Long-term evaluation of a forward osmosis-nanofiltration demonstration plant for wastewater reuse in agriculture

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Abstract

Hybrid forward osmosis (FO) processes such as forward osmosis with membrane bioreactors (FO-MBR), electrodialysis (FO-ED), nanofiltration (FO-NF) or reverse osmosis (FO-RO) present promising technologies for wastewater reuse in agriculture as they meet high effluent quality requirements, especially regarding boron and/or salt content. An FO-NF demonstration plant for this application was built and operated treating 3 m^3 h^{-1} of real wastewater with a salinity of 3-5 mS cm^{-1} and 1.5 mg L^{-1} of boron in continuous mode for 480 days. Three draw solutions (DS) were evaluated in different periods of experimentation. Sodium polyacrylate led to reversible fouling on the FO and NF membranes and the permeate was not suitable for irrigation. Magnesium sulphate, used as DS in a second phase, generated severe irreversible fouling on NF membranes and therefore it was discarded. Finally, magnesium chloride showed the best performance, with FO-NF membranes presenting a stable permeability and low membrane fouling during long-term operation. The FO-NF permeate showed high quality for irrigation, achieving a conductivity value of 1 mS/cm, a boron concentration below 0.4 mg L^{-1} and an average SAR of 1.98 (mequ $L^{-1})^{0.5}$. DS replacement costs were reduced by working with high rejection NF membranes. However, energy consumption costs associated with the NF step make the global process more energy intensive than conventional technology.

***Keywords*:** Forward osmosis, hybrid FO-NF system, membrane fouling, economic analysis, demonstration plant, water reclamation.

1. INTRODUCTION

Forward osmosis (FO) processes use a draw solution (DS) to create an osmotic pressure gradient that induces water from a feed solution to flow through a semi-permeable membrane that prevents the passage of most solutes. This is generally followed by a process to reconcentrate the diluted DS and produce water, except in the case of particular applications where no DS reconcentration is necessary [1], [2]. For the application studied here, forward osmosis-nanofiltration (FO-NF) was identified as a promising option because NF presents a high rejection of multivalent ions and a sufficiently low pressure to achieve high recovery rates [3], [4]. Several authors have studied this hybrid technology, validating its application for divalent and organic DS separation with high flux and acceptable salt rejection [5]–[8]. FO-NF may even offer many benefits over the stand-alone RO process for desalination of brackish water [9].

The concept of fertiliser-driven FO (FDFO) coupled with NF membranes for indirect fertigation has been widely studied by Phuntsho et al. [10]–[13] at batch lab- and pilot-scale and with full-scale simulation, obtaining useful information about reverse diffusion, accumulation of feed solutes, membrane fouling and energy consumption. However, the results obtained in these studies are not comparable to those of conventional technologies at demonstration scale, working continuously and using real wastewater, for instance as regards energy and DS consumption, clean-in-place (CIP) frequency, or fouling deposited on FO and NF membranes.

Only a few publications [13]–[17] have provided an energy consumption comparison between hybrid FO technologies and conventional RO, all of which were only performed theoretically and all indicate that RO is more energy efficient because the DS recovery step implies high energy input. The only exceptions would be an FDFO-NF hybrid system using a thin film composite (TFC)-FO membrane [13] and a lab-scale FO-ED process [18], which present lower energy consumption than RO.

Meanwhile, CIP chemical consumption in FO processes is highly dependent on fouling propensity. One of the main advantages reported for the FO process compared with conventional membrane technologies when applied to wastewater treatment, is the low fouling tendency of FO membranes. This is because the lack of hydraulic pressure, and thus fouling layer compaction [17], [19], reduces the need for cleaning chemicals throughout the entire process, leading to a corresponding reduction in plant shutdowns in comparison with RO membrane systems. Some authors have studied the FO fouling phenomenon using deionised water as feed water matrix [20]–[22], while others have used more representative feeds [23]–[25], but none have assessed fouling performance during long-term operation. Although some studies in the literature have evaluated the influence of flux, temperature, pH, feed or DS on fouling, these were all based on experiments performed at bench scale using simulated feed and focusing solely on the FO step [21], [26], [27]. No studies have been identified that investigated fouling occurrence and chemical cleaning frequency in FO membranes and membranes from the DS recovery step alike.

To the best of our knowledge, no experimental research has been conducted on hybrid FO-NF technology under realistic conditions at close-to-market scale. For the first time, the present study implemented a hybrid FO-NF demonstration plant at commercial scale over a long period of time (480 days) using real feed water in order to evaluate this technology considering fouling propensity, energy and chemical costs and permeate water quality for agricultural purposes. Plant construction was guided by the conclusions drawn from a preliminary pilot-scale study [4] aimed at identifying the most suitable DS and FO membrane modules. Additionally, this study evaluated operational costs and compared them with those of the main alternative, UF-RO, in order to determine the feasibility of this emerging technology.

2. MATERIALS AND METHODS

2.1. ***FO-NF hybrid system***

The FO-NF demonstration plant was located next to a wastewater treatment plant (WWTP) in San Pedro del Pinatar (Murcia), based on membrane bioreactor (MBR) technology. As feed water, the FO-NF demonstration plant used the MBR effluent, which is free from solids and pathogens. Figures 1.a and 1.b present a diagram and a picture, respectively, of the plant. NF technology and TFC-FO flat-sheet (FS) membranes were selected according to a preceding work [4], hence, two racks of six FO commercial FS membranes (model number PFO 100) were used, comprising an area of 84 m^2 of TFC (Porifera, CA, USA). The active layer was in contact with the feed solution, and co-current contact was implemented according to instructions from the manufacturer. Two pressure vessels were installed with four NF membranes (Filmtec), each one, model numbers NF 270 4040 (TFC, high flux) or NF 90 4040 (TFC, high rejection), with an area of 60.8 m^2. Some parameters, such as conductivity, redox potential, pH, flow rate, pressure and temperature were automatically monitored, registered and controlled at different points in the plant using a supervisory control and data acquisition system (SCADA) from Rockwell Automation (Allen Bradley). All the instrumentation was acquired from Endress+Hauser (Switzerland). An FO control loop was implemented between the permeate flow rate and the fresh DS dose to maintain the permeate flow rate constant by means of a set-point. NF membrane permeate flow rate and FO permeate flow rate were coordinated so that both processes worked simultaneously [28].

2.2. ***Feed water (FW)***

The MBR effluent from San Pedro del Pinatar WWTP was characterised. Table 1 compiles the main parameters of the effluent. Except for conductivity and boron, which were higher than expected due to marine intrusion, the values of the parameters measured were in the range of those typical for MBR effluent from an urban wastewater treatment plant. In line with Spanish water reuse legislation (RD1620/2007) [29] for irrigation purposes, these values thus indicated the need for treatment with a desalination process to reduce both salinity and boron concentration.

2.3. *Chemicals*

According to a previous study [4], three DS were selected to test: sodium polyacrylate, magnesium sulphate and potassium pyrophosphate. The last one was replaced by magnesium chloride. The high molecular weight polymer DS (sodium polyacrylate with 6500 Da previously diluted, 43% w/w) was purchased from Kemira Ibérica (Spain). The two inorganic DS tested, magnesium sulphate with 98% purity (2% of impurities mainly consisting of silicates, gypsum and iron) and magnesium chloride with >99% purity, were purchased from Barcelonesa de Drogas y Productos Químicos (Spain), as were the CIP chemicals, hydrochloric acid (25% purity) and sodium hydroxide (50% purity). Genesol 703, a commercial cleaning product that is particularly effective against aluminium silicate, was acquired from Genesys.

2.4. *Demonstration plant operation*

A continuous flow of 3 m^3 h^{-1} of MBR effluent, from the WWTP at San Pedro del Pinatar, was treated in the FO modules of the demonstration plant using 2 m^3 h^{-1} of concentrated DS (sodium polyacrylate, magnesium sulphate or magnesium chloride). The diluted DS stream was treated by NF membranes. Filter cartridges of 5 µm passage were installed just before the FO and NF membranes in order to protect membranes from thicker suspended solids. The permeate flow rate (water for irrigation) set-point was kept constant at 200 L h^{-1}, which corresponds to a flux of 2.4 L m^2 h^{-1} for FO and 3.3 or 6.6 L m^2 h^{-1} for NF depending on the period. A DS osmotic pressure of about 10 bar, according to Corzo et al. [4], was set. As an exception, the permeate flow rate was increased on days 160 and 187 to 350 L h^{-1}.

The demonstration plant was maintained in operation for 480 days. During the operation, different changes (three different DS, changes in NF membrane type and number of modules) were introduced with the aim of reducing the operation expenditures (OPEX). The reason for each change is described further in the results section. During 480 days of operation, five different operational periods were clearly distinguished (Table 2). When DSs were changed, the operation of the plant was stopped and all elements (pipes, pumps, tanks and membranes) were flushed with deionized water. When replacing NF membranes, flushing out the membrane preservative solution was done for at least 30 minutes.

2.5. Monitored parameters

Permeability (Perm) or normalised specific flux was calculated continuously in FO and NF membranes as follows:

$$\text{Perm} = \frac{Jw(25^{\text{o}}C)}{NDP} \qquad \text{(eq. 1)}$$

$$Jw(25^{\text{o}}C) = \frac{Jw}{TCF} \qquad \text{(eq. 2)}$$

$$\text{TCF}=\frac{1}{(2.10^{-9}\cdot(\text{T}^6)-3.85^{-7}\cdot(\text{T}^5)+2.88^{-7}\cdot(\text{T}^4)-1.14^{-3}\cdot(\text{T}^3)+2.62^{-2}\cdot(\text{T}^2)-3.82^{-1}\cdot\text{T}+3.96)} \qquad \text{(eq. 3)}$$

where Jw (25ºC) represents the flux corrected at 25ºC [L m^{-2} h^{-1}] obtained by equation 2 and 3, to be TCF the temperature correction factor and NDP the net driving pressure [bar] which is obtained by equation 4.

$$NDP = \text{Pf} - \left(\frac{\delta P\text{f,c}}{2}\right) - \text{P}_{\text{p or DDS, CDS}} - \Pi_{\text{f,c}} + \Pi_{\text{p or DDS, CDS}} \qquad \text{(eq. 4)}$$

where P is the hydraulic pressure, Π the osmotic pressure and δP the differential pressure [bar]. The subscripts f, c, p, DDS and CDS indicate feed, concentrate, permeate, diluted DS and concentrated DS, respectively.

Permeability is an intrinsic parameter of each type of membrane and thus monitoring this parameter allows fouling problems or alteration of structural parameters to be inferred. The water from the region of Murcia has extreme temperatures during summer and normalization at 25ºC has been applied to Jw, Js and P using the TCF (eq. 3). Magnesium or sodium mass balance (depending on the DS employed) between DS and FW streams was used to check normalised reverse salt diffusion (Js) from the DS side to the feed water side. Conductivity water quality was monitored online. FO and NF membrane CIP was implemented when membrane permeability was observed to decrease. DS and energy consumption was recorded in order to determine OPEX.

2.6. ***NF autopsy***

A detailed examination of two nanofiltration elements (one NF 270-4040 and one NF 90-4040) located in the 1st position of the demonstration plant pressure vessel was conducted. The examination included external inspection of the elements, autopsies and analytical tests of the active layer surface, as well as an analysis of deposited matter by means of quantification, moisture determination, the loss on ignition (LOI) test and scanning electron microscope with energy dispersive X-ray analysis (SEM-EDX).

The LOI test was performed under oxidant conditions, from room temperature to 550ºC, in order to determine the composition of the organic and inorganic solid matter present on both NF elements subjected to autopsy. The EDX analysis was conducted to identify membrane fouling components. Samples of deposited solid on the membrane surface were dried and calcined before EDX analysis. The SEM-EDX analysis identified the elements in the solid deposited on the membrane surface. SEM was performed using a Philips XL30 ESEM microscope and an EDX analyser from EDAX.

2.7. *Analytical methods*

The parameters to be evaluated in the demonstration plant laboratory were analysed weekly. Osmotic pressure was measured using an Osmomat® 030 Cryoscopic Osmometer from Gonotec. TDS and conductivity measurements were performed with a Crison CM 35 conductivity meter with temperature compensation. Sodium, magnesium and boron were determined by ICP-mass spectrometry using an ICP-MS 7500cx spectrometer from Agilent Technologies and isotopic dilution analysis. For calcium analysis, potentiometric titration was carried out with a Titrando 809 system controlled by PC control software following SM 2340 C. COD was analysed by using LCK 414 kit from Hach Lange.

3. RESULTS AND DISCUSSION

3.1. *FO-NF performance at demonstration scale*

Hydraulic performance, water quality and OPEX due to DS replenishment, energy consumption and CIP frequency, were monitored and evaluated over the 480 days of demonstration plant operation in order to determine the feasibility of the FO-NF system. Three different DS and some modifications in NF membranes and configuration were implemented, divided into 5 different demonstration plant operation periods, as detailed in Table 2.

A general overview of hydraulic performance is presented in Figure 2, which includes permeate flow rate and specific flux for both membranes. Figure 3 shows the evolution of the hydraulic pressure required in the NF process and Figure 5 presents the evolution of both FO feed and NF permeate conductivity, as well as the boron and sodium adsorption ratio (SAR) over the 480 days of experimentation. Figure 6 (Table S-2) gives the number of parameters that indicated whether the water produced were acceptable or unacceptable for use in irrigation from the total of 32 listed in Table S-1. Finally, Table 4 includes OPEX calculated from DS replenishment, cleaning processes and energy consumption.

3.1.1. *First period: sodium polyacrylate as DS and 8 NF-270 4040 elements*

The first period encompassed days 1 to 58 of operation using sodium polyacrylate as DS and 8 NF 270 4040 membranes. As shown in Figure 2, FO permeability was observed to decrease over this period, falling over the first 10 days of operation and then remaining stable for the rest of this period. Meanwhile, a substantial change was observed in the NF unit over the experimental period, with a considerable reduction in permeability. This loss of NF hydraulic properties was probably caused by a fouling episode, as shown in Figure 3, where a steep rise in nanofiltration membrane differential pressure can be observed between days 40 to 58.

To clarify the causes of this fouling event, an autopsy was carried out on one of the NF membrane elements (see section 2.6) before applying chemical cleaning. As the NF membrane feed was basically DS diluted in water, fouling must have been produced by the DS selected [30]. An initial visual examination of the NF membrane element suggested that organic fouling had settled on the membrane surface. The element was completely covered by a thin brown-grey layer, as depicted in Figure 4. A solid sample from the surface was collected for subsequent analysis. A LOI analysis showed that the solid from the element contained 86.30% water. These results may indicate that, due to the capacity of the DS for water absorption, a jellied layer had formed, which considerably reduced the hydraulic properties of the NF module. Calcination of the previously dehydrated solid sample indicated that its composition corresponded to 89.72% organic matter and 10.28% inorganic matter. SEM-EDX analyses of the dehydrated solid revealed the presence of C, O and N, and to a lesser extent, of the elements Al, Si, Fe, P, S, K, Mg and Cl. Regarding the calcined solid, there was a higher proportion of the elements O, Si and P followed by a lower proportion of Fe, Al, K, Ca, Mg, C, Cu, Na and S. Therefore, the SEM-EDX analyses confirmed the existence of organic matter in the solid. In addition, the analyses showed that the inorganic fraction of the solid could be composed of silicates of aluminium, iron and other metals, as well as possibly metallic oxides, hydroxides, and phosphates.

In light of these results, the FO and NF membranes were subjected to conventional chemical cleaning, which comprised the steps shown in Table S-3. Table 3 shows the results of the hydraulic test (Table S-4) carried out in order to determine the effect of chemical cleaning on the membranes. The most relevant observation was that this cleaning procedure restored almost 100% of the initial permeability of the NF membrane. Thus, it can be concluded that only reversible fouling of this membrane occurred when using sodium polyacrylate as DS. In contrast, the FO membrane only recovered 78% of its initial permeability, with only 13% being due to reversible fouling. Some 22% of losses in terms of specific flux could be attributed to an initial membrane maturation period [31].

Product water from the FO-NF demonstration plant during period 1 reached some of the quality standards required for agricultural reuse. For instance, figure 5 shows that boron values were constantly below 0.4 mg L^{-1} and the average conductivity was 0.9 mS cm^{-1}, meeting the legislative requirements. However, SAR was higher than expected (SAR > 100 (mequ $L^{-1})^{0.5}$), which exceeded the limit established in RD1620/2007 [29]. This can be attributed to the removal of divalent ions by the NF membrane and the high presence of sodium. Adjustment with Ca^{2+} or Mg^{2+} salts would therefore be necessary in order to comply with reuse requirements.

As shown in Figure 6, the percentage of parameters indicating that water was acceptable for irrigation only increased from 50% up to 75% when water was treated by FO-NF using sodium polyacrylate as DS. Nevertheless, the results showed that the permeate water still presented a moderate to high content of salts, especially sodium and, consequently, was not suitable for irrigation uses.

Since the DS selected in this period was organic, COD monitoring was performed. Results are presented in Figure 7. COD permeate values were unstable over the first 40 days but subsequently stabilised to below 100 mg L^{-1}, an admissible value for WWTP effluents according to European legislation (91/271/CEE) [32]. This phenomenon was attributed to wide variations in the molecular weight of the sodium polyacrylate. As the DS was operating in a closed loop, when the DS regeneration process started, the low molecular weight fractions of the DS would have passed through the NF membrane and the DS would have thus been enriched in the high molecular weight fractions. This may have increased rejection and permeate quality until only the high molecular weight fractions remained in the DS, at which point rejection and permeate quality stabilised.

Given these results, it can be concluded that the demonstration plant operation under period 1 conditions produced water which complied with the quality standards required for agricultural reuse except for SAR. Furthermore, as shown in Table 4, the use of sodium polyacrylate as DS was expensive (2.97 € m^{-3}) due to the high cost associated with, first, its replacement and, second, the higher CIP frequency needed because of the reversible fouling occurring in the NF process.

3.1.2. *Second period: magnesium sulphate as DS and 8 NF-270 4040 elements*

The second period encompassed operational days 59 to 83. As shown in Figure 2, at the start of the second period, the NF-specific flux recovered its initial performance and operation with magnesium sulphate, as DS remained reasonably stable without the need to apply CIP. However, as can be seen in Figure 5, permeate conductivity reached mean values of around 2 mS cm^{-1}. This was attributed to significant DS loss because of the higher diffusion coefficient of divalent electrolytes as compared to high molecular weight polymers [33]. Figure 5 also shows that SAR and boron were reduced to around 0.5 (mequ $L^{-1})^{0.5}$ and 0.4 mg L^{-1}, respectively.

Figure 6 shows that the permeate water obtained using an inorganic DS based on magnesium sulphate, presented acceptable values for more than 90% of irrigation quality parameters such as sodium content, H. Green rules, Wilcox rules and the Scott index among others (table S-1). Therefore, the permeate obtained using magnesium sulphate as DS presented a suitable quality for irrigation purposes.

3.1.3. *Third and fourth periods: magnesium sulphate as DS and 8 and 4 NF-90 4040 elements, respectively*

The third and fourth periods lasted for more than 8 months of demonstration plant operation, from days 84 to 226 and days 226 to 327, respectively.

When the third period started, the 8 NF-270 4040 elements were changed for the same number of higher rejection NF-90 4040 membranes. Immediately after the installation of the new NF system, DS losses in permeate decreased significantly, which represented considerable savings in DS replenishment and reduced the total process costs (see Table 4). Although this change entailed a slight increase in the energy required for the process, this was by far counterbalanced by the reduction in DS losses obtained with the tighter membranes.

As described in Figure 2, operation with magnesium sulphate was practically stable in the third period and fouling did not occur. However, from day 160 it was decided to increase permeate flow rate by increasing DS osmotic pressure, and shortly afterwards, irreversible fouling appeared on the NF membranes~~,~~ as shown in Figure 3. As this figure also shows, when the third period started, the pressure gap increased up to 4 bars. One reason for this might be that the high rejection NF membranes offered more resistance than high flux NF membranes (second period). From day 160, the pressure gap increased due to fouling occurrence. Therefore, in order to recover the initial hydraulic properties of the NF membranes, an element autopsy followed by a chemical cleaning were performed.

As shown in Figure 8, the element was covered by a thin layer of dark, wet, brown-grey powder that suggested inorganic fouling. This substance could not be collected in sufficient quantity to be quantified by means of LOI. The most relevant information was drawn from an SEM-EDX analysis, which confirmed the presence of inorganic matter on the thin layer. Several constituents were detected, including alumina silicates, iron and metallic oxides and hydroxides. Gypsum did not appear on the membrane surface, but a high retention of this material was detected inside the cartridge filters that protected the NF membranes. Thus, it was confirmed that NF fouling was produced by the DS content in impurities (section 2.3).

Conventional cleaning was performed with the aim of recovering the initial NF hydraulic properties, following the procedure set-up shown in Table S-3. Table 5 gives the results of the standard test (Table S-4) carried out in order to determine membrane performance before and after conventional chemical cleaning. The NF membrane only recovered 59% of its initial permeability after chemical cleaning. About 21% of flow loss was caused by reversible fouling and 41% by persistent fouling. The effect of this cleaning only increased NF permeability for a few days, as shown in Figure 2.

In period 4 (from day 226), the number of NF-90 4040 elements was reduced by half, from 8 to 4. The main objective was to increase NF cross flow velocity to double in order to prevent fouling, but an additional goal was to optimise savings in chemical consumption by means of enhancing NF rejection. Figure 2 shows that NF permeability increased, but Figure 3 indicates that the pressure gap also increased up to 6 bars because of foulants deposited on the membrane surface. Since foulants in general, and alumina silicates in particular, are difficult to remove, chemical cleaning was performed with a special cleaner, Genesol 703, following the procedure shown in Table S-5. Table 5 gives the results obtained, where only the 63% of the initial permeability was recovered by the NF membrane. Only about 11% of flux was recovered following this special cleaning, and 37% of losses in terms of specific flux were caused by irreversible fouling. Thus, although Figure 5 indicates high permeate water quality during these periods; the marked fouling detected entailed higher energy costs in the regeneration process (see Table 4).

3.1.4. *Fifth period: magnesium chloride as DS and 4 NF-90 4040 elements*

The fifth and longest demonstration plant operation period lasted from days 328 to 480. During this period, magnesium chloride was used and evaluated as DS, having been selected because it is an economical substance with high magnesium content. Furthermore, diffusivity and the Van't Hoff coefficient are higher than in magnesium sulphate [34]. When using magnesium chloride, less DS was required to achieve the same osmotic pressure, and there was less internal concentration polarisation on the FO membrane; therefore, a lower quantity of chemical was lost in the recovery step in comparison with the prior period.

It can be observed in Figure 2 that NF permeability increased significantly during the fifth period. Figure 3 shows a pressure gap increasing trend during the fifth period probably due to initial NF membrane maturation and an operational problem: a slight rise in the permeate flowrate up to 250 L h^{-1} from the 367 to 381 day (see Figure 2). Thereafter, this tendency was higher but quite stable, the pressure gap returned to below 4 bars and low fouling was detected, with the consequent reduction in NF energy consumption throughout the entire period (Table 4). On the other hand, as can be seen in Figure 5, permeate conductivity increased to around 1 mS cm^{-1}. Chloride is more conductive than sulphate, thus, when using magnesium chloride, the electrical conductivity was higher than in the previous period [35]. Most of the water quality parameters maintained acceptable standard values. FO membrane boron rejection was constant at around 70%, thus boron values remained below 0.4 mg L^{-1} throughout the entire operation. Although the mean SAR value increased from 0.92, when using magnesium sulphate as DS, to 1.98 (mequ $L^{-1})^{0.5}$ when using magnesium chloride, irrigation quality parameters were acceptable in more than 90% of cases (Figure 6), primarily due to the low sodium content. Like SAR and conductivity, some other parameters were higher in period 5 than in period 3 or 4. In this case, Riverside rules classified period 5 permeate as high salinity water and with moderate hardness (Table S-1). Therefore, the permeate presented a suitable quality for irrigation purposes as regards both irrigation quality parameters and legislation [29].

As shown in table 4, after implementing several improvements in every period, the operational costs per cubic meter of product water were reduced. The fifth period presented stable operation and the lack of fouling problems extends the standard CIP frequency. With these results, the FO-NF demonstration plant operation was completed and the data obtained were used for the comparison purposes included in section 3.2.

3.2. *Comparison between FO-NF and UF-RO*

The cost per cubic metre of product water obtained by the state-of-the-art technology for desalination as tertiary treatment, UF-RO process is estimated at large-scale, 0.35-0.45 € m^{-3} [36] while, according to this study, the cost of product water obtained by FO-NF technology reached 0.96 € m^{-3}.

As can be drawn from the previous section, the FO-NF process consumes less chemical product than UF-RO. The FO membranes do not require chemical cleaning and NF fouling depends directly on the DS used. The only significant chemical cost is caused by DS losses (NF permeate and reversal flux), but this is offset by the fertilising properties provided by the residual magnesium chloride content in the reclaimed water, which is beneficial for some crops [37], leading to savings in agricultural costs. Furthermore, if a divalent waste liquid stream with low fouling potential was identified as DS [38], no chemical consumption cost would be entailed. However, the UF-RO feed needs pH, coagulant and antiscalant dosage adjustments. According to the manufacturer's instructions, UF chemically enhanced backwash (CEB) must be performed once daily, whereas CIP is normally performed once per month using sodium hypochlorite, caustic soda and hydrochloric acid [39]. Moreover, the RO cleaning solution is usually applied monthly with the consequent expense in caustic soda, hydrochloric acid, ethylene diamine tetra-acetic acid and sodium lauryl sulphate [40]. Furthermore, a remineralisation process must be implemented with lime or limestone and carbon dioxide in order to achieve acceptable SAR values.

As regards energy requirements, total energy consumption of the FO-NF process is about 40% higher than the UF-RO process, as shown in the simulation presented in Table S-6. However, it should be borne in mind that the FO-NF values given in Table 4, refer to a demonstration plant rather than a large-scale plant. Large-scale cost estimation would be desirable, as the scale factor significantly affects energy consumption. It has been estimated that pilot-scale plants may consume between 2 and 10 times more energy than a full-scale plant [41], and therefore, costs at large-scale might be substantially more economical. Consequently, a large-scale estimation for FO-NF technology might reduce the cost per cubic metre of product water to a level similar to that for UF-RO (around 0.4 € m^{-3}).

4. CONCLUSIONS

The application of a hybrid FO-NF system for wastewater reclamation was studied at demonstration plant scale. Over the 480 days of demonstration plant operation, some adjustments were carried out in order to improve performance and minimise OPEX. The obtained results suggest that the use of sodium polyacrylate as DS promotes fouling and generates permeate quality issues. When employing magnesium sulphate as DS, permeate quality showed to be suitable for irrigation but irreversible fouling occurred on NF membranes. On the other hand, the use of high rejection NF membranes and magnesium chloride as DS significantly reduced operating costs throughout the last operational period. Low fouling was observed and no chemical cleaning was required. Conductivity, boron, SAR and other irrigation parameters reached the quality standards required for agricultural reuse. The only significant chemical cost is caused by DS losses although total energy consumption of the FO-NF process is about 40% higher than the UF-RO process.

This study has demonstrated that FO is a low-fouling technology that can achieve a stable, high quality permeate for wastewater treatment and reuse in the long-term. Chemical consumption is only relevant in terms of DS losses, and the residual content present in product water can serve as fertiliser for watering crops. However, further optimisation is required in terms of energy and DS consumption to transform the hybrid-FO process into a competitive technology for water reuse.

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6. REFERENCES

[1] S. Phuntsho, H. K. Shon, S. Hong, S. Lee, S. Vigneswaran, and J. Kandasamy, “Fertiliser drawn forward osmosis desalination: The concept, performance and limitations for fertigation,” *Rev. Environ. Sci. Biotechnol.*, vol. 11, no. 2. pp. 147–168, 2012.

[2] D. Roy, M. Rahni, P. Pierre, and V. Yargeau, “Forward osmosis for the concentration and reuse of process saline wastewater,” *Chem. Eng. J.*, vol. 287, pp. 277–284, 2016.

[3] H. Luo *et al.*, “A review on the recovery methods of draw solutes in forward osmosis,” *Journal of Water Process Engineering*, vol. 4, no. C, pp. 212–223, 2014.

[4] B. Corzo, T. de la Torre, C. Sans, E. Ferrero, and J. J. Malfeito, “Evaluation of draw solutions and commercially available forward osmosis membrane modules for wastewater reclamation at pilot scale,” *Chem. Eng. J.*, vol. 326, pp. 1–8, 2017.

[5] C. H. Tan and H. Y. Ng, “A novel hybrid forward osmosis - nanofiltration (FO-NF) process for seawater desalination: Draw solution selection and system

configuration," *Desalin. Water Treat.*, vol. 13, no. 1–3, pp. 356–361, 2010.

[6] J. Su, T. S. Chung, B. J. Helmer, and J. S. de Wit, "Enhanced double-skinned FO membranes with inner dense layer for wastewater treatment and macromolecule recycle using Sucrose as draw solute," *J. Membr. Sci.*, vol. 396, pp. 92–100, 2012.

[7] N. T. Hau, S. S. Chen, N. C. Nguyen, K. Z. Huang, H. H. Ngo, and W. Guo, "Exploration of EDTA sodium salt as novel draw solution in forward osmosis process for dewatering of high nutrient sludge," *J. Membr. Sci.*, vol. 455, pp. 305–311, 2014.

[8] R. Kumar and P. Pal, "A novel forward osmosis-nano filtration integrated system for coke-oven wastewater reclamation," *Chem. Eng. Res. Des.*, vol. 100, pp. 542–553, 2015.

[9] S. Zhao, L. Zou, and D. Mulcahy, "Brackish water desalination by a hybrid forward osmosis-nanofiltration system using divalent draw solute," *Desalination*, vol. 284, pp. 175–181, 2012.

[10] S. Phuntsho, S. Hong, M. Elimelech, and H. K. Shon, "Forward osmosis desalination of brackish groundwater: Meeting water quality requirements for fertigation by integrating nanofiltration," *J. Membr. Sci.*, vol. 436, pp. 1–15, 2013.

[11] S. Phuntsho *et al.*, "Fertiliser drawn forward osmosis process: Pilot-scale desalination of mine impaired water for fertigation," *J. Membr. Sci.*, vol. 508, pp. 22–31, 2016.

[12] S. Phuntsho *et al.*, "A closed-loop forward osmosis-nanofiltration hybrid system: Understanding process implications through full-scale simulation," *Desalination*, pp. 1–10, 2016.

[13] J. Eun *et al.*, “Environmental and economic impacts of fertilizer drawn forward osmosis and nanofiltration hybrid system,” *Desalination*, vol. 416, no. April, pp. 76–85, 2017.

[14] N. M. Mazlan, D. Peshev, and A. G. Livingston, “Energy consumption for desalination - A comparison of forward osmosis with reverse osmosis, and the potential for perfect membranes,” *Desalination*, vol. 377, pp. 138–151, 2016.

[15] D. L. Shaffer, J. R. Werber, H. Jaramillo, S. Lin, and M. Elimelech, “Forward osmosis: Where are we now?,” *Desalination*, vol. 356, pp. 271–284, 2014.

[16] R. K. McGovern and J. H. Lienhard, “On the potential of forward osmosis to energetically outperform reverse osmosis desalination,” *J. Membr. Sci.*, vol. 469. pp. 245–250, 2014.

[17] N. Akther, A. Sodiq, A. Giwa, S. Daer, H. A. Arafat, and S. W. Hasan, “Recent advancements in forward osmosis desalination: A review,” *Chem. Eng. J.*, vol. 281, pp. 502–522, 2015.

[18] S. Zou and Z. He, “Electrodialysis recovery of reverse-fluxed fertilizer draw solute during forward osmosis water treatment,” *Chem. Eng. J.*, vol. 330, no. May, pp. 550–558, 2017.

[19] M. Xie, J. Lee, L. D. Nghiem, and M. Elimelech, “Role of pressure in organic fouling in forward osmosis and reverse osmosis,” *J. Membr. Sci.*, vol. 493, pp. 748–754, 2015.

[20] S. Zhao, L. Zou, C. Y. Tang, and D. Mulcahy, “Recent developments in forward osmosis: Opportunities and challenges,” *J. Membr. Sci.*, vol. 396. pp. 1–21, 2012.

[21] J. Heo *et al.*, “Organic fouling and reverse solute selectivity in forward osmosis: Role of working temperature and inorganic draw solutions,” *Desalination*, vol. 389, pp. 162–170, 2016.

[22] N. M. Mazlan *et al.*, “Organic fouling behaviour of structurally and chemically different forward osmosis membranes. A study of cellulose triacetate and thin film composite membranes,” *J. Membr. Sci.*, vol. 520, pp. 247–261, 2016.

[23] A. Achilli, T. Y. Cath, E. A. Marchand, and A. E. Childress, “The forward osmosis membrane bioreactor: A low fouling alternative to MBR processes,” *Desalination*, vol. 238, no. 1–3, pp. 10–21, 2009.

[24] H. Zhang, Y. Ma, T. Jiang, G. Zhang, and F. Yang, “Influence of activated sludge properties on flux behavior in osmosis membrane bioreactor (OMBR),” *J. Membr. Sci.*, vol. 390–391, pp. 270–276, 2012.

[25] S. Phuntsho, S. Sahebi, T. Majeed, F. Lotfi, J. E. Kim, and H. K. Shon, “Assessing the major factors affecting the performances of forward osmosis and its implications on the desalination process,” *Chem. Eng. J.*, vol. 231, pp. 484–496, 2013.

[26] P. Xiao, J. Li, Y. Ren, and X. Wang, “A comprehensive study of factors affecting fouling behavior in forward osmosis,” *Colloids Surfaces A Physicochem. Eng. Asp.*, vol. 499, pp. 163–172, 2016.

[27] G. Blandin, H. Vervoort, P. Le-Clech, and A. R. D. Verliefde, “Fouling and cleaning of high permeability forward osmosis membranes,” *J. Water Process Eng.*, vol. 9, pp. 161–169, 2016.

[28] B. Corzo, T. de la Torre, A. Molina, M. Micó, and J. J. Malfeito, “REFO®. Procedimiento de control de sistema combinado de ósmosis directa y nanofiltración u ósmosis inversa.” PCT/ES2016/070925. Patent Pending, 2016.

[29] Spanish Legislation, “Real decreto de reutilización de aguas depuradas RD 1620/2007,” pp. 50639–50661, 2007.

[30] P. Zhao *et al.*, “Explore the forward osmosis performance using hydrolyzed

polyacrylamide as draw solute for dye wastewater reclamation in the long-term process," *Chem. Eng. J.*, vol. 273, pp. 316–324, 2015.

[31] Networking, "IDA World Congress," 2015.

[32] MAGRAMA, "Directiva 91/271/CEE sobre el tratamiento de las aguas residuales urbanas. Manual de interpretación y elaboración de informes," p. 133, 1991.

[33] E. R. Cornelissen *et al.*, "Membrane fouling and process performance of forward osmosis membranes on activated sludge," *J. Membr. Sci.*, vol. 319, no. 1, pp. 158–168, 2008.

[34] A. Achilli, T. Y. Cath, and A. E. Childress, "Selection of inorganic-based draw solutions for forward osmosis applications," *J. Membr. Sci.*, vol. 364, no. 1–2, pp. 233–241, 2010.

[35] R. C. Weast, *CRC Handbook of Chemistry and Physics*, 70th Editi. Boca Raton, Florida, 1989.

[36] R. Iglesias, E. Ortega, G. Batanero, and L. Quintas, "Water reuse in spain: Data overview and costs estimation of suitable treatment trains," *Desalination*, vol. 263, no. 1–3, pp. 1–10, 2010.

[37] H. Azzouzi, K. Ouzaouit, A. Aboulaich, Y. Dali, A. Kaddami, and I. Akalay, "Managem Products Potentially used in Fertilizers Industry," *Procedia Engineering*, vol. 138, pp. 302–307, 2016.

[38] M. J. Luján-Facundo, J. L. Soler-Cabezas, J. A. Mendoza-Roca, M. C. Vincent-Vela, A. Bes-Piá, and S. Doñate-Hernández, "A study of the osmotic membrane bioreactor process using a sodium chloride solution and an industrial effluent as draw solutions," *Chem. Eng. J.*, vol. 322, pp. 603–610, 2017.

[39] Pentair, *Operation & Maintenance - X-Flow dead-end UF systems - Cleaning In Place*, Technical. 2012.

[40] *Dow Water & Process Solutions, FILMTEC^{TM} Reverse Osmosis Membranes,* Technical. 2011.

[41] B. Lesjean, “European projects on MBR technology delivered. A report on the final MBR-Network workshop,” no. April, pp. 1–8, 2009.

Table 1. Comparison of San Pedro del Pinatar. MBR effluent parameters analyzed and RD1620/2007 criteria for irrigation purposes.

Table 2. Operation conditions in every period.

Table 3. Results of hydraulic test[1] for both membranes showing the conventional CIP effect during the first period.

Table 4. Overall real OPEX calculated from DS replenishment, cleaning processes and energy consumption at demonstration plant.

Table 5. Results of hydraulic test[1] for NF 90 4040 membrane showing the conventional CIP effect in the third period and the special CIP in the fourth.

Figure 1a. Scheme of the demonstration plant. **1b.** Picture of the demonstration plant.

Figure 2. Hydraulic performance of the demonstration plant in their different periods.

Figure 3. Evolution of the hydraulic pressure required in NF process in order to observe the fouling trend.

Figure 4. Membrane sheet picture and solid sample collected from the membrane surface.

Figure 5. Comparison between feed water and permeate quality. Zoom for SAR in the first 60 days.

Figure 6. Quantification of irrigation parameters that classify the water samples as acceptable or unacceptable for this purpose.

Figure 7. Evolution of COD along the first experimentation period.

Figure 8. Membrane picture and solid sample collected from the membrane surface.

Table 1

Parameter	***Units***	***MBR effluent average***	***RD 1620/2007 limit***
E.coli	CFU/100 mL	0	100
Suspended solids	mg/L	<1	20
Turbidity	NTU	0.22	10
Conductivity	dS/m	5.33	3
Sodium adsorption ratio	$(\text{mequ L}^{-1})^{0.5}$	10.6	6
Boron	mg/L	1.17	0.5
Arsenic	mg/L	0.0015	0.1
Chrome	mg/L	0.0041	0.1
Copper	mg/L	0.002	0.2
Manganese	mg/L	0.018	0.2
Molybdenum	mg/L	0.002	0.01
Nickel	mg/L	0.0016	0.2
Selenium	mg/L	<0.004	0.02

Table 2

Period	*Draw Solution*	*NF membranes*	*Number of membranes*[1]
1	Sodium Polyacrylate	NF 270 4040	8
2	Magnesium Sulphate	NF 270 4040	8
3	Magnesium Sulphate	NF 90 4040	8
4	Magnesium Sulphate	NF 90 4040	4
5	Magnesium Chloride	NF 90 4040	4

1) 4 membranes per pressure vessel

Table 3

Comments	**NF 270 4040 Specific Flux (L m^{-2} h^{-1} bar^{-1}) at 25ºC**	**PFO 100 Specific Flux (L m^{-2} h^{-1} bar^{-1}) at 25ºC**
Initial conditions	8.55	0.26
Before Chemical cleaning	4.44	0.17
After Chemical cleaning	8.49	0.20

1) Hydraulic test procedure was presented in supplementary material, table S-4.

Table 4

Period	FO Jw[1] (L m^{-2} h^{-1})	FO Js[1] (g m^{-2} h^{-1})	Js/Jw (g L^{-1})	DS losses in permeate (g L^{-1})	Cost of replacement[3] (€ m^{-3})	FO process energy consumption[4] (KWh m^{-3})	NF process energy consumption[4] (KWh m^{-3})	Cost of energy[5] (€ m^{-3})	FO CIP frequency (CIP year^{-1})	NF CIP[6] frequency (CIP year^{-1})	CIP cost (€ m^{-3})	Overall cost (€ m^{-3})
1	2.51±0.11	0.18±0.01	0.07[2a]	0.85±0.05	2.50	0.45	4.12[7]	0.46	NR	18	0.01	2.97
2	2.16±0.07	0.41±0.03	0.19[2b]	1.52±0.03	1.68	0.41	3.03	0.34	NR	NR	-	2.02
3	2.04±0.05	0.35±0.03	0.17[2c]	0.91±0.03	1.06	0.42	3.44[7]	0.39	NR	NA	-	1.45
4	2.37±0.04	0.40±0.02	0.17[2d]	0.82±0.02	0.97	0.41	4.14[7]	0.46	NR	NA	-	1.43
5	2.58±0.10	0.49±0.03	0.19[2e]	0.39±0.04	0.52	0.38	4.00	0.44	NR	NR	-	0.96

1) Normalized at 25ºC

2) DS Osmotic pressure (concentration) average: a = 9.28 bar (221.5g L^{-1}); b=8.99 bar (41.0g L^{-1}); c=7.79 bar (34.9g L^{-1}); d=8.08 bar (36.3g L^{-1}); e=7.57 bar (10.6g L^{-1})

3) DS price is referred to a small-scale order

4) Measured by means of an energy counter. It must be taken into account that the values refer to a demonstration plant, and this pumping energy will be significantly reduced in a full-scale plant due to the scale factor.

5) 0.10 KWh/m^3 is assumed

6) Applied when 20% of permeability losses are quantified

7) NF Membranes fouled

NR) Not required during the experimentation time

NA) Not applicable due to cleaning inefficacy. Irreversible fouling

Table 5

Comments	**NF 90 4040 Specific Flux under conventional CIP** **(L m^{-2} h^{-1} bar^{-1}) at 25ºC**	**NF 90 4040 Specific Flux under special CIP** **(L m^{-2} h^{-1} bar^{-1}) at 25ºC**
Initial conditions	4.69	4.69
Before Chemical cleaning	1.78	2.44
After Chemical cleaning	2.77	2.95

1) Hydraulic test procedure was presented in supplementary material, table S-4.

Figure 1

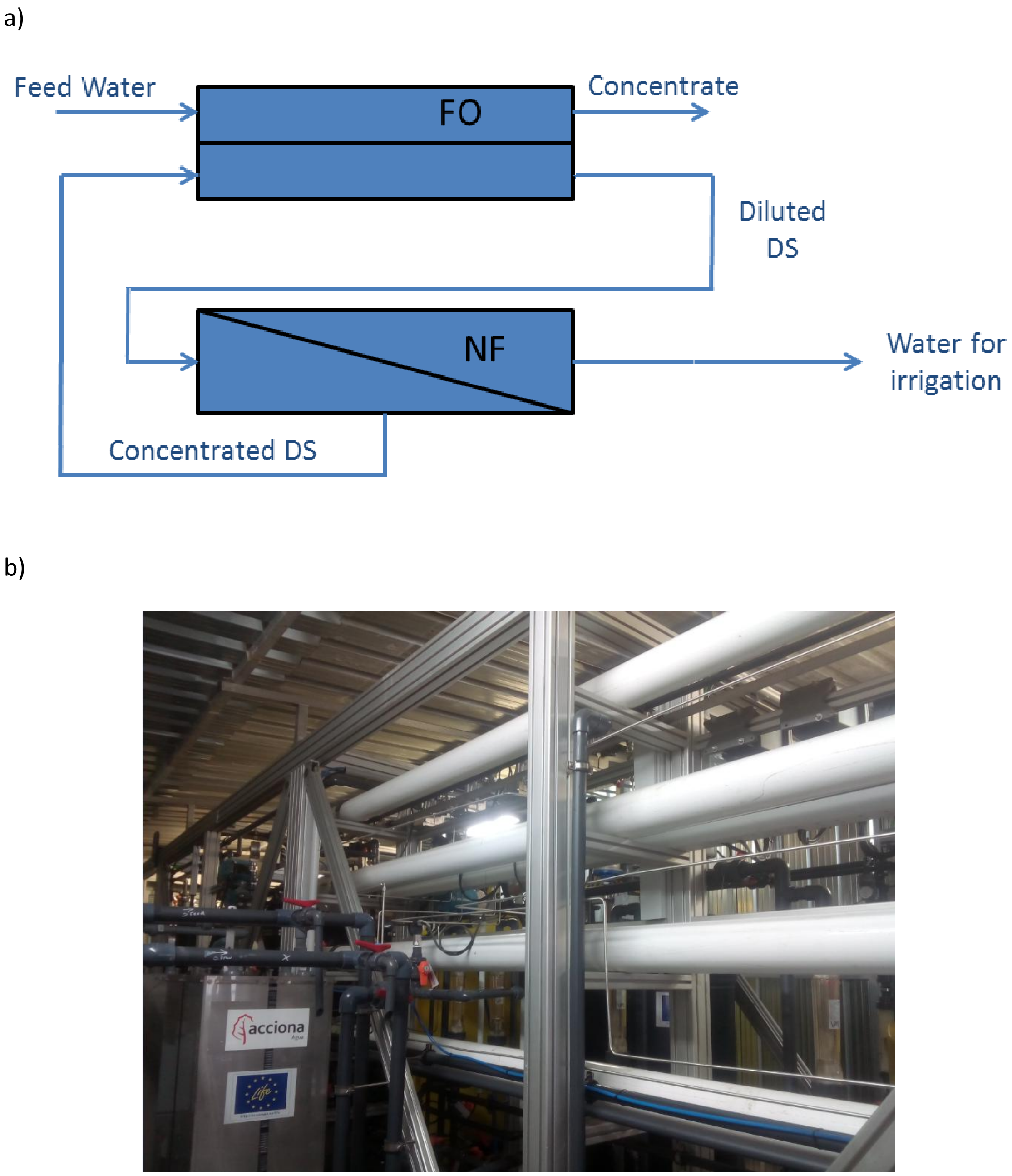
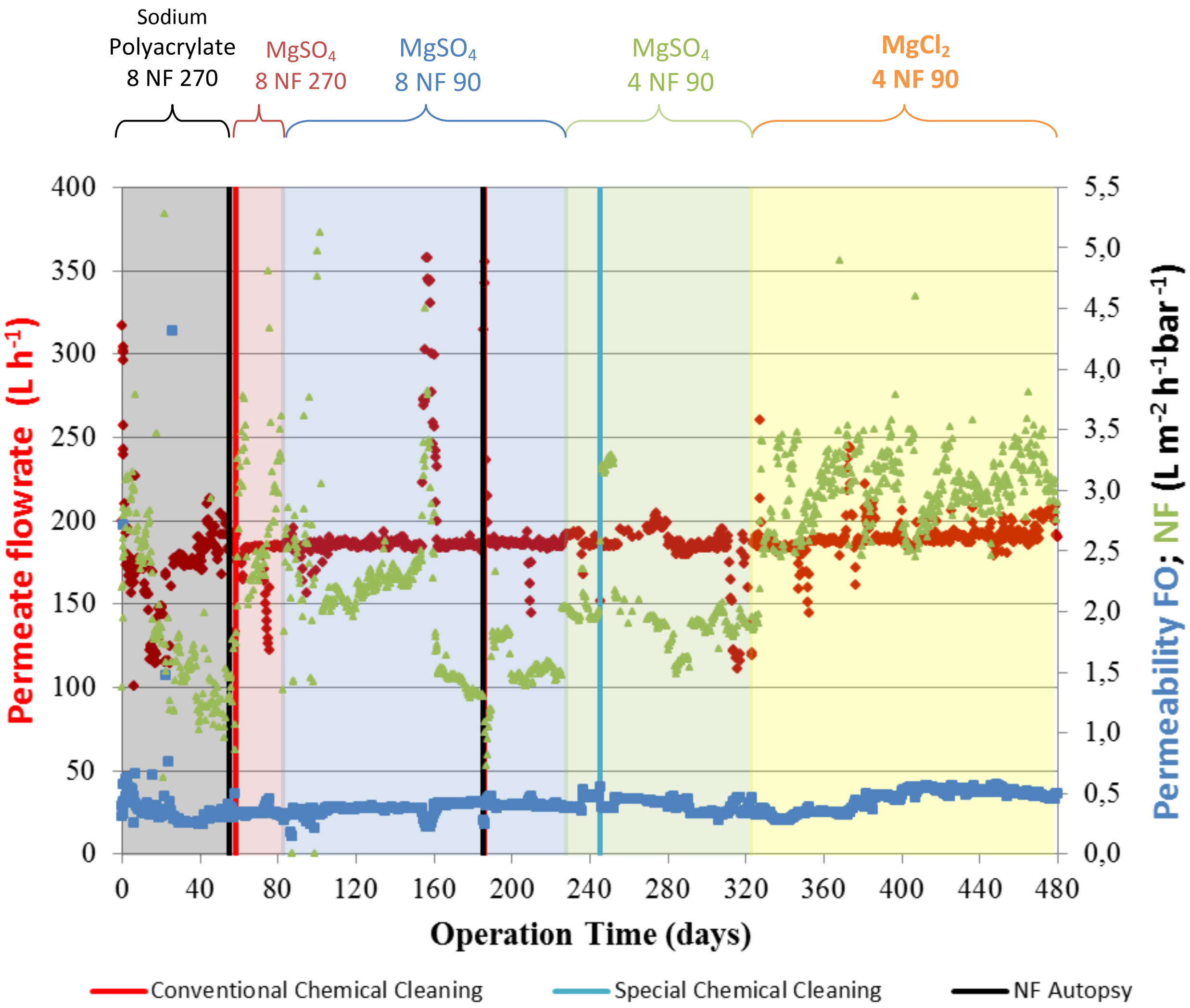

a)
Feed Water
FO
Concentrate
Diluted DS
NF
Water for irrigation
Concentrated DS
b)
acciona
Life

Figure 2



Sodium Polyacrylate
8 NF 270
$MgSO_4$
8 NF 270
$MgSO_4$
8 NF 90
$MgSO_4$
4 NF 90
$MgCl_2$
4 NF 90
Permeate flowrate (L h^{-1})
Permeability FO; NF (L m^{-2} $h^{-1}$$bar^{-1}$)
400
350
300
250
200
150
100
50
0
5,5
5,0
4,5
4,0
3,5
3,0
2,5
2,0
1,5
1,0
0,5
0,0
0
40
80
120
160
200
240
280
320
360
400
440
480
Operation Time (days)
Conventional Chemical Cleaning
Special Chemical Cleaning
NF Autopsy

Figure 3

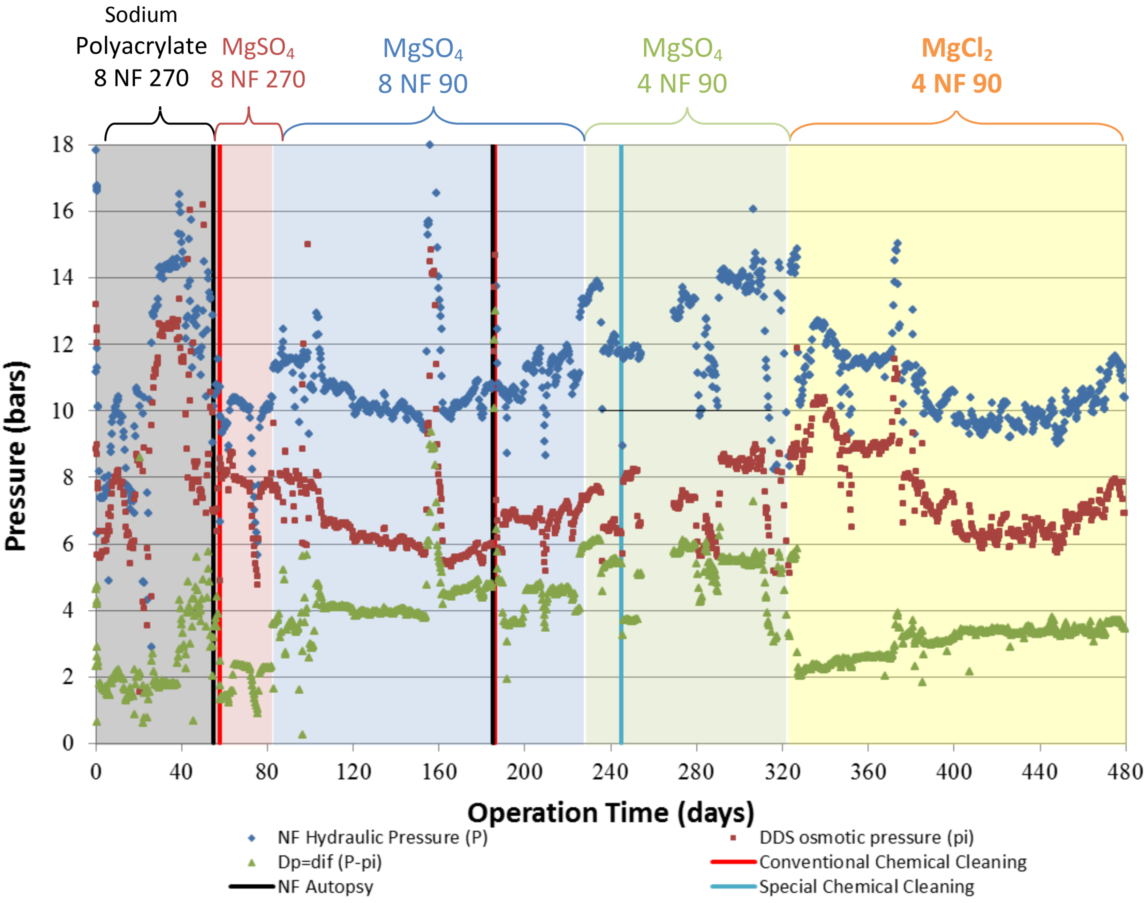

Sodium Polyacrylate 8 NF 270
MgSO4 8 NF 270
MgSO4 8 NF 90
MgSO4 4 NF 90
MgCl2 4 NF 90
Pressure (bars)
0
2
4
6
8
10
12
14
16
18
0
40
80
120
160
200
240
280
320
360
400
440
480
Operation Time (days)
NF Hydraulic Pressure (P)
DDS osmotic pressure (pi)
Dp=dif (P-pi)
Conventional Chemical Cleaning
NF Autopsy
Special Chemical Cleaning

Figure 4

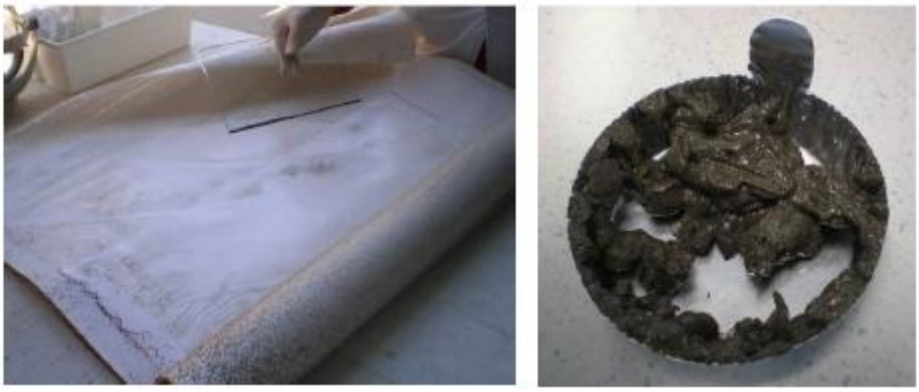


Figure 5

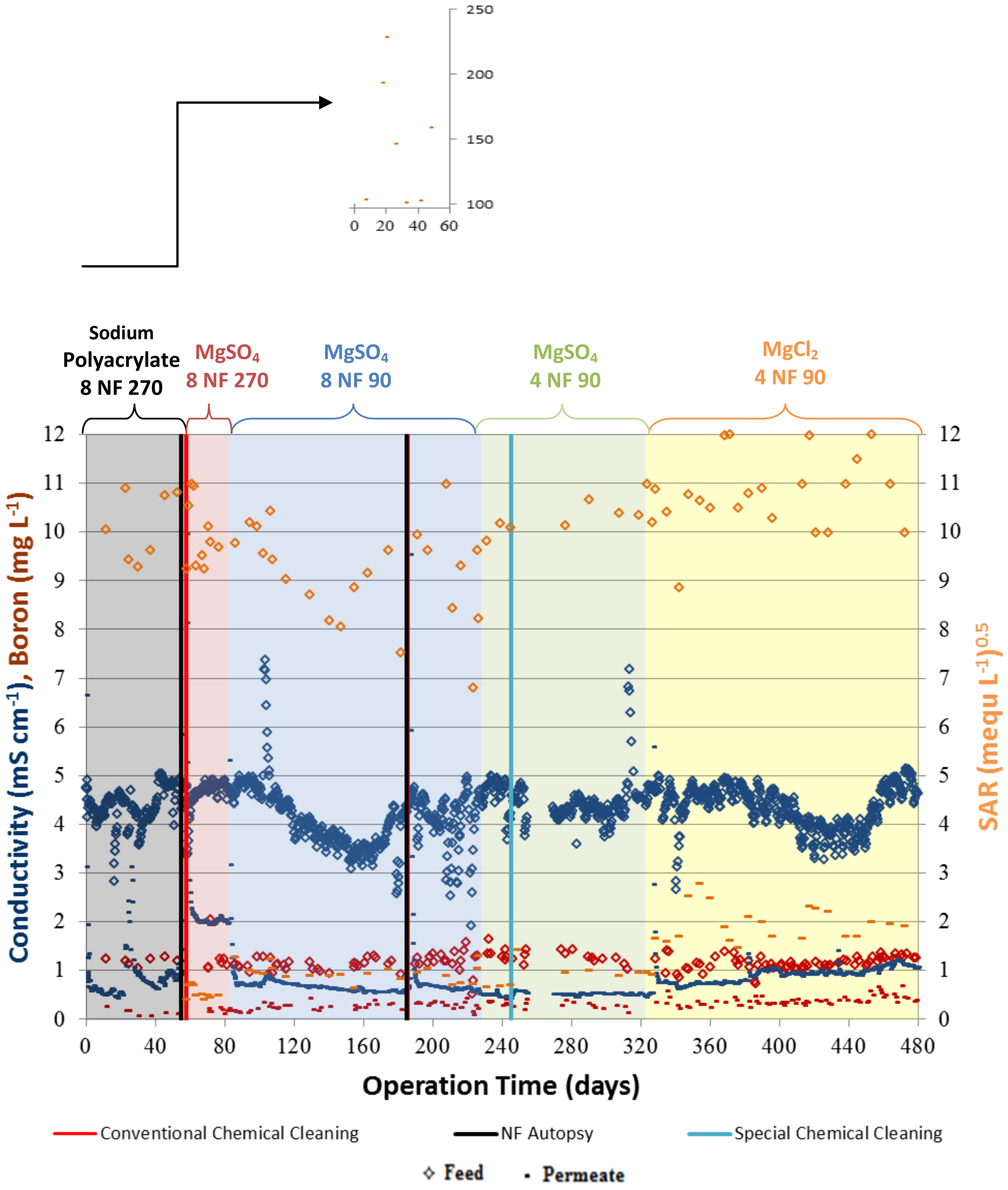

250
200
150
100
0
20
40
60
Sodium Polyacrylate 8 NF 270
$MgSO_4$ 8 NF 270
$MgSO_4$ 8 NF 90
$MgSO_4$ 4 NF 90
$MgCl_2$ 4 NF 90
12
11
10
9
8
7
6
5
4
3
2
1
0
Conductivity (mS cm^{-1}), Boron (mg L^{-1})
SAR (mequ L^{-1})$^{0.5}$
0
40
80
120
160
200
240
280
320
360
400
440
480
Operation Time (days)
Conventional Chemical Cleaning
NF Autopsy
Special Chemical Cleaning
◇ Feed
▪ Permeate

Figure 6

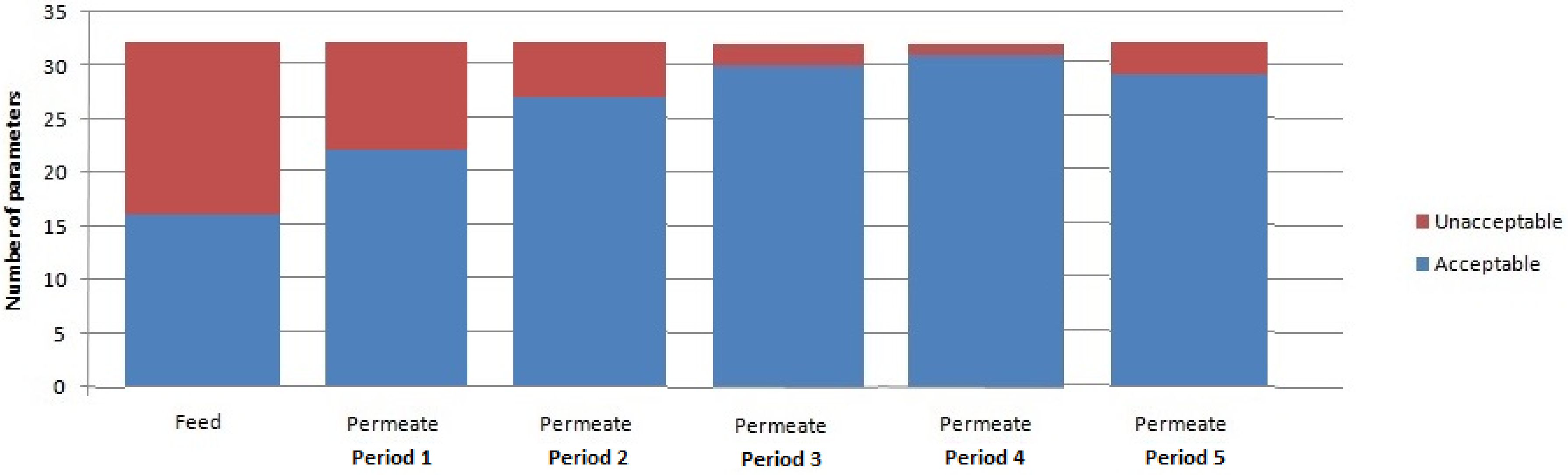

Number of parameters
35
30
25
20
15
10
5
0
Feed
Permeate Period 1
Permeate Period 2
Permeate Period 3
Permeate Period 4
Permeate Period 5
🟥 Unacceptable
🟦 Acceptable

Figure 7

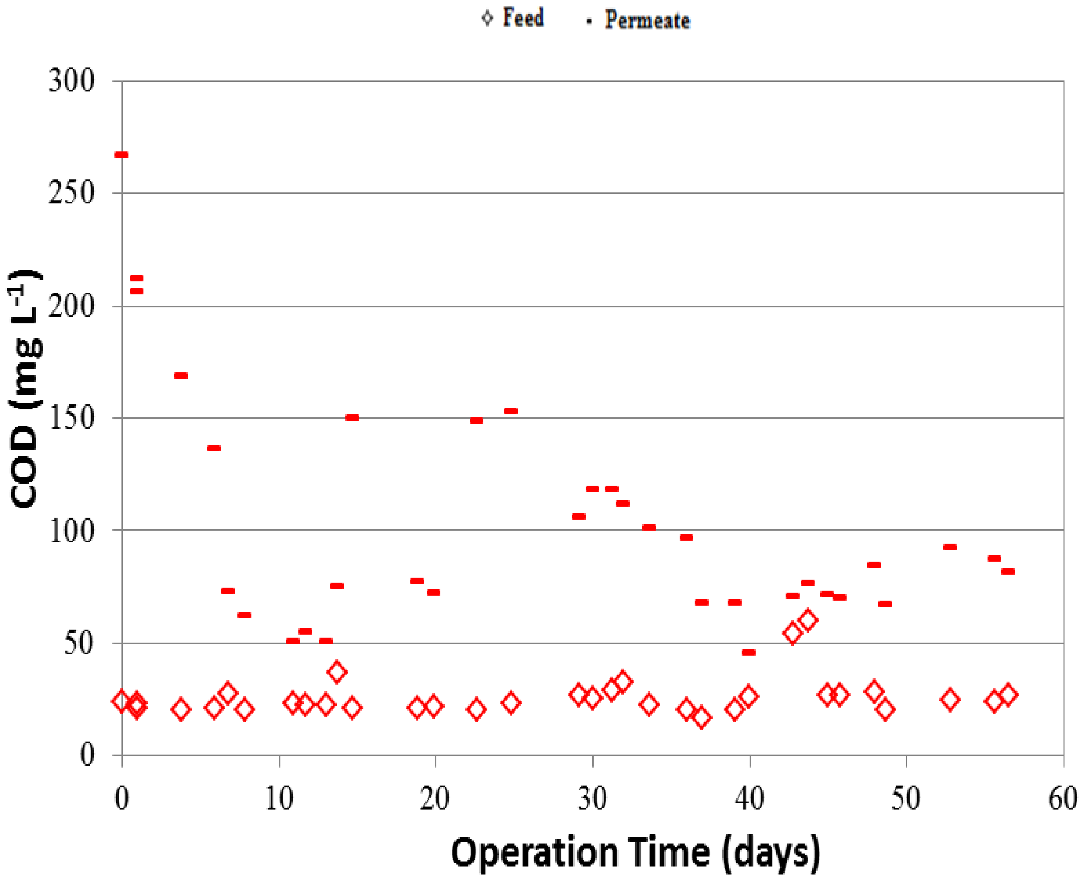

◇ Feed
▪ Permeate
300
250
200
150
100
50
0
COD (mg L-1)
0
10
20
30
40
50
60
Operation Time (days)

Figure 8