RO MEMBRANE BIOFOULING: PROBLEMS AND SOLUTIONS

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Abstract

It is well known that biofouling is among the most common and the most problematic types of fouling of reverse osmosis membranes. Biofouling is the excessive growth of the biofilm present on a membrane surface.

Major typical consequences are low availability rates due to high chemical cleaning frequencies, high electricity and chemical consumption, underperformance in permeate quantity and quality, mechanical damage of spiral wound membrane elements due to excessive delta p, chemical damage of membranes due to inappropriate use of biocides and shortened membrane life.

Severe membrane biofouling commonly occurs if significant concentrations of nutrients are present in warm feed water. Those nutrients mainly consist of biodegradable organic matter that allows the growth of heterotrophic microorganisms and mineral nutrients (e.g. ammonia) responsible for the growth of autotrophic microorganisms. Other nutrients like phosphorous and certain trace elements need also to be present in the feed water.

Different methods can be used to control reverse osmosis membrane biofouling. The use of oxidising biocides is restricted by the incompatibility of polyamide membranes with strong oxidisers. Mono-chloramine is used successfully in wastewater applications, but it cannot be applied on surface or ground water.

Continuous chlorination and dechlorination upstream the reverse osmosis membranes is known be counterproductive. Chlorine transforms some refractory organic compounds into biodegradable compounds and furthermore no biocide is left that would protect the membranes from biofilm formation after dechlorination with bisulphite. Non-oxidising reverse osmosis membrane compatible biocides are efficient, but cannot be used on-line in drinking water production.

Alternative biofouling control methods are also available or under development. Most of them are based either on prevention or reduction of biofilm adhesion or on restriction of biofilm growth by nutrient limitation.

The paper addresses 3 subjects related to reverse osmosis biofouling
- Inventory of causes, consequences and possible solutions
- Case study of a successful biofouling control by nutrient limitation at an 84 MLD plant
- Introduction of a new innovative biofouling control method destined to reverse osmosis plants with ultrafiltration or microfiltration as pretreatment including performance results from a pilot trial.

I. INTRODUCTION

As on any surface in contact with water, a biofilm is formed on the surface of reverse osmosis (RO) membranes. A biofilm can also be formed on the surface of feedspacers present in spiral wound RO membrane elements. Depending on the feed water, membrane and module design and on the operations conditions, the biofilm may grow excessively and thus become a more or less severe operational issue. This excessively growing biofilm is commonly called biofouling. Gentle biofouling causes increased operation costs, whereas severe biofouling may even result in insufficient performance in terms of treated water quantity or/and quality. The biofouling layer consists of microorganisms incorporated in a sticky structure of extracellular polymeric substances (EPS). Commonly solids originating from the feed water are also present.

The issue of RO biofouling and its possible consequences are commonly recognized. Different approaches to control RO biofouling are used on plants with different levels of success. RO biofouling is also a subject of extensive R&D efforts in order to improve the understanding of involved mechanisms and to develop monitoring tools and appropriate counter measures.

The aim of this paper is to provide a concise inventory on causes, consequences and possible solutions, to discuss some field experience in form of a case study of a RO plant operated by Veolia Water Korea and to present a new innovative RO biofouling control technology under development by Veolia Water Solutions & Technologies.

II. CAUSES OF RO MEMBRANE BIOFOULING

2.1 Necessary conditions

2.1.1 Presence of nutrients – Phototrophic microorganisms are absent in RO membrane biofilms as there is no light inside the membranes. Therefore all microorganisms in the biofilm are heterotrophs or chemoautotrophs. This means that organic nutrients (biodegradable organic matter) or inorganic nutrients (ammonia, nitrite, ferrous iron, sulphur, hydrogen sulphide, etc.) need to be available for the growth of the biofilm. The microorganisms also need some phosphorous and some other trace elements. The potential growth rate of the biofilm or, in other words, the degree of biofouling is correlated to the concentration of nutrients present in the water.
The absence of biofouling on most RO plant treating ground water can be explained by the quasi-absence of biodegradable organic matter in the water. The biodegradable fraction of the organic matter is biodegraded by a natural slow biofiltration in the soil.

2.1.2 Presence of microorganisms – Microorganisms are ubiquitous. Water without any micro-organisms is something very uncommon and RO feed water without microorganisms simply does not exist. Hence this condition is always fulfilled. A high concentration of microorganisms accelerates the formation of the biofilm on a clean membrane. With a mature biofilm on the membrane however, the concentration of microorganisms in the feed water has a rather negligible impact on the biofouling rate.

2.2 Conditions favouring biofouling

2.2.1 Temperature – There are two major reasons responsible for amplified biofouling during warm water periods. The first is the impact of temperature to microbial growth kinetics. The second reason is the coincidence of seasonal conditions with high raw water temperature. The amount of organic nutrients available in surface water is correlated to photosynthetic activity. During summer the photosynthetic activity is the highest because the extent of presence of sunlight is the longest and also because the kinetics of photosynthesis is temperature dependant as well.

2.2.2 Flux rate and tangential velocity – The concentration polarisation of any solute including the nutrients on the membrane surface is correlated to flux rate and tangential velocity. Consequently biofouling also increases with rising flux rate as well as with decreasing tangential velocity. However, it has also been reported that high tangential velocity enhances the attachment of the biofouling layer to the membranes and therefore reduces its chemical cleanability [1].

2.2 Biofilm formation

The first step of the formation of a biofilm is the adsorption of organic molecules which are generally EPS from upstream biological activity. The second step is the attachment of microorganisms to the membrane surface, in a first place by pioneer bacteria strains. Other microorganisms can attach only to a mature biofilm with a sufficiently developed EPS structure. The EPS matrix structure is formed through secretion of EPS by the microbes growing in the biofilm and by deposition of EPS compounds present in the feed water.

On a mature biofilm there is some detachment of microorganisms. This allows them to colonise new surfaces. At high nutrient concentrations, the increase of the biofilm thickness by growth of microorganisms is significantly higher then biofilm thickness reduction by detachment. In this case only chemical cleaning can reduce the thickness. At a certain age of the biofilm the removal by chemical cleaning is not complete any more and the biofouling becomes partially irreversible. Subsequently, biofouling may become more and more irreversible. Furthermore, the protection of microorganisms against biocides by the EPS structure generally increases with the age of the biofilm.
Often biofouling appears in combination with particulate or/and colloidal fouling. In some cases, this can reinforce the biofilm structure and contribute to the irreversibility of the biofouling.

The primary attachment of microorganisms or/and the beginning of the irreversibility of the biofouling can be more or less delayed by an intensive pretreatment (e.g. with ultrafiltration membranes) or other low-fouling conditions (e.g. low flux rate, modified membrane surface, etc.).

III. CONSEQUENCES OF RO MEMBRANE BIOFOULING

There are numerous possible consequences resulting from biofouling:

- *Increased feed pressure* due to high delta p (feed to concentrate pressure drop), reduced permeability and higher osmotic pressure caused by increased concentration polarisation [2]. The result of increased feed pressure is high electricity consumption. An insufficient margin in feed pumping capacity may result in insufficient production of treated water.
- *Low plant availability and increased chemical costs* due to high chemical cleaning frequency and the use of biocides.
- *Mechanical damage of membrane elements* caused by too high delta p, especially if water hammers occur during transient phases of operation.
- *Chemical damage of membranes* caused by inappropriate use of cleaning agents or/and oxidising biocides.
- *Quality degradation of treated water* due to concentration polarisation or/and damaged membranes.

- *High membrane replacement costs* because of shortened membrane life.

IV. POSSIBLE SOLUTIONS TO RO MEMBRANE BIOFOULING

4.1 Conventional approaches: Use of chemicals

4.1.1 Frequent chemical cleaning of the membranes – A high chemical cleaning frequency can be a way to control biofouling or to contribute to the control of biofouling. This is a common approach for small RO plants treating difficult water in a high added value application. For a large drinking water plant this is not likely to be a cost efficient solution.

4.1.2 Oxidising biocides – Most RO membranes used today are composite membrane with a polyamide active layer that has a very limited resistance to chlorine. The experience with the combination of chlorination and dechlorination (by sodium bisulphite) upstream RO generally is quite unsatisfactory (see case study in chapter V). Chlorination-dechlorination rather enhances biofouling than controlling it. A chlorine resistant RO membrane with a performance similar to currently used polyamide composite RO membranes does not yet exist.
Mono-chloramine injection (without injection of bisulphite) is performing well on RO membrane plants treating tertiary effluents, but has not been successfully used in seawater RO plants with polyamide membranes.
Chlorine dioxide can be compatible, under certain conditions and to a certain extent, with polyamide composite RO membranes. It is used on some plants, but there is no long-term experience yet.
Peracetic acid can be used under certain conditions for sanitation after a chemical clean. This may result in some delay for the regrowth of the biofilm.
Some microbes that can be present in biofilms have some resistance to oxidising biocides.

4.1.3 Non-oxidising biocides – There are many polyamide RO membrane compatible biocide products available. They are based on two different non-oxidising biocide chemicals: 2,2-dibromo-3-nitrilo-propionamide (DBNPA) and isothiazolone.
They are used successfully on some RO plants [3]. Nevertheless, its online injection in drinking water plants is not recommended and would not be allowed by public health authorities in many countries. Off-line sanitation with those type of products is a possibility, but off-line sanitation corresponds to some down-time and thus to a loss of availability of the plant and production.

4.2 Approaches targeting the prevention of biofilm formation

4.2.1 Membrane surface modification – There are low fouling brackish water membranes available with an improved membrane surface (generally reduced roughness and/or increased hydrophilicity and/or reduced surface charge). Biofilm formation can be delayed by such membranes and cleanability can be better compared to conventional membranes.

4.2.2 Operation at a sub-critical flux – It has been reported that a biofilm is formed when the critical flux of the microbes has been exceeded [4].

4.2.3 Disinfection step in the pretreatment – It is still widely believed that disinfection of the water upstream the RO membranes can reduce or avoid biofouling. Possible technologies to do this are, other than the chlorination-dechlorination as mentioned above, ultrafiltration (UF) microfiltration (MF) and ultraviolet (UV) light treatment. However, UF hardly ever exceeds about 5 logs of reduction of microbes. This means that water feeding an UF with a total bacterial count of e.g. 10^5 u/mL will still have a total bacterial count of 1 u/mL or 10^3 u/L or 10^6 u/m^3 after this membrane “disinfection”. UF only allows to delay primary formation of the biofilm and its maturation. It also may delay the biofilm regrowth after a membrane cleaning or/and sanitation. The situation is quite similar with UV treatment: after some delayed biofilm formation and/or maturation, the effect is generally close to zero [5].

4.2.3 Quorum sensing disruption – Quorum sensing is the intercellular communication of micro-organisms via the production and response to signal molecules. Disruption of intercellular communication related to biofilm formation can be an efficient tool against RO membrane biofouling. This approach is still in an early R&D phase.

4.3 Techniques targeting in limitation of consequences of the biofilm

4.3.1 Membrane elements with different feed spacers – Membrane elements with a thicker feed spacer (34 mil) have a reduced delta p, as the cross-sectional area for the water flow is higher. This does not avoid the growth of the biofilm, but the impact on performance is significantly reduced. They also have a better cleanability. A more recent technology is based on a 34 mil feed spacer that is chemically enhanced by a biostatic agent. It also has an improved geometry that further reduces delta p [6].

4.3.2 Nutrient limitation by biofiltration – As stated by Hans-Curt Flemming [7], RO membrane biofouling is a “biofilm reactor in a wrong place”. This means that a bioreactor in the right place, i.e. in the pretreatment upstream the RO, allows to avoid or at least significantly reduce biofouling. Conventional pretreatment includes a granular media filters. In those filters, if they are operated without biocide or with biocide limited to occasional shock treatment, a biofilm is formed on the media biodegrading nutrient that downstream are no longer available for the growth of the biofilm on the RO membrane surface. An even better biodegradation is achieved with media types like activated carbon or expanded clay that are more adapted biomass supports than sand or anthracite.

4.3.3 Phosphorous limitation – Nutrient limitation can also be in form of phosphorous limitation. A way to remove phosphate in water that has been proposed [8] is coagulation with an iron salt. If phosphorous limitation is used for biofouling control, any phosphonate based antiscalant would need to be replaced by a polymer based antiscalant.

V. CASE STUDY: 84 MLD RO PLANT IN DAESAN, SOUTH KOREA

Severe biofouling combined with some colloidal fouling of the RO membranes of a plant at Daesan in South Korea has been an issue since its start-up in the 1992. The plant has a nominal capacity of 84 MLD and is operated by Veolia Water since 2000.

The raw water fed to this plant is mainly brackish water from a reservoir close to the sea (Daeho Lake) with some addition of soft water from another reservoir (Asan Lake). The water treatment configuration is shown below in the simplified process flow diagram in figure 1. Bleach is injected upstream the clarifiers and, in its original configuration, dechlorination was done by sodium bisulphite injection prior to the cartridge microfilters.

Coagulation is done in the circular clarifiers by injection of ferric chloride and flocculation is achieved with a low dose rate of an anionic polyelectrolyte. There is no coagulant injection prior to both filtration steps that would enhance filtration performance. The RO step consists of 12 trains with a capacity of

292 m^3/h each, operating at a recovery rate of 87%. 10 trains are in a 3-stage configuration and 2 trains have a 2-stage configuration.

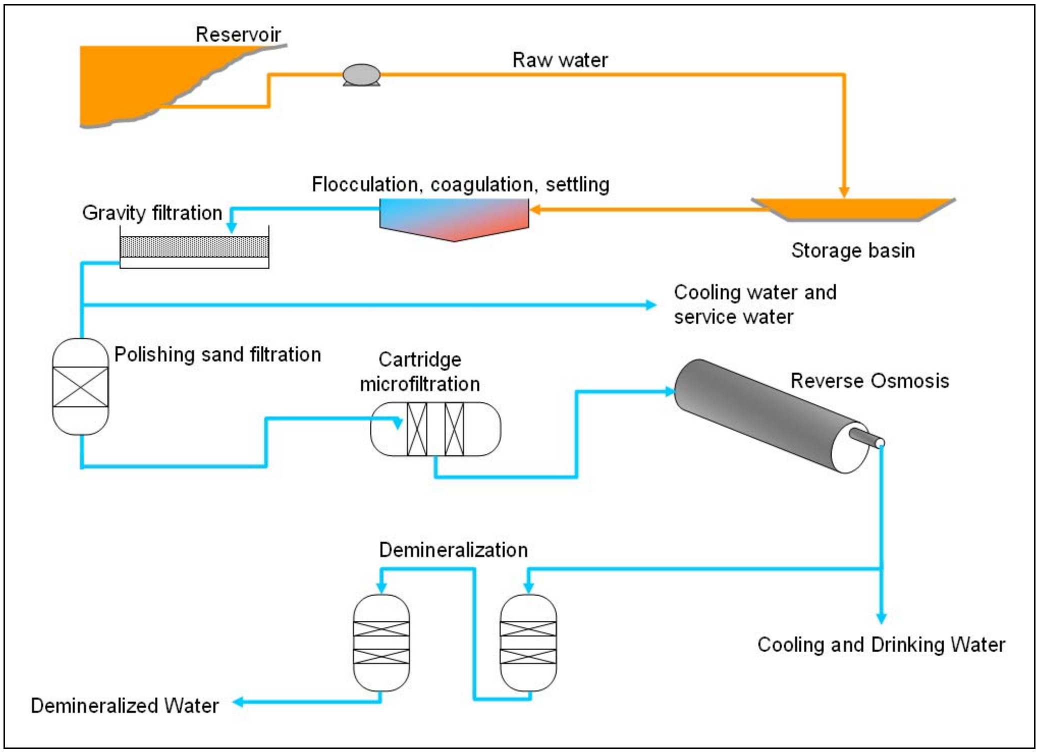

Figure 1: Simplified PFD of the plant

Among the consequences of the severe biofouling there have been a high chemical cleaning frequency of about once per week and an average membrane life of only 3 years. As it can be seen in figure 2, the delta p of the first stage has been very high with a maximum value of 12 bar.

Several modifications in 2006 have allowed operating the membranes with significantly reduced biofouling. The most important improvement has been removal of a major part of biodegradable organic matter in the pretreatment by operating the two filtration stages without the presence of free chlorine. This has been achieved by operating the chlorination prior to clarifiers close to the break-point and by addition of a granular activated carbon layer to the gravity filters. The activated carbon does not only remove eventual residual free chlorine, it is also a good support for the biomass. Complementary measures have been the use of a more efficient alkaline cleaning agent and the use of 34 mil feed spacer elements as replacement membranes.

The major results of the significantly reduced biofouling are a membrane life that has more than doubled and a chemical cleaning frequency that has been reduced by a factor of 4. It is quite likely that a major part of the remaining slow increase of delta p of the RO membrane elements is due to colloidal fouling.

In figure 2 it can be seen that in 2006 (after the modifications) and in 2007 the 1st pass delta p is gradually decreasing (both minimum and maximum values) to a normal level. The decreasing minimum values mean that the irreversible part of biofouling gradually turned back to reversible biofouling. The jump in mid-2008 to even lower delta p values of the 1st and 2nd pass corresponds to a membrane replacement with new 34 mil feed spacer elements.

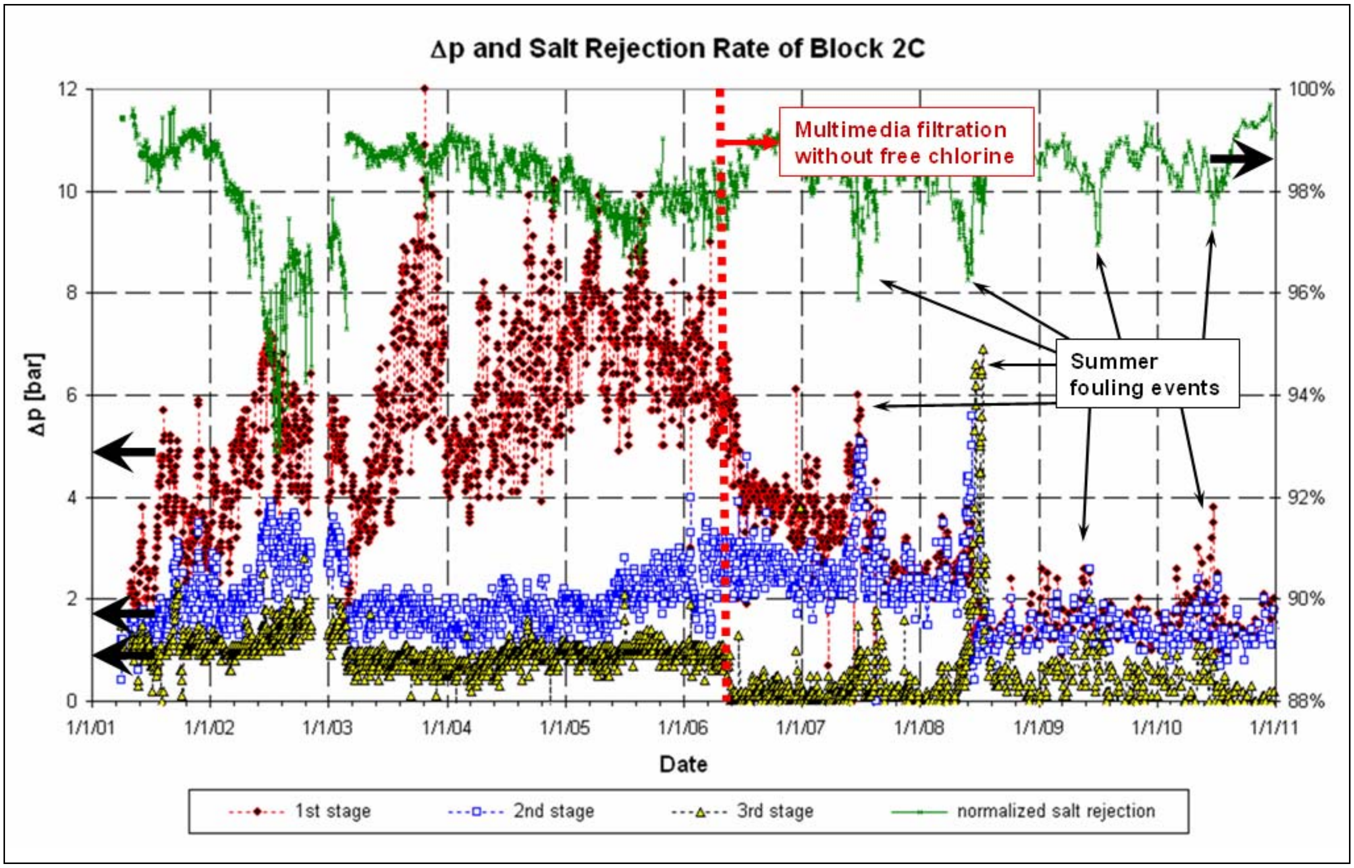

Figure 2: Evolution of Δp of each stage and of normalized salt rejection of Daesan RO block 2C (Membrane replacements: all three stages in 02-2003 and 07-2005; stage 1&2 in 06-2008; 3rd stage in 05-2010)

Nevertheless, every summer, there is period of about one or two months with a difficult raw water during which biofouling on the RO membranes still occurs. However, chemical cleanings after the end of these periods are always very efficient and no increase in irreversible fouling is observed after these summer fouling events (see figure 2).

VI. A NEW INNOVATIVE BIOFOULING CONTROL TECHNOLOGY[1]

6.1 Introduction

Nowadays RO pretreatment by UF or MF becomes more and more popular. These membrane filtration processes allow to achieve a better removal of small particulates and colloids than granular media filtration.

Their major drawback compared to granular media filtration is the quasi-absence of biological activity. Any RO plant with only UF (or MF) as pretreatment has a high risk of RO membrane biofouling, especially if it treats warm water containing nutrients. It often takes a very long time for the RO membrane biofilm formation due to the high feed water quality in terms of solids and microbes. It may

[1] BiopROtector™, Veolia Water Solutions & Technologies

take a year or two until the biofouling starts to become irreversible. In case that any pilot trial has been done before the design and construction of the plant, it is very likely that the duration of the trial was too short to see these long term effects.

In some cases this high risk of biofouling has been recognized and some biofiltration has been added as a complementary step to the UF (or MF) pretreatment. Even though biofouling control by nutrient limitation a quite appropriate option, the implementation of a second filtration process in addition to a high performance membrane filtration doesn't make much sense.

The new technology (patent pending) is a novel and innovative fixed bed bioreactor, but not a biofilter, i.e. it is reasonably inefficient in filtration, but performing well in biodegradation of nutrients. It is aimed to be used for the RO membrane biofouling control of plants with UF (or MF) as pretreatment filtration step.

The advantage compared to a biofilter is its simpler design and simpler operation with lower capital costs and lower operation costs as consequences. It can be placed either upstream or downstream the membrane filtration step. The major advantage of the position downstream the UF (or MF), is the absence, in most cases, of the necessity to clean the fixed bed. The major advantage of the upstream position is a reduction in fouling of the UF (or MF) membranes.

6.2 Seawater pilot trial

The pilot trial has been done with Mediterranean seawater from an open intake at a site close to Toulon in France. The raw water quality is described in a previous publication [9].

The treatment line using the bioreactor technology consists of:
BiopROtector™ – loose UF membrane filtration – 5 µm cartridge filtration – reverse osmosis (1 element 4040). No chemicals are used on this line.
The BiopROtector™ itself comprises 2 fixed bed bioreactors in series with empty bed hydraulic retention time of 4.3 minutes each.

The reference line consists of: dual media filtration (coagulant 1 mg/L Fe, 9 m/h, 80 cm anthracite/pumice 1.5 mm, 80 cm sand 0.66 mm) - 5 µm cartridge filtration – reverse osmosis (1 element 4040).

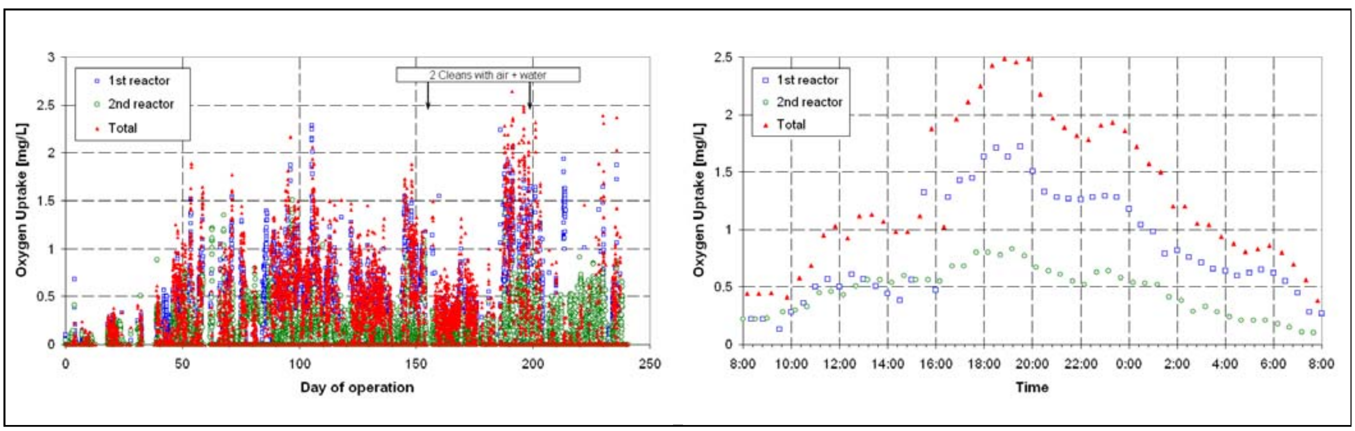

Figure 3: Bioreactor oxygen uptake rates during the trial and typical 24 hour profile

Nutrient biodegradation is difficult to quantify as assimilable organic carbon (AOC) and biodegradable dissolved organic carbon (BDOC) methods generally suffer from interferences and unadapted strains of microorganisms. However oxygen uptake rate is a relatively simple method for monitoring of biological activity.

Figure 3 shows the oxygen uptake rates during the trial as well as a typical 24-hour profile. Approximately 70% of the total oxygen uptake happens in the first reactor. In the 24-hour profile an increase of the oxygen uptake during daytime and a decrease during the night is observed. A correlation between photosynthetic activity in the sea and nutrients available could be a plausible explanation for this phenomenon.

The evolution of delta p of the RO elements is shown in figure 4. The delta p of the RO element downstream the bioreactor/UF pretreatment line is significantly more stable compared to the reference line with the dual media filter. It needs to be noted also that in previous trials [9] the RO with a dual media filter pretreatment had significantly less fouling than the RO with UF membrane (without bioreactor) pretreatment .

The evolution of the RO permeability has been similar on both lines. Furthermore it has been observed that the UF performed somewhat better, with less fouling compared to previous trial without bioreactor upstream the UF.

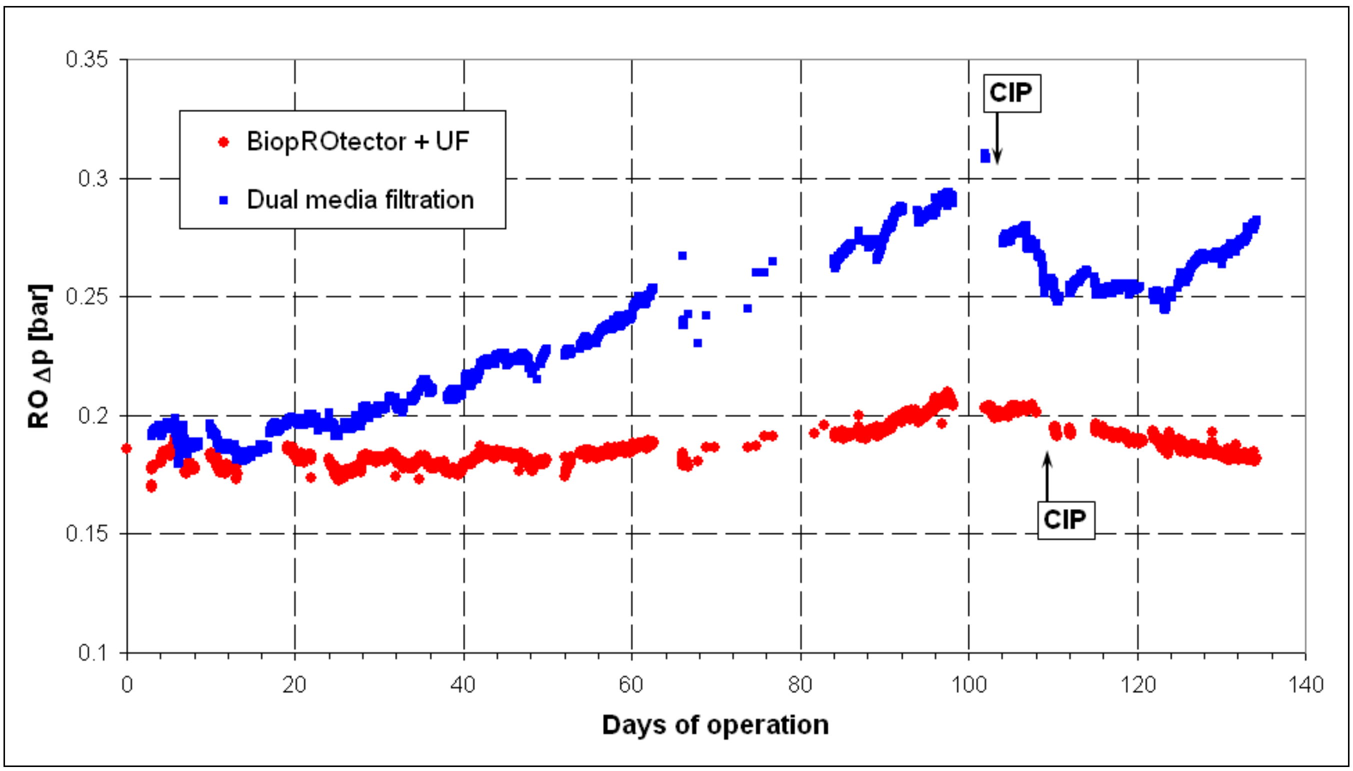

Figure 4: Evolution of delta p of the reverse osmosis membrane

VI. CONCLUSION

RO membrane biofouling is a common issue on RO plants treating surface water. It increases operational costs and therefore there is some strong demand for efficient biofouling control strategies. Many different approaches exist already or are under development.

Biofouling control by nutrient limitation has been successfully implemented on a large RO plant that previously suffered from the most severe RO membrane biofouling ever experienced by Veolia Water. A new innovative technology based on a fixed bed bioreactor aimed for biofouling control of RO membranes with UF/MF as pretreatment is under development. A pilot trial on seawater with this new technology gave very promising results.

VII. ACKNOWLEDGEMENTS

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REFERENCES

1 - J.S. Vrouwenvelder, "*Biofouling of Spiral Wound Membrane Systems*", PhD thesis, Delft University of Technology, 2009.

2 - M. Herzberg, and M. Elimelech, "*Biofouling of reverse osmosis membranes: Role of biofilm enhanced osmotic pressure*", Journal of Membrane Science, 295, 2007, p.11–20.

3 - K. Majamaa, U. Bertheas, V. Gomez Cortes, J. Cugat Mata, A. Arzu, "*Field Trial to Optimize the Use of DBNPA in WRU Application*", IDA World Congress, Dubai, 2009 (DB09-076).

4 - H. Winters, A. G. Fane, B. Nicolaisen, "*Microbial Membrane Fouling: Microbial Cake Enhanced Osmotic Pressure (CEOP) or Thermodynamic Restriction?*", IDA World Congress, Maspalomas, Gran Canaria , 2007 (MP07-267).

5 - C. Pelekani, S. Jewell, G. Kilmore, "*Design, Operating and Research Experience at the Penneshaw Seawater Desalination Plant, South Australia*", IDA World Congress, Maspalomas, Gran Canaria, 2007 (MP07-126).

6 - R. Franks, C. Bartels, A. Anit, "*Demonstrating improved RO System Performance with New low Differential (LD) Technology*", http://www.membranes.com/docs/papers/New Folder/Demonstrating Improved RO System Performance with New Low Differential (LD) Technology.pdf, 2010.

7 - H.C. Flemming, "*Reverse Osmosis Membrane Biofouling*", Experimental Thermal and Fluid Science, 14, 1997, p. 382-391.

8 - M. Kennedy, H. Bae, J. Jacobson, G. Amy, J. Schippers, "*Controlling Biofouling by Limiting Phosphate in RO Feedwater*", IDA World Congress, Dubai, 2009 (DB09-277).

9 - P.-J. Remize, J.-F. Laroche, J. Leparc, J.-C. Schrotter, "*A pilot-scale comparison between granular media filtration and low-pressure membrane filtration for seawater pretreatment*", Desalination and Water Treatment 9, 2009, p. 22-27.