

Removing biofilm from membranes – a practical approach.

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Abstract

Within the lifetime of most reverse osmosis (RO) systems some fouling will adversely affect membrane performance. One of the major foulants identified on lead membranes during a decade of membrane autopsy at the Genesys Membrane laboratory is biological fouling (biofouling).

All raw water sources contain microorganisms such as algae, bacteria and fungi. They also contain compounds which provide nutrients and energy sources which promote biological growth. In addition current methods of control such as chlorination will increase the availability of nutrient compounds.

The effects of biofouling on membrane operation include a reduction in flux, increase in pressure drop and salt passage and potentially membrane degradation and failure. Current technology favours the use of biocides to control biofouling; however bacteria in biofilm are more resistant to biocides than planktonic organisms. In addition using biocides produces an accumulated biomass which encourages active re-growth of the population. Therefore the successful approach must kill the biological population and successfully remove it from the membrane surface to prevent rapid re-growth.

This paper explores the processes for developing and testing a cleaning product Genesol 703 which removes biofouling from RO/NF/UF systems. The results of removing biofilm from membranes are presented. Product efficacy was determined by comparison of membrane flux rates before and after cleaning and visual inspection by scanning electron microscopy (SEM). The results demonstrate that Genesol 703 is a technically and economically viable cleaning chemical product for the removal of biofouling from membranes.

Keywords: reverse osmosis, membranes, cleaning, biofilm, fouling, autopsy, **Genesol 703**

1. Introduction

Biofouling is referred to as the undesired development of microbial layers on surfaces [1]. All raw water sources and therefore reverse osmosis (RO) feed waters contain microorganisms such as algae, bacteria and fungi, in addition they contain both nutrient and energy sources which promote growth of the bacterial population.

Biofouling has been recognized as the most serious problem in RO systems [2,3]. Membrane Autopsy procedures at the Genesys laboratories in Madrid have proved that over a 5 year period biofouling accounts for 35% of failures of all membranes tested; the most frequently detected foulant.

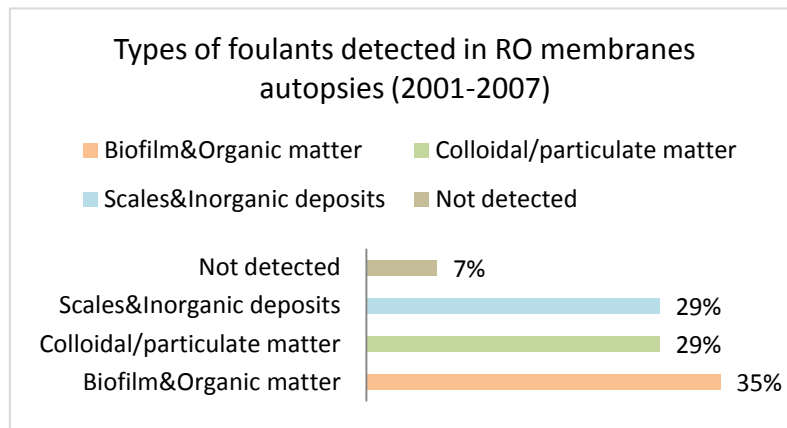


Figure 1. The main types of foulant identified on membrane elements from the first position during autopsy (2001-2007). Source: GMP laboratories statistics

The effects of biofouling on both Brackish water (BWRO) and Sea Water (SWRO) RO membranes include an increase in pressure drop, decrease in flux, and can also affect salt passage. In extreme cases membrane degradation and failure can occur. As all of these consequences will impact directly on operating expenditure a variety of different operating procedures are regularly implemented during pre-treatment to control the population of microorganisms in RO feed waters.

Pre-treatment and chemical procedures are required to prevent and control membrane fouling but have been found to be rarely totally effective in removing microorganisms and nutrients from the feed water system. In addition differences in RO system design, operating procedures and the ability of microorganisms to adapt and multiply successfully in membrane environments makes it difficult to rely on a single method of control. In addition some of the methods currently in wide use to control biofouling can encourage growth if applied incorrectly. The following sections give an overview of some of the processes involved in biofouling and the development of a specific cleaning product. Results from laboratory scale tests are presented with an explanation of the unique mechanisms which make this product effective.

2, Background –Membrane biofouling.

All RO feed water sources contain a population of microorganisms and compounds which act as nutrients or energy sources. It is not the purpose of this paper to outline in detail the

different types and species of microorganisms which may be present and also the complex methods of interaction and protection they employ to survive and multiply in the aquatic membrane environment. A brief description of the microbial populations in the membrane environment will help explain how current control methods are limited and how a dual approach is required to control operational problems associated with membrane biofouling.

In RO systems the pre-treatment, pipe work and membrane elements provide a large surface area for the attachment and growth of free living bacteria entering in the feed water. A biofilm is described as bacterial aggregates attached to a surface; the biofilm structure includes a matrix of bacterially produced Extracellular Polymeric Substances (EPS). The EPS is composed of polysaccharides, proteins and nucleic acids [4] and has been proven to play a major role in biofouling formation and its behaviour; effectively altering the porosity, density, water content, charge and sorption properties [1,5] of the biofilm. EPS enhances the structural integrity and adhesiveness of biofilms through 3 different forces: 1. electrostatic, 2. hydrogen bonds and 3. London dispersion forces [6]. This adhesiveness and elasticity makes the biofilm difficult to remove from membrane surfaces and also provides protection from biocides. In addition the presence of divalent cations such as calcium and magnesium increase the strength of biofilm by forming salt bridges between the membrane surface and negatively charged bacteria [6].

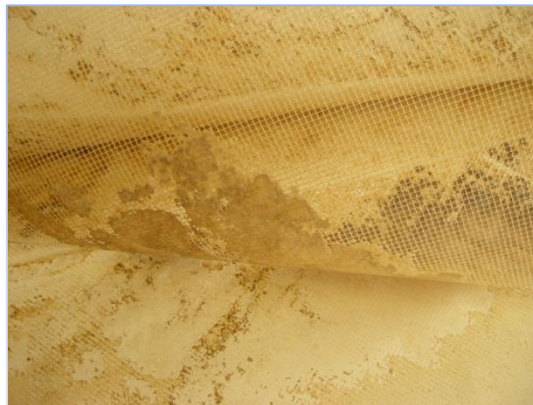


Figure 2.- Detail of a biofilm fouled membrane with deposit attached to spacer material.

2.1 Methods of Control biofouling

Genesys Membrane Autopsy results prove that biofilm formation does not occur equally within all areas of the membrane system, as the RO membranes filter out bacteria and nutrient sources from the feed water the bulk of the biofouling occurs in the first element of a pressure vessel. However in extreme cases formation can occur on the product side contaminating permeate water. Time of formation differs widely between RO systems; from a few days to a few weeks, however in an RO system operating on biologically active feed water a biofilm will appear within 3-5 days of inoculation [7].

In order to limit biofouling in a membrane system bacteria and nutrient/energy sources are intended to be removed from the feed water (preventive action). Pre-treatments in RO facilities have largely evolved in the last years including in some cases membrane technologies as Microfiltration (MF) or Ultrafiltration (UF). Even these last generation and extensive pre-treatment designs are rarely a 100% efficient processes and survival of a very small number of viable cells will lead to multiplication and possible biofouling in the membranes. In addition to this approach disinfection stages in the pre-treatment system using

biocides or UV are also used. Factors which must be considered when designing a method of disinfection include feed water quality (particularly; bacteria levels, pH and analysis of both organic and inorganic compounds), contact time and membrane element type (material). Cost of biocide application must also be considered as dosage rates will be affected by the size of the system and level of biofouling.

The chemistry and use of chlorine as a disinfectant is widely covered in literature. It is extensively used in industrial and municipal applications due to its' relatively low cost and widespread availability. It has significant limitations in terms of application in RO systems; thinfilm composite polyamide membranes are sensitive to levels of chlorine with oxidative degradation occurring at between 200-1000 hours of exposure to 1ppm of free chlorine [7], therefore chlorine must be removed from the feed system prior to entering the membrane, either by activated carbon or dosing Sodium Metabisulphite. Therefore any viable bacterial population or biofilm in the membrane will not be affected. In addition chlorine breaks down natural organic matter (NOM) present in the feed water to more easily biodegradable products offering a nutrient source to micro-organisms. As no chlorine is present on the membrane surface biofilm growth can occur leading to a requirement for more frequent sanitization. At this point, it is important to consider the role of EPS in membrane fouling and performance rather than counts on viable cells on membranes. Within a membrane system a biofilm level of 10^3cfu/cm^2 for aerobic bacteria is considered normal with operational problems generally occurring with bacterial counts $>10^5\text{cfu/cm}^2$ [8]. Recent studies show that chlorine-inactivated bacteria may also produce a biofouling layer on the RO membrane surface [9]. Chlorine is effective in inactivating microorganisms but not in decreasing EPS concentration, so no improvements in flux decline related to these fouling processes are observed [5].

Alternative non-oxidising biocides such as DBNPA (2,2-dibromo-3-nitrilopropionamide) and isothiazalones are approved by membrane manufacturers; however dose rates and therefore application costs are significantly higher than chlorine making continual dosing impractical. These chemicals are also not approved for dosing online in potable applications.

Importantly these biocide products are unable to adequately penetrate the protective biofilm layer and lyse/dissolve these foulants thus preventing re-growth on the membrane [9].

2.2 Membrane Cleaning

Membrane cleaning-in-place (CIP) is also used as a means of biofouling control, primarily aimed at disrupting and removing the biofilm layer from the membrane system. As reported by C. Whittaker et al [9] "strongly bactericidal compounds were not necessarily effective in removing biofouling layers, and cleaning solutions that were effective in biofilm removal were not necessarily bactericidal". In any case, disinfections have to be completed by the removal of the killed cells, which otherwise would adhere to membrane surface.

In practice CIP processes do not fully remove biomass from membranes, particularly in severe cases when plugging of the feed path restricts transport of cleaning chemicals into the blocked region. The remaining biomass, rich in nutrients, allows for rapid re-growth after cleaning. The use of CIP as a means of removing biofilm is often ineffective due to a combination of incorrect chemical selection – inability to fully penetrate the biofilm layer, poor cleaning practice (with respect to parameters such as pH, temperature, contact time and/or improper recirculation flow rates) and delays in CIP application. Poorly applied

membrane cleaning procedures will limit the recovery of the system to design operating parameters (flux, pressure drop and permeate quality) and incomplete removal of biomass may accelerate the growth of bacteria in other parts of the system.

3. Genesol 703 - new cleaning approach

Cleaning agents can affect fouling materials present on a membrane surface in three ways: (i) foulants may be removed, (ii) morphology of foulants may be changed (swelling, compaction) and/or (iii) surface chemistry of the deposit may be altered, such that the hydrophobicity or charge is modified [10]. Reported foulant-cleaning agent reactions are hydrolysis, peptization, saponification, solubilisation, dispersion (suspension) and chelation.

If an inappropriate cleaning agent is chosen negative effects can appear and membrane performance can be adversely affected. Membrane manufacturers [11] clearly state the consequences of applying inefficient cleaning techniques: “If foulant is not successfully removed, the membrane system performance will decline faster as it is easier for the foulant to deposit on the membrane surface area. The time between cleanings will become shorter, resulting in shorter membrane element life and higher operating and maintenance costs. Most effective cleaning allows longer system operating time between cleanings and results in the lowest operating costs”.

Genesol 703 was developed and tested as an effective cleaning compound for the removal of clay deposits [12]. Genesol 703 is a 100% active chemical powder based on a combination of high pH phosphate cleaners, a blend of chelants, surfactants and other active compounds. The product is approved under NSF/ANSI 60 guidelines. This combination of products has a detergent and surfactant effect on the colloidal foulants and in addition creates high ionic strength at the membrane surface. Due to the relevance of biofouling problems detected in Genesys Membrane Products laboratories (detected in 35% of membranes autopsied) and synergistic properties of this formulated cleaner, trials against biofilm removal under laboratory conditions were conducted.

The Genesol 703 mode of action can be described as follows: the first stage of attack occurs at the water/surface inter-phase of the biofilm and is due to the synergistic mode of operation of the combined speciality chemicals. This process works by reducing the surface tension of the deposit allowing the surfactant to become more effective in overcoming the impermeability of the EPS material; this allows the cleaning solution to penetrate into the biofilm structure. The foulant layer then becomes more porous increasing the permeability to water and consequently increasing the surface area of the deposit allowing more active chemical to penetrate and disrupt the “body” of the deposit. Genesol 703 provides a secondary physical action which increases cleaning efficiency at the membrane surface allowing a “double edged” approach to deposit removal. This action removes blockages from the membrane pores caused by the biofilm layer.

In normal operation of an RO system the pressure provided by the high pressure pump (HPP) overcomes the osmotic pressure of the feed water. During cleaning, the Genesol 703 solution is introduced to the system at a cleaning pressure below 4 bar. The feed water salinity will increase. It is possible that at the membrane surface the local osmotic pressure may become higher than the Net Driving Pressure (NDP) of the feed water. If this were the case then potentially there may be some localised forward osmosis taking place. Any movement of permeate water through the membrane to the feed water may assist lifting of the biofilm

around the membrane pores. This in turn would allow greater access to the surfactant cleaning chemicals to remove deposits. The removal of deposits away from the membrane into the concentrate stream is likely to help minimise membrane abrasion. This phenomenon may go some way to explain the effectiveness of the cleaning formulation. Further work is required to try and observe what is actually happening at the membrane surface during cleaning.

In addition to the effectiveness of Genesol 703 in removing biofilm deposits its application also serves as a means of “shock treatment” of a reverse osmosis system to reduce the biofouling potential through lysis of microorganisms; in turn this helps to prevent further system contamination. Cell lysis occurs due to the semi permeable nature of the membrane surrounding the microorganism; the cleaning solution creates the movement of water from the cell cytoplasm resulting in the eventual removal of the membrane from the cell wall. In addition to removing the biofilm layer from the membrane surface this effect helps to destroy remaining active cells preventing swift repopulation of the system.

Laboratory tests (as indicated below) proved this product to be much more effective at removing biofouling deposits than conventional acid and alkaline cleaning products.

5. Testing Genesol 703 efficiency - Experimental set up and procedures

In order to establish the efficiency of Genesol 703 in removing biofouling from a membrane surface, several cleaning tests were carried out in the Genesys Membrane Products S.L. laboratories using membrane coupons from three actual RO membrane elements in which biofouling was identified. In order to verify that the deposits on these membrane elements were mainly composed of biofilm, several observations (deposit morphology, moisture and organic matter content) and techniques were taken into consideration:

- a) Microbiological counts on membrane surface
- b) Membrane surface/deposit inspection by Scanning-electron microscopy – Energy dispersive X-ray analysis (SEM-EDAX) is used to study the membrane surface and to verify the elemental composition of its foulant and deposits detected. Elemental determination with the SEM-EDXA system is based on analysis of X-rays produced via electron beam excitation of a sample area.
- c) Foulant/membrane surface analysis by Attenuated Total Reflectance Infrared Spectrometry (ATR/IR). This technique can provide valuable information related to chemical structures and characterize the fouling layer from membrane surfaces. In the mid-infrared, absorption of radiation is related to fundamental vibrations of the chemical bonds. Internal reflection spectrometry provides information related to the presence or absence of specific functional groups. IR spectra were carried out for the foulant taken from the membrane surface in all case studies. In all of the 3 cases the identified compounds are protein derivatives that are commonly related to the presence of microorganisms / biofilm (bands at 1639 and 1561 cm^{-1}).

Data for membranes selected for this study are summarized in Table 1.

Cleaning experiments were performed with a laboratory scale cross-flow test rig unit. Rectangular flat sheet membrane coupons from RO elements were housed in a stainless steel cell, with an effective membrane area of 231 cm^2 . Feed water was circulated under the

characterisation conditions (pressure and salinity) established by the membrane element manufacturer in order to establish a baseline for each membrane sample. Data achieved is normalized to 25°C conditions. Different cleaning solutions were later re-circulated at 40 psi. The cleaning chemical used on each membrane and the test conditions are described below. After re-circulating the cleaning solution the membrane is rinsed with deionised water and characterised with the same conditions as used in step one. The cleaning efficiency of the product is then evaluated in terms of flux and rejection percentual variations. Additional analysis and visual inspection can be carried out to provide further evaluation.


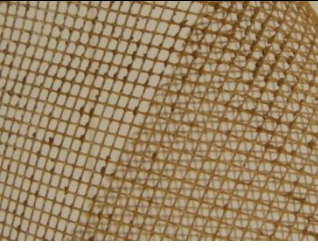

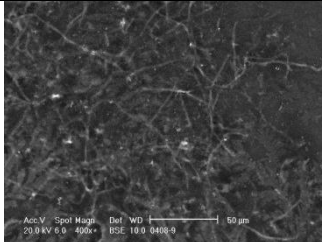
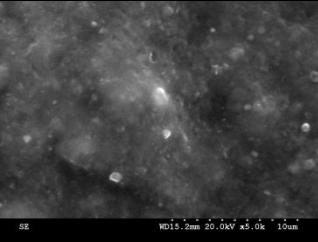
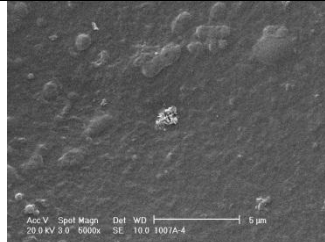
	CASE 1	CASE 2	CASE 3
Membrane type: (Characterization conditions)	TorayTM820E-400 (800psi, 32.000ppm NaCl, 1000ml/min)	Dow Filmtec BW30-400 (225psi, 2000ppm NaCl, 1000ml/min)	Hydranautics ESPA2+ (150 psi, 1,500mg/l NaCl, 1000ml/min)
Foulant description:			
	A brown orange coloured deposit was observed all over the membrane surface	Dark brown deposit covering both membrane space and spacer. Aluminosilicates also detected.	Membrane surface was homogeneously covered by a brown and jelly deposit
LOI:	Not performance (NaCl interference)	Moisture: 73.4 % Organic matter: 53,3%	Moisture: 94.2 % Organic matter: 86.3%
Microbio. counts:	Aerobic Bacteria 1.5x10 ³ Sulphite-ReducingBact.<1 Pseudomonaesp<1 Moulds and Yeasts 13	Aerobic Bacteria 8.2x10 ³ Sulphite-ReducingBact.<1 Pseudomonaesp<1 Moulds and Yeasts 19	Aerobic bacteria 3.1x 10 ⁴ Sulphate Reducing Bact.<1 Pseudomonaesp 35 Moulds & Yeasts 9
ATR-FTIR:	Proteins derivatives related to biofilms presence confirmed (1639 and 1561 cm ⁻¹ bands)	Proteins derivatives related to biofilms presence confirmed (1639 and 1561 cm ⁻¹ bands)	Proteins derivatives related to biofilms presence confirmed (1639 and 1561 cm ⁻¹ bands)
SEM-EDAX:			

Table 1: Summarized data for membrane samples used in laboratory scale tests

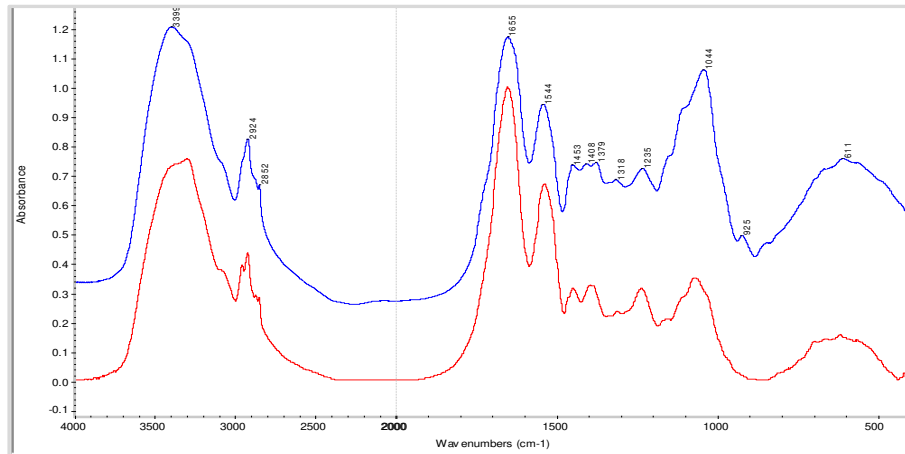


Figure 3.ATR-FTIR spectrum for membrane surface in case 3 (blue line). Comparison with database compounds – protein derivatives related to biofilms (red line).Source: GMP laboratories data base.

6. Testing Genesol 703 efficiency - Results and discussion

In order to check Genesol 703 efficiency, several cleaning programs were designed according to the membrane manufactures guidelines for removing this type of foulant. Established limits of pH and temperature have also been applied. In order to achieve comparative results, contact time in each trial has been set up in 2 hours. The results obtained in the different cleaning tests and the conditions applied (temperature, pH and contact time) are summarized in Table 3. Figure 3 depicts a graphical summary from different case studies showing the percentage flux change of each membrane coupon section after the cleaning process. Individual chemical cleaning solution relate to those shown in table 3.

	Cleaning solution	Temp.	pH	Time	Flow rate (l/m ² h 25°C)			% Salt Rejection	
					Before	After	%	Before	After
Case 1	C1.1 Genesol 703 (1 wt%)	35°C	11.5	2hrs	23.89	30.81	+29.0	99.68	99.66
	C1.2 Na ₄ EDTA (1 wt%) + sodium tripolyphosphate STP (2 wt%)	35°C	11.5	2hrs	29.19	35.61	+22.0	99.67	99.72
	C1.3 Sodium dodecyl benzene sulfonate (0.25 wt%) + Na ₄ EDTA (1 wt%)	35°C	11.5	2hrs	28.10	32.18	+1.7	99.60	99.68
Case 2	C2.1 Genesol 703 (1 wt%)	35°C	11.5	2hrs	9.77	23.22	+138	94.89	97.92
	C2.2 Na ₄ EDTA (1 wt%) + sodium tripolyphosphate STP (2 wt%)	35°C	11.5	2hrs	10.98	20.84	+89.8	96.29	97.94
	C2.3 Sodium dodecyl benzene sulfonate (0.25 wt%) + Na ₄ EDTA (1 wt%)	35°C	11.5	2hrs	8.92	16.58	+85.9	95.03	97.71
Case 3	C3.1 Genesol 703 (1 wt%)	35°C	11.5	2hrs	27.17	39.97	+47.1	99.59	99.24
	C3.2 Na ₄ EDTA (1 wt%) + sodium tripolyphosphate STP (2 wt%)	35°C	11.5	2hrs	24.60	30.79	+25.2	99.48	99.39
	C3.3 Sodium dodecyl benzene sulfonate (0.25 wt%) + Na ₄ EDTA (1 wt%)	35°C	11.5	2hrs	29.80	34.26	+15.0	99.58	99.48

Table 2: Summarized data for cleaning test conditions and results

The data obtained in this experimental work demonstrates that Genesol 703 is more efficient in removing this kind of biological foulant than the other chemical blends in term of flux improvements. With regards to the evaluation of salt rejection data the results are inconclusive - as in most cases a decrease in salt rejection was observed after chemical

cleaning. It is important to point that in this experiment fouled membrane samples come from real plants and they have been operating under fouling conditions a variable period of time in each case. Although biofilm has been documented as more significant fouling in these samples, it is widely assumed that biological fouling is seldom found alone (“composite fouling”) and its properties for enhancing particulate fouling. A reasonable explanation to these results would be membrane abrasion which is frequently documented in membranes fouled by colloids [12] and operation under high differential pressure conditions.

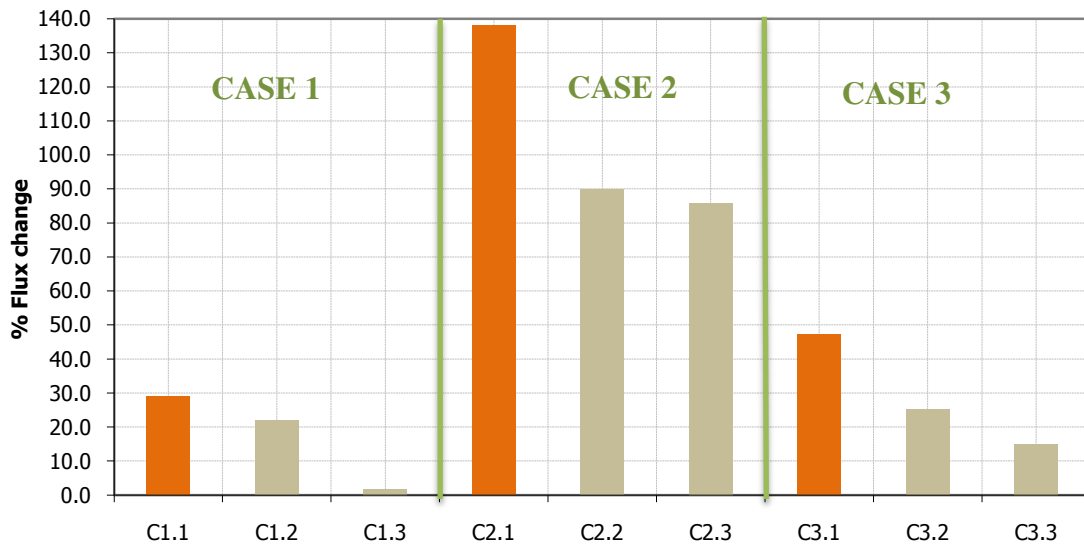


Figure 3: Percentual flux improvements achieved in cleaning tests. Comparative data.

In order to confirm foulant removal from membrane surface, SEM inspection for membrane surface before and after cleaning was conducted. Results for case study X are shown in Figure 4.

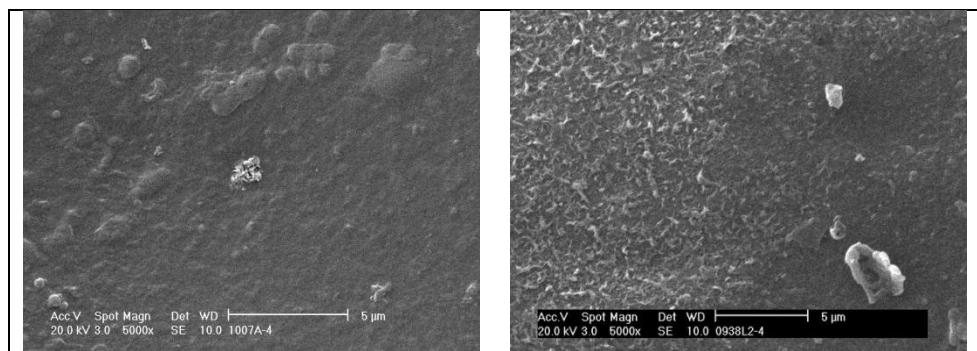


Figure 4: SEM inspection for membrane coupons before and after cleaning with Genesol 703 (Case 3).

7. Conclusions

The results of Genesys membrane autopsy laboratory data support the fact that biofouling is a common foulant occurring primarily on the membrane elements in the first position and that it can occur in all RO feed waters.

Improvements in pre-treatment can be considered although practical experience shows that bacteria cannot be completely removed from feed streams. In order to prevent membrane

damage, remedial action should be taken immediately when the first symptoms of fouling are detected.

Laboratory studies indicate that Genesol 703 is more effective at removing biofouling from membrane surfaces at a dosage rate of 1%. This is significantly lower than traditional cleaning chemicals. In these analyses real membrane samples have been used which have been affected by biological fouling during their natural operation and the effectiveness of the product has been proven in terms of the results of significant increases in membrane flux and foulant layer removal (SEM inspection). Although design values has not been achieved in all cleaning trials, it is important to point out that only one step with 2 hours contact time tests were established as the objective of this work is compare efficiency between different available cleaning options.

The product has been used in over fifty operating plants with biofouling problems with encouraging results. In real operational plants, cleaning protocols have been designed with appropriate contact times and combining Genesol 703 with additional cleaning steps (biocides, acidic cleaners) according to each plant conditions. Rejection values have been reported to either improve or be maintained. In some cases, rejection has decreased after the cleaning procedure. Behaviour in salt rejection values depends on the type of foulant and condition and how they affect membrane rejection properties. The product has been tested in line with the membrane compatibility testing protocol established by DOW Filmtec and results confirm no effects on membrane rejection properties.

Further studies will be conducted and the authors hope to present additional case study information in the future.

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