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Characterization of seawater reverse osmosis fouled membranes from large scale commercial desalination plant

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ABSTRACT

The objective of this work is to study the ageing state of a used reverse osmosis (RO) membrane taken in Algeria from the Benisaf Water Company seawater desalination unit. The study consists of an autopsy procedure used to perform a chain of analyses on a membrane sheet. Wear of the membrane is characterized by a degradation of its performance due to a significant increase in hydraulic permeability (25%) and pressure drop as well as a decrease in salt retention (10% to 30%). In most cases the effects of ageing are little or poorly known at the local level and global measurements such as (flux, transmembrane pressure, permeate flow, retention rate, etc.) do not allow characterization. Therefore, a used RO (reverse osmosis) membrane was selected at the site to perform the membrane autopsy tests. These tests make it possible to analyze and identify the cause as well as to understand the links between performance degradation observed at the macroscopic scale and at the scale at which ageing takes place. External and internal visual observations allow seeing the state of degradation. Microscopic analysis of the used membranes surface shows the importance of fouling. In addition, quantification and identification analyses determine a high fouling rate in the used membrane whose foulants is of inorganic and organic nature. Moreover, the analyses proved the presence of a biofilm composed of protein.

Capsule Summary: This study reveals an autopsy study of a fouled seawater reverse osmosis membrane, used for two years in Benisaf Water Company desalination plant in Algeria, to study membrane performance degradation.

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INTRODUCTION

Reverse Osmosis (RO) is a well suited and commonly used process in desalination and advanced wastewater treatment (Thuy et al., 2007). In the last few years, the seawater reverse osmosis (SWRO) desalination has gained much popularity

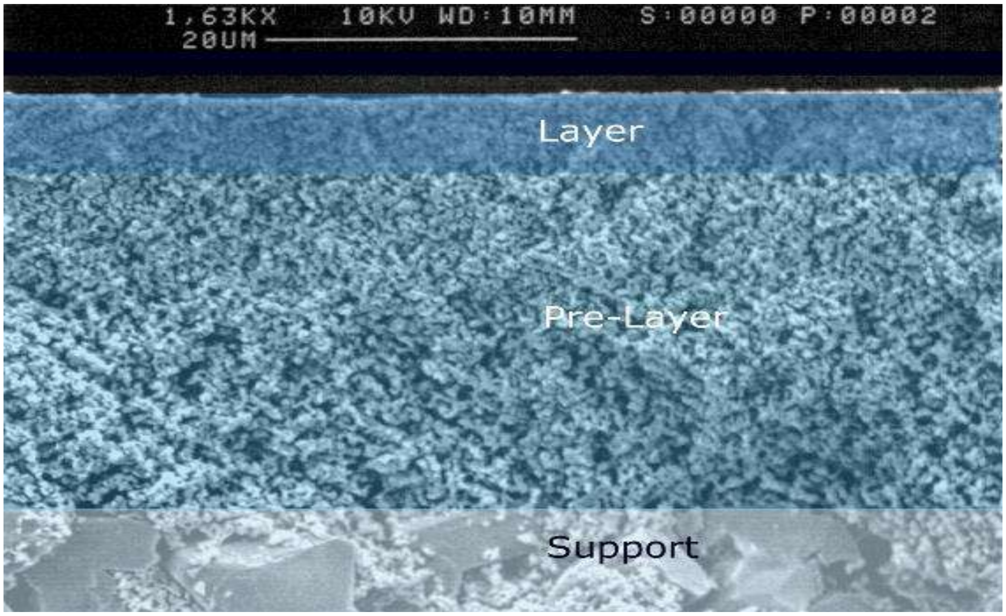


Fig. 1: Thin film composite polyamide membrane composition

Fig. 2: The fouled RO membrane element

which will become one of the important methods to solve the problem of fresh water deficit and seawater. The technology of RO process has gone through a remarkable transformation. The new high rejection and high flow membranes were allowed operating at high pressures (up to 80–90 bar), and thus making conversions to 55–60% economically feasible. A higher efficient energy recovery device as pressure exchangers (PX), that in the past was only used in small RO seawater plant, is also slowly gaining use in large desalination plants. Hydraulic efficiency of this type of equipment is in the range of 90–94%. All these advances have simplified the RO processing from a two-stage treatment shift to a single-stage array and have resulted in lowering RO system capital and operating costs (Yan-yue et al., 2006). However, like other membrane filtration processes, fouling is a major obstacle in the efficient operation of RO systems. Fouling refers to the deposition of undesirable material on the membrane which affects the installation operation by a decline in product water flux and/or increased salt passage (Siobhan et al., 1997). Membrane fouling causes deterioration of both the quantity and quality of treated water which consequently results in higher treatment costs. Foulants may be classed into one of four major categories: sparingly soluble inorganic compounds, colloidal or particulate matter, dissolved organic substances and microorganisms (Thomas et al., 2007). Successful development of membrane materials followed by further modifications to increase its performance played a crucial role in the global application of this technology. Many commercial RO membranes are thin film composite (TFC) polyamide (PA) membranes which consist of three layers: a polyester supportive backing layer (120-150 µm thickness), a microporous polysulfone interlayer (40 µm) and an extremely thin polyamide active layer on the membrane surface (0.2 µm) (Petersen and Lal, 1990). Commercial materials are developed for effectiveness despite heterogeneity caused by the manufacturing process. The active layers can vary chemically across the membrane as well as throughout the depth of the surface layer (Siobhan et al., 1997). Figure 1 shows the composition of a thin film of a polyamide membrane.

Membrane manufacturers typically recommend that cleaning should be conducted when there is a significant drop in performance. The standard advice has not been changed in over 30 years. The DOW Filmtec Technical Manual states on Page 122 that: "Elements should be cleaned when one or more of the below mentioned parameters are applicable:

- The normalized permeate flow drops 10%
- The normalized salt passage increases 5 - 10%
- The normalized pressure drop (feed pressure minus concentrate pressure) increases 10 -15%

If you wait too long, cleaning may not restore the membrane element performance successfully. In addition, the time between cleanings becomes shorter as the membrane elements will foul or scale more rapidly." This is the same message offered in Hydranautics Technical bulletin of 1992: "If permeate flow drops the product water quality decreases or applied pressure must be increased to maintain normal productivity more than 10 to 15 percent, then the elements need to be cleaned." Analysis of the results of 500 membrane autopsies by Peña & al 2013, had shown that 60% of the main foulants are biological and particulate/colloidal fouling (Yan-yue et al., 2006). Clay and biofilm tend to build up in layers and become compressed into the membrane surface if left to accumulate (Stephen et al., 2002).

The research works in the last years are focused on developing methods for diagnosis and control of fouling. A set of coherent tools has been developed for (i) determining the fouling potential of feed water and (ii) analysing the fouling of RO membranes. An overview of the tools applied in practice and had proven their values are shown in Table 1. One of these tools will be illustrated in more detail in this paper (Vrouwenvelder et al., 2003).

In most cases membranes are sent for integral diagnosis (autopsy) because they have failed or are underperforming significantly. That is salt passage, flow, flux and pressure differentials are outside of the design specifications. The first stage of membrane autopsy is to record the element model, serial number, position in the plant along with the chemical applied treatment regimes. External examinations and photographs are taken to record the physical condition. Samples can be taken from the feed inlet and outlet. The outer casing is removed and membrane leaves unrolled in readiness for an internal examination of the membrane sheets, glue lines, vexar and permeate carrier. Representative deposit samples are taken from the membrane surface and photographs are taken. Membrane samples are cut and prepared for characterization (Stephen et al., 2002). Early findings revealed that metallic oxides play a critical role in cohesion of the scale formed or fouling-layer .A primary foulant can inhibit back diffusion of soluble ions and lead to secondary fouling that has even more serious consequences (Min and Lal, 2001).With an accelerating deterioration of water quality, especially for a micropolluted water source, organic matters and/or microorganisms have become the main foulant in membrane systems (Min and Lal, 2001). A very large 200,000m^3/day, sea water RO plant in the Ouest of Algeria was commissioned in August 2016. A programme of predictive maintenance was a key feature of the operation of this plant. In June 2017 a Hydranautics SWC5 RO lead membrane element from the first stage of the plant was sent for autopsy. A used SWC-5 membrane autopsy results are discussed to identify the foulants.

MATERIAL AND METHODS

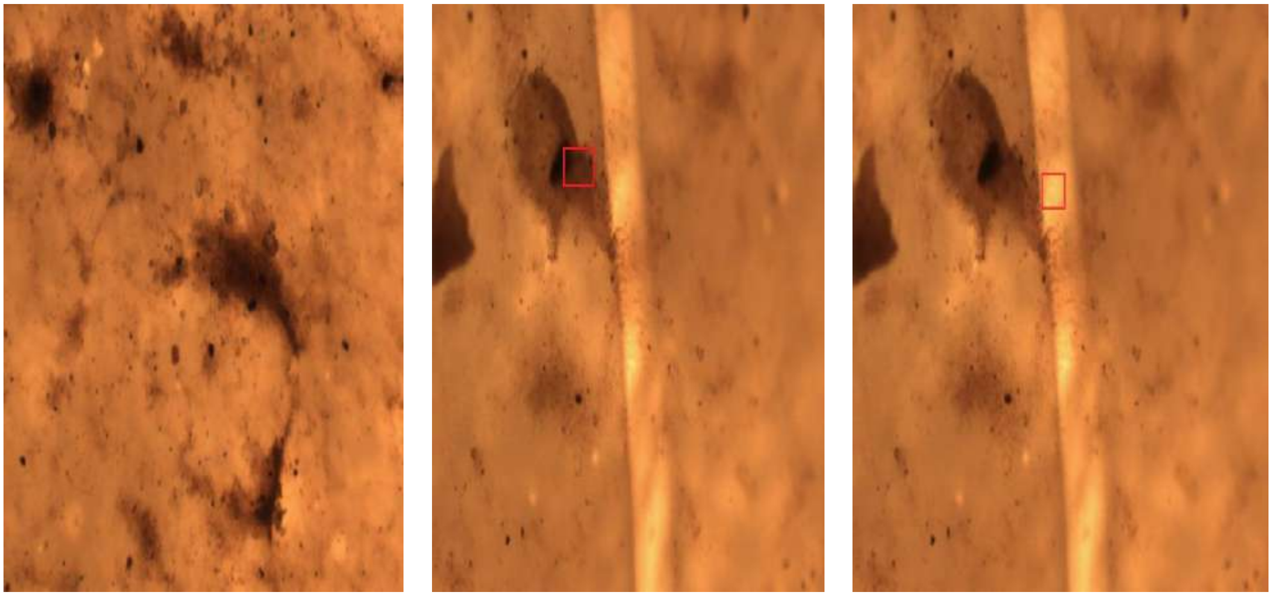
Desalination plant process

The water treatment process at the Beni Saf plant consists of a collection system and pumping of sea water through a single round plug connected to the seawater pump tank by a pipe 2.4 m in diameter, submerged at 1400 m from the coast at a depth of 18 m.

Pre-treatment by sand/anthracite filtration and micro- filtration using polypropylene cartridge filters,followed by demineralization by reverse osmosis, and finally evacuation of brine and by-products through an outlet 1.8 m in diameter at 8 m depth below sea-level, discharging 2 m above the bottom through a single diffuser (1 m diameter at an inclination of 45º) (Abdelmalek et al., 2017).

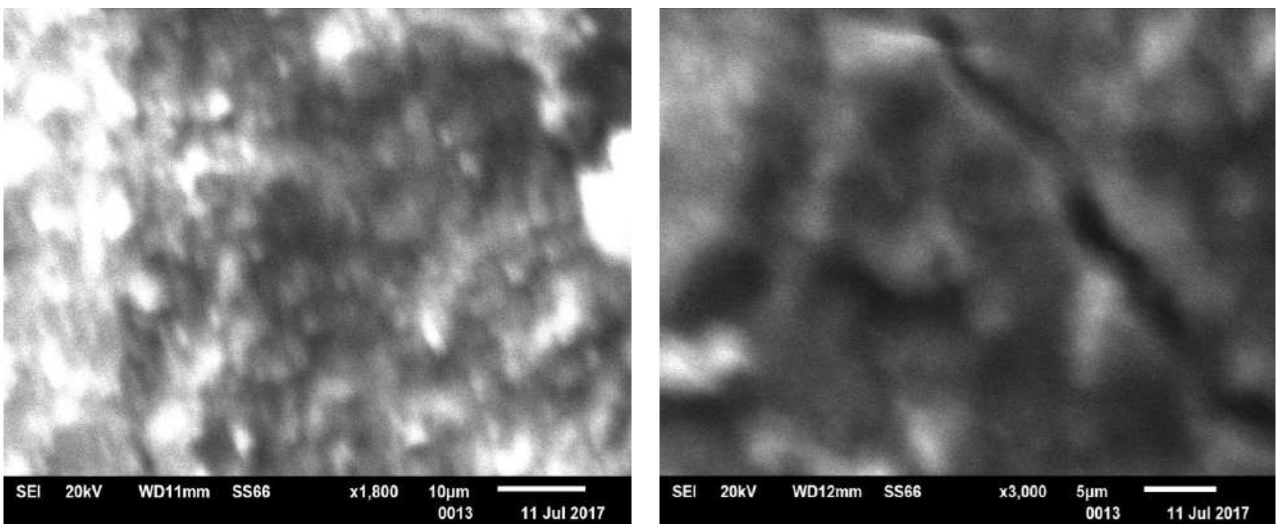
The fouled spiral wound RO membrane element

The fouled RO membrane element (HYDRANAUTICS SWC 5) serial number: A1497030 selected for the autopsy study had been in service for nearly 2 years in a water treatment facility operated by Benisaf Water Company of Ain Temouchent in the Ouest of Algeria. The RO desalination plant was integrated into the water treatment facility in response to the increased salinity of sea water in the region. The plant was capable of producing 200000 m3/day of permeate and included a concentrate recycle stream to improve recovery up to 45%. A maleic acid-based antiscalant was used in the RO operation. Prior to the RO treatment, the raw water from catchments in the Grampians Ranges and stored in open reservoirs had undergone a pre-treatment process including coagulation (iron chloride), pH correction, and cartridge filtration using 5 and 1 mm pore size filters. The filtered water had a pH of 7.18 and a turbidity of 0.08 NTU. Chemical



A B C

Fig. 3: Optical images of the membrane surface (b) in the vicinity and (c) in site of the feed spacer



A B

Fig. 4: SEM images of the membrane surface

analysis of the filtered water was carried out and the results are presented in Table 2.

Atomic absorption spectrometry (AAS)

Atomic absorption spectrometry (AAS) is an analytical technique that measures the concentrations of elements. Atomic absorption is so sensitive that it can measure down to parts per billion of a gram (µg dm^{-3}) in a sample. The technique makes use of light wavelengths specifically absorbed by an element. They correspond to the energies needed to promote electrons from one energy level to another higher energy level. Surface deposits were digested in duplicate with 1:1 HNO_3 on a hotplate (Thuy et al., 2007), prior to analysis by using a Perkin Elmer AAnalyst 100 Laboratory Atomic Absorption Spectrometer. A general scan including Al, Ca, Cu, Fe, K, Mg, Mn, Na, Si,B and Zn elements was carried out. Only the elements detected in trace levels and above are reported in the results.

ATR/FTIR analyses

The Attenuated total reflectance infrared is a technique that can provide valuable information related to the chemical structure of membrane or characterize the fouling layer that may be present on the membrane surface. The material used

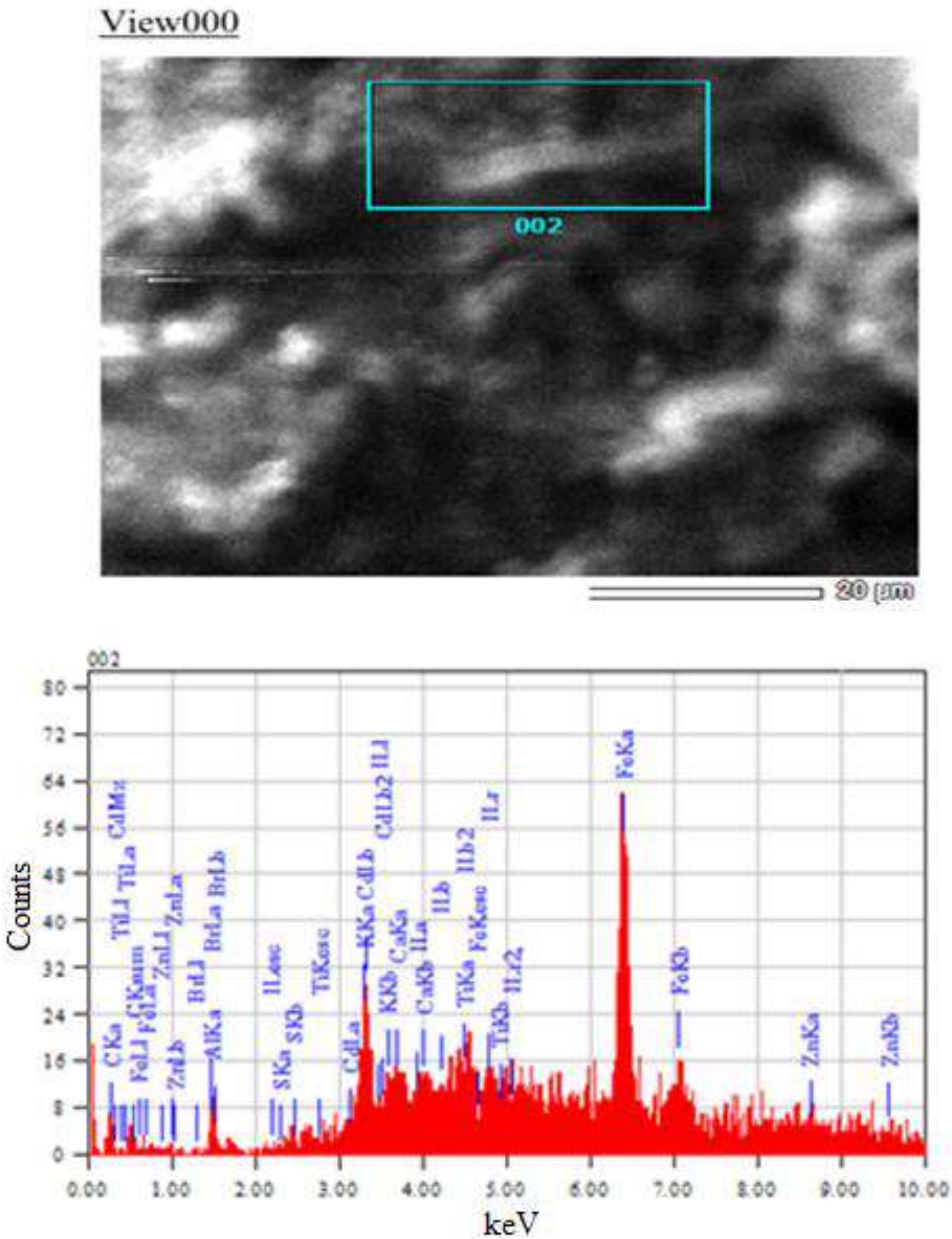


Fig. 5: SEM image and micrograph of the membrane surface – out of the feed spacer

for the study is a spectrometer IR-TF Tensor-27 (Bruker Optik, Ettlingen, France).

The samples of fouling deposits were taken randomly on the used membrane leaflets and dried in an oven at 105 °C during 24 hours before analysis in FTIR. Indeed, water absorbs strongly at 1640 cm^{-1} (Chittur, 1998), corresponding to the vibrations of deformation of the OH bond. Thus it can represent a signal as a parasite for the band. The maximum of absorption is around 1650. Thus drying had solved this problem. A few grains of dried product

Table 1: Overview of tools available for determining the fouling potential of feed water and fouling diagnosis of N F and RO membranes used in water treatment (Vrouwenvelder et al., 2003).

Tools	Fouling diagnosis	Comments
Integral diagnosis (autopsy)	Biofouling inorganic compounds and particles	Diagnosis of foulant in membrane elements
Biofilm monitor and AOC(activity in drinking water distribution networks under oligotrophic conditions)	Biofouling	Prediction and prevention of biofouling by determining the (,growth) potential of water
SOCR Specific Oxygen Consumption rate	Biofouling	Non-destructive method for determining active biomass in Membrane systems
MFI-UF (Modified Fouling Index-Ultrafiltration)	Particulate	Particulate fouling potential of water
ScaleGuard	Scaling	Optimising recovery, acid dose and anti-scalant dose

Table 2. Chemicals used for processing at desalination plants (Abdelmalek et al., 2017).

Products	Symbol	Utilization
Sodium hypochlorite	NaOCl	Disinfection
Ferric chloride	FeCl3	Coagulant
Sodium sulphite	Na2SO3	Remove residual chlorine
Dispersant	–	Anti-scale
Sulphuric acid	H2SO4	pH correction

are dispersed in sodium chloride and a pellet is made. Then the produced pellets are placed as they are on the analysis support.

The acquisition of spectrums is made in the interface solid-air at room temperature (20±2 °C). The spectrums are collected at a resolution of 2.Each spectrum obtained is an average of 32 scans and is recorded under the OPUS software. Finally for each spectrum a baseline is made to keep only the specific signals for the sample to be analyzed.

Optical and electron microscopic analyses

An Olympus OLS 4100 Optical Microscope was used for general observation of the fouled membrane sections. The SEM EDS technique is used to study the membrane surface and to verify the elemental composition of its fouling and detected deposits. Elemental determination with the SEM-EDXA system is based on analysis of X-rays produced via electron beam excitation of a sample area. This technique allows analysis of a sample in selective areas (Nuria et al., 2013). Microstructures of the surface deposits were analyzed using a JEOL 6610 (LA) field emission SEM operating at 20 KV in conjunction with EDS and ZAF method standard less quantitative analysis with 0.5226 as fitting coefficient.

RESULTS AND DISCUSSION

Optical microscopy observations

Figure 3 shows the optical images of the membrane surface at different locations Microscopic observation of samples reveals the importance of fouling deposition in the membrane surface. We notice that the distribution of the fouling charge is unequal on the surface with the presence of brown stains. We can also observe that the zone outside the feed spacer (Figs. 3–b) is more charged than the area below it (Figs. 3–c). The fouling particles act as a barrier and prevent the water from diffusing through the membrane which reduces the performance of the operation. The SEM images show the morphological aspect of the fouling as well as the importance of the thickness of the layers (Fig. 4). The deposits were distributed unevenly across the membrane surface. We also notice that the zone outside the feed spacer is more loaded than the other zone as shown in figure 5. Inspection by SEM EDS confirms the diversity of the fouling composition layer across the surface of the membrane and provides a better understanding of the nature and method of layer development. As shown in Figures 5–6, a typical fouled membrane surface consisted of particulate matter embedded in an apparently amorphous matrix (Thuy et al., 2007). Associated EDS analyses indicate that the particulate matter had relatively high levels of C, O, Al and Si.

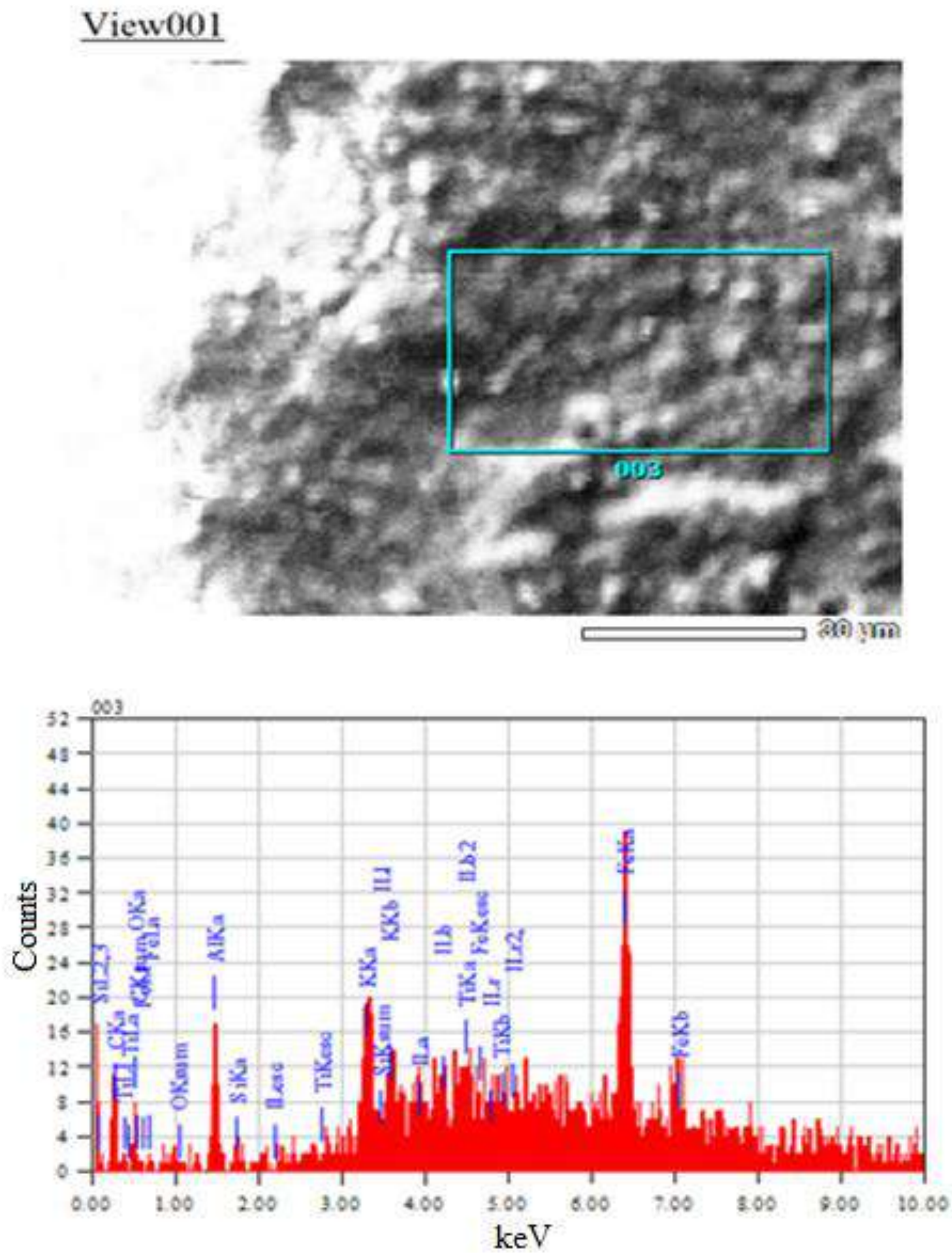


Fig. 6: SEM image and micrograph of the membrane surface – under the feed spacer

The C and O peaks are likely due in part to organic and/or biological materials. The high levels of Al and Si in the particulate matter suggest that it was mainly aluminium silicates which are common foulants in RO operations (Thuy et al., 2007). The use of iron chloride as coagulant prior to the RO treatment could also elevate the Fe concentration in the RO feed which can prove the presence of iron dioxide in the foulants.

ATR/FTIR analyses results

Figure 7 shows the FTIR spectrum obtained for the fouled membrane. A typical FTIR spectrum of the fouled membrane extract is shown in Fig. 7. The main absorption bands were in the vicinity of 1020 cm-1(Si-O and Al-O) of silicate. In addition, the mass around 575 cm^{-1} suggests that the fouling is composed of amorphous structures of phosphates. The band in the vicinity of 613 cm-1 indicates the presence of iron sulfate, 600–800 cm−1 could be due to aromatic compounds, 1400 cm-1 could be due to aliphatic C–H deformation, C–O stretching and O–H deformation of phenol.

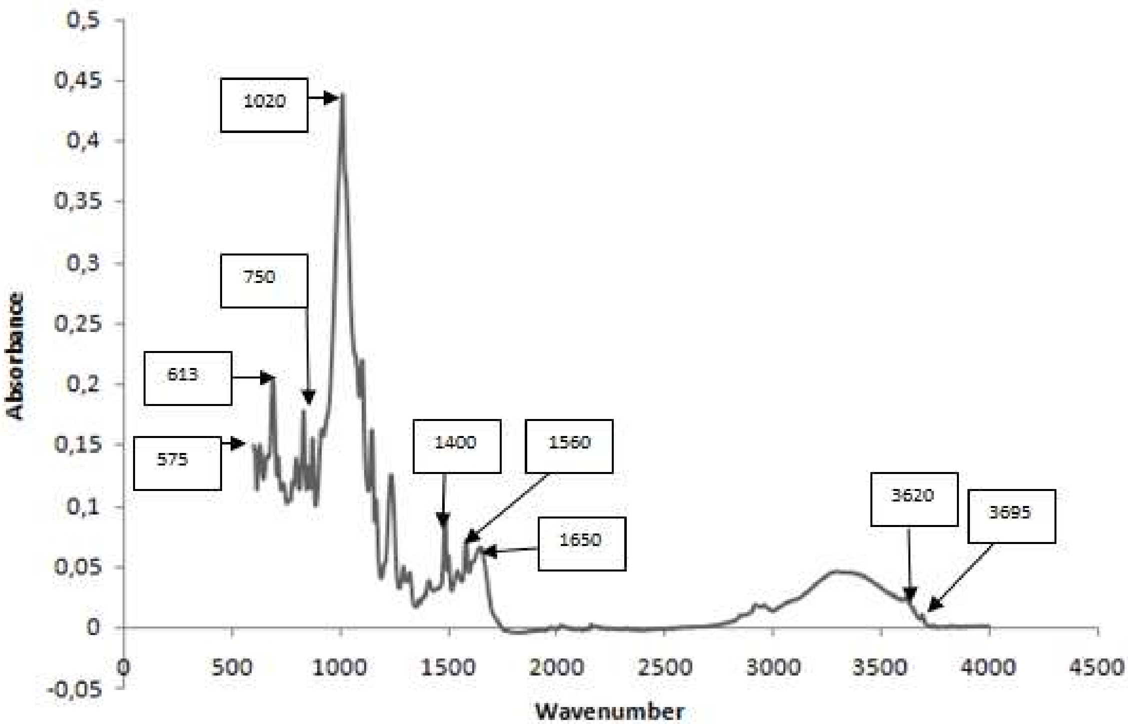


Fig. 7: FTIR spectrum of the fouled membrane extract

Table 3: Results of chemical analysis of filtered water prior to RO treatment process

Parameter	Concentration
Ph	7.18
Conductivity (µS/cm)	46600
salinity	34020
Turbidity (NTU)	0.08
CaCO3 (mg/L)	65.06
CO3-2 (mg/L)	00
HCO3- (mg/L)	79.32
Ca2+ (mg/L)	25.65
Cl2 (mg/L)	0.58
Langelier Saturation Index	0.02

Table 4: Results of SAA analyses of deposits scraped from the fouled membrane surface

Elements	Concentration (ppm)
Al	580
Ca	450.9
Cu	0.0340
Fe	0.2577
K	434.1
Mg	551.7
Si	392.5
Na	186.5
B	1.404
Zn	0.1595
Mn	0.0175

The bans in the range of 1500- 1650 cm^{-1} are due to (amide I and N–H deformation + C–N stretching of amide II, symmetric stretching of COO–). This band may indicate the presence of protein, 3620 cm-1 and 3695cm-1 aluminum silicate.

Atomic absorption spectrometry (AAS) results

Chemical analysis of filtered water prior to RO treatment process are shown in Table 3. The results from SAA analysis are shown in Table 4. The majority of detected elements included Al (580 ppm), Mg (551.7 ppm), Ca (450.9 ppm), K (434.1 ppm) and Si (392.5). Lesser amounts of Fe (257 ppm), and Na (186.7 ppm) were also present. Low levels of B, Cu, Zn and Mn were also identified in the deposits. The presence of negative ions such as bicarbonates in the feed water encourages the precipitation of various compounds. Common deposits found in the fouled membrane are aluminium silicates, metal ions especially Ca^{2+} can form complexes with natural organic matter (NOM). Generally, during the formation of fouling layers on the membrane surface can beg and generate the back diffusion of dissolved salt ions which generates an increase in the concentration of salt ions on the side of the membrane surface. Results revealed that the membrane performcae may change due to organic and inorganic matter in water during osmosis process, which needs to tackle by modifying the membrane with advanced material (Anis et al., 2019; Badruzzaman et al., 2019; Croll et al., 2019; Ghaemi and Khodakarami, 2019; Ghaseminezhad et al., 2019; Joseph and Damodaran, 2019; Liu et al., 2019; Nguyen et al., 2019; Rehman et al., 2019; Shakeri et al., 2019; Tang et al., 2019; Weinman et al., 2019; Zou et al., 2019).

CONCLUSIONS

This paper presents an autopsy report of a spiral wound RO membrane that has been used for two years taken from a seawater desalination plant in western Algeria. This membrane autopsy has been carried out using optical and electron microscopic methods, FTIR and SAA. The membrane surface is observed and analyzed in order to better understand the method of the development and the composition of the fouling layer. The results obtained are consistent and complementary to each other. From the results of the study the following conclusions can be drawn; the extent of fouling was uneven on the membrane surface with the areas below or near the feed spacer being most affected. The fouling in areas further away from the strands was generally less loaded. Inorganic elements found with a high percentage are Fe, Al. The use of iron chlorides as coagulant and maleic acid-based as antiscalant can contribute to the increase in the percentage of these elements in the fouling. The adhesive complex is composed of a particulate colloidal matter (Al, Fe, Si) and organic substance. It can accelerate the formation of fouling. Adsorption of organic and colloidal matter can also play a crucial role in the development of fouling layers.

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