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Fouling development in direct contact membrane distillation: Non-invasive monitoring and destructive analysis

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Abstract

Fouling development in direct contact membrane distillation (DCMD) for seawater desalination was evaluated combining *in-situ* monitoring performed using optical coherence tomography (OCT) together with destructive techniques. The non-invasive monitoring with OCT provided a better understanding of the fouling mechanism by giving an appropriate sampling timing for the membrane autopsy. The on-line monitoring system allowed linking the flux trend with the structure of fouling deposited on the membrane surface. The water vapor flux trend was divided in three phases based on the deposition and formation of different foulants over time. The initial flux decline was due to the deposition of a 50-70 nm porous fouling layer consisting of a mixture of organic compounds and salts. Liquid chromatography with organic carbon detection (LC-OCD) analysis revealed the abundance of biopolymer in the fouling layer formed at the initial

phase. In the second phase, formation of carbonate crystals on the membrane surface was observed but did not affect the flux significantly. In the last phase, the water vapor flux dropped to almost zero due to the deposition of a dense thick layer of sulfate crystals on the membrane surface.

Keywords: Direct contact membrane distillation (DCMD); Fouling mechanism; Scaling; On-line monitoring; Optical coherence tomography (OCT); Seawater desalination.

1. Introduction

Desalination by membrane distillation (MD) is a technology that combines distillation and membrane separation processes. MD uses a porous hydrophobic membrane that acts as a barrier between the liquid-vapor interfaces allowing the transportation of water vapor through its dry pores. MD is suitable for high saline water desalination (Xu et al., 2016). Unlike reverse osmosis (RO), the driving force of the MD process is the partial water vapor pressure difference which is determined by transmembrane temperatures between feed and permeate sides. In addition, the mass transfer in MD process is determined by the structural parameters of the membrane (e.g. pore size, membrane thickness, porosity and tortuosity). However, like other membrane processes, a major drawback of the MD process is membrane fouling which causes a decline in the membrane permeability due to the deposition of foulants on the membrane surface and within its pores leading to pore wetting (Al-Obaidani et al., 2008; Francis et al., 2014; Hsu et al., 2002; Kharraz et al., 2015; Tijing et al., 2015; Zhang et al., 2015). Accordingly, several studies on MD membrane fouling have been conducted to better understand fouling behavior and thus develop mitigation and control strategies.

In seawater desalination using MD, fouling can be categorized by three groups of foulants;

inorganic and organic compounds, and biological fouling. In most cases and in real MD operations, fouling by a single mechanism does not occur but is the complex combination of different types of fouling (Tijing et al., 2015).

Organics in seawater can be problematic as they can cause wetting of the membrane due to their high affinity with membrane material and diffusability of their volatile portions that evaporates through the membrane pores (Gryta et al., 2001; Srisurichan et al., 2005). Naidu et al. (2014a) studied the characteristics of organic compounds by analyzing the changes in organic fractions and their mass in both feed and permeate. The focus on humic substances was because of a specific property, thermal disaggregation of humic substances to low molecular weight (LMW) organics (i.e. LMW humics and building blocks). In addition, different disaggregation rates of humic substances were found when humic substances were in presence of salts such as sodium chloride (NaCl) and calcium sulfate (CaSO_4) (Naidu et al., 2015). Another major fouling is membrane scaling by sparingly soluble salts and silicate, which can lead to dramatic flux decline and pore wetting. Since MD is a thermally driven process, scaling is intensified by the inverse solubility of gypsum and calcium carbonate with increasing temperature (Curcio et al., 2010; Nghiem and Cath, 2011; Shin and Sohn, 2016). Scaling behaviors are difficult to predict since various factors such as pH, temperature, operating pressure, and flow velocities can be influenced on the scale formation (Gryta, 2008a; Naidu et al., 2014b; Warsinger et al., 2015). Nghiem et al. (Nghiem and Cath, 2011) investigated the scaling mechanism using calcium carbonate (CaCO_3) and CaSO_4 feed solution at various feed temperature ranges. Scaling by CaSO_4 led to a severer flux drop than that by CaCO_3 . By increasing the feed temperature, an inducted time for scaling formation tended to be shortened and more large crystals were formed. Wong et al. (2016) investigated the fouling due to the deposition of particles using feed solutions

71 containing different concentrations of TiO_2 from 0 to 9 g/L at different flow-rates.

72 In spite of numerous studies on MD membrane fouling, most of them have focused on
73 individual foulants and only few studies have been conducted with real feed water (e.g. seawater).
74 Considering the complexity of the process, the use of a real feed is necessary for a more
75 comprehensive understanding of fouling characteristics and interactions between various
76 foulants (Nguyen et al., 2017; Qin et al., 2017).

77 In membrane processes, there are needs for monitoring the fouling development on the
78 membrane surface. In MD, the scaling/fouling on the membrane represents one of the main
79 challenges, hindering the commercialization of full-scale desalination plant (Ji et al., 2010;
80 Mericq et al., 2010). The use of *in-situ* or non-destructive techniques in membrane filtration
81 system has been increasing in recent years. Optical coherence tomography (OCT) is able to
82 monitor the filtration system under continuous operation, providing real-time information of the
83 fouling layer without stopping the operation or disassembling modules. The OCT is the only
84 technique that enables to provide “a window” on the system during operation without the use of
85 any contrast agent. So far it has been mostly employed for the *in-situ* investigation of the
86 biofouling. OCT was used in a submerged system to monitor the dynamic evolution of the
87 biomass layer formed, over short-term (Fortunato et al., 2017b) and long-term operations
88 (Fortunato et al., 2017c). In spacer-filled channel, the OCT was used to perform time-resolved
89 and spatial-resolved evaluation of biofouling development (Fortunato et al., 2017a; Fortunato
90 and Leiknes, 2017; West et al., 2015). Moreover, the OCT enables a non-destructive scan of the
91 membrane surface at the end of the experiment prior to the membrane autopsy. This procedure is
92 important to assess the homogeneity of the fouling deposited on the membrane and to check the
93 samples to analyze through membrane autopsy (Fortunato et al., 2016). To understand the

fouling behavior in MD, a real-time monitoring is necessary (Lee et al., 2018). Particularly for MD that is a thermal separation process and where the fouling structure is not maintained when operation is shut-downed and samples are taken from the membrane module.

The objective of this work is to investigate the fouling development in a direct contact membrane distillation (DCMD) process operated using real seawater. The DCMD process was chosen due to its simplest configuration and relatively higher permeate flux. Real seawater collected from the Red Sea, Saudi Arabia, and deionized (DI) water were used as feed and permeate solutions, respectively. Different characterization techniques were employed aiming to relate the scaling formation with the performance decrease. To our knowledge, this is the first trail to use OCT to monitor fouling (or scaling) in MD. The OCT was used to monitor the system *in-situ* non-destructively under continuous operation allowing the scaling development to be related with the flux decline. Selected samples were taken to perform membrane autopsy and foulant characterization. Scanning electron microscopy with energy dispersive X-ray (SEM-EDX) analysis was performed to characterize the scaling formation at different operational times.

2. Materials and methods

2.1. Laboratory-scale DCMD coupled with OCT

Figure 1 shows a bench top laboratory-scale DCMD set-up used for the fouling experiments. Two gear pumps (Micro gear pump, Cole Parmer) were employed to supply the steady flow rates to feed and permeate inlets. Red Sea water (as a feed) was heated up to the desired feed temperature by the hotplate (IKA C-MAG HS7) with temperature controller (IKA ETS-D5) and it was circulated through the feed channel, while DI water (as a cooling water), which is cooled down using a coiled SUS tube submerged in water bath was circulated through the permeate

channel in a counter-current flow manner.

A commercial flat sheet hydrophobic micro porous membrane purchased from General Electronic (GE, US) was used. The average contact angle of the membrane was about $140\pm4^\circ$ (it was measured by using Theta optical tensiometer (Attension, Sweden). The detailed properties provided by the manufacturer are summarized in Table 1. The acrylic membrane module was manufactured with a window having 5 mm thickness on the upper module to facilitate the OCT monitoring. The channel dimensions (length, width and height) of channel of the membrane module were 60 mm, 150 mm and 2 mm respectively, giving an effective membrane area was of 0.0009 m^2 . The OCT device was placed on the feed side of the module to observe the fouling and scaling behavior in a real-time (Figure 1).

Figure. 1. A schematic diagram of laboratory-scale DCMD coupled with OCD set-up.

Table 1. Detailed specifications of the MD membrane.

Material	Polytetrafluoroethylene (PTFE)
Thickness (μm)	179
Nominal pore size (μm)	0.2
Porosity (%)	75 $\pm$ 5
Effective area (m^2)	0.0009
Mean contact angle ($^\circ$)*	140 $\pm$ 4

*Measured in our laboratory.

2.2. Feed and permeate solution

Red Sea water was collected from the intake line of the KAUST commercial seawater reverse osmosis (SWRO) desalination plant (Rahmawati et al., 2012). After collection, the feed solution was filtered through a GF/C membrane (Whatman, 1.2 μm) to remove large suspended solids and algae. The initial pH and conductivity of raw seawater were 7.98 and 60.89 mS/cm, respectively. After filtering the feed solution was stored in 4 $^\circ\text{C}$ cold room. In the DCMD experiment, 2 L of filtered seawater and 1 L of deionized (DI) water were used as feed and cooling solutions, respectively.

2.3. Operational conditions

A high temperature difference between feed and permeate inlet can lead to high permeate flux. Thus, the inlet temperature of feed and permeate sides were kept at 70 $^\circ\text{C}$ and 20 $^\circ\text{C}$, respectively. In order to reduce the temperature polarization in the DCMD process, turbulent flows were maintained in both feed and permeate channels (1.2 and 0.8 L/min (LPM) of inlet feed and permeate flow rates, respectively) (Alsaadi et al., 2014). The resulting Reynold number (Re) in the feed side was 5,697 which represents a turbulent flow condition ($\text{Re} > 2300$). The permeate side flow-rate was set at 0.8 LPM which is lower than feed side to prevent the

membrane from being bent to up-side. During the MD experiments, the feed water was collected for further water analysis and additional experiments were carried out for membrane autopsy. After finishing operations, conductivity of the permeated water was measured to check for membrane wetting or penetration of salt to the permeate side.

2.4. Analytical methods

Considering the complex nature of the feed solution, different analytical techniques were employed to understand the fouling phenomenon based on the flux variation. Sample taken for the autopsy data experiment were analyzed using inductively coupled plasma optical emission spectrometry (ICP-OES) and liquid chromatography – organic carbon detection (LC-OCD) to identify the nature of the deposits on the membrane surface. To collect autopsy samples, whole membrane was submerged in 45 mL of Milli-Q water right after experiments. Then it was sonicated and stirred for 10 min to detach foulants from the membrane. In the LC-OCD technique, the sample is supplied in a mobile phase (phosphate buffer, 12.5 g KH_2PO_4 (Fluka, USA) + 7.5 g $\text{Na}_2\text{HPO}_4 \times 2\text{H}_2\text{O}$ (Fluka, USA) to 5 L) at a flow rate of 1.5 mL/min to the chromatographic column – a weak cation exchange column based on polymethacrylate. Injection volume and retention time for all samples were 2,000 μL and 180 min, respectively. Chromatograms were processed on the basis of area integration using a customized software program (ChromCALC). The main fractions identified by the LC-OCD technique are biopolymers (BP), building blocks (BB), low molecular weight (LMW) acids and neutrals. The definitions and molecular weight size ranges assigned to organic fractions obtained from LC-OCD analyses were given by Jeong et al (2013).

2.5. SEM-EDX image analysis

To examine the surface of fouled membranes at zero and tilted angles, samples were mounted on flat and 45-degree pre-tilted aluminum stubs. To examine the cross section and determine the thickness of membrane sample deposited at the end of the observation period, the sample was freeze-fractured inside liquid nitrogen and the fractured sample was mounted on the 45-degree pre-tilted aluminum stub. To dissipate charging during SEM imaging and EDX analysis, mounted samples were coated with either 5 nm Iridium inside Q150TS sputter coater (Quorum Technologies) or with 10 nm carbon inside K950X evaporator (Quorum technologies). Quanta 200FEG SEM equipped with ETD secondary electron detector and Magellan SEM equipped with a lens secondary electron detector were used for SEM imaging. Quanta 200SEM equipped with EDX detector (EDX) was also used to determine the elemental compositions of foulants on the membranes.

2.6. Optical coherence tomography (OCT)

A spectral domain OCT system device from Thorlabs, GmbH (Germany) armed with the scan lens (LSM 03BB) was used to assess the fouling development non-invasively in the flow cell of the DCMD module. The OCT probe was mounted on the flow cell for continuous monitoring in a fixed position. Scans were acquired each hour for the whole period of observation. The cross sectional scans (2500 x 1024 pixel) corresponding to 5.00 mm x 2.77 mm (width x depth) were taken within a fixed rectangular area of 5.0 x 2.0 mm. The OCT scans were processed with FiJI software. The images were filtered to reduce the noise. Then the contrast and brightness were adjusted. The images were cropped from 2500 x 1024 pixels to 954 x 184 pixels corresponding to 0.50 x 1.90 mm for visibility. The properties of the fouling layer were estimated using a

customized MATLAB code.

3. Results and discussion

3.1. *In-situ non-destructive scaling (fouling) assessment with OCT*

In this work, the OCT technique was used for the first time to assess the scaling formation on a membrane surface in the MD process. Therefore, it was possible to relate the flux trend with scaling structure observed via an *in-situ* monitoring of the membrane surface. Three phases can be noted depending on the flux decline pattern (Figure 2): (i) initial decreased phase, (ii) stationary phase and (iii) sharp decreased phase. In the initial operational period, the volume concentration factor (VCF) from 1.00 to 1.80, the normalized flux dropped by 40%. At the end of this phase, after 13 h of operation, a slight flux recovery from VCF 1.80 to 2.00, corresponding to a jump in the flux, was observed. This might be due to the detachment or breakage of the deposited layer from the membrane surface (see details in the next sections). The following phase is characterized by a stable phase with constant flux (VCF from 2.00 to 3.05). Afterwards, in the last phase, the flux dropped to attain almost to zero.

As shown in Figure 1, the OCT was mounted directly on the membrane flow cell allowing the acquisition of cross-sectional scans in correspondence of each specific step of the DCMD process.

In Figure 3, the OCT scans show the fouling development on the membrane surface over time. In the early stage, when the slight drop occurs in the first 12 h corresponding to VCF 1.85, no significant deposition on the membrane was observed. After 16 h, corresponding to VCF 1.98, spherical depositions were observed on the membrane surface. At the end of the observation period corresponding to VCF 3.20 (24 h), a fouling layer characterized by an irregular

219 morphology was observed, which was the most possible reason of the sudden flux drop.

220
221 **Figure 2.** Normalized flux pattern versus VCF. The experiment was run in parallel in order to
222 perform destructive analysis at different time intervals (VCF 1.20, 2.50 and 3.20).
223

224
225 **Figure 3.** Cross-sectional OCT scans of the fouling deposited on the membrane surface over
226 time.

In this study, OCT proved to be a useful tool for fouling monitoring in MD application for two features: (i) directly and *in-situ* monitoring the membrane under operation in a real time, and (ii) guiding the membrane autopsy. Furthermore, the use of OCT enables the visualization of the membrane cross section and therefore, allows linking the scaling/fouling formation on the membrane surface observed in a real time with the decrease in the water vapor flux. In other words, it was possible to gain information about the system during the whole experiment without any sampling procedure.

3.2. Fouling characterization in DCMD

Fouling in MD is complex and depends on different aspects of the process. A better understanding of its nature is necessary to minimize the fouling formation and to achieve better performances. Different kinds of fouling can occur in MD processes. Depending on the nature of the pollutants and the fouling layer characteristic, the fouling layer deposited or formed on the membrane surface can provide additional thermal and hydraulic resistances. The flux decrease is attributed to two different types of fouling layers: porous and non-porous (Gryta, 2008b).

The use of different characterization techniques is necessary to gain a better understanding of fouling nature in membrane processes (Fortunato et al., 2016; Wu and Fane, 2012). The objective of this study is to investigate the fouling development in MD seawater desalination, and therefore it is not possible to use the OCT as a stand-alone technique. In fact, the OCT is only able to provide structural information about the fouling, not distinguishing between different scalants formed on the membrane surface. In the OCT scans it is only possible to observe the presence of a deposit on the membrane surface, without any information about the composition

of the deposits. When real seawater is used as feed, the different pollutants and salts are formed at different operational times on the membrane resulting in different impacts on the flux decline. As described in the experimental section of SEM-EDX imaging analysis, additional destructive imaging techniques were employed in this study to characterize the scaling formed on the membrane surface. The SEM analysis provides images at high resolution of the fouling. In the case of scaling, the classification of different scalants is only possible based on the shape of the crystals in SEM observation (Zarga et al., 2013). Coupling SEM with EDX is necessary to have a qualitative classification of the scaling on the membrane surface (Figure S1).

In this study, experiments were run in parallel in order to collect samples at different time intervals. This allowed performing destructive qualitative analyses (i.e. membrane autopsy) on the samples corresponding to each specific phase. This procedure also allowed relating the OCT scans with fouling characterization, and coupling the information gained *in-situ* non-destructively (via OCT) with the ones performed *ex-situ* and destructively (via SEM).

3.2.1. SEM analysis

SEM is the most commonly used imaging technique in the characterization of fouling in membrane-based processes. Comparing with OCT, it enables the acquisition of high-resolution images of the fouled membrane, allowing a detailed investigation of deposition morphology. However, SEM is destructive and requires different steps for sample preparation such as staining and coating. In this study, the SEM investigation was performed at the end of the three experiments run in parallel. The samples were collected at VCFs of 1.20, 2.50 and 3.20, corresponding to 4, 20 and 24 h of operational times. Figure 4 shows the SEM images of the fouling deposited on the membrane surface for each phase at different magnifications.

In the first phase (VCF 1.20), although the OCT was not able to detect any scales on the surface in corresponding to the first drop in flux (Figure 3), the SEM analysis performed on the membrane coupon revealed the presence of a thin layer on the membrane surface (Figure 4A). At this stage, the fouling layer covered most of the available surface but the layer has a porous structure allowing the water vapor transport through the layer. The presence of this layer on the membrane surface decreased the flux by 40%. The structural properties of layer formed such as the pore size, porosity, tortuosity and thickness may contribute to the reduction of permeate flux in terms of mass transfer (Tijing et al., 2015). In Figure 4B-C, it is possible to see the membrane surface through some fractures in the fouling layer, however these fractures are probably due to the drying of the sample.

As shown in Figure 4, the fouling at the early stage is not characterized by specific crystal on the membrane surface but it is represented by a thin layer with some crystals embedded in it. The SEM-EDX analysis allowed the characterization of the crystals surrounded in a homogeneous fouling layer (Figure S2).

Figure 4. SEM images of the fouling layer at three different VCFs. A) Low magnification image of the fouling after 4 h at VCF 1.20. B) Higher magnification (2,500 X) of the same fouling layer. C) The same membrane imaged at higher magnification (25,000 X) and at 70 degree stage tilt showing topography of the fouling surface. D) Low magnification of the fouling layer after 20 h at VCF 2.50. E) Higher (1,000 X) magnification F) The same membrane imaged with 70 degree stage tilt and at higher magnification (25,000 X) showing rosette-like clusters. G) Low magnification image of the fouling layer after 24 h at VCF 3.20. H), and I) Higher magnification of the same membrane showing calcium sulfate crystals presented in plate shaped with different length-to-width ratios. The surface of these crystals appears very smooth.

The SEM investigation made it possible to estimate the fouling layer thickness by tilting the sample at specific angles, revealing a thickness of only hundreds nm (Figure 6). However, the OCT was not able to detect the layer deposited at this stage as its resolution limit is in the micrometer range.

The second phase is characterized by the achievement of a constant flux between VCF 2.00 and 3.00. Figures 5A-C show a comparison between the two imaging techniques. Through the OCT scans (Figure 5A-B) it is possible to assess the presence of spherical particles on the membrane surface. The SEM analysis performed at VCF 2.50 confirmed the presence of rounded crystals on the membrane surface, showing the crystal morphology (Figure 4D-F and Figure 5C). The EDX analysis provided a qualitative evaluation of the scaling, revealing the presence of calcium carbonate (CaCO_3) crystals (Figure S1). As shown in Figures 3, 4 and 5, in this phase the crystals did not cover the whole surface but only approximately 20%. Moreover, the carbonate deposited on the membrane surface was found as a single particle or as aggregates of particles (Figure 4D-F). The image analysis performed on the OCT scans and the SEM images (by tilting the sample) showed deposits having an average thickness of 5-10 μm (Figure 6B). The crystals were deposited directly on the membrane surface. Indeed, as shown in Figure 4E-F, at VCF of 2.50, the thin fouling layer formed at the early stage was no longer present on the surface. The slight flux increase shown in Figure 2 is attributed to disappearance/breakage of the layer and the formation of calcium carbonate crystals on the surface. The formation of crystals may also have contributed to the breakage of the first layer deposited in the early stage on the membrane.

In the last phase (after 24 h operation, around VCF 3.20), the flux dropped to zero. From the OCT scans acquired on-line under operation (Figure 3), the presence of a layer with a thickness

of about 40-50 μm can be observed. SEM images confirm the presence of a thick and dense layer on the membrane surface (Figure 4G-I). Since the fouling deposited at this stage was covering the whole membrane surface (Figure 4G), it was possible to examine the cross section of the sampled membrane coupon. The cross sectional analysis performed on the SEM images showed a thickness of about 60-80 μm .

EDX analysis showed that the layer deposited at the end of the experiment was mainly composed of sulfate (Figure S1). At the end of the experiment the sulfate is presented as platelet structures of different sizes (Figure 4G-I). These structures are the characteristic of calcium sulfate (CaSO_4) bulk precipitation.

Figure 5. Comparison between OCT scans and SEM images at different time intervals. A) OCT scans at VCF 2.50. B) Cropping of the boxed area at VCF 2.50. C) SEM tilted surface image at

VCF 2.50. D) OCT scans at VCF 3.20. E) Cropping of the boxed area at VCF 3.20. F) SEM cross-section image at VCF 3.20.

Figure 6. Thickness analysis of the fouling layer deposited at different VCFs through SEM images. A) Tilted sample at VCF 1.20. B) Tilted sample at VCF 2.50. C) Cross section analysis at VCF 3.20.

3.2.2. Membrane autopsy

As shown in Figure 4, the first phase was characterized by the deposition of a homogenous thin fouling layer on the membrane surface. The SEM-EDX analysis (Figure S1) is limited in the quantification of elements present in the layer, but can be used for a qualitative estimation. Moreover, in the case of a thin layer, it was not possible to distinguish between the signal coming from the layer and the one coming from the membrane, given that EDX has a depth in the range of 5-10 μm , and the thickness of the layer deposited in this phase was only about 40-60 nm. In this case, it was not possible to measure the carbon content in the layer, since the layer was coated with carbon. Therefore, as reported in fouling characterization section, a detailed analytical characterization was performed on another membrane coupon collected at VCF 1.20. The ICP analysis (Table S1) confirmed the results observed by the SEM-EDX. The qualitative

investigation revealed an abundance of Mg, Na, K and Ca in the fouling layer observed at the early stage. Moreover, the SEM-EDX allowed the analysis of subareas in the imaged samples (Figures S1 and S2), where Mg, K and Ca appeared to be embedded in the layer. Na abundance in this phase is probably due to the presence of NaCl deposit in the fouling layer (Figure S2).

Figure 7. Organic composition in the feed solution at different VCFs (X-axis: mass in feed solution in terms of DOC characterized by LC-OCD).

The LC-OCD analysis revealed which organic compounds participated in the fouling or scaling formation at each stage. The organic matter presents in the seawater (VCF 1.00 corresponding to time 0) is mainly characterized by mostly HS, BB and LMW acids and neutrals

and BP, which is high MW organic compounds, (about of 5% of total organic compounds). The dissolved organics contributed to fouling in the early stage (by VCF 1.50) was negligible. However, as shown in Figure 7, from VCF 1.00 to VCF 1.50, the LMW organics increased while the HS decreased. This is due to the high temperature required in the MD process. This phenomenon has been previously reported where at high temperatures as in MD the thermal disaggregation of HS to LMW compounds can occur (Drastík et al., 2013; Naidu et al., 2015). It is worth mentioning, that at VCF 1.50 the concentration of BP dropped significantly, since most of BP were deposited on the membrane surface as observed from the analysis performed at VCF 1.20 (Figure S3). The analysis revealed the abundance of BP and some of LMW in the fouling layer in the early stage (Figure S3). In fact, the hydrophobicity of the MD membrane enhances the adsorption of organic materials onto the membrane surface (Gryta, 2008b). As stated by Xu et al. (2004) the proteins have a high affinity to deposit on the hydrophobic membranes. Afterwards, organics including HS and LMW neutrals were adsorbed in the scalants formed on the membrane. The HSs are considered as one of the major foulants in membrane based filtration systems (Li et al., 2016; Lin, 2000; Yuan and Zydney, 1999).

3.3. *Scaling development in DCMD*

Scaling formation in bulk is due to the solubility product of the salts, which depends on the composition of the feed solution and in part on the concentration polarization. Additionally, as reported by Curcio et al. (2010), another factor involved in the scaling formation in MD is represented by the membrane proprieties. In fact, the membrane physico-chemical proprieties play a significant role in the nucleation mechanism. In this study, the seawater feed solution was recirculated over time leading to a continuous increase of salt concentration in the feed.

Carbonate is less soluble than the sulfate, leading to the formation of carbonate crystals before sulfate ones. In fact, as shown by the SEM-EDX analysis the second phase is characterized by the formation of rounded calcium carbonate crystals on the membrane surface. Carbonate scales can occur in three anhydrous crystalline polymorphs: calcite, aragonite and vaterite. Aragonite is characterized by a needle structure and is the most dominant species at high temperature (Sawada, 1997; Zarga et al., 2013). Li et al. (2015) reported that high concentrations of Mg ions in the feed water could promote the formation of aragonite with respect to the vaterite.

Calcium sulfate deposition on the membrane surface occurred around a VCF 3.10. The sulfate scaling on the membrane surface has a significant impact on the flux in DCMD (He et al., 2008). The sharp decrease in the flux occurs when the feed water became supersaturated with calcium sulfate, which over the time reached supersaturated conditions in the feed, leading to the bulk crystallization of calcium sulfate. Calcium sulfate exists in three different forms: gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), bassanite ($\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$) and anhydrite (CaSO_4). Among the three crystallographic species, gypsum is the most thermodynamically stable and it has the lowest solubility. Gypsum can arise in different structures depending on the supersaturation ratio and the kinetics of the crystallization (Lee and Lee, 2000). In addition, the feed composition affects the formation of sulfate crystals, since the presence of bicarbonate and magnesium delays the formation of gypsum nucleus. In fact, the solubility constant of each salt changes depending on the co-precipitation (Gryta, 2009). Moreover, the sulfate crystals were formed in larger amount on the membrane surface compared to the carbonate crystals observed at VCF 2.00. This is due to the higher concentration of sulfate in seawater feed solution. The formation of a thick non-porous sulfate layer on the surface led to a complete decrease of the flux. Nghiem et al. (2011) reported that sulfate scaling is severer than the carbonate scaling or silicate, and it is

characterized by a longer induction time. However, the deposition of scaling on the membrane surface did not promote pore wetting. No increase in permeate conductivity was observed at the end of the experiment.

4. Conclusions

Fouling development in a lab-scale DCMD desalination process treating seawater collected from the Red Sea was investigated. This study firstly employed OCT technique for on-line monitoring enabling the *in-situ* non-destructive fouling assessment during continuous MD operation. In addition, destructive fouling investigations including SEM-EDX image analysis were carried out to characterize the fouling formation at different stages. Key findings obtained from this study are as follow.

- The *in-situ* monitoring with OCT in combination with destructive techniques is suitable for the evaluation of fouling development in the DCMD process. In addition, the OCT coupled with membrane autopsy provided a better understanding of the fouling mechanism to give an appropriate sampling timing.
- OCT was able to monitor the fouling development on the membrane surface over time and allowed relating the scaling/fouling formation on the membrane surface observed in a real time with the flux decline. The flux trend in MD was divided into three phases based on the deposition and formation of different scalants over the time: (i) initial decreased phase, (ii) stationary phase and (iii) sharp decreased phase.
- At early stage, the flux decreased by 40% due to the presence of a porous fouling layer in the range of 50-70 nm covering the membrane surface. LC-OCD analysis revealed the

abundance of the thermal disaggregation of HS to LMW compounds and significant deposition of BP on the membrane surface were observed.

- The second phase showed a constant flux between VCF 2.00 and 3.00. Rounded crystals 5-10 μm thick (mostly, CaCO_3) were observed on the membrane covering approximately 20% of its surface. Interestingly, the formation of crystals led to the removal of the thin fouling layer formed at the early stage.
- In the last phase where the flux dropped to almost zero (at about VCF 3.20), the presence of a thick and dense fouling layer (about 60-80 μm) on the membrane surface was observed and CaSO_4 formation was revealed.

Supporting information

Figures showing additional SEM-EDX analysis of the fouled membrane coupons at different VCFs (Figure S1), subarea in the fouled membrane at VCF 1.20 (Figure S2), and organic composition of the foulants deposited on the membrane surface at VCF 1.20 (Figure S3) are presented in the SI. A table showing ICP analysis of the fouling layer at VCF 1.2 (Table S1) is also given.

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Supplementary Figures

Figure S1. SEM-EDX analysis of the fouled membrane coupons at different VCF.

Figure S2. SEM-EDX analysis of subarea boxed in red in the fouled membrane at VCF 1.20.

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594 **Figure S3.** Organic composition of the foulants deposited on the membrane surface at VCF 1.20.

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596 **Table S1.** ICP analysis of the deposited fouling layer at VCF 1.20.

	Ca	K	Mg	Na
mg/m ²	240	267.5	687.5	550

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Highlight

- A comprehensive analysis of fouling and scaling behavior in DCMD was investigated.
- OCT was employed to monitor the deposition layer in real-time during MD operation.
- Variations of permeate flux with VCF were studied under different conditions.
- Flux trend was divided in three phases based on the deposition of foulants over time.
- Deposits are composed of a mixture of organic compounds, salts, carbonate & sulfate crystals.