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An experimental approach to explore cleaner systems for desalination membranes

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ABSTRACT

Organic fouling massively influences the performance of polymer membranes used in desalination processes. Due to the complexity of the fouling processes there is no complete picture of the involved interactions yet and targeted strategies to overcome membrane fouling are missing [1]. Defined and reproducible testing strategies are essential for the successful development of effective cleaner systems. To address this need, we introduce a multicomponent fouling model mimicking the initial biomolecular adsorption of proteins, humic acids and polysaccharide substances onto membrane surfaces. Utilizing well defined thin films made of polyamide mimicking the outermost layer of TFC-membranes allowed us to study the adsorption and subsequent removal of (model-) fouling components. Adsorption and desorption (cleaning-) experiments were done utilizing quartz crystal microbalance (QCM) and ellipsometry. Cleaning efficiency of acids, surfactants and chelats was analyzed. The results show chelats to be most effective as cleaning agents.

Keywords: RO/NF membranes; Organic fouling; Chelats; Acids; Surfactants

1. Introduction

Organic fouling is one of the most critical problems associated with the use of materials and devices in contact with biosystems [2,3]. Examples include the undesired deposition of biomass on ship hulls, cooling systems, sensors and many others. Among the affected applications, membranes are particularly demanding as the deposition of molecules, particles and assemblies thereof at the membrane surface can lead to a significant flux decline [4] and changes in the separation characteristics, resulting in an often dramatic loss of performance [5,6]. Accumulated materials involved in the organic fouling of membranes can be colloidal, organic, bacterial or of inorganic (mineral) origin. The initial formation of molecular adsorption layers of organic matter obviously depends on the surface characteristics of the membrane material, the composition of the fluid brought into contact and the transport conditions at the interface. In the sequence of events, the primary deposition of biomolecules of different type critically determines subsequent bacterial settlement which is the base for the formation of mature biofilms and, through this, decisive for the overall fouling effect by controlling later events, including adhesion and growth of 'macrofoulers' such as algae.

Polymer membranes used in reverse osmosis processes for desalination represent particularly challenging materials with respect to organic fouling. Here, the biofilm formation is known to reduce both permeate flux and salt rejection. The latter is caused by the increased overall hydraulic resistance for water permeation through the membrane and a hindered back-diffusion of salts

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through the biofilm (commonly referred to as "biofilm enhanced osmotic pressure" leading to an enhanced salt passage through the membrane) [7]. These phenomena create a need for both the in situ prevention of the involved processes and the removal of deposited materials from the membrane surfaces after use [7–10]. Efforts were undertaken recently to explore the basic interfacial processes resulting in the fouling of reverse osmosis membranes [11,12], the propensity of different membrane materials to organic fouling [13] and to identify the efficacy of substances added as 'antifoulants' and 'cleaners' [14,15]. While the main constituents of the fouling layers were identified to be polysaccharides, silicate and hematite [8] the complexity of the involved interactions still aggravates the development of effective strategies to overcome membrane fouling in situ and ex situ [1]. Defined but robust and simple screening approaches to evaluate organic fouling of membrane materials are therefore critically important for the targeted design of effective antifouling and cleaner systems.

To address this need, we introduce here a multicomponent early stage organic fouling model layer which is compatible with an array of powerful analytical methods. Polyamide thin films are used as base materials representing the separation layers of commonly used RO membranes applied in desalination. Fouling model layers prepared on top according to specifically adapted protocols combine polysaccharidic substances, proteins, and humic acids mimicking the initial biomolecular adsorption at membrane surfaces [16]. Complementary analytical methods including quartz microbalance and ellipsometry were applied to evaluate the deposition and retention of the biomolecular model layers on the membrane polymer materials in the presence of relevant electrolyte solutions. Together, these analytical methods permit to draw conclusions on the interactions involved in binding/retention/release. Combining defined model fouling layers and complementary analytical methods, the introduced analytical approach is eventually used to evaluate the efficacy of various antifouling and cleaner systems and to identify optimal conditions for their application.

2. Experimental

2.1. Polyamide thin film preparation

Freshly cleaned planar silicon oxide carrier materials [(silicon wafers 15×20 mm, TU Dresden, Germany or SiO_2-coated QCM-D crystals, Q-sense, Sweden) were oxidized in a mixture of aqueous ammonia solution (Acros Organics, Geel, Belgium) and hydrogen peroxide (Merck, Darmstadt, Germany)] were hydrophobized with hexamethyldisalazane (ABCR, Karlsruhe, Germany). Subsequently thin films of polyamide were immobilized applying spincoating from PA-12 solutions (VESTAMID, Evonik Industries, Germany). Solutions of 0.2% of VESTAMID were dissolved in hexafluoroisopropanol (Fluka, Germany) and subsequently spincoated at 3000 rpm for 30 s (RC 5 Suess Microtec, Garching, Germany). The polyamide thin films showed a thickness of 19 ± 2 nm (ellipsometry, SE 400, Sentech, Berlin, Germany). The static contact angle of 76.3 ± 1° (OCA 30, Dataphysics, Filderstadt, Germany) shows the hydrophobic characteristic of the films.

2.2. Measurement of single model fouling component adsorption by quartz crystal microbalance (QCM)

Adsorption of model fouling components on polyamid thin films was analyzed at constant temperature (23°C) by using QCM-D E4 (Q-Sense AB, Gothenburg, Sweden). The polyamid-coated QCM-D crystals were swollen in MilliQ to achieve a stable baseline and subsequently incubated with 0.25 or 0.5% [w/v] alginate (AG; medium viscosity, Sigma-Aldrich, Deisenhofen, Germany), 200 pm bovine serum albumin (BSA; Sigma-Aldrich) or 20 ppm humic acid (HA; Sigma-Aldrich) dissolved in MilliQ. Stability/desorption of the resulting single component layer was evaluated by rinsing with MilliQ. By monitoring frequency and dissipation shifts induced by adsorbed/desorbed components in real time at the third, fifth and seventh overtone (15, 25 and 35 MHz, respectively), layer thicknesses could be determined using Q-tools software (Q-Sense AB).

2.3. Preparation of multi-component fouling layers

Fouling layers were prepared by dipping polyamide thin film substrates into an excess volume of 0.25 or 0.5% [w/v] alginate (AG; medium viscosity, Sigma-Aldrich) and 200 ppm bovine serum albumin (BSA; Sigma-Aldrich) dissolved in MilliQ. After 15 min adsorption under stirring, the substrates were removed and dried at 60°C for 5 min. To stabilize these layers, the adsorption process was either performed directly in presence of 8% [w/v] $CaCl_2$ (Merck) or the dried substrates were dipped into a concentrated $CaCl_2$ solution (8% [w/v]) for 10 s followed by an additional drying step at room temperature.

Optimized layer preparation in presence of humic acid (HA; Sigma-Aldrich) was done by directly covering the polyamid thin film substrate with a solution of 0.25% AG, 200 ppm BSA and 20 ppm HA. After 10 min adsorption, the excess liquid was removed by carefully tilting the wafers followed by a subsequent drying step at 60°C for 5 min. The fouling layers were stabilized by dipping them into a concentrated $CaCl_2$ solution (8% [w/v]) for 10 s followed by an additional drying step at room temperature. This type of layers was used for all subsequent cleaning experiments.

Prior to the cleaning experiments, all fouling layers were dipped in MilliQ for 1 min and dried at room

temperature. Resulting layer thickness was analyzed by ellipsometry.

2.4. Evaluation of cleaning efficiency

Selected cleaning conditions (alkaline pH) and agents (surfactants, acids and chelats) were tested for their potential to decrease the thickness of multi-component fouling layers. The following substances were used: 0.01 M NaOH (pH 12; Sigma-Aldrich), sodium dodecylbenzenesulfonate (LAS; BASF, Ludwigshafen, Germany) dissolved in 0.01 M NaOH, 0.2 and 2% [v/v] methanesulfonic acid (Lutropor® MSA; BASF), 0.2 and 2% [v/v] phosphoric acid (Sigma-Aldrich), 0.2 and 2% [v/v] sulfamic acid (Sigma-Aldrich), 0.2 and 1% [v/v] tri-sodium salt of methylglycindiacetic acid (Trilon® M; BASF), 0.2 and 1% [v/v] sodium salt of modified anionic polyamine (Trilon® P; BASF), 0.2 and 1% [v/v] amino tri-(methylene phosphonic acid) pentasodium (Dequest® 2006; Solutia/Thermphos). Unless otherwise indicated, all substances were dissolved in MilliQ. The organic fouling model layers were immersed in aqueous solutions containing the selected agents for 5 min at room temperature followed by rinsing in MilliQ and drying at room temperature. Remaining layer thickness was determined by ellipsometry. Cleaning efficiency was calculated according to the formula cleaning efficiency = (1 – (remaining layer thickness/initial layer thickness)×100%.

2.5. Determination of layer thickness by ellipsometry

Layer thickness was determined using a micro-focus ellipsometer Sentech SE-400 from Sentech Instruments GmbH, Germany with a wavelength of λ = 632.8 nm. The angle of incidence was set to 65°, 70° and 75°. For further thickness measurements a multilayer model was applied to calculate the thickness of the fouling layers and the underlying polyamid thin films. The refractive indices were: $n_{(Si)}$ = 3.858; $n(_{SiO_2})$ = 1.4571; $n_{(Polyamid)}$ = 1.47 and $n_{(fouling\ layer)}$ = 1.47.

3. Results and discussion

Subsequently, we report and discuss experiments performed to establish model fouling layers on polyamide thin films and summarize data obtained when analyzing the effect of cleaner components using this model fouling system.

3.1. Fouling layer preparation

Alginate (AG), bovine serum albumin (BSA), and humic acid (HA) were selected as relevant biomolecular components to mimic initial stages of fouling processes, i.e. the deposition of biomolecules from solution on the membrane surface. First, adsorption experiments of the single components were performed to investigate their affinity to polyamide surfaces. The hydrophilic polysaccharide AG showed –independently of the applied concentration — no adsorption on polyamide films (Fig. 1). No spreading of AG solutions on the polyamide layer was observed. In contrast, the amphiphilic BSA showed a clear tendency to adsorb onto the polyamide surface (Fig. 1), which resulted in the formation of protein layers of about 2.5 nm thickness. Increasing the BSA solution concentration (up to 1000 ppm, data not shown) did not alter the adsorbed amount. Furthermore the BSA adsorption was found to be irreversible upon rinsing with MilliQ (for 30 s), as obvious from the unchanged layer thickness before and after rinsing (Fig. 1). These results underscore the amphiphilic character of BSA, resulting in its massive adsorption to many different surfaces [17]. HA adsorbed to the polyamide films in lower amounts (layer thicknesses of ~0.5 nm) but similarly showed high degrees of retention upon rinsing in MilliQ, (Fig. 1).

Starting from these observations, adsorption from solutions containing 0.25% or 0.5% AG, respectively, and 200 ppm BSA was investigated. In contrast to the pure alginate system a very significant AG layer formation was obtained in those systems (~20 nm for 0.25% and ~80 nm for 0.5% AG plus 200 ppm BSA; Fig. 2). Since similar results were obtained if BSA was pre-adsorbed (data not shown) it could be concluded that BSA acts as a 'primer' for the alginate. However, the AG layers obtained from the AG/BSA mixtures were found to be of limited stability as rinsing with MilliQ (for 30 s) removed a major fraction of the surface bound biopolymer layers (Fig. 2). Therefore, additional experiments aimed at stabilizing AG/BSA layers. The use of multivalent cations was expected to offer a powerful means for that purpose since Ca^{2+}-containing solutions were extensively applied for the gelation of AG to produce stable hydrogel matrices [18].

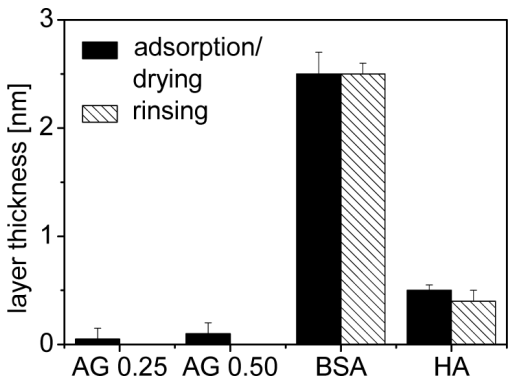

Fig. 1. Adsorption/stability of model fouling components on polyamide thin films, analyzed by QCM-D. Adsorption and drying (solid bars): alginate (AG) from solutions containing 0.25% and 0.5%, bovine serum albumin (BSA) from solutions of 200 ppm, humic acid (HA) from solutions of 20 ppm, rinsing in MilliQ water for 30 s and drying (striped bars).

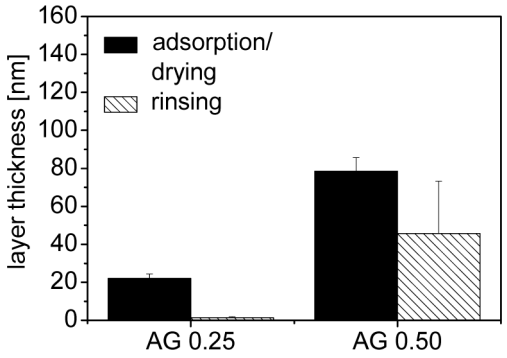

Fig. 2. Adsorption/stability of model fouling components on polyamide thin films, analyzed by ellipsometry. Adsorption from solutions of 0.25 or 0.5% alginate (AG) + 200 ppm bovine serum albumin (BSA), adsorption/drying (solid bars), rinsing in MilliQ water for 30 s and drying (striped bars).

Two different procedures were tested to stabilize the AG/BSA-layers. According to Method A (Fig. 3, left) $CaCl_2$ (8% [w/v]) was added to AG/BSA mixtures resulting in an ill-defined increase of the solution viscosity accompanied by particle formation. Adsorption experiments with this solution resulted in the adsorption of higher alginate amounts from the 0.25% AG/BSA mixture (~50 nm for 0.25% compared to the pure AG/BSA system ~20 nm, Fig. 3, left), while the layers formed from 0.5% AG/BSA mixtures remained unchanged (Fig. 3, left). The rather heterogeneous adsorption of particles and bigger aggregates was found to be largely reversible, leading to a nearly quantitative removal upon rinsing with MilliQ-water (Fig. 3, left). For Method B (Fig. 3, right) a pure AG/BSA-layer was adsorbed onto the polyamide surface followed by a stabilization step consisting of dipping the layered sample into a concentrated $CaCl_2$ solution. This treatment lead to the gelation of the AG/BSA layers, as it was obvious from the significant increase in layer thickness (Fig. 3, right). Rinsing with MilliQ resulted in layer thicknesses comparable to the initially adsorbed AG/BSA layers, independent of the applied AG solution concentration upon formation (Fig. 3, right). The stabilized layers were shown to resist prolonged rinsing procedures in MilliQ at pH 12 (30 min, data not shown). From these results we concluded, that amphiphilic proteins can mediate the formation of interfacial AG layers while multivalent cations are crucial for the stability of the layered substrates. The latter observation is in line with published findings on the crucial role of multivalent cations in fouling processes [19]. Thus, the stabilization of multicomponent biopoymer layers by Ca^{2+} ions can be clearly seen to add to the relevance of our model system.

To further improve the relevance of our model, we additionally added humic acid (HA), one of the main organic components of any aquatic systems [20,21]. For this, we applied a mixture of 0.25% AG and 200 ppm BSA as main components and added 20 ppm HA. With the applied concentration of HA we refer to published reports on the maximum concentration of humic substances in the feed of desalination plants [22]. Furthermore the layer preparation method was optimized with respect to stability and reproducibility. In our final procedure the polyamide thin film substrate was directly covered with the three-component solution described before. After 10 min adsorption, the excess liquid was removed by carefully tilting the wafers followed by a subsequent drying step at 60°C for 5 min. In consequence, the initial layers were thicker compared to the former application process (Fig. 4 left and Fig. 3 left, ~50 nm vs. ~20 nm). The ongoing procedure was similar to the former method, stabilization in a $CaCl_2$-solution and washing and drying finalized the preparation. The presence of 20 ppm HA within the mixture did slightly decrease the layer thickness remaining after the rinsing step, pointing at a destabilizing effect of HA within the three-component system (Fig. 4).

In summary, defined and robust early stage organic fouling model layers were formed from mixed solutions of major biomolecular components of relevant fluids: An

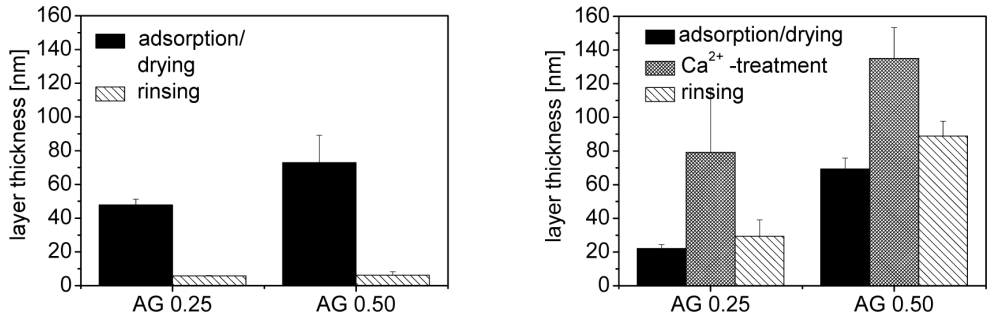

Fig. 3. Adsorption/stability of model fouling components on polyamide thin films, analyzed by ellipsometry. Left: alginate (AG) 0.25% or 0.5% + 200 ppm bovine serum albumin (BSA) + $CaCl_2$, adsorption and drying (black bars), rinsing in MilliQ water for 30 s and drying (striped bars). Right: 0.25% or 0.5% AG + 200 ppm BSA, adsorption/drying (black bars), stabilization with 8% $CaCl_2$ solution for 10s (grey bars), rinsing in MilliQ water for 30 s and drying (striped bars).

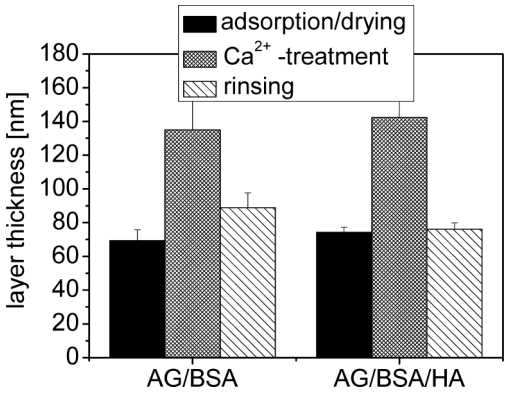

Fig. 4. Application of mixed biopolymer solutions for the formation of model fouling layers on polyamide thin films. Left: 0.25% alginate (AG) + 200 ppm bovine serum albumin (BSA), application (black bars), stabilization with 8% $CaCl_2$ for 10 s (grey bars), rinsing in MilliQ water for 30 s and drying (striped bars). Right: 0.25% alginate (AG) + 200 ppm bovine serum albumin (BSA) + 20 ppm humic acid (HA), application (black bars), stabilization with 8%-$CaCl_2$ for 10 s (grey bars), rinsing in MilliQ water for 30 s and drying (striped bars).

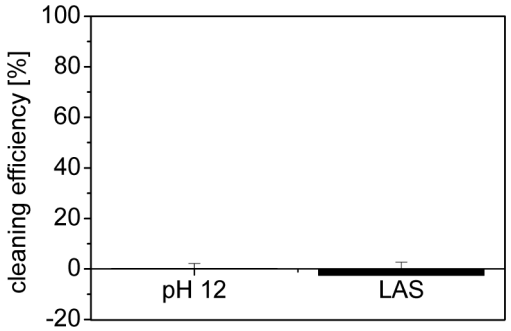

Fig. 5. Cleaning experiments on model fouling layers, analyzed as percentage of layer removal by ellipsometry. Application of fouling layers prepared from 0.25% alginate (AG) + 200 pm bovine serum albumin (BSA) + 20 ppm humic acid (HA). Cleaning efficiency (5 min, RT) of 0.01 M NaOH (pH 12) and 0.025% sodium dodecylbenzenesulfonate (LAS) in 0.01 M NaOH.

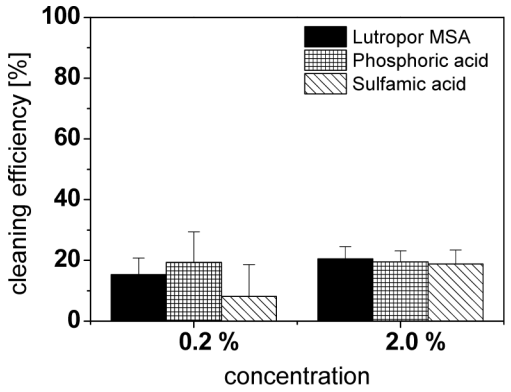

Fig. 6. Cleaning experiments on fouling layers, analyzed as percentage of layer removal by ellipsometry. Application of fouling layers prepared from 0.25% alginate (AG) + 200 ppm bovine serum albumin (BSA) + 20 ppm humic acid (HA). Cleaning efficiency (5 min, RT) of methanesulfonic acid (Lutropor® MSA), phosphoric acid, and sulfamic acid dissolved in MilliQ.

amphiphilic globular protein (BSA) was combined with a polysaccharidic substance (AG) and humic acid (HA). BSA was found to act as a primer for the anchorage of AG. The obtained layers were stabilized when applying solutions containing multivalent cations.

3.2. Cleaning experiments

The developed early stage organic fouling model layers were subsequently used in experiments to evaluate the efficacy of selected cleaner components. The measurements were performed in aqueous solution at room temperature with a contact time of 5 min. No cleaning effect was observed when applying sodium hydroxide (0.01 M NaOH, pH = 12) and the "standard" anionic surfactant sodium dodecylbenzenesulfonate (LAS) dissolved in 0.01 M NaOH (both chemicals were dissolved in MilliQ, resembling the permeate of a desalination plant, Fig. 5). Thus, neither alkaline pH values nor the presence of anionic surfactants were sufficient to attack the biomolecular layer.

Next, different organic and inorganic acids were tested at 0.2 and 2%. At 0.2%, methanesulfonic acid (Lutropor® MSA) and phosphoric acid turned out to be more efficient in foulant removal than sulfamic acid (cleaning efficiency of MSA and H_3PO_4 ~20 % vs. ~10 % for sulfamic acid, Fig. 6). An increase in the acid concentration to 2% resulted in an increase of the cleaning efficiency for sulfamic acid only. At this concentration all acids showed a similar cleaning efficiency of ~20% (Fig. 6).

Finally, three different chelats, the tri-sodium salt of methylglycindiacetic acid (Trilon® M), the sodium salt of modified anionic polyamine (Trilon® P), and amino tri-(methylene phosphonic acid) pentasodium (Dequest® 2006) were tested with respect to their cleaning efficiency. In contrast to the acids all chelats showed a very impressive removal of more then 90 % of the biomolecular layer even at the lower concentration of 0.2% (Trilon® M/Trilon® P ~94%, Dequest® 2006 ~89%, Fig. 7).

Increasing the concentration up to 1% further enhanced the cleaning efficiency. Here, Trilon® M showed the best results of ~99%, followed by Trilon® P with 96% and Dequest® 2006 with 95% (Fig. 7).

The results clearly showed a tremendous effect of the chelates when compared to the application of acid based cleaners. Swelling and acidic attack seems to be much less efficient compared to the binding and removal of stabilizing cations, namely divalent calcium ions which

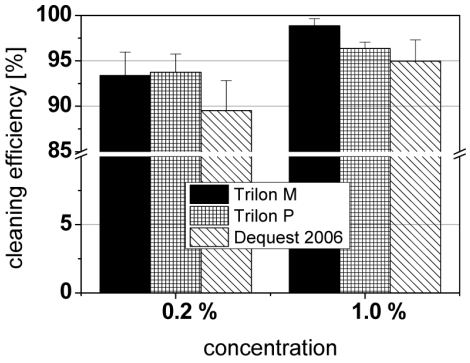

Fig. 7. Cleaning experiments on fouling layers, analyzed as percentage of layer removal by ellipsometry. Application of fouling layers prepared from 0.25% alginate (AG) + 200 ppm bovine serum albumin (BSA) + 20 ppm humic acid (HA). Cleaning efficiency (5 min, RT) of tri-sodium salt of methylglycindiacetic acid (Trilon® M), sodium salt of modified anionic polyamine (Trilon® P) and Amino tri (methylene phosphonic acid) pentasodium (Dequest® 2006) dissolved in MilliQ.

significantly contribute to the stability of the biomolecular fouling layers. This finding is fully in line with previous studies on wastewater treatment membranes [23] , clearly pointing at Ca^{2+}-removal being the crucial factor for fouling layer destabilization and removal. Ongoing work will explore the effect of combinations of surfactants and chelats to simultaneously destabilize the polysaccharidic and the proteinaceous components of the fouling layer.

4. Conclusion and perspective

Defined and robust early stage organic fouling model layers were formed from mixed solutions of major biomolecular components on polyamid thin films to mimic the initial biomolecular coverage of desalination membranes. The layered samples were applied to screen the efficacy of various cleaner components. First results revealed the outstanding effect of chelats, presumably acting by removing multivalent cations that complex and stabilize interfacial polysaccharide components. Ongoing work is dedicated to the compositional analysis of the developed multicomponent organic fouling layers using fluorescence labeling and confocal laser scanning microscopy. Through this, information about the depletion of individual molecular components within the fouling layer will be obtained. This is expected to unravel the interplay of different constituents of the system and allow for the development of strategies for their targeted removal. Using the extended methodology, we will systematically study the efficacy of various cleaner systems and combinations thereof.

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