Problems of operation and main reasons for failure of membranes in tertiary treatment systems

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Abstract This paper presents and discuss the results of the long term operation and monitoring of membrane fouling at several full-scale MF/RO water recycling facilities operated by Agbar in Spain. It was demonstrated that membranes are very reliable treatment enabling the production of high-grade recycled water, well disinfected and with the removal of all priority substances. The high organic and salt concentrations of raw wastewater combined to extremely high variations justified the implementation of sand filtration to protect MF/RO membranes. Membrane autopsy was used to better understand the predominant fouling mechanisms and optimise down-stream operation and membrane cleaning strategy. The main membrane pathologies are described with recommendation of an adequate cleaning strategy.
Keywords: cleaning strategy, membrane autopsy, membrane fouling, microfiltration, reverse osmosis

INTRODUCTION

Agbar Agua is the principal operator of wastewater treatment plants in Spain (500 WWTP, 12,500,000 p.e.). Over 28% of the total treated volume (1000 Mm^3/yr) undergoes tertiary treatment for beneficial reuse mainly in the Mediterranean cost and the Balearic and Canaries Islands. The majority of the tertiary treatment trains includes only a disinfection step of UV irradiation or chlorination. The increasing demand of high quality recycled water with reduced total dissolved salt content promoted the implementation of advanced membrane treatments. Reverse osmosis (RO) and electrodialysis reversal (EDR) have been chosen to reduce total dissolved solids, thus enabling water recycling for urban and golf course irrigation, as well as the irrigation of salt sensitive crops.

Microfiltration (MF) has been chosen as the best available pre-treatment of RO, which was successfully used since 1995 in West Basin Water Recycling Plant in California in replacement of conventional lime clarification and filtration (Lazarova et all., 2003).

At the end of 2002, according to a recent survey of WERF (Foussereau *et al*., 2003), over 25 recycling facilities used MF/RO technologies, from which 20 plants in the USA. More recently, 4 large tertiary treatment UF&MF/RO facilities have been constructed in Singapore in Bedok, Kranji, Seletar and Ulu Paladan with treatment capacities from 32,000 to 148,000 m^3/d.

A number of pilot and full-scale investigations confirmed the advantages of MF and ultrafiltration (UF) as reliable pre-treatment stage before RO allowing a small footprint and high rejection level for many fouling agents at competitive costs. Nevertheless, because the high variation of wastewater quality in terms of concentrations of metals, silica, salinity and organic matters, the control of membrane fouling remains the major challenge in operation of membrane facilities.

In this context, the main objective of this paper is to present the most common problems of operation and analyse the reasons for failure of membranes used in MF/RO tertiary treatment schemes applied for the treatment of relatively high concentrated urban wastewater in terms of levels of organic matter and salinity. Special attention was made on the investigation of RO fouling mechanisms and optimisation of membrane cleaning.

MATERIALS AND METHODS

8 full-scale wastewater treatment plants (WWTP) in Spain with different membrane combinations as tertiary treatment have been evaluated (UF+RO, MBR+RO, EDR). From which, 4 MF/RO units implemented at two plants operated for over 3 to 5 years (Table 1), have been evaluated in details in terms of reliability of operation and control of fouling. Wastewater and recycled water characteristics have been followed on weekly basis using Standard Methods. Special attention has been dedicated on the control of membrane fouling and optimisation of cleaning procedure, in particular of RO membranes. The concept of membrane autopsy has been applied to better understand the predominant fouling mechanisms and consequently, apply the most appropriate pre-treatment and cleaning strategies.

Table 1. Main characteristics of investigated MF/RO water recycling facilities located in Spain

Plant index and start-up	Treatment capacity, m^3/d	Tertiary treatment train and equipment		
		Pre-treatment	Low pressure membranes	Desalination (RO and EDR)
Plant 1, (2001)	12,000 (4 lines)	Dual contact sand filtration (6 units)	External MF, Memcor M10C, (0.2 µm, 1.5 bar), 180 modules	Line 1 to 3: Reverse osmosis (3 steps, 168 units), Dow Filmtec BW 365FR; Renewed by Ropur Toray TML20-370 (2 steps, 126 units, 12 bar), Line 4: Electrodialysis reversal (1 module of 3 lines with 2 steps each
Plant 2 (2004)	4,800 (12,000 of secondary treatment)	Pulsed-bed sand filtration (3 units)	External MF, Memcor M10, (0.2 µm, 1.5 bar), 96 modules	Reverse osmosis (2 steps, 90 units, 12 bar), Dow Filmtec BW 30-365 FR

Figure 1. View of the flat sheet cleaning rig used for membrane autopsy

Membrane autopsy was used as the most common way to understand the causes of the loss of membrane permeability and flux. This destructive technique allows evaluating both membrane polymer condition and foulant nature. Membrane autopsy methodology may vary depending on type of foulant or problem suspected. In all cases, the general purpose is as follows:

- Testing integrity of membrane element and visual inspection,
- Visual inspection of membrane surface (after external housing removal),
- State of the membrane permeability and rejection properties using a flat sheet test rig,
- Observations by electronic microscopy of the state of the polymer and/or the presence of deposits,
- Characterization of deposits detected on membrane surface by different analytical techniques. Fourier Transmission by Infrared (FTIR), X-ray Photoelectron Spectroscopy (XPS) and scanning electron microscope (SEM) connected to energy dispersive X-ray analysis (EDAX) have been used to characterises in more details the RO membranes fouling. Depending on foulant properties, other techniques may be used (Magnetic Nuclear Resonance, X-Ray Difraction, etc.).
- Counting and identification of bacteria on the surface of the membrane.

A detailed description of the analytical procedure is provided elsewhere (Darton *et al*., 2004).

Several samples of aged and/or fouled RO membranes situated either in the 1st and 2nd stages have been removed for an autopsy in a specialised laboratory. After external inspection, the first step consists in removal of various A4-size pieces of RO membranes, which were characterised by means of the flat sheet- test rigs under standard operating pressure, saline solution and flux conditions settled by membrane manufacturer (Figure 1). In some cases, once preliminary studies have been completed, supplementary test works were performed on a full size element.

This methodology is also used for testing several chemicals and cleaning protocols with the aim of optimising the cleaning procedure, which is usually carried out during routine operation. Such cleaning-up tests make it possible to evaluate the reversibility of membrane fouling.

RESULTS AND DISCUSSION

Membrane operation, performances and failures

As illustrated by Table 2 and Figure 2, the MF/RO tertiary treatment allowed to consistently produce high-grade recycled water (<5 mg/L of suspended solids and BOD, as well as <30 mgCOD/L) with not detected coliforms. Moreover, the analysis of micropollutants demonstrated that metals (Al, As, Ba, Cu, Cr, Sn, Fe, Mn, Hg, Ni, Pb, Zn), and 29 pesticides and other organic priority substances are far under maximum concentration limits (MCL) in drinking water.

Table 2. Water quality monitoring data: raw sewage, secondary effluent and recycled water (Jan 2005 – May 2007, weakly records, 127 samples of blended MF and RO permeate)

Parameter	Raw sewage (Plant 2)	Secondary effluent		Tertiary MF/RO permeate	
		Plant 1	Plant 2	Plant 1	Plant 2
COD mg/L	349-1592		41 (13-119)	<30	
BOD_5 mg/L	110-600	35	11 (5-29)	<5	8 (5-13)
TSS mg/L	153-1330	30	14 (5-47)	<5	
NTK mg/L	32-102		25 (4-39)		
P_{tot} mg/L	9-45	4.5	2.4 (0.3-7.5)	<0.5	
Conductivity, µS/cm	1734-9400		2485 (1315-5700)	<50	
E.coli/100 mL	10^5-10^7		10^4-10^5	not detected	

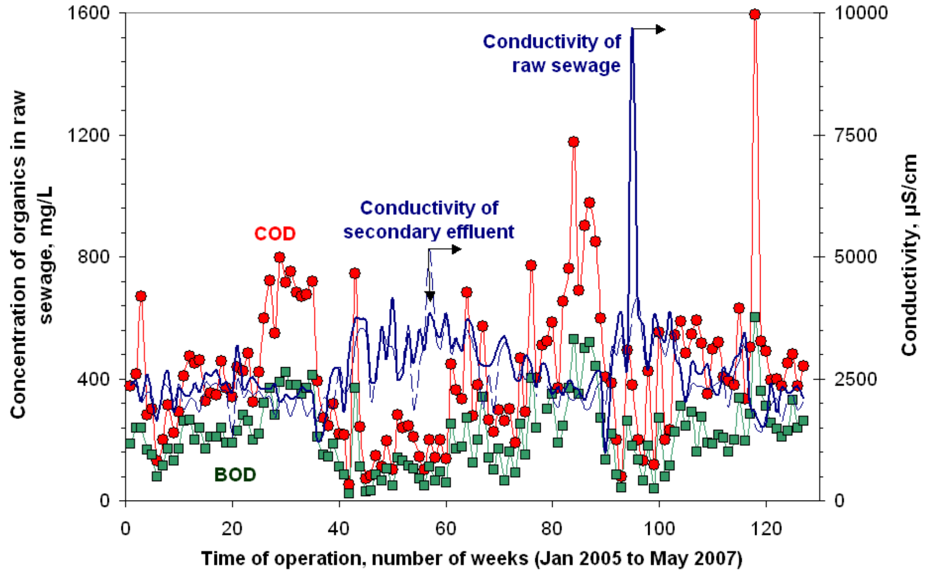


Figure 2. Evolution of organic content and salinity of raw wastewater

It is important to underline that raw wastewater treated in these two recycling facilities is very concentrated in terms of organic and nitrogen concentrations. In addition, wastewater salinity is extremely high with peak concentrations up to 5,700-9,400 µS/cm (see Figure 2). High salinity is due to sea water intrusion in sewers favoured by specific climate conditions.

Because the high concentrations and high variability of raw wastewater characteristics (55±2% for TSS, COD and BOD and 32% for conductivity for 3-year monitoring in the plant 2, for example), a robust pre-treatment by advanced contact filtration was implemented before MF/RO treatment.

The major problem during the start-up of the two MF/RO facilities was the failure of automation and PLC systems. As a rule, manufacturers provide too rigid PLC or software systems that cannot be managed by local operators and cannot be easily adapted to the constraints of inlet wastewater. Consequently, water quality was sometimes not in compliance with expectations. It is important to notice that the seasonal and daily variations of the quality of secondary effluents in the inlet of tertiary treatment require an adjustment in real time of operating parameters of membrane systems.

The main challenge in operation is to preserve membrane permeability close to initial value. Since the plant start-up, it is necessary to define an effective strategy to prevent the most common and typical membrane pathologies as colloids, biofouling, scaling, as well as an efficient methodology for membrane cleaning to avoid the loss of output in long term.

As illustrated by Figure 3, deterioration of water quality (variation of salinity from 1734 to 3142 µS/cm) leads to a significant decrease in membrane flux combined to increase in salt passage above 2.5% (average RO recovery 72%).

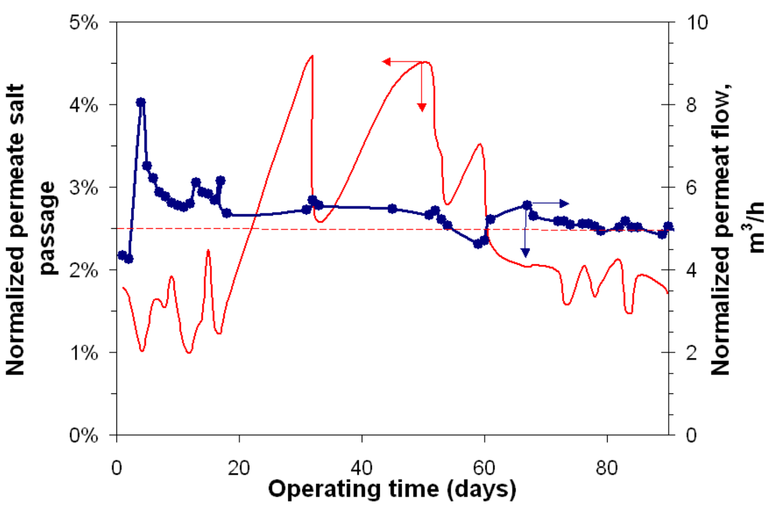


Figure 3. Performance of polyamide RO membranes

Role of membrane autopsy for the control of membrane fouling

Few long-term problems of operation appeared in reverse osmosis membranes in the two water recycling plants, which are generally more sensitive than those of EDR to poor wastewater quality and pre-treatment. These problems resulted in progressive loss of membrane flux, leading to frequent repairs, and in some cases, to a fast membrane replacement at the end of the first years of operation (3 to 4 years).

Following an extensive study of membrane fouling in the four full-scale units using autopsy procedure, it was found that main problems were related to presence of organic foulants and biofilms on membrane surface. Despite the MF pre-treatment, low molecular weight dissolved organics reach membrane surface and act as nutrients for microorganisms. As observed by Darton *et al.* (2004), all polyamide membranes support a viable biofilm unless continuously treated with a non-oxidizing biocide, independently of the pre-treatment system. In wastewater membrane treatment, biofilm control becomes a goal, and consequently, specific preventive and corrective actions must be considered such shock dosage of membrane-compatible non-oxidant biocides and periodical alkaline cleaning with surfactants at high temperature (35ºC) and high flux (membrane manufacturer guidelines must be always considered).

It is important to stress that inorganic deposition in membrane surface is commonly considered as the main cause of failure in sea water and brackish water RO desalination systems. Main scaling agents as calcium carbonate, calcium sulphate or barium/strontium sulphate are seldom a problem when appropriate pre-treatment is designed. Effectiveness of commercial antiscalants have been largely tested in desalination plants. Main target when operating wastewater membrane units is to avoid calcium phosphate deposits, an unusual foulant until quite recently. Calcium phosphate has a low solubility that is readily exceeded even for low concentrations of phosphates in feed water. Calcium phosphate forms a thin deposit layer, covering completely membrane surface (Figure 4). Membrane permeability is dramatically affected and decreases by nearly 50% in flux have been observed for very short periods of operation (6 hours). In this case, rejection properties are not affected after foulant removal, as opposite of other common scales referenced above. The best cleaning strategy to overcome calcium phosphate deposits is acid cleaning.

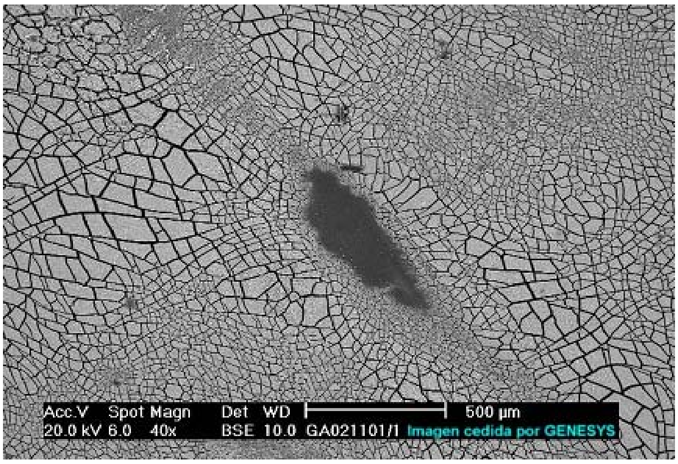


Figure 4. SEM-EDAX micrograph illustrating a calcium phosphate deposit on a membrane surface

Other foulants that can adversely affect membrane performance in WWTP are:

- Colloidal matter that can be difficult to remove from feed water,
- Coagulants and flocculants, mostly overdosed in previous stages of wastewater treatment. Aluminium-based coagulants and organic polymeric flocculants are molecules with high affinity to charged membrane surface that can dramatically affect its permeability,
- Oils and fats.

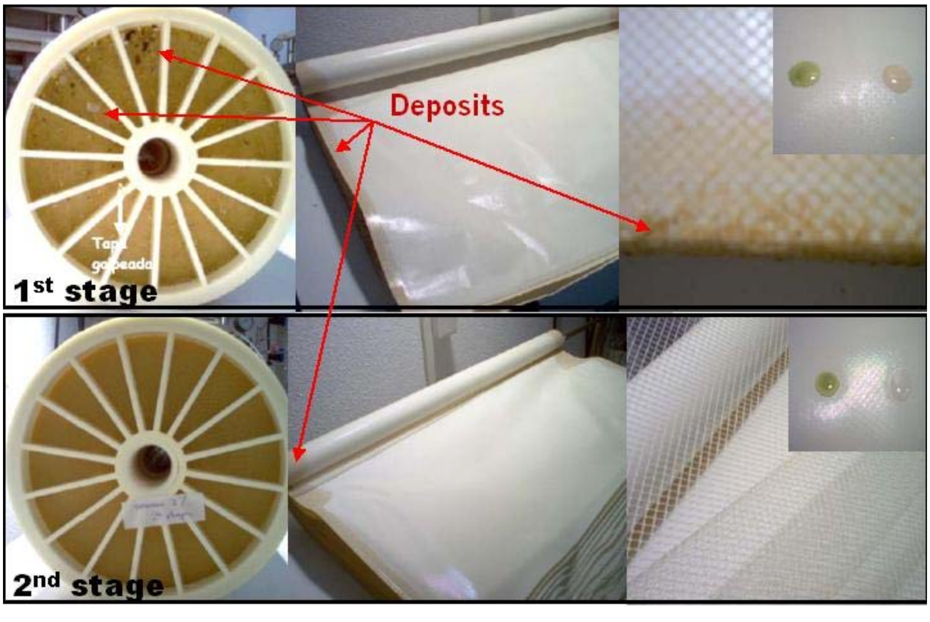
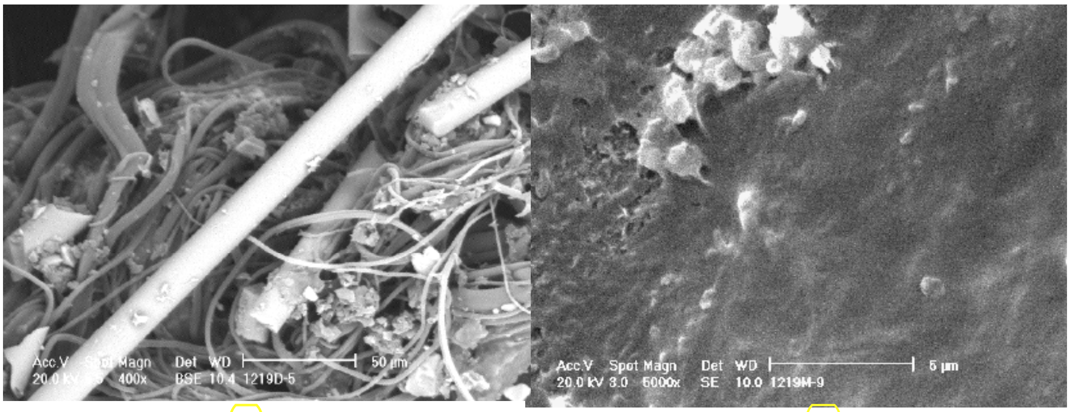


Figure 5. Feed end and full view of the RO membranes (1st and 2nd stage from plant 2)

To better understand the mechanism of membrane fouling, two RO polyamide modules (1st and 2nd stage) have been removed for autopsy. The visual inspection (Figure 5) indicated the presence of a significant number of particles and deposits on the feed-end of the 1st stage RO membrane, as well as a very fine yellow deposit covering partially the open membrane. The 2nd stage membrane seems visually clean. Colorimetric tests indicated the absence of carbonates and Fe^{2+}, but the presence of Fe^{3+} (very slight coloration for the 2nd stage membrane). Average measured flux was 20 and 23.8 L/m².h for the 1st and 2nd stage, respectively, which is well below the nominal value of 45 L/m².h. Salt retention remains into the limits of design values (99.0-99.5%).

As shown on Figure 5, the highest amount of deposits was observed on the feed end of the first membrane. SEM-EDAX and FTIR investigation of membrane samples confirmed that this fibrous material (Figure 6a) is predominantly organic (proteins and polypropylene) with trace amounts of iron, alumino-silicate, as well as some phosphorous and calcium compounds.



a) b)

Figure 6. SEM micrographs (a) feed end and (b) full view on the 1st stage RO membrane

The very fine deposit observed on the membrane surface is not homogenous and is concentrated mostly near the feed side. As illustrated by the SEM micrograph on Figure 6b, a thin layer of exopolymers with few bacterial colonies can be detected.

The infrared spectra (Figure 7) demonstrated that this fine layer is composed predominantly by proteins, which could correspond to an early stage of biofilm development (surface conditioning by excreted soluble proteins).

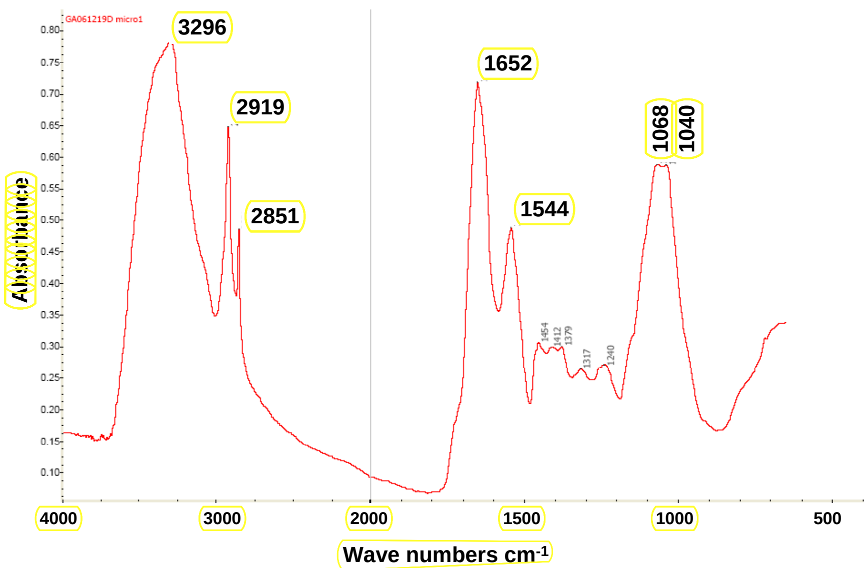


Figure 7. Infrared spectrum of the fine layer on the membrane surface

These samples and the previous autopsies confirm that biofouling is one of major pathologies of wastewater RO membrane treatment despite the biocide addition. The main challenge is to control this biofilm avoiding any excessive growth. According to the statistical review of 150 membrane autopsies, Darton and Fazell (2001) concluded that as a rule, biofilms does not affect system performance as long as bacterial count remains<10^4 cfu/cm². In the case of our investigation, aerobic bacterial counts remained lower than this value, but membrane permeability was greatly affected due to the thin protein layer. Using flat sheet test rig, a 3-step cleaning protocol (alkaline-acid-alkaline) using proprietary/formulated cleaning chemicals was specifically designed for the MF/RO facilities of concern. Different conditions such us pH, soaking time and cleaning solution temperature were tested in order to optimize cleaning results and recover the flux up to design values established by membrane manufacturer.

Optimisation of membrane cleaning

As a rule, many difficulties are faced in RO wastewater recycling plants when an optimisation of cleaning process is needed. The ideal cleaning situation occurs when the type of foulant that is affecting the given plant is known, the cleaning process restores the membrane element performance to original start-up data, the chemical cleaning frequency is relatively low (few per year) and the membrane elements last more than 3 years. However, the reality is commonly far away from such ideal situation: what is on the membrane is not know, cleanings are not restoring original performance, frequent cleanings are needed and the membrane life is relatively short (<3 years).

The first step of the optimisation of membrane cleaning is the establishment of relevant criteria to decide when the chemical cleaning becomes necessary. First of all, it is important to emphasise that external factors such as changes in the feed quality, temperature, pressure availability etc., could lead the operator to the wrong assumption that the plant is not performing well. For this reason, the operating data should always be normalised. Taking this into account, a cleaning should be done when one (or more) of the following three criteria occurs:

1) The normalised flow decreases by 10%,
2) The pressure drop increases by 10-15%, and/or
3) The normalised salt passage increases by 5-10%.

Once a lost in membrane performance has been detected, the major source has to be identified. For this purpose, the following steps should be taken into account:

- Initial inspection of the lead element and the feed scroll in order to find possible suspended solids. In WWTP with an UF or MF prior to the RO system, no suspended solid should reach the RO elements.
- Inspection of the scroll of the rear elements to find possible scaling.
- Autopsy.

The most common types of fouling and scaling affecting wastewater RO systems and the recommended cleaning procedures are described as follows:

Figure 8. Example of a biological/organic fouling

Biological/Organic fouling. The most typical causes for biological and organic fouling are usually related to improper membranes preservation, presence of biological and organic matter in the feed water and/or improper pre-treatment. This type of fouling (Figure 8) can be recognized by the strong odour of the elements, by the discoloration of the scroll end, as well as by the low permeate flow, high salt rejection and high pressure drop. A commonly recommended biofouling cleaning solution consists of a 0.5-1% (wt) Na-EDTA and 0.1% (wt) NaOH, pH 12 and 30ºC. Contact time is critical and several overnight soaks might be necessary to restore the system performance. (Dow Water Solutions, Technical Manual).

Some organics, such as oils, are especially difficult to remove from the surface of the membrane. In such circumstances, the cleaning solutions should contain a surfactant like Na-DSS (sodium salt of dodecylsufate) or some commercially available specific detergents. One possible cleaning procedure might be then a caustic cleaning (0.1% wt NaOH + 0.025% wt Na-DSS at pH 12 and 30ºC) followed by acid cleaning (0.2% wt HCl at pH 2 and at a maximum temperature of 45 ºC). If the cause of the organic fouling is an overfeeding of a coagulant, the order of cleanings can be reversed, *i.e*., first acid cleaning followed by a caustic cleaning.

Carbonate, sulphate and phosphate scaling. Carbonate scaling usually occurs due to feed water improper conditioning such as high hardness and high pH or due to high recoveries rates. In general, scaling can be identified when the plant presents a low permeate flow, poor salt rejection and high pressure drop. In addition, elements suffering from scaling are heavier than normal ones due to the extra weight of the precipitates. Acid cleanings have shown to be effective against carbonate and phosphate scaling. Hycrochloric acid, citric acid, phosphoric or sulfamic acid are commonly used to deal with such precipitates. Sulphate scaling is more complicated to remove. Usually a caustic cleaning (Na-EDTA + NaOH) is suggested, however the reaction is slow and overnight soaking and recirculation is commonly necessary.

Colloidal fouling. Colloidal or silt fouling occurs mainly due to inadequate pre-treatment, which allows water with high turbidity and high content in suspended solids to reach the membranes. It can be identified through a physical inspection of the elements, when the feed scroll end is especially dirty. In addition, an element suffering from silt fouling presents a low permeate flow together with a poor salt rejection or a high permeate salt with a very poor salt rejection. The extra weight of the element can be also an indication of colloidal fouling. This type of fouling is not easy to clean. Caustic cleaning solutions mixed with Na-EDTA can give successful results. Commercially available detergents can also be a feasible solution to restore the initial element performance.

CONCLUSIONS

The long-term operation of four MF/RO units at two recycling facilities in Spain demonstrated the ability to produce high-grade recycled water that is totally disinfected and free of priority pollutants. The major challenge of operation was the control of membrane fouling. The regular follow-up of wastewater characteristics, membrane performances and the application of membrane autopsy enabled to better understand the predominant fouling mechanisms in MF/RO systems. Biofouling was identified as the major cause of decrease in membrane permeability even when only a very thin layer of proteins was present. To improve membrane operation and lifetime, adequate criteria must be applied to decide the chemical cleaning frequency and select the most appropriate cleaning protocol depending on predominant foulants and/or scalants.

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