Desalination and Water Treatment
www.deswater.com

34 (2011) 361–366
October

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doi: 10/5004/dwt.2011.2805

Membrane fouling characterization and cleaning adaptation in wastewater reclamation plants: from plant to lab

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Received 3 September 2010; Accepted 3 January 2011

ABSTRACT

Membrane biofouling represents an important drawback in full-scale water reclamation plants as it affects energy consumption, permeate productivity and even quality. Due to the high number of water-/membrane-/site-specific variables affecting membrane fouling and lifetime, cleaning and maintenance procedures need to be specifically designed for each application. Cleaning activities cannot directly be optimized onsite due to the necessity of ensuring a constant and safe product water flow and quality. For this reason, cleaning optimization needs to be transposed from plant to lab. In this work, a Spanish wastewater reclamation plant was selected to optimize cleaning procedures. For this, a reverse osmosis element was sampled and submitted to several cleaning protocols at lab-scale. The influence of the basic cleaning agent nature, pH and presence of additives on cleaning efficiency was studied. The optimal membrane cleaning conditions were achieved with a NaOH solution at pH 12 containing 0.03% SDS. At these conditions, permeate flux after cleaning was two fold greater than fouled membrane permeate flux. In this work, lab-scale membrane cleaning tests have shown to be a successful tool to optimize cleaning activities for full-scale plants and understand the influence of cleaning variables on membranes restoring efficiency.

Keywords: Membrane technology; Reverse osmosis; Fouling; Autopsy; Cleaning; Wastewater reclamation

1. Introduction

Water is a natural resource that needs to be preserved to ensure future human life development. Nowadays, around 600 m^3 of water per capita/year are abstracted worldwide [1]. Water consumption, together with the expected population increase and climate change, will sharply increase the number of people facing water scarcity problems in a near future [2]. Alternative supply options such as desalination, groundwater recharge, water reuse and rainwater harvesting are being more and more implemented in order to decrease natural water abstractions. Water reclamation is achieved through several treatment units installed after secondary treatment, whose configuration depends on many factors such as feed water quality, product water requirements and site area availability. Membrane technologies are being more and more selected to reclaim water as they are efficient and robust technologies to meet stringent quality needs required for reuse [3,4].

Despite its high treatment efficiency, membrane operation is strongly affected by fouling, which is usually the process bottleneck in terms of energy requirements, consumption of chemicals and water production. Mechanisms and compounds involved in fouling formation need to be identified and controlled to minimize

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Presented at the AMS6/IMSTEC10, The 6th conference of the Aseanian Membrane Society in conjunction with the 7th International Membrane Science and Technology Conference, Sydney Australia, November 22–26, 2010

fouling impact on membrane performance. However, this is not the only action to be implemented to reduce membrane fouling impact. Optimization of feed water pretreatment, membrane material, module hydrodynamics and cleaning protocols is also needed to soften fouling impact on treatment performance [5] and thus on process economy.

In full–scale installations, cleaning conditions must be specifically designed due to the huge variety of fouling processes taking place. The aim of this work was to study the influence of chemical cleaning variables on membrane properties restoration. As biofouling is considered as one of the most difficult to remove fouling types [6], an extremely-biofouled reverse osmosis (RO) element (permeability loss higher than 75%) used for several years in a water reclamation plant was selected for this study. The element was autopsied and submitted to several cleaning conditions to assess the influence of pH, cleaning agent nature and additives impact on cleaning efficiency. The results have demonstrated that lab-scale tests are useful for, apart from understanding the impact of the abovementioned variables on cleaning efficiency, designing and optimizing cleaning protocols for full-scale RO units.

2. Methodology

2.1. Membrane

A municipal water reclamation plant in Spain was selected to optimize the cleaning of the 8-inch RO membrane elements installed as final step in the tertiary treatment section. A 8-inch element (Hydranautics, model LFC1), with a cumulative filtration life of around four years, was selected and extracted from the lead position of the first pressure vessel in the RO section of the plant. Element origin and location were selected so that cleaning could be studied in a membrane exhibiting a high biofouling load. As it is well known, biofouling degree is higher in lead than in tail position, being the latter more affected by scaling [7].

Virgin and fouled membrane permeability and retention were measured in flat-sheet membrane samples obtained from a new 4-inch element and the 8-inch membrane element selected for this study, respectively. Permeability and retention were obtained from permeate flux and conductivity values measured when a 1500 mg/l NaCl solution was filtered through the membrane sample being characterized. Characterization tests were performed at 16 bar of transmembrane pressure (TMP), 25°C of temperature (T) and 1 m/s of crossflow velocity (v_f). Characterization protocol details can be found in section 2.3. Fouled membrane permeability (0.74 ± 0.08 l/hm^{2}bar) and salt retention (92.2 ± 1.2%) were 76% and 7% lower than those for the virgin membrane, respectively. Virgin and fouled membrane permeability and retention of the element studied indicate that, after around four years of operation, hydraulic characteristics were strongly damaged whereas selectivity was practically unaffected. Due to the sharp permeability loss, it can be stated that the selected membrane was practically at the end of its lifetime. Despite this operational limitation, the membrane represented a potential tool to study the impact of cleaning conditions on the partial restoration of a highly-fouled/-damaged element. The fouled element was first autopsied and characterized in order to rationally design the cleaning experiments. Fouling was found to be mainly formed by biofouling although scaling was also detected (phosphor and calcium presence). Accordingly, basic cleaning protocols were selected to clean the membrane as they are known to be effective for biofouling and organic fouling removal [8].

2.2. Chemicals and cleaning solutions

At full scale, sodium hydroxide at pH 12 was used for cleaning the elements installed in the selected reclamation plant when needed. In this work, the cleaning efficiency of this solution and of other formulations was assessed at lab-scale. In order to prepare the cleaning solutions to be tested, commercially-available reagents were dissolved in deionized water (27.2 ± 0.28 μS/cm). Two alkaline formulations were studied; one was based on sodium tripolyphosphate (STPP) and the other on sodium hydroxide. Apart from testing the cleaning efficiency of monocomponent formulations, bicomponent solutions were also studied. Bicomponent solutions were formed by the combination of STPP or sodium hydroxide with a surfactant (sodium dodecylsulfate - SDS or sodium dodecylbenzene sulfonate - DBS) or a chelating agent (sodium salt of ethylenediaminetetraacetic acid, EDTA). Furthermore, monocomponent solutions of EDTA, SDS and DBS were also studied in order to assess the influence of each substance dissolved in bicomponent formulations. Sodium chloride was used to prepare membrane characterization solutions (1500 mg/l NaCl), which were employed to characterize fouled and cleaned membrane properties. In the following section, the detailed membrane characterization protocol is presented.

2.3. Cleaning protocol

Cleaning experiments were performed in a lab-scale crossflow filtration unit. The unit, schematized in Fig. 1, was composed of a temperature-controlled feed tank (1), a pump equipped with an adjustable speed drive (2), a flat-sheet filtration cell (4) manufactured by GE Osmonics (model SEPA CF II), a backpressure

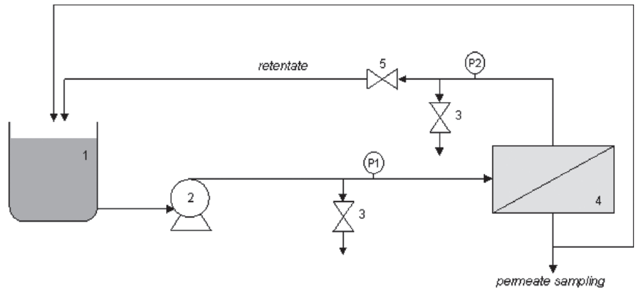

Fig. 1. Membrane cleaning experimental set-up.

valve (5) and two purge valves (3). Two pressure gauges were installed (P1 and P2) to monitor TMP. A BEL Engineering balance was installed in the permeate outlet to monitor permeate mass and thus obtain permeate flux. A multimeter (Crison) was used to analyze permeate and feed pH and conductivity.

Cleaning experiments were composed of three main steps: initial membrane characterization, cleaning protocol and final membrane characterization. Initial membrane characterization consisted in filtering through a fouled membrane sample a 1500 mg/l NaCl solution at 16 bar of TMP, 25°C of T and 1 m/s of v_f. At the steady-state, feed and permeate conductivity (C_f and C_p, respectively) as well as permeate flux (J_{bc}) were measured (period: 10 min). When C_p and J_b variations were lower than 5%, average values and standard deviations of C_p and J_b flux were obtained from the last three values. Average C_p and C_f were employed to obtain salt retention of fouled membrane (R_{bc}), which was calculated according to Eq. (1).

$$R_{bc}(\%) = 100 \times \left(1 - \frac{C_P}{C_f}\right) \tag{1}$$

Cleaning tests were performed after completing the initial membrane characterization step and pouring the remaining characterization solution out of the system. A cleaning test started by placing a previously-prepared cleaning solution in the feed tank and filtering it, following the same procedure than for characterization, at low TMP (2 bar), 25°C and at a 1 m/s of v_f. Cleaning experiments duration (t) was 2 h. Depending on the goal of each set of experiments, cleaning variables were adjusted. In this paper, the effect of pH, cleaning reagent and surfactant or chelating agent presence on membrane cleaning efficiency is presented. Hence, pH, agent nature and combination were varied according to the purpose of each test.

After cleaning the membrane, the solution that remained in the system was poured out and the feed tank was filled again with characterization solution. Then, the cleaned membrane was characterized following the same protocol than for the fouled membrane in order to calculate the restoring efficiency achieved. In this case, J_{ac} and R_{ac} represent cleaned membrane permeate flux and retention, respectively. The restoring capacity of the cleaning performed was assessed through the permeate flux gain, expressed by the ratio J_{ac}/J_{bc}, as it is commonly used in previous works [9,10]. Absolute R_{bc} and R_{ac} values were also compared to assess salt selectivity recovery achieved although, as abovementioned, this property was not found to be strongly affected in the RO element studied.

3. Results and discussion

3.1. Agent and pH impact on cleaning efficiency

In this section, the effect of the cleaning agent and bulk solution pH on cleaning efficiency is discussed. A first selection of cleaning agents as well as their combination and concentration was carried out according to the general recommendations of RO membrane manufacturers [11]. Solutions of STPP+EDTA, STPP+SDS, NaOH, NaOH+SDS and NaOH+EDTA were thus tested at pH 10, 11 and 12 at 25°C. As Fig. 2 demonstrates, STPP-based solutions were less effective than NaOH-based ones at pH 12. However, at pH 10 and 11, their activity was similar. STPP functions as an inorganic-based chelating agent and detergent [11] whilst NaOH cleaning mechanism can be explained by hydrolysis and dissolution or even saponification [12]. Hence, the higher efficiency achieved with NaOH could be explained by the membrane fouling nature (mainly biofouling), and thus its affinity to be more easily removed by NaOH than STPP.

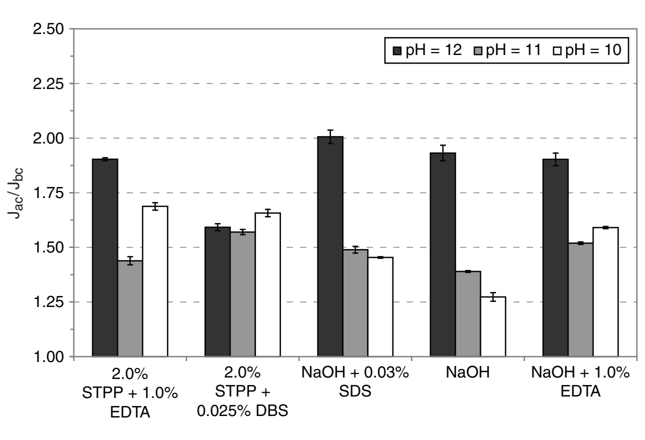

Fig. 2. Influence of cleaning agent and pH on permeate flux gain t = 2h; TMP = 2 bar; v_f = 1 m/s; T = 25°C.

By comparing NaOH-based solutions efficiency at pH 10 and 11, it can be stated that SDS and EDTA presence slightly improved NaOH cleaning activity. This could be explained by the emulsification and dispersion capacity of surfactants that may enhance cleaning efficiency [12]. Surfactants ability to solubilize organic compounds (present in organic and biological foulants) in micelles formed in the bulk solution and/or in the membrane surface vicinity may also contribute to the efficiency improvement [13]. EDTA chelation capacity for inorganics explains the cleaning efficiency enhancement observed when it was present in the formulation [14]. When increasing pH from 11 to 12, for all the NaOH-based solutions, a significant improvement on cleaning efficiency was achieved. This can be related to the fact that an increase on pH (i.e., concentration) results into a higher NaOH activity, as demonstrated in previous literature [9,15]. The highest permeate flux gain observed (2.01 ± 0.03) in this set of experiments was for NaOH+0.03% SDS at pH 12. This flux gain was 4% higher than the one obtained with the formulation used at full-scale conditions (NaOH at pH 12). Hence, the improvement achieved when NaOH+SDS at pH 12 was tested could have a significant impact on water production in high-capacity plants. Lab-scale experiments have thus shown to be useful for optimizing cleaning and process efficiency of full-scale RO elements.

Retention behavior of fouled and cleaned membranes was also assessed. Fouled and cleaned membrane retentions, obtained when testing the influence of agent and pH on cleaning efficiency are grouped in Fig. 3. In this figure, solid bars represent fouled membrane retention (black for pH 12, grey for pH 11 and white for pH 10) whilst textured bars represent cleaned membrane retention. As Fig. 3 shows, the highest salt retention observed after cleaning was 95.7 ± 0.1%. These results were achieved for the NaOH+0.03% SDS solution at pH 12, which was the formulation that also gave the highest J_{ac}/J_{bc}.

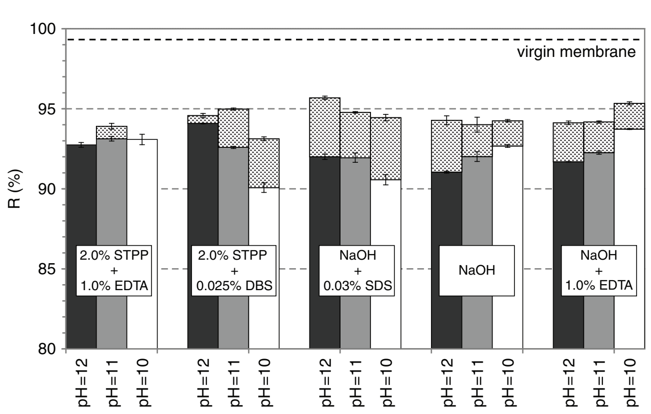

Fig. 3. Influence of cleaning agent and pH on membrane retention t = 2h; TMP = 2 bar; v_f = 1 m/s; T = 25°C. Solid bars represent fouled membrane retention and textured bars cleaned membrane retention.

Cleaned membranes retention, as shown in Fig. 3, did not follow a clear trend with cleaning agent nature and pH. This can be the result of to the huge variability observed in fouled membrane retention data. Retention variability can be attributed to the fact that each experiment was performed with a new fouled membrane sample. Thus, it seems logical to state that, depending on the sampling area, fouling changed in extent and/or nature, which in turn affects rejection properties. Instead, J_b remained practically constant regardless of the membrane sample and thus sampling area. It can therefore be concluded that permeate flux gain is a more appropriate cleaning efficiency indicator than retention, at least for the tested membrane and conditions.

3.2. Additive impact on cleaning efficiency

In the preceding section, it was demonstrated that binary NaOH-based solutions were highly active for restoring membrane permeate flux. In this section, the role of single components forming binary solutions on cleaning efficiency is presented. Fig. 4 shows the influence of surfactant (DBS or SDS) or chelating agent (EDTA) presence, on permeate flux gain, in NaOH solutions at pH 12. The figure also presents the results of the experiments performed with monocomponent solutions of NaOH, EDTA, DBS or SDS at the same concentration than when they were dissolved in bicomponent solutions.

Flux gain for monocomponent solutions of NaOH was significantly higher than that achieved for EDTA, DBS and SDS monocomponent solutions. This behavior agrees with results published by Madaeni and Samieirad (2010) concerning the assessment of the impact of cleaning variables on wastewater-fouled membranes cleaning [15]. The authors observed that single NaOH

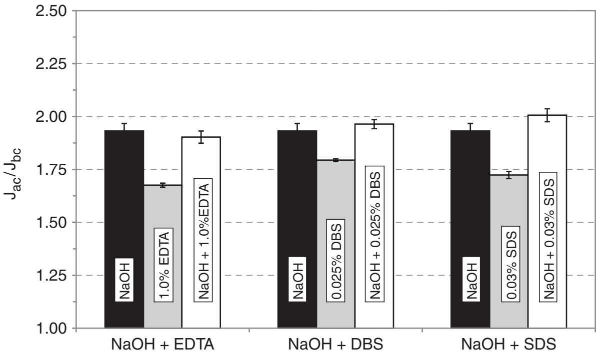

Fig. 4. Influence of additives in NaOH-based solutions on permeate flux gain t = 2h; pH = 12; TMP = 2 bar; v_f = 1 m/s; T = 25°C.

solutions were more effective for fouling removal than single surfactant formulations. Fig. 4 shows that EDTA was less effective for removing fouling than SDS and DBS. This can be attributed to the fact that EDTA is an inorganic chelating agent and is thus, in principle, active for removing inorganic compounds and minerals but not for biofouling [14]. Instead, anionic surfactants are useful for both attracting and confining positively-charged inorganic ions in the hydrophilic head of micelles or monomers and dissolve organic compounds in the micellar hydrophobic cores [16].

Cleaning efficiency of binary NaOH-based solutions was, as Fig. 4 demonstrates, slightly higher than for single surfactant or chelating agent solutions. Again, these results agree with those published by Madaeni and Samieirad (2010), which demonstrated that combined NaOH+SDS solutions were more active than those prepared with single NaOH or SDS [15]. As Fig. 4 shows, when NaOH+EDTA, NaOH+DBS and NaOH+SDS formulations were tested, permeate flux gain was 13%, 9% and 17% higher than for single EDTA, DBS and SDS solutions, respectively. As Fig. 4 demonstrates, J_{ac}/J_{bc} was 1.93 ± 0.04 and 2.01 ± 0.03 for NaOH and NaOH+SDS, respectively. Therefore, an improvement of 4% on the permeate production could be obtained by replacing the NaOH solution (used in the full-scale plant selected) by the bicomponent NaOH+SDS formulation.

Fouled and cleaned membrane retention for this set of experiments is presented in Fig. 5. As the figure shows, a retention improvement was observed in all the tests, regardless the cleaning conditions. The highest cleaned membrane retention, which was obtained with the NaOH+SDS solution, was 95.7 ± 0.1%. Hence, complete restoring of rejection was not possible at least at the tested conditions. This may indicate that either cleaning solutions were not efficient enough for removing fouling or that, what is more probable, irreversible fouling was deposited on the membrane and/or part of the membrane performance had been lost during its operation (four years).

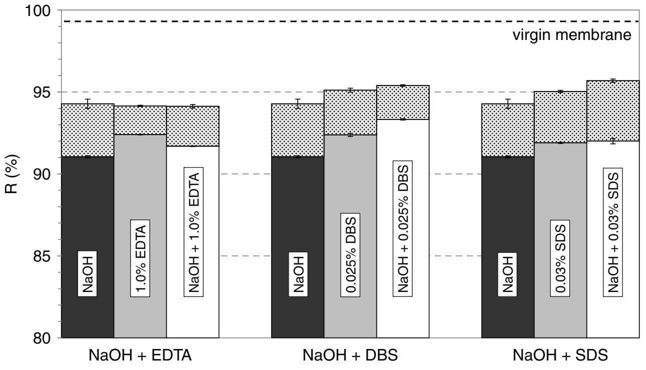

Fig. 5. Influence of additives in NaOH-based solutions on membrane retention t = 2h; pH = 12; TMP = 2 bar; v_f = 1 m/s; T = 25°C. Solid bars represent fouled membrane retention and textured bars cleaned membrane retention.

4. Conclusions

Permeate flux gain was found to be a more reliable indicator to assess membrane cleaning efficiency than retention recovery because, when cleaning conditions were modified, no significant and clear differences on retention were observed. This may be explained by the variability of fouled membrane retention, whose value depended on the sampling area. Moreover, due to the fact that membrane retention for fouled membrane was only 7% lower than virgin membrane rejection, retention improvements achieved by cleaning could not be macroscopically observed. Instead, as permeate flux had been strongly affected by process operation, cleaning efficiency could be satisfactorily assessed through its gain measurement.

The results have shown that a RO membrane, which had been under operation in a water reclamation plant during four years, could be partially cleaned with basic formulations. Cleaning efficiency was found to be affected by pH, cleaning agent and presence of additives. NaOH-based solutions were found to be more active for fouling removal than STTP-based formulations. Moreover, by appropriately selecting cleaning pH, fouling removal efficiency could be optimized. For instance, when a NaOH solution was tested, cleaning efficiency increased around 30% when pH was raised from 10 to 12. It was thus demonstrated that an increase on pH results into a permeate flux restoring efficiency improvement. Presence of surfactants, such as SDS or DBS, in NaOH-based solutions was found to enhance fouling removal efficiency probably due to the increased solubilization capacity (for organic fouling and biofouling components) of the cleaning solutions containing surfactants. To sum up, lab-scale cleaning experiments have shown to be a useful instrument to optimize membrane cleaning protocols and understand the impact of cleaning variables on membrane restoration efficiency. Thus, lab-scale cleaning optimization studies represent a potential tool for full scale membrane plant operators.

Acknowledgements

The ACC1Ó agency of the *Generalitat de Catalunya* is gratefully acknowledged for co-funding this project (OPTIMECA, ref. RD08-2-0023). The authors are indebted to the *Consejo Insular de Aguas de Gran Canaria* (CIAGC) for its support in the project.

Symbols

C_f — Feed concentration (mg/l) or conductivity (µS/cm)
C_p — Permeate concentration (mg/l) or conductivity (µS/cm)
DBS — Sodium dodecylbenzene sulfonate
EDTA — Sodium salt of ethylenediaminetetraacetic acid
J_{ac} — Permeate flux measured after cleaning (l/h·m^2)
J_{bc} — Permeate flux measured before cleaning (l/h·m^2)
SDS — Sodium dodecylsulfate
STPP — Sodium tripolyphosphate
t — Cleaning duration (h)
T — Temperature (°C)
TMP — Transmembrane pressure (bar)
v_f — Crossflow velocity (m/s)
R_{ac} — Salt retention measured after cleaning
R_{bc} — Salt retention measured before cleaning
RO — Reverse osmosis

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