis by-products such as cyclopentenone and methyl cyclopentenone were indicators of the presence of polysaccharides in the organic layer. Toluene, styrene, pyrrole, and methyl pyrrole confirmed the presence of proteins. The detection of furanmethanol, a DNA pyro-fragment, is an indicator of living or recently dead microorganisms [33]. This pyrolysis fingerprint demonstrates the biological origin (biofilm) of the foulant. Remarkably, previous investigations have similarly reported recalcitrant foulants consisting of polysaccharides, aminosugars, and proteinaceous structures (i.e., mainly of bacterial origin) after backwash [34].

3.2.4. *Change of nanomechanical properties of virgin membranes after chemical cleaning under controlled laboratory conditions*

The values of the mechanical properties of Xiga virgin-chemically cleaned were statistically processed by probability density functions (i.e., Lognormal and Gauss distributions) where no peak values significantly deviated from the fitting functions (Figure S5a-f). A similar trend was observed only for Xiga Virgin (Figure 2). Briefly, the mean roughness and adhesion forces of Xiga virgin-chemically cleaned were similar to those of Xiga virgin, while its mean LogDMT modulus was double in magnitude. Along with a slightly lower deformation and a higher Peak Force, this latter result suggests a stiffer Xiga membrane surface after chemical cleaning. Nevertheless, this type of chemical cleaning did not impact the nanomechanical properties of Xiga virgin to the extent of causing peak values highly deviating from the probability density functions as observed in Xiga left, Xiga center, and Xiga right samples (i.e., harvested membranes were exposed to higher C.t, 267 CEBs, fouling, and 57,150 m³ of feed water). Also, the PES/PVP composition of the Xiga virgin and Xiga virgin-chemically cleaned membranes were recorded by FT-IR analysis (Figure S10). The spectrum recorded for the Xiga virgin-chemically cleaned hollow fiber showed no significant reduction in the intensity of the peak at 1650 cm⁻¹ and corresponding to C=O vibration of the PVP amide group. However, a small intensity band centered at 1720 cm⁻¹ was detected after chemical oxidation (OCl⁻ at pH 12) of Xiga virgin, which can be attributed to the formation of succinimide groups [35]. These results indicate that virgin membranes would fairly maintain their mechanical properties after subjected to a chemical cleaning process as performed in the current study.

3.2.5. *Link between macroscopic properties and nanomechanical characteristics of membranes*

The transmembrane pressure (TMP) of UF-1 (Xiga) modules was recorded approximately 88 times per day during the entire pilot-scale operation (Figure S11). This data was statistically processed by probability density functions to calculate mean (μ) TMP at varied time frames. At the beginning of the operation, the mean TMP was 0.168 bar and increased to 0.278 bar by the first 31 days. Nevertheless, TMP peaks of up to 0.6 bar were recorded in the following 90 days, indicating an aggressive fouling. By the first 6 months of operation, the mean TMP was recorded as 0.205 TMP. Finally, by the end of the year the mean TMP slightly increased to 0.235 bar, resulting in a 40% increase with respect to the TMP recorded at the beginning of the operation. This result suggests a link between the macroscopic properties and nanomechanical characteristics of membranes. Specifically, the applied CEB process was not able to fully recover the initial TMP of the hollow fiber membranes, indicating the occurrence of irreversible fouling. This type of fouling highly impacts the characteristics of membranes and decrease their performance. This phenomenon was clearly evidenced during the analysis of the nanomechanical properties of harvested membranes, where highly adhesive foulants of low elastic properties and biological origin (i.e., consisting of polysaccharides, DNA pyro-fragments, and proteinaceous structures) were also detected.

4. Conclusions

The current investigation exploited the analytical advantages of QNM technique to conduct a rigorous analysis of the nanomechanical properties of UF hollow fiber membranes harvested from pilot scale units after extended operation. Briefly, a Quantitative Nanomechanical Mapping (QNM) of adhesion, dissipation, deformation, and LogDMT modulus was generated while simultaneously acquiring a topographic image of the membrane samples. From these results, the following key conclusions were outlined:

- Virgin membranes: Every nanomechanical mapping of virgin membranes revealed surfaces of heterogeneous properties. Due to this heterogeneity, a rigorous statistical analysis by probability density functions was conducted to describe these properties (μ and σ).
- Harvested membranes showing no foulant adsorption: Although clean harvested membranes displayed a similar mean roughness to those of virgin membranes, they also showed a higher mean modulus and dissipation, and a lower deformation. These results indicate stiffer membranes of lower elastic deformation. However, a significant fraction of these measurements displayed peak values deviating from the distribution; thus, representing regions of the membrane with properties highly differing from the probability density function. These change in mechanical properties would be a result of feed quality, foulant adsorption, and reaction to cleaning agents (i.e., 57,150 m³ of feed water, 267 CEBs).
- Harvested membranes showing foulant adsorption: Foulants were recorded partially and completely coating a scanning area. Pyrolysis GC-MS indicated the biological origin of the foulants; mainly consisting of polysaccharides, DNA pyro-fragments, and proteinaceous structures. Unlike virgin and clean harvested membranes, no statistical analysis could be performed to describe the mechanical properties of foulant layers due to their high heterogeneity in morphology and nanomechanical properties. Remarkably, all foulant layers displayed high roughness, adhesion forces, and dissipation (low elastic deformation). The presence of these foulants after chemical cleaning and their nanomechanical properties (e.g., high adhesion) would be a direct nanoscale evidence of irreversible fouling.
- Macroscopic properties of membranes: After a year of operation, the mean TMP experienced a 40% increase with respect to the TMP recorded at the beginning of the operation. The applied CEB process was not able to fully recover the initial TMP of the hollow fiber

membranes, indicating the occurrence of irreversible fouling (i.e., permanent change in membrane characteristics and decrease in performance). Therefore, this result suggests a link between the macroscopic properties and nanomechanical characteristics of membranes.

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Supplementary Data

Supplementary data associated with this article can be found in the online version at:

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Figure 1. a) Height sensor, b) Peak Force error, c) LogDMT Modulus, d) Adhesion, e) Deformation, and f) Dissipation images of Xiga virgin membrane. Scan area: 2×2 μm .

Figure 2. Probability density functions describing a) roughness, b) adhesion, c) Peak Force error, d) dissipation, e) LogDMT Modulus and f) deformation of Xiga virgin membrane

Figure 3. a) Height sensor, b) Peak Force error, c) LogDMT Modulus, d) Adhesion, e) Deformation, and f) Dissipation images of Xiga Center membrane. Scan area: $5 \times 5 \mu\text{m}$.

Figure 4. a) Height sensor, b) Adhesion, c) Deformation, d) Dissipation, e) LogDMT Modulus, and f) Peak Force error images of Xiga right membrane showing adsorption of foulant. Scan area: $5 \times 5 \mu\text{m}$.

Figure 5. a) Height sensor, b) Adhesion, c) Deformation, d) Dissipation, e) LogDMT Modulus, and f) Peak Force error images of Xiga Left fouled membrane. Scan area: $2 \times 2 \mu\text{m}$.