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# NOM characterization by LC-OCD in a SWRO desalination line

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ABSTRACT

The quantification and characterization of natural organic matter (NOM) in seawater reverse osmosis desalination (SWRO) is of great importance to improve our understanding of NOM role and to evaluate the performance of the different units involved in desalination facilities. In this study, we compared the effectiveness of two pre-treatment methods, operated in a pilot facility fed with Mediterranean seawater, in terms of determining NOM composition and NOM removal using liquid chromatography coupled with organic carbon detection (LC-OCD). LC-OCD was also used to assess the SWRO operation. Conventional pre-treatment using a flotation unit followed by dual-media filtration achieved 12% of dissolved organic carbon (DOC) removal. The same level of DOC removal was achieved by coupling flotation and ultrafiltration. In both pre-treatment methods, low-molecular-weight (LMW) neutrals and biopolymers were reduced by 33–40% and 18–19%, respectively. Reverse osmosis (RO) membranes acted as almost a complete barrier for humics, building blocks, and LMW neutrals, which had a rejection rate of over 97%. Despite this, 31 $\mu gC\,L^{-1}$ of LMW acids and 48 $\mu gC\,L^{-1}$ of biopolymers were found in the RO permeate. LMW acids could also be found in the RO permeate due to the affinity these compounds have with the membrane material. However, biopolymers should be more effectively rejected due to their structure and molecular weight (>20 kDa). The hypothesis proposed to explain the presence of biopolymers in permeate is a possible biofilm growth in the permeate side of the membrane module.

*Keywords:* Pre-treatment; SWRO; Seawater desalination; Reverse osmosis; Natural organic matter (NOM); Liquid chromatography with organic carbon detection (LC-OCD)

## 1. Introduction

The availability of freshwater resources is limited, due to overuse and misuse, and is being increasingly depleted at an alarming rate in many regions of the world [1–3]. Seawater and saline aquifers account for 97.5% of the Earth's water resources and thus represent a potential source of water fit for human consumption, as long as it can be treated effectively [4]. Thus, desalination techniques involving seawater reverse osmosis (SWRO) have emerged as important candidates in securing these water supplies [1,3].

SWRO desalination has advanced significantly in the past decade, particularly due to the development of more robust membranes and improved energy

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recovery systems [1], which reduce the final cost of the desalinated water to below 4 kWh $m^{-3}$ [5,6]. Nevertheless, the issue of membrane fouling has not yet been resolved [3,7].

In SWRO desalination plants, the RO membranes are considered to be the backbone of the process while the pre-treatment methods are the key steps [2,8,9]. Pre-treatment is required to remove mineral, particulate, organic, and biological contaminants from seawater that negatively affect the performance of the RO membranes and which would otherwise accumulate onto the membrane surfaces [10–15]. The pre-treatment configurations in SWRO desalination plants depend largely on the characteristics of the feedwater [3]. Conventional pre-treatments involve the process of conditioning raw seawater by coagulation and flocculation, followed by filtration through one or more layers of granular media (e.g. anthracite, sand) [16]. However, currently almost all new desalination plants are equipped with double barrier technology, consisting of an additional microfiltration (MF) or ultrafiltration (UF) system upstream from the RO membranes instead or in combination with the conventional pre-treatment system [15,17–20].

The present study focuses specifically on the effectiveness of size-exclusion liquid chromatography coupled with organic carbon detection (LC-OCD) in order to better characterize the natural organic matter (NOM) fractions and assess the impact of each pre-treatment on the different LC-OCD fractions, as well as on the RO unit.

## 2. Material and methods

### 2.1. Seawater characteristics

The experiments were carried out in a pilot plant located at El Prat de Llobregat (Barcelona, Spain). A summary of raw seawater characteristics—the focus of this study—is detailed in Table 1.

Data retrieved for seawater temperature, pH, and conductivity were in accordance with that published in other studies in the Mediterranean region [21,22]. Compared with other water types, seawater samples have low levels of organic matter (dissolved organic carbon (DOC) = 0.89 mg C $L^{-1}$; $A_{254}$ = 0.74 $m^{-1}$) and of biodegradability [23].

### 2.2. Desalination line

The seawater pre-treatment process used in this study consisted firstly of dissolved air flotation (DAF) using $FeCl_3$ as a coagulant. In DAF units, water is brought into contact with small air bubbles to float light particles and organic substances (algae, fine silt, oil, grease, etc.) contained in seawater [24,25]. These particles are collected at the top of the unit, leaving an effluent with a low turbidity level further downstream. In the present study, the AquaDAF® unit was used, which was developed by Degrémont. The water then flowed along two different treatment pathways, as shown in Fig. 1.

In the first pathway, the seawater is fed through a dual-media filter (DMF) unit of anthracite–sand, which operates in down-flow mode at 14 m $h^{-1}$. The characteristics of the filter media are shown in Table 2. DMF is designed to reduce turbidity and the presence of colloids in the water by physically trapping them [15,26]. In the second pathway, seawater is passed through an out/in UF hollow fiber membrane (Polyvinylidene fluoride; 0.02 µm nominal pore size). The UF permeate is then passed through 5-µm security cartridge filters and fed through an RO module (thin film composite membrane operating at 14 L $m^{-2}$ $h^{-1}$ and 45% of recovery).

Table 1
Characteristics of NW Mediterranean seawater

| Parameter | Unit | Mean value (±SD) |
|---|---|---|
| Temperature | ℃ | 19.2 (±4.2) |
| pH | – | 8.1 (±0.1) |
| Conductivity | mS $cm^{-1}$ | 56.1 (±1.5) |
| Turbidity | NTU | 2.4 (±4.2) |
| TDS | gNaCl $L^{-1}$ | 32.1 (±1.5) |
| $A_{254}$ | $m^{-1}$ | 0.74 (±0.18) |
| DOC | mgC $L^{-1}$ | 0.89 (±0.10) |
| Total bacterial count | cells $mL^{-1}$ | $6.7 \times 10^5$ ($\pm 3.0 \times 10^5$) |
| Algae | cells $mL^{-1}$ | 331 (±307) |

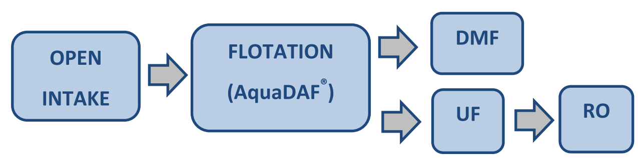


Fig. 1. Flow diagram of the pilot treatment line.

Table 2
Media (height and size) of the DMF

| Media | Height (cm)/size (mm) |
|---|---|
| Anthracite | 55/0.95 |
| Sand | 45/0.28 |

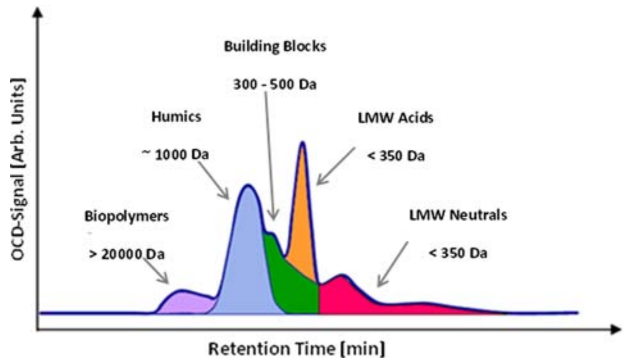


Fig. 2. LC-OCD fractions over the SEC chromatogram with OCD.

### 2.3. Liquid chromatography with organic carbon detection

LC-OCD is a fractionation method based on size-exclusion chromatography coupled with different on-line analyzers such as organic carbon detector (OCD) and UV absorbance at 254 nm. According to the literature, these facilitate the distribution of organic matter over five different fractions named: (1) biopolymers that are composed of polysaccharides and proteins, (2) humics (and fulvics), (3) building blocks that correspond to breakdown products of humics, (4) low-molecular-weight (LMW) organic acids, and (5) LMW neutrals (alcohols, aldehydes, ketones, and amino acids) [27]. Fig. 2 shows the LC-OCD fractions, defined based on the size-exclusion chromatogram and size range. In order to assess the performances of the different treatments, the LC-OCD analysis was performed on raw seawater, DMF filtrate, UF permeate, and on both outlet streams in the RO: permeate and retentate.

## 3. Results

### 3.1. Pre-treatment effectiveness on NOM removal

The results of NOM distribution over treatment line by LC-OCD are shown in Table 3. Seawater was mainly composed of LMW neutrals and humic substances, which represented more than 70% of the total DOC. Seawater was also characterized by a low content of biopolymers (8% of total DOC) that were the more readily biodegradable substances [23]. It also emerged that they may be possible biofouling precursors [28].

The combination of the AquaDAF® + DMF unit affected the LMW neutrals and the biopolymer fraction, eliminating 113 and 35 $\mu gC\,L^{-1}$, respectively, which in turn caused a reduction of these fractions by 18 and 33%, respectively. The combination of AquaDAF® + UF removed 40% of biopolymers and 19% of LMW neutrals. Although UF could act as a barrier for

Table 3
LC-OCD results of seawater, DMF filtrate, and UF permeate and % of DOC removal (% rem) referred to seawater inlet

| LC-OCD fractions | Seawater | DMF filtrate | | UF permeate | |
|---|---|---|---|---|---|
| | ($\mu gC\,L^{-1}$) | ($\mu gC\,L^{-1}$) | (% rem) | ($\mu gC\,L^{-1}$) | (% rem) |
| Biopolymers | 105 ± 5 | 70 ± 4 | 33 | 63 ± 3 | 40 |
| Humics | 361 ± 18 | 361 ± 18 | 0 | 361 ± 18 | 0 |
| Building blocks | 220 ± 11 | 214 ± 11 | 3 | 214 ± 11 | 3 |
| LMW neutrals | 636 ± 32 | 523 ± 26 | 18 | 515 ± 26 | 19 |
| LMW acids | 73 ± 4 | 66 ± 3 | 10 | 69 ± 3 | 5 |
| $DOC_{TOTAL}$ | 1,395 ± 70 | 1,234 ± 62 | 12 | 1,222 ± 61 | 12 |

the biopolymer fraction, 63 $\mu gC\,L^{-1}$ of biopolymers were found in the UF permeate, meaning that the RO feed could contain biopolymers even downstream from the UF membrane. This is highlighted in similar studies [29]. No significant impact was observed on humics, building blocks, or LMW acid fractions.

Both pre-treatment processes achieved overall DOC removals rates of 12%, with the biopolymers and the LMW neutrals being the most effectively removed fractions. Thus, for the raw seawater inlet quality used in this study, the AquaDAF® + DMF and AquaDAF® + UF pre-treatments were equally efficient at removing NOM from seawater. The LC-OCD compositions of seawater and the effluents of both pre-treatments are shown in Fig. 3. These results do not differ significantly with those described by other authors [30], who achieved 13% of overall DOC removal using coagulation-flocculation + DMF and <5% using a MF alone as a pre-treatment. Furthermore, results show that membrane processes such MF or UF remove only a small fraction of the NOM [8,22,31].

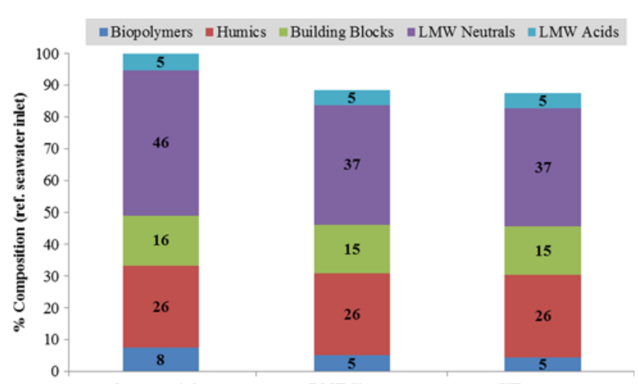


Fig. 3. Seawater inlet, DMF filtrate, and UF permeate composition.

### 3.2. Distribution of NOM in the RO unit

In the RO unit was achieved a rejection rate of 92% for DOC, using the UF permeate as feed water (see Table 4). RO should act as a complete barrier for the humics, building blocks, and LMW neutrals (97–100% rejected); however, poor rejections were observed for LMW acids (55%)—as reported by other authors [32,33]—and biopolymers (24%). In the RO permeate were found 31 and 48 μgC L$^{-1}$ of LMW acids and biopolymers, respectively.

Organic molecules included in the LMW acid fractions may be able to cross the RO membranes due to their affinity with the material composing the RO membrane [34], but biopolymers should be retained, given their high molecular weight (>20 kDa) and macromolecular structure.

Mass balances for all the LC-OCD fractions were performed on the RO unit accordingly to Fig. 4.

Terms of generation, $\Delta_G$, have been considered in the mass balances to explain the results. In an ideal case of 100% rejection of all the LC-OCD fractions by RO and no term of generation, the DOC found in the feed should be found in the retentate. Nevertheless, as shown above, some DOC was also found in the RO permeate. However, even considering the DOC present in permeate and retentate, a term of generation is needed to meet the mass balance in some of the fractions. This may mean some transformation of DOC among fractions, because no generation is detected in the global mass balance.

Table 5 shows the terms of the mass balance starting from 100 L h$^{-1}$ of RO feed and a recovery rate of 45%.

The results highlight that some fractions of the LC-OCD need a significant term of generation in order to satisfy the mass balance. In this sense, $\Delta_G$ obtained for biopolymers and LMW acids were significantly different from zero. The presence of biopolymers in the permeate stream could be associated to a possible membrane damage. However, this hypothesis was rejected because the salt rejection of the RO membrane

Table 4
LC-OCD results of the RO feed, RO permeate, and % DOC rejected (% rej) referred to raw seawater

| LC-OCD fractions | RO feed (μgC L$^{-1}$] | RO permeate (μgC L$^{-1}$) | (% rej) |
|---|---|---|---|
| Biopolymers | 63 ± 3 | 48 ± 2 | 24 |
| Humics | 361 ± 18 | 1 ± 1 | 100 |
| Building blocks | 214 ± 11 | 3 ± 1 | 99 |
| LMW neutrals | 515 ± 26 | 14 ± 1 | 97 |
| LMW acids | 69 ± 3 | 31 ± 2 | 55 |
| $DOC_{TOTAL}$ | 1,222 ± 61 | 97 ± 5 | 92 |

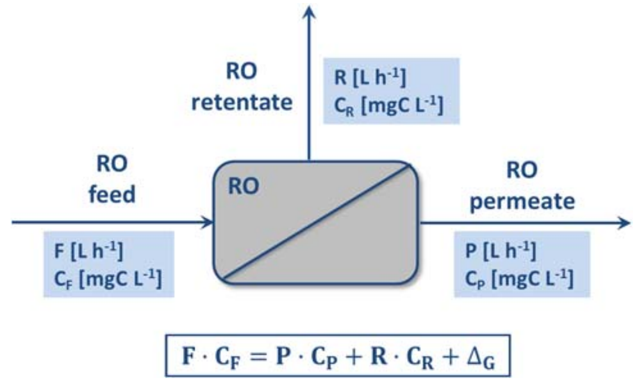


Fig. 4. RO unit operation and mass balance.

Table 5
RO mass balance (feed = 100 L h$^{-1}$; recovery = 45%)

| LC-OCD fractions | RO feed $F \cdot C_F$ (mgC h$^{-1}$) | RO permeate $P \cdot C_P$ (mgC h$^{-1}$) | RO retentate $R \cdot C_R$ (mgC h$^{-1}$) | Generation $\lvert\Delta_G\rvert$ (mgC h$^{-1}$) |
|---|---|---|---|---|
| Biopolymers | 6.3 ± 0.3 | 2.2 ± 0.1 | 6.7 ± 0.3 | 2.5 ± 0.8 |
| Humics | 36.1 ± 1.8 | 0.0 ± 0.1 | 39.3 ± 2.0 | 3.3 ± 3.8 |
| Building blocks | 21.4 ± 1.1 | 0.1 ± 0.1 | 19.4 ± 1.0 | 1.9 ± 2.1 |
| LMW neutrals | 51.5 ± 2.6 | 0.6 ± 0.1 | 49.6 ± 2.5 | 1.3 ± 5.1 |
| LMW acids | 6.9 ± 0.3 | 1.4 ± 0.1 | 7.1 ± 0.4 | 1.6 ± 0.8 |
| Total | 122 ± 6.1 | 4 ± 0.2 | 122 ± 6.1 | 4 ± 12.4 |

(99.9% without taking into account boron), which was monitored during all experimental period, underwent no change. The salt rejection level showed a normal operation of the membrane. It is important to note that values of $\Delta_G$ obtained for humics, building blocks, and LMW neutrals were not significantly different from zero. However, this does not mean that it can actually be slightly negative. Probably, this is the case because the generation term in the overall balance is not significantly different from zero. The generation of biopolymers could be linked with the growth of microorganisms and therefore the release of extracellular polymeric substances in the permeate side of the membrane module.

Nevertheless, it is important to consider that the fractions that increase slightly in the RO module are those with a lower contribution of DOC (10%) to the total DOC in the RO feed. Thus, more research is required to establish the LC-OCD composition in each RO stream and to confirm whether biological activity is taking place.

## 4. Conclusions

Seawater contains low levels of NOM, measured as DOC. NOM has low aromaticity despite the fact that humics (and building blocks) account for more than 40% of the total DOC. Two conventional pre-treatment processes, one using AquaDAF® + DMF, and another using AquaDAF® + UF, both achieved a DOC removal rate of 12%. The most effectively removed fractions were biopolymers (33–40%) and LMW neutrals (18–19%). Nevertheless, 63 $\mu$gC $L^{-1}$ of biopolymers were still found in the RO feed.

The RO membranes were capable of rejecting almost all (97–100%) the humics, building blocks, and LMW neutrals. However, poor rejections were achieved for the biopolymers and LMW acids (24 and 55%, respectively). Therefore, 48 $\mu$gC $L^{-1}$ of biopolymers were found in the RO permeate. These results highlight the possibility that biomass growth may occur in the permeate side of the membrane module.

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