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Autopsy of ultrafiltration membranes for drinking-water production with in-line coagulation and ozonation pre-treatments

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ABSTRACT

Membrane autopsies were performed after a pilot-scale study with ultrafiltration (UF) membranes for drinking-water production from humic-rich influents where $FeCl_3$ coagulation–flocculation (CF) and ozonation (OZ) were used as pre-treatments. Membrane fragments and extracted residues were analysed to identify the foulants and evaluate the condition of the respective modules used. The amount of deposits on the membrane surface proved higher for CF-UF system, although microbial activity was more remarkable in OZ-UF, as significantly more SMP was detected. Bacterial growth was confirmed by the spongy and fully developed biofilm found for both systems with scanning electron microscopy (SEM). XRF showed Fe content to be predominant for the CF-UF membrane, while elements such as Al, Si or Ca were also found, though these were not as abundant as in the OZ-UF system. Cross-section analyses with SEM/energy dispersive spectrometer (EDS) revealed the presence of Fe combined with P inside the membrane pores for CF-UF fragments. By contrast, OZ-UF fragments revealed the presence of aluminosilicates with no visible effect on membrane pores. Finally, ATR-FTIR profiles showed that neither the chlorine used in the chemical cleaning nor the pre-treatments had damaged the chemical structure of the membranes. However, the main absorption bands were masked for OZ-UF in comparison to CF-UF system, indicating that fouling was more severe after the application of ozone.

Keywords: Drinking water; Ultrafiltration membrane autopsy; Biofilm; Foulants; Coagulation–flocculation; Ozonation

1. Introduction

Membrane technology is applied to drinking-water production worldwide. However, as the membranes are porous materials, the accumulation of aquatic substances on and/or inside the membrane matrix may cause permeability loss [1], which can be reversible or irreversible. This phenomenon, known as fouling, mainly reduces the permeate flux or raises the operating pressure, in addition to progressively deteriorating the membrane. Consequently, energy consumption rises and membrane modules need replacement, raising operational and maintenance costs [2].

Given that the nature and extent of fouling are strongly influenced by raw-water composition, membrane characteristics and operating conditions [3], these factors are relevant in devising strategies for

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fouling control. Research on materials [4], surface properties [5], configurations and hydrodynamics [6] seeks to make the modules more fouling resistant in the membrane-manufacturing process. On the other hand, considering the great influence of the nature of the foulants, the feed water is commonly pre-treated. Optimization of the operating variables and application of backwashing, aeration and chemical cleanings are also frequent, having proved effective for fouling control [1]. However, these operations often alter membrane selectivity, surface morphology and pore structure [7], thereby shortening the membrane's service life. Thus, it is essential to quantify the effects that the above-mentioned practices exert on the membranes so as to find a solution that facilitates the filtration process without compromising membrane integrity.

Together with the physicochemical analysis of the raw water, membrane autopsy is a valuable technique to determine the causes of fouling. In fact, although it is a destructive technique, autopsy is considered the only reliable method for determining the true identity of the foulant with confidence and, once the causes have been identified, recurrence of the problem can often be prevented [8].

The authors of the present study have taken part in a project supported by the Spanish Ministry of Science and Innovation, in which real-scale ultrafiltration (UF) membranes were tested for drinking-water production from low-quality influents. A spiral-wound membrane configuration was chosen for having high surface and packing density [9] as well as being compatible with aeration [10]. Direct UF was tested first, concluding that single-treatment UF was not recommendable when the quality of the influent was low [11]. The poor dissolved organic carbon removal achieved, together with the quick growth of trans-membrane pressure (TMP), obliged subsequent research to include the application of pre-treatments. Thus, different processes were applied in order to compare the results of respective membranes performance and thereby determine the most effective option for that particular water quality.

Of the possible pre-treatments available, coagulation–flocculation was chosen for being a useful way to reduce organic matter content and control fouling, as several studies have reported [12–15]. Pre-oxidation, another traditional process employed for water purification, was selected so as to compare the efficiency of two different action mechanisms for the same influent water quality. In particular, ozone was chosen for being a powerful oxidant less commonly applied with polymeric membranes [16] as well as for its capacity to break double bonds and aromatic cycles frequently present in natural organic matter (NOM) [17]. Both pre-treatments were compared in terms of fouling generation and permeate quality throughout pilot-scale testing. However, only the increase in TMP was quantified during the operation but not the fouling itself. It was necessary to identify the foulants and evaluate their possible influence on the membrane modules. Thus, after each experimental period, membrane autopsies were performed to assess the condition of the different modules used, for which extracted residue and membrane fragments were analysed.

The present study focuses on the results of the autopsies conducted for in-line coagulation and ozonation (OZ) pre-treatments, the results being compared to each other as well as to a virgin membrane. The specific objective of this work is to determine the way in which the pre-treatments applied influence membrane fouling and ageing, attending to the chemical structure, surface condition, and pore clogging of the modules used.

2. Materials and methods

2.1. Membrane characterization

The membrane modules autopsied were spiral-wound SpiraSep 960 by TriSep Corporation (Goleta, California, USA); made of polyvinyliden fluoride (PVDF), with 0.03 µm effective pore size, (500 kDa MWCO) and 20.9 m^2 filtration area. The contact angle was 45–50°, corresponding to hydrophobic membrane elements.

Before being put into service the modules were preserved in 1% (m/m) $NaHSO_3$ solution. The modules were operated submerged and vacuum-driven. Maximum TMP recommended by the supplier was −0.7 bar.

2.2. Influent-water quality

The influent used was synthetic humic-rich water with a natural matrix, i.e. surface water from Canales reservoir (Granada, Spain). A mixture of humic/fulvic acids (Carbotecnia Húmico 10–10 solution, 10% fulvic extract, 10% humic extract, Carbotecnia S.L., Spain) was added to the matrix water to reach an average DOC concentration of 7.5 ± 1 mg/L, i.e. medium- to low-quality influent, according to Hepplewhite et al. [18]. The molecular weight (MW) of the humic/fulvic acids was determined by fractioning them using centrifugal UF methods described by Rojas-Serrano et al. [11]. Table 1 shows the physicochemical characteristics of the influent water.

2.3. Overview of the pilot-scale experiments prior to the membrane-module autopsies

The pilot-scale plant used in the preceding study was located in Parque de las Ciencias (Granada, Spain). The facility was composed basically of an UF module equipped for applying in-line coagulation–flocculation (CF-UF) and ozonation (OZ-UF) pre-treatments.

The membrane working conditions consisted of constant flux (48 LMH) production periods alternating with backwashing phases. Aeration was continuous, with a flow rate equal to 18 Nm^3/h. The coagulant dose applied was 50 mg $FeCl_3/L$, while the ozone concentration was 25 g O_3/Nm^3, equivalent to a transferred ozone dose of 3.7 mg O_3/L on average. The timetable was 6 d operating/1 d off with 240-min long assays. The total operating time for each membrane module was approximately 550 h.

The cleaning process applied for the different operating periods was the same. Cleaning in place (CIP) was carried out on a weekly basis. During CIP, the membrane tank was emptied and filled with permeate with 50 mg NaClO/L doses. Once the membrane tank was full, the permeate-NaClO mixture was recycled to the permeate tank for 20 min. Then, the membrane tank was emptied and filled with tap water, the membrane module remaining soaked with an extra dose of NaClO until the next operating period.

2.4. Autopsy procedure

After each operational period, the corresponding membrane module was immediately removed and replaced. Then, autopsy was conducted. Each membrane was dissected according to the following protocol: First, the protective casing was cut and removed to unroll the membrane and separate sheets and feed spacers for visual inspection. Then, two complete sheets taken at random were fragmented into 5 cm^2 pieces, each sheet being approximately 4,250 cm^2 usable surface. Three fragments from each sheet were separated and stored under dry conditions, whereas other three were preserved in glutaraldehyde (3%) in PBS (130 mM NaCl and 10 mM Na_2HPO_4/NaH_2PO_4, pH 7). The rest of the pieces were preliminarily washed with distilled water (MilliQ, Millipore Corporation) and then immersed in new distilled water to be subjected to 5 ultrasound pulses of 20 min per pulse [19] for a fuller separation of the deposits. After the cleaning, three fragments per sheet were removed and preserved under dry conditions whereas another three were preserved in glutaraldehyde (3%) in PBS. All the distilled water used for membrane washing was kept separately for further analyses of the residue (for simplicity, the term “liquid waste” will be used to refer to the water-residue mixture). Lastly, the membrane fragments and the residue were analysed separately.

Table 1
Physicochemical characteristics of the influent water

Description	Influent water
SS (mg/L)	–
Turbidity (NTU)	5.4 ± 0.2
DOC (mg/L)	7.6 ± 0.2
UVA_{254} (m^{-1})	18.5 ± 0.1
SUVA (mg/mL)	2.5 ± 0.1
$Colour_{436}$ (m^{-1})	3.0 ± 0.1
Total aerobic bacteria (22˚C) (CFU/mL)	<10
pH	8.2 ± 0.0

2.4.1. Residue characterization

The liquid waste resulting from washing the membrane fragments was analysed in the following way:

2.4.1.1. Gravimetric analyses and hydrophobicity. Suspended solids (SS) were determined after filtering three 50 mL samples through glass-fibre filters (Millipore AP4004705). Loss on ignition at 105˚C (LOI) enabled the quantification of volatile and fixed fractions (SS_V, SS_F) [20].

Relative hydrophobicity of the residue and humic substances was determined according to Liu et al. [21].

2.4.1.2. Characterization of the organic fraction: carbohydrates, proteins and humic acids. Soluble microbial products (SMP) and exopolysaccharides (EPS) were extracted by centrifuging 10 mL samples at 5,000 gX for 10 min. As a result, respective pellets and supernatants were separated. The supernatants were then passed through a 0.22-μm filter (Millipore GSWG047S6) with the resulting filtrates containing SMP. The pellets were resuspended in Milli-Q water. Then, 30 mL of ethanol (−20˚C) were added and each sample was kept at 4˚C for 24 h. Finally, the samples were centrifuged at 15,000 gX for one h and the supernatants were filtered through 0.22 μm, the filtrates containing EPS.

Carbohydrates, proteins and humic acids were analysed in both extracted EPS and SMP. The protein content was determined by the spectrophotometric method proposed by Frølund et al. [22] with bovine serum albumin as the standard (Sigma Aldrich). The carbohydrate content was analysed with the phenol-sulphuric acid spectrophotometric method introduced by DuBois et al. [23], using D-glucose (Panreac) as the standard. Finally, humic acids were analysed according to Frølund et al. [22], using humic acids (Sigma Aldrich) as the standard. Each determination was replicated three times to establish the average values for each parameter.

2.4.1.3. X-ray fluorescence (XRF) and elemental analyses (EAN). A variable volume of liquid waste (minimum 1 L) was completely dried at 105˚C and calcined at 550˚C. The resulting solid residue was milled before the aforementioned analyses were performed. A wavelength dispersive sequential spectrometer with an X-ray generator (Philips Magix Pro PX-2440) was used for the XRF analyses. Additionally, an elemental analysis was performed using a FISSON CARLO ERBA EA 1108 analyser equipped with a TCD detection system for C–N–H and for sulphur traces.

2.4.2. Membrane analyses

Both cleaned and unwashed membrane fragments were analysed through different techniques. Additionally, a new membrane sheet was available. Thus, all the analyses described within this section were also performed for new membrane fragments, so that the condition of the membrane used could be compared to that of the new one.

2.4.2.1. Zeta potential. Zeta potential of the cleaned membrane-fragment surface was determined with Zeta CAD (CAD Inst., France) via tangential streaming potential measurement. The difference in potential was measured alternatively in two-flow with a continuous increase of pressure from 0 to 400 mbar (18 ± 2˚C). The measurements were performed with 5 mM KCl solution (0.7 mS/cm conductivity and 5.43 pH on average).

2.4.2.2. Scanning electron microscopy (SEM)/energy dispersive spectrometer (EDS). Membrane fragments preserved in glutaraldehyde (3%) in PBS were cut into smaller pieces (1 cm^2) and analysed separately. Both the top surface and the cross section of membrane pieces were visualized with high-resolution variable pressure field-emission scanning electron microscope (VPSEM, Zeiss SUPRA40VP) with an X-ray dispersive energy detector (X-Max 50 mm) for chemical microanalysis. The fragments were previously dehydrated using critical-point drying (POLARON CPD 7501) and then placed on double-sided carbon tape. For the cross-section analyses, the samples were embedded in a polymeric resin with their cross sections oriented perpendicular to the electron beam. After the resin hardened, the samples were polished with various grades of diamond paste using an oil-based lubricant prior to the analyses.

2.4.2.3. ATR-FTIR. Both the cleaned and the unwashed membrane fragments were dried prior to the analyses with attenuated total radiation-Fourier transform infrared spectroscopy (ATR-FTIR). JASCO 6200, software SPECTRA MANAGER 2.0. FTIR worked in the mid-infrared range (600–4,000 cm^{-1}) with 2 cm^{-1} and 100 scan resolution.

3. Results and discussion

3.1. Influent organic matter characterization

The fractionation of the humic acids in the influent revealed that 7% were more than 0.22 μm sized, substantially above the average membrane pore size. This implies that although this fraction can be easily removed by UF membranes without pre-treatment, they significantly increase organic fouling after low-pressure filtration. The consequence of the latter was the formation of a deposit layer that increased TMP during permeate production. However, given the nature of these compounds, this layer allowed the filtration process to continue, somehow preventing the pores from blocking [1]. By contrast, the MW of most of the filterable fraction (<0.22 μm) was below the membrane module cut-off, with 24% being below 3 kDa (Fig. 1). Particles measuring close to the membrane pore size are more prone to causing pore blockage or constriction, resulting in more significant losses of membrane permeability [1].

On the other hand, the relative hydrophobicity of the humic substances was 56%, proving hydrophobic [24]. These substances have a complex molecular structure, with aromatic groups and great adsorptive properties, together with a negative charge density due to acidic functional groups. Given the hydrophobic characteristics of the membrane, a high adsorption of humic/fulvic substances was expected, although their negative charge density could also favour electrostatic exclusion [24]. However, the relative hydrophobicity reached for the lowest fractions of the humic acids used was only 7%, which made it difficult to predict their influence on a hydrophobic membrane.

3.2. Membrane visual inspection

The removal of the protective casing of the membrane subject to CF-UF process revealed an orange sludge on the edges and on the top cross section of

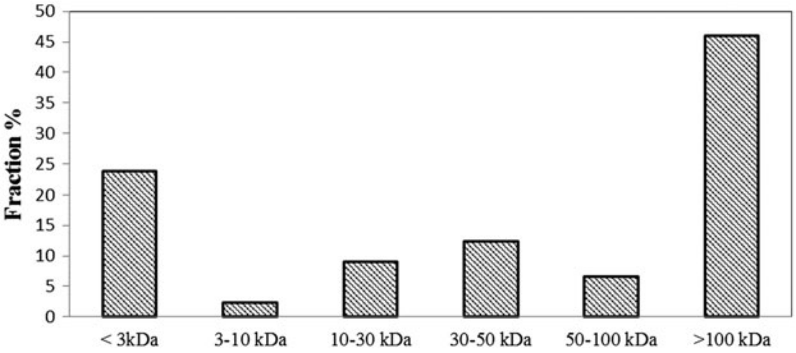

Fig. 1. Molecular-weight distribution for the humic/fulvic acids used in the influent.

the element that could be manually removed. In addition, both the top and bottom sections of the membrane presented several incrustations. Membrane unrolling showed the imprints of the feed spacers on the filtering side of each sheet, in opposition to the spacer-free surface covered by deposits. This phenomenon has been mentioned by other authors [19,25]. Most of the surface was covered with the same orange-coloured deposits. However, no biofilm was visible to the naked eye.

Regarding the module used during OZ-UF, the visual inspection was analogous, as the same marks caused by the feed spacers were observed, although the sludge found on the sheet surface was brownish and substantially less abundant than in the previous case. No signs of damage were noted for any membrane, and the permeate side seemed to be unaffected.

3.3. Residue characterization

LOI confirmed that the concentration of solids on the membrane surface was considerably higher for the element used for CF-UF experiments than that for OZ-UF. While 23.2 g/m^2 were removed as SS from the surface of the CF-UF module, only 7.3 g/m^2 were released from the OZ-UF module. Moreover, the volatile content of the SS was 77% for CF-UF membrane, markedly above OZ-UF figure, 54.7%, despite that the same quality of feed water had been used. These results are consistent with the effluent quality achieved during the pre-coagulation period, when the highest DOC rejection was reached.

EAN of the dry residue after CF-UF resulted in nearly 9% C, 3% H, and less than 1% N, with an insignificant presence of S. The same analysis for OZ-UF resulted in 30% C, 5.6% H, 3% N and again an insignificant percentage of S. According to the TOC determination, more than 99% of the C determined by the EAN was organic. Only 1% inorganic carbon content indicates that the presence of carbonate precipitates on the membrane surface can be disregarded. A major fraction of the organic carbon resulted from microbial activity products, such as SMP and EPS, which were extracted and quantified (Table 2). The EPS content for both membranes was similar; although given the different amount of deposits extracted, the percentages were different as well, with 3.2% for CF-UF and 11.8% for OZ-UF. The situation was analogous for SMP, although the differences between the two systems were more remarkable. Additionally, the composition of the EPS was similar for the two cases analysed, proteins and carbohydrates being predominant. For SMP, humic substances were the most significant. The presence of SMP and EPS in the deposits extracted for the two membranes revealed biofilm development in both cases, although this was more significant after pre-ozonation. The reason for this could be organic-matter fragmentation after chemical oxidation [26] given that the application of ozone may have increased bacterial food source [27], resulting in greater development of bacteria and thus of biofilm.

Relative hydrophobicity analyses of the deposits indicated a certain degree of hydrophilicity, with values of 15.5 and 23.9% for CF-UF and OZ-UF, respectively. The presence of polysaccharides and proteins resulting from biofilm development [24], and the retention of the most hydrophilic fractions of the influent, explain these values.

XRF analyses showed the percentage of the major chemical elements found in the residue as oxides (Table 3). The concentration of each element per square meter of membrane surface was calculated taking into account the concentration of total and volatile SS. The results showed significant differences in the composition of the main inorganic deposits. For the CF-UF membrane, Fe content was predominant,

Table 2
Proteins, carbohydrates and humic acids in EPS/SMP in liquid waste

	CF pre-treatment		OZ pre-treatment	
	EPS	SMP	EPS	SMP
Proteins (mg/m^2)	289.69	34.73	482.51	236.75
Carbohydrates (mg/m^2)	282.92	16.56	328.34	161.89
AAHH (mg/m^2)	161.32	58.82	51.14	957.81
Total (mg/m^2) (%)	733.93 (3.2)	110.11 (0.5)	861.99 (11.8)	1356.45 (18.6)

Table 3
XRF analyses

	Membrane (g/m^2)		Percentage of deposit (SS)	
	CF-UF membrane	OZ-UF membrane	CF-UF membrane	OZ-UF membrane
Si	0.099	0.664	0.42	9.10
Al	0.039	0.539	0.17	7.38
Fe	3.240	0.244	13.97	3.35
Mn	0.001	0.001	0.01	0.02
Mg	0.003	0.071	0.01	0.97
Ca	0.020	0.174	0.08	2.38
Na	nd	0.008	0.00	0.11
K	0.018	0.043	0.08	0.58
Ti	0.153	0.014	0.66	0.19
P	0.052	0.026	0.22	0.36

representing almost 14% of the deposits on the membrane surface. The use of $FeCl_3$ in coagulation–flocculation processes preceding membrane filtration results in a high Fe content in membrane surface deposits [28], especially when the membrane is a direct barrier for the retention of flocs. This fact explains the differences in the Fe content for each membrane. However, despite that no coagulant was used, the presence of Fe was noticeable in the membrane subject to pre-ozonation, Fe reaching 3.3%.

The deposits from the OZ-UF membrane included other elements such as Al, Si or Ca, with significant concentrations of the same order of magnitude as Fe. These elements were also present in the deposits extracted from the surface of the CF-UF membrane but in lower amounts. Concentrations of Si, Al and Fe and, to a lesser extent, Ca, Mg or K, indicate the presence of aluminosilicates, very common in different types of water [19,29,30]. The origin of some of the cations found for both membrane deposits could certainly be the presence of aluminosilicates in the influent water. However, given that the influent water was the same, there must be a particular influence of OZ, since the accumulation of these elements in the extracted residue was much more significant for the membrane used for OZ-UF than for that used for CF-UF. Previous works [27,31] have also revealed a major presence of Fe, Al or Ca cations in the deposits extracted from nanofiltration membranes subjected to OZ than in those resulting from other processes for the same influent-water quality. Considering that oxidation can break some of the bonds between humic molecules, boosting their adsorption capacity and enabling their association to metallic polymers or hydroxides [32], it seems probable that oxidized humic acids and metal hydroxides were partially retained by the membrane, accounting for the higher presence of metallic elements in the OZ-UF membrane deposits.

3.4. Membrane zeta potential

The zeta potential for the virgin membrane analysed was −13.3 mV. According to Phuntsho et al. [33], the zeta potential of fouled membranes is generally less negative than for virgin membranes. Nevertheless, in both cases, this value was more negative for the fouled membranes, −19.6 and −27.1 mV for CF-UF and OZ-UF, respectively. Jermann et al. [34] reported that humic acid adsorption onto the membrane surface shifts the membrane zeta potential to more negative values, and therefore, this behaviour can be considered normal given the humic-rich feed water used. On the other hand, the addition of a coagulant reduces the foulant specimen's negative net charge, explaining why the zeta potential in the element subjected to coagulation–flocculation pre-treatment was less negative than after pre-ozonation.

The fact that the zeta potential was more negative than for the new membrane indicated hydrophilicity loss [35], which could have prevented deposit accumulation on the membrane surface since the net repulsive forces between the membrane surface and the foulant specimens would have increased, resulting in lower electrostatic attraction [33]. However, molecular-weight reduction and increased hydrophilicity are also consequences of OZ [17,26], and they appear to have exerted a more significant effect on the higher adsorption of humic substances on the OZ-UF membrane surface than diminished zeta potential.

3.5. Scanning Electron Microscopy/Energy Dispersive Spectrometer

Fig. 2 shows SEM micrographs of the membrane fragments used in the study at different magnifications. A layer of deposits covered the entire surface of both membranes, except the area occupied by the spacer (first picture in B column), which was considerably cleaner. Particles of different sizes were visible, all of which

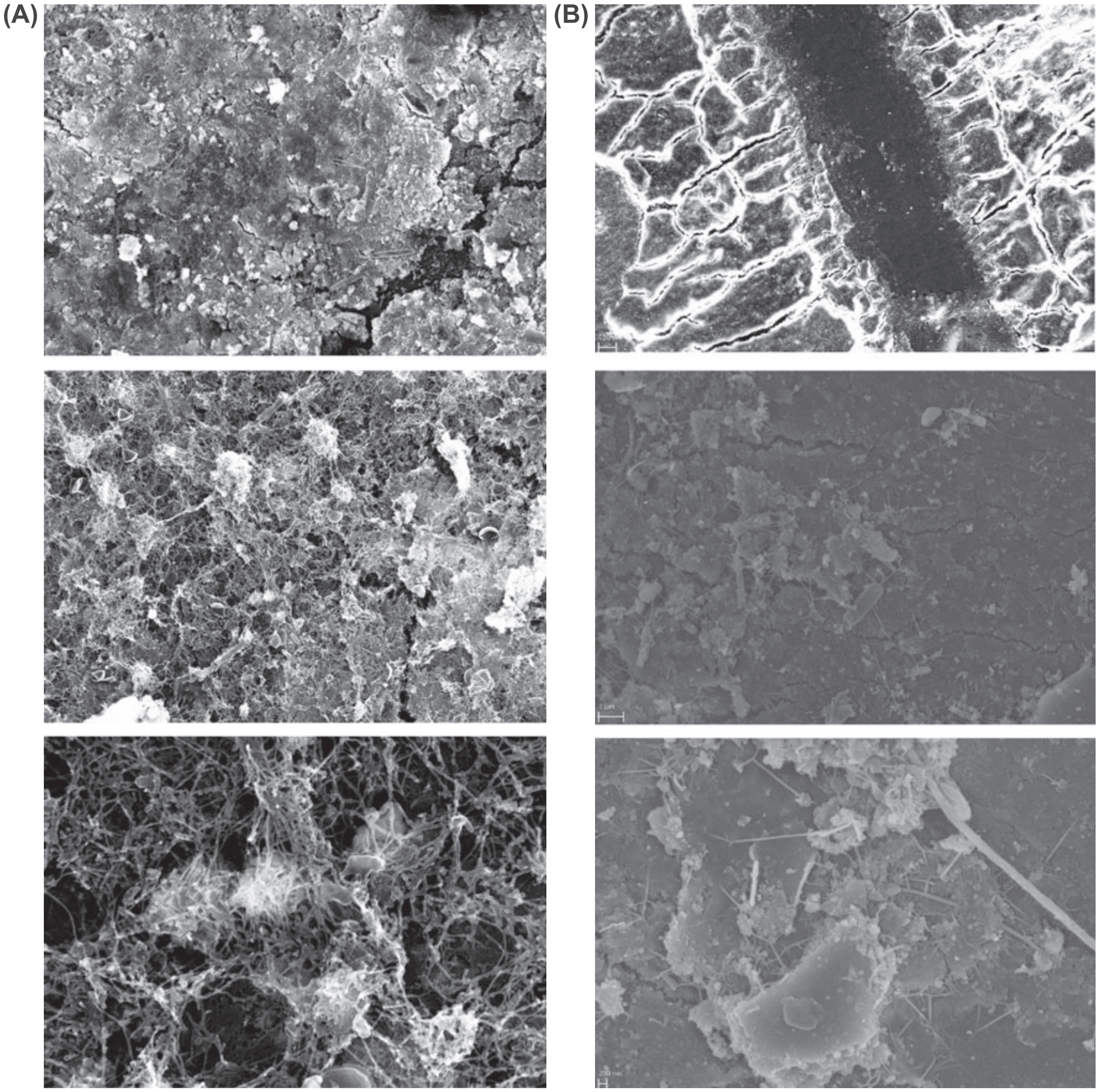

Fig. 2. SEM micrographs of fouled membranes for CF-UF system (A) and OZ-UF system (B). Magnification increases downwards (100–0.2 μm).

were amorphous, with no crystalline particles being found. The absence of a solid/liquid separation system prior to the membrane caused the accumulation of particles of different sizes and nature, this increasing the risk of membrane-surface damage by erosion, roughness, scratches or cuts [19]. However, despite the presence of large particles, no cracks or abrasion were detected on the membrane surface.

When the surface was magnified, a thick biofilm layer became visible in both membranes. The biofilm was spongy and fully developed, indicating that it did not correspond to an early stage. In addition, bacteria of different morphologies were abundant, *Bacilli* and cocci being the most common although *Spirilla* and *Spirochaetes* also appeared.

The lack of disinfection before a coagulation–flocculation process prior to UF causes living bacteria to accumulate on the membrane surface, which, together with many organic substances on the surface, can result in biofilm formation [1]. One of the most common mechanisms to control biofilm formation for drinking-water-production membranes is periodical chemical cleaning with biocides such as chlorine [16]. In particular, PVDF membranes are resistant to high chlorine concentration at pH of 12, and therefore, weekly cleaning with NaClO was the option chosen for both CF and OZ pre-treatments. However, sometimes biofilms can develop even after the application of continuous or shock chlorination [36]. The influent being humic-rich and the use of a coagulant caused quick deposition of organic substances, acting as a protective barrier for the biofilm formed on the surface of the CF-UF membrane. On the other hand, despite the continuous application of ozone and the chemical cleanings, the corresponding OZ-UF membrane also presented mature biofilm. Not only was there biofilm but also it was more significant than for the CF-UF system even though more deposits had been removed from the CF-UF fragments. These results confirm that the use of ozone increased humic acid transformation and fragmentation, making the deposits more easily adsorbed onto the biofilm at the same time as they became more metabolisable for the bacteria [17]. The development of the biofilm was the consequence of the nutrients being more available.

The cross-section analysis (Fig. 3) showed the fouling layer on the membrane surface to be thickness variable, depending on the fragments. The thickness for the fragments analysed from CF-UF averaged around 250 μm (Fig. 3(a)), whereas for the fragments from OZ-UF measured around 175 μm (Fig. 3(b)). Apparently, two different layers were found from the standpoint of chemical composition for both membranes. A thin layer with a thickness between 5 and 10 μm was visible directly on the surface, followed by a second one that was less dense. These results agree with the formation of a compact cake after coagulation–flocculation [37,38] responsible for easing the filtration process, as demonstrated by the lower fouling rates that had been achieved for this pre-treatment during pilot testing. For the membrane from OZ-UF, a cake was visible as well, with apparently a more heterogeneous composition.

EDS microanalysis revealed the composition of a new membrane surface (C, O and F) and confirmed C, O, Fe, Al, Si, P and Ca as major fouling constituents for the membranes analysed in the study. The main difference between the two pre-treatments analysed was the presence of Fe, in accordance with the XRF results. Fe was consistently detected in CF-UF membranes but only occasionally in OZ-UF. In fact, Fe was the dominant element in the residue for the CF-UF membrane fragments. Other elements, such as Ca or P, were also abundant in this membrane, although less significant. In addition, Al and Si comprised the resi-

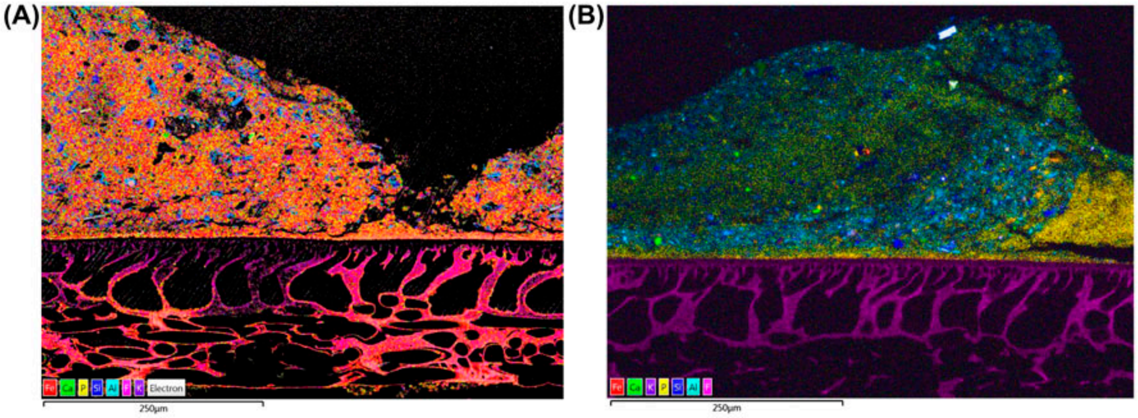

Fig. 3. SEM/EDS cross section of the different fragments analysed CF-UF (A) and OZ-UF (B).

due also, the origin of which was apparently the clay present in the source water, since these elements were invariably present in identical layers [19]. However, aluminosilicates were clearly constituents of the external fouling, as opposed to Fe, which was found as part of the cake but also inside the membrane pores. In fact, a certain interaction between Fe and the membrane matrix would have been possible, threatening membrane condition over the medium and long term. Additionally, P was also found inside the membrane pores, suggesting a possible combination between Fe^{3+} in the coagulant and phosphates present in the humic/fulvic acid mixture used to prepare the synthetic water, resulting in ferric phosphates, which would have precipitated. Fe^{3+} added to water forms cationic hydrolytic species and weakly charged or uncharged precipitates. Then, negatively charged NOM fractions coagulate due to the adsorption to Fe precipitates or metal-NOM complexation and precipitation [1].

The elements found on the membrane surface in the OZ-UF samples were nearly the same as in CF-UF with the only exception of Fe, which was present in very minor concentrations, according to XRF analyses. Silicate content of the matrix water must have been higher than in the former stage since more Al and Si

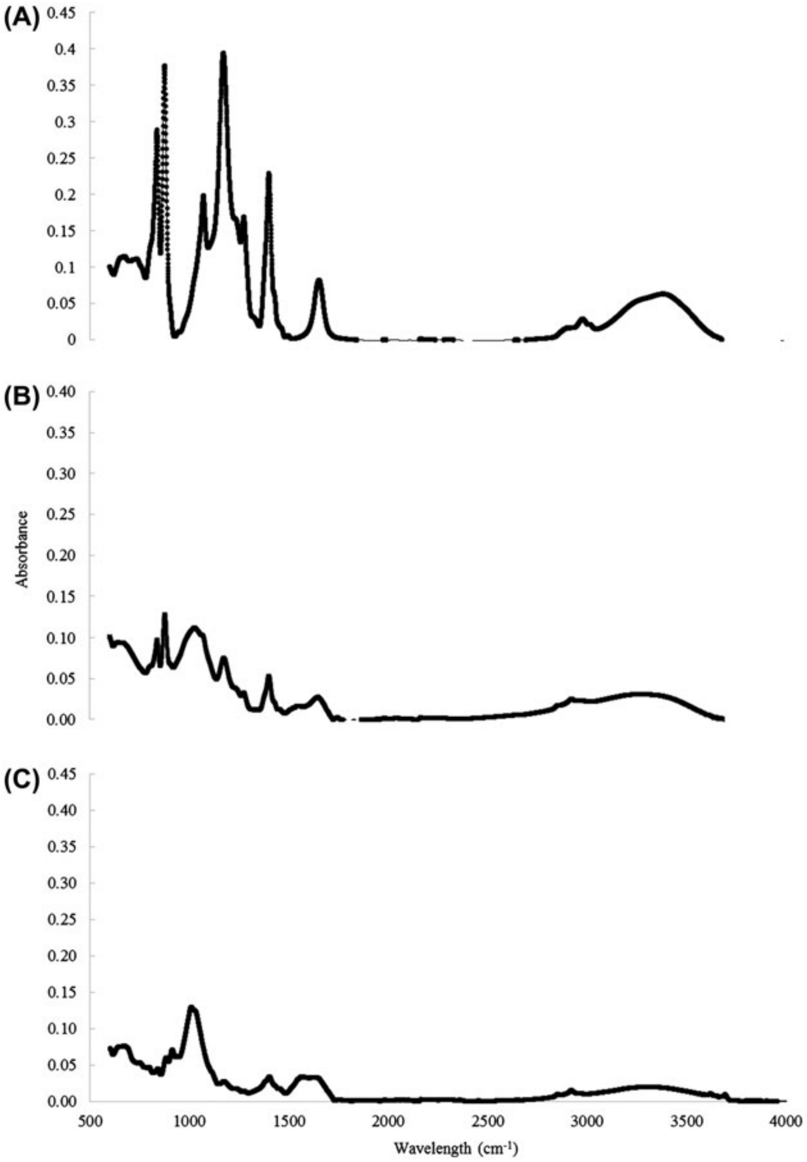

Fig. 4. ATR-FTIR spectra of the membrane fragments analysed. New membrane (A), CF-UF membrane (B) and OZ-UF membrane (C).

were found in the superficial membrane deposits, although ozone, by increasing the association of humic acids and metallic hydroxides, probably had an influence as well [32]. In addition, Ca was also present. On the other hand, the hypothesis of phosphates combining with ferric ions for the CF-UF system is feasible, considering that the feed-water quality was the same for the two pre-treatments and, in the absence of Fe^{3+}, no P inside the membrane pores was found.

Microanalyses of the cross section also confirmed two phases of different composition formed within the cake for both CF-UF and OZ-UF membrane fragments; a first layer where the inorganic materials were more abundant, with a significant predominance of clays composed by Si, Al and Ca or ferric phosphates, and a second one where the organic compounds dominated, dotted with clay materials.

3.6. ATR-FTIR

Fig. 4 compares the absorption spectrum for a new membrane and for the membranes used before being cleaned. The new membrane showed a typical absorption profile for PVDF membranes, with 1,072, 1,170, 1,402 and 1,646 cm^{-1}, bands assigned to C-C stretching, asymmetric stretching of C–F, C–H wagging and C=O stretching of amide I band, respectively [39]. Other characteristic bands appeared at 840 and 880 cm^{-1}, corresponding to CH_2 rocking vibration and CH out-of-plane deformation vibration, respectively [40]. Bands characteristic of virgin membranes remained hidden for the fouled membranes due to the deposits on the surface, although some major bands such as those for 840, 880, 1,170, 1,402 and 1,646 cm^{-1} were visible for the CF-UF system. Nevertheless, none of these could be found for the membrane subjected to pre-ozonation, which showed a very different profile. Compared to the new membrane, the infrared absorption was weaker, especially for OZ-UF. In addition, new bands appeared on the fouled membranes, i.e. a broad band at 1,013–1,045 cm^{-1} and a single band at 1,247 cm^{-1} for CF-UF system. Single bands at 907, 1,003 and 1,390 cm^{-1} and a broad band at 1,563–1,632 cm^{-1} appeared for the OZ-UF membrane. Zularisam et al. [24] described the FTIR spectra of NOM from two different water sources, finding bands corresponding to the C-O stretching of alcoholic compounds (1,034–1,040 cm^{-1}), the origin of which was mainly polysaccharides, or bands corresponding to C=O stretching of amide I and N–H amide II bonding vibration (1,550–1,640 cm^{-1}). Although the NOM of the influent involved mainly humic substances, those absorption bands were also observed in the ATR-FTIR profile of the membranes used in this study, evidencing the presence of polysaccharides and proteins [41]. As indicated in Section 3.3, these substances were presumably generated by bacteria forming a biofilm on the membrane surface [39], this being more significant in the OZ-UF membrane fragments.

The ATR-FTIR profile for the new membrane fragments and for the membrane fragments after the deposit removal (Fig. 5) shows the absence of new bands appearing or disappearing in the spectra of cleaned membranes. Apparently, the polymer constituting the membrane did not change substantially, although the relative intensity of the bands did change for the used membranes. In fact, the intensity of all the characteristic bands changed simultaneously

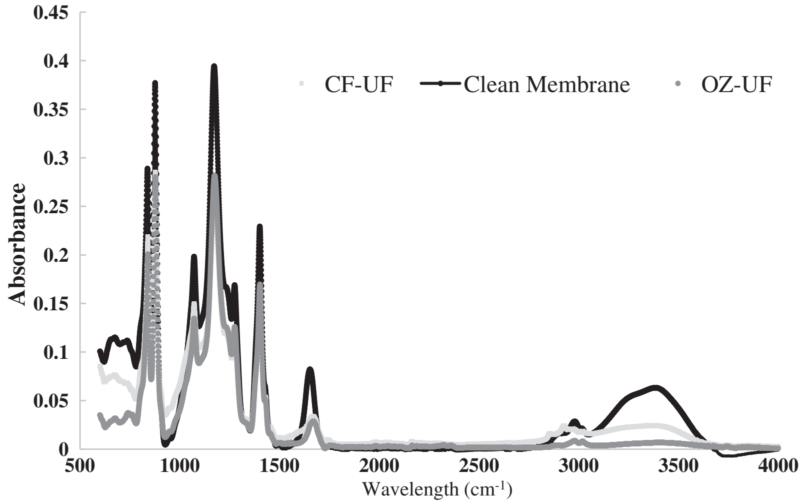

Fig. 5. Comparative ATR-FTIR spectra.

while alterations of a single band were not detected. These results indicate that neither the chlorine used in the chemical cleaning nor ozone or $FeCl_3$ used for the application of pre-treatments had damaged the chemical structure of the membranes.

Even though ozone is reportedly incompatible with most polymeric UF membranes [1,16], the membrane autopsy in the present study showed that neither fissures nor changes in the internal membrane structure were caused by OZ, so that the PVDF membrane used can be considered compatible with the ozone doses assayed. Nonetheless, the greater masking of the main absorption bands in the fouled membranes with respect to CF-UF system was attributed to fouling, more severe in the OZ-UF membrane, in accordance with the greater TMP increase found for that combination during the pilot tests.

4. Conclusions

The pre-treatment applied to drinking water production by UF membranes affects the characteristics and type of deposits that accumulate on the surface. Previous coagulation–flocculation involves greater deposit accumulation on the membrane surface than does pre-ozonation, as indicated by LOI and SEM cross-section analyses. A double-layer was visible for the two pre-treatments, the first one being composed mainly of aluminosilicates while the nature of the successive substances accumulated was organic. The organic layer was more relevant when coagulation–flocculation was applied. By contrast, the presence of aluminosilicates inside the deposit matrix was more significant for OZ in spite of having used the same influent water quality. On the other hand, there was a remarkable presence of precipitates of Fe^{3+} with P derivates inside the membrane pores for the membrane subject to coagulation–flocculation.

A mature biofilm developed in both cases even when chlorine had been used for chemical cleanings. Particularly, OZ involved greater biofilm generation despite the ozone-oxidising nature, confirming that the fragmentation of the influent organic matter increased food source for microorganisms as it was more readily available for them. The analyses of EPS and SMP extracted from the liquid waste were consistent with SEM micrographs.

Despite the presence of large particles, no cracks or signs of abrasion were detected on the membrane surface in the SEM micrographs for any of the pre-treatments applied. In fact, the ATR-FTIR profile for the cleaned membrane fragments exhibited the absence of new bands appearing or disappearing in the spectra, demonstrating that the polymer constituting the membrane did not change substantially as a consequence of the application of pre-treatments or chlorine chemical cleanings. The differences in the intensity of the bands compared to the ATR-FTIR spectra for a virgin membrane were due to fouling. The greater masking of the main absorption bands in comparison to pre-coagulation system suggests a negative effect of the application of ozone on fouling.

In summary, according to autopsies results, both OZ and in-line coagulation–flocculation pre-treatments are innocuous in terms of altering membrane chemical composition or surface condition. However, coagulation–flocculation is a more recommendable option for drinking water production from humic-rich influents.

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