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# Pre-treatment optimisation studies for secondary effluent reclamation with reverse osmosis

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## Abstract

Physical–chemical pre-treatment was used for the reverse osmosis unit for reclamation of secondary effluents. The pilot plant was equipped with a variety of tertiary treatment units to prevent fouling and biofouling of the cellulose-acetate reverse osmosis membranes used. The optimisation of pre-treatment involved application of various concentrations of lime to raise the pH to 10.3–12.1, and to stabilise the sludge generated, as well as different dosages of ferric chloride (15, 20, and 25 mg/L) for the coagulation and solid–liquid separation. Sodium hypochlorite (8 mg/L) and UV disinfection are used for microbiological control. The water quality obtained, under the optimum conditions (pH = 10.5; $FeCl_3$: 25 mg/L; anionic flocculant: 0.5 mg/L; sodium hypochlorite: 8 mg/L) was high, showing an average conductivity of 66 μS/cm and low COD values 4 mg $O_2$/L. The product water is suitable for injection into a groundwater aquifer to counteract seawater intrusion. © 2002 Elsevier Science Ltd. All rights reserved.

*Keywords:* Cellulose-acetate membranes; Lime clarification; Pilot plant; Reclamation; Reuse; Reverse osmosis

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## 1. Introduction

Spain is one of the most arid countries in Europe with great differences in precipitation from north (wet) to south (almost dry). Thus, the interest of wastewater reclamation and reuse has increased considerably over the past several years; however, its implementation is still limited. This is particularly true for water reuse involving membrane-based advanced treatment and groundwater recharge scheme. The study was conducted using an experimental pilot plant (100 $m^3$/day) located within the 10,000 $m^3$/day municipal wastewater treatment plant of La Barrosa, Chiclana de la Frontera, Province of Cádiz, Spain. The purpose of this pilot plant study was to define the optimum conditions for physical–chemical pre-treatment of secondary effluent for successful reverse-osmosis (RO) operation.

After physical–chemical treatment of secondary effluent, the water was passed to a RO unit using cellulose-acetate (CA) membranes. The product water was then injected directly into a local groundwater aquifer. The treatment processes consist of coagulation with ferric chloride; disinfection with sodium hypochlorite; lime clarification; lamellar settler; external sludge recirculation; sand filtration; irradiation by UV rays; cartridge filtration (5 μm); pH neutralisation (pH = 5.0 to minimise CA membrane hydrolysis); anti-scaling; dechlorination with sodium bisulphite; RO; and air stripping. In this study, CA membranes were used due to lower fouling propensity compared to composite polyamide membranes [1]. This is mainly attributed to the relatively smooth appearance of CA membranes while composite membranes show a pronounced surface roughness. This is an important factor in fouling rate of RO membranes, although colloids and membrane surface charges, and high recoveries are also important [2].

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## 2. Material and methods

### 2.1. Brief description of the plant

The plant is completely automated and has four interconnecting modules: settling, filtration, RO and the monitoring and laboratory unit. Fig. 1 shows a schematic diagram of the pilot treatment plant. The lamellar settler has a settling area of $3\,m^2$ and a maximum ascensional velocity of 3.37 m/h. The plant has three sand filters with a diameter of 1.13 m (cross-section $1.0\,m^2$). Each consisted of 72 cm layer of coarse sand (2–0.2 mm). Average filtration velocity was $5.6\,m^3$/h. During experiment there was only one filter in operation, once silted, it was replaced for other one for the cleaning process. General practices of sand cleaning with air and filtered water were used. An anti-scaling agent (Osmoprot 36, a polyacrilate solution) was used to prevent salt precipitation on RO membranes. The RO membranes employed in these trials were manufactured by Hydranautics, model number 4040-MSY-CAB2 and were made of CA. Seven pressure vessels containing 42 membrane modules ($40 \times 40$) were arranged in two stages; the first one with four vessels and the second with three. The first stage brine is the second stage feed water. This arrangement leads to a recovery of 75%, with a nominal production of $100\,m^3$/day.

The laboratory is fully equipped to enable researchers to carry out the daily analyses required in the monitoring and control of the processes (pH, conductivity, turbidity, permanent and temporary alkalinity, calcium, magnesium and total hardness levels and chlorides). All other testing (microbiological analyses, $BOD_5$, COD, suspended solids, sulphates, nitrates, nitrites, calcium, magnesium, phosphates) were carried out in the facilities of the Environmental Technology Research Group at the Faculty of Marine and Environmental Sciences of the University of Cadiz. Standard methods for water analysis [3] were employed in the examination of the different parameters under study. Silt density index (SDI) values were obtained in accordance with ASTM D 4189-95 standard (standard test method for SDI of water). SDI measures the fouling potential of the water, measured by filtering a water sample through a micron filter (0.45 μm). In RO systems, SDI should be maintained at or below 5.

In order to examine the performance of the CA membranes in different water qualities, three levels of treatment were applied to the water fed into the RO unit, namely: *intense treatment, moderate treatment,* and *minimum treatment*. In this paper, only the best resulting experiment is shown, which corresponds with the intense treatment (25 mg/L of ferric chloride and high pH). Preliminary jar testing proved extremely useful in determining the appropriate concentration levels to be employed in pilot plant trials. This method was employed to identify the most suitable pH value and, in addition, it was used to evaluate the optimum concentration levels of ferric chloride, anionic flocculant

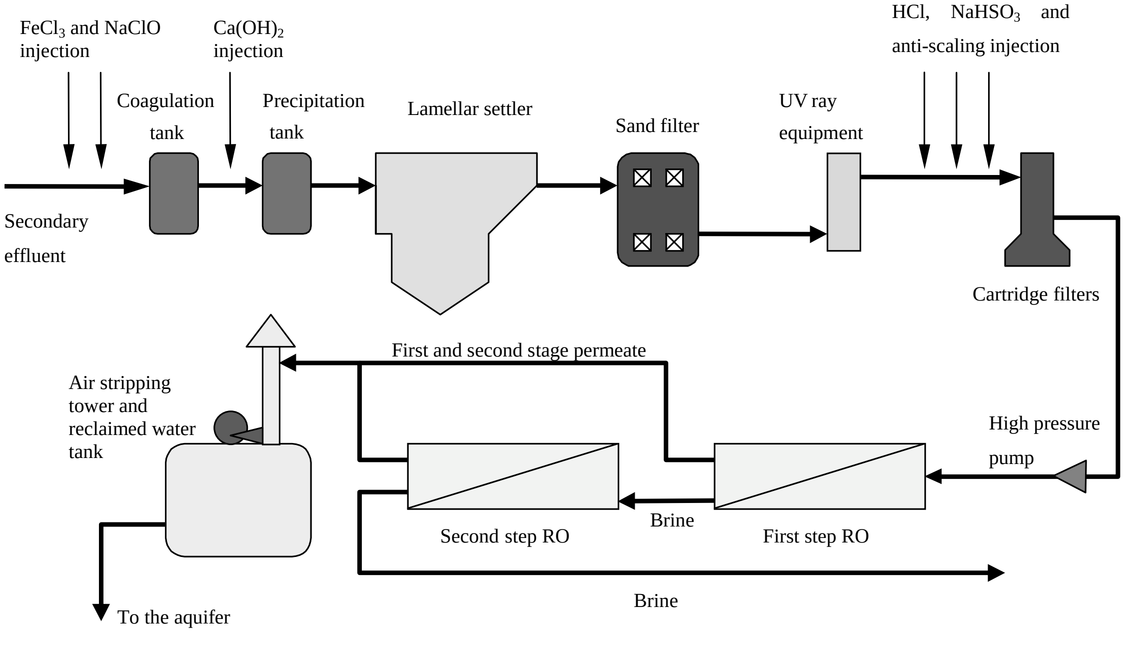

Fig. 1. Flow diagram of the treatment employed.

and sodium hypochlorite, for subsequent application in plant experiments.

## 3. Results and discussion

The optimum conditions found in the laboratory test and the pilot plant operations are presented.

### 3.1. Laboratory tests

These laboratory tests using jar tests enabled the determination of the following optimum conditions for commencing pilot plant operation:

- Ferric chloride: 25 mg/L.
- Flocculant (anionic charge, PASAFLOC FI-35): 0.5–1 mg/L.
- pH: 10.5 (adding calcium hydroxide).
- Sodium hypochlorite: 4.0–9.0 mg/L.

### 3.2. Pilot plant operation

Data are analysed with respect to the three unit operations.

#### 3.2.1. Sedimentation

The experiment that showed the best results, among several carried out, was that using 25 mg/L of ferric chloride; this dosage has, therefore, been selected for the experiment.

The conditions employed for the experiment were as follows (see Fig. 1):

- Ferric chloride: 25 mg/L.
- pH: this was varied between 10.3 and 11.9, by the addition of calcium hydroxide.
- Flocculant: 0.5 mg/L (concentration obtained from previous experiments).
- Sodium hypochlorite: 8 mg/L.

Based on the bench-scale results, the addition of 25 mg/L of ferric chloride with a contact time of about 10 min in the coagulation tank and the further addition of lime (pH = 10.5) and flocculant produced an excellent and well-formed floc inside the lamellar settler.

Fig. 2 shows turbidity of the secondary effluent (input water) and the clarified water, together with the pH values of the clarified water during the experiment. With respect to pH, two distinct stages can be observed. The first with pH fairly stable at 10.5 up to day 12, with turbidity of the clarified water exceeding that of the secondary effluent; the second, with pH gradually increasing above 10.5 from day 12 onwards, when turbidity of the clarified water was diminishing. The explanation for this variation is that the increase in pH produces higher density sludge; thus greater removal of colloids and suspended solids, due to calcium carbonate and magnesium hydroxide precipitation. The former resulted in sweep coagulation process where only large particles are entrapped, and the latter resulted in positive superficial charge, which attracts the colloid particles inducing adsorption and the agglomeration [4].

In previous tests conducted, a minimum of conductivity was observed around pH = 10.5 (pH range studied: 9.0–12.5). At higher pH values than 10.5 the conductivity increased, even above of secondary effluent conductivity, due to the excess of added lime to increase the pH. Fig. 3 shows conductivity of the clarified water, which declines as a result of precipitation of certain compounds (mainly calcium carbonates and hydroxides) due to the increase in pH that was produced by the addition of lime. This precipitation represents a double advantage: reducing a possibility of precipitation of

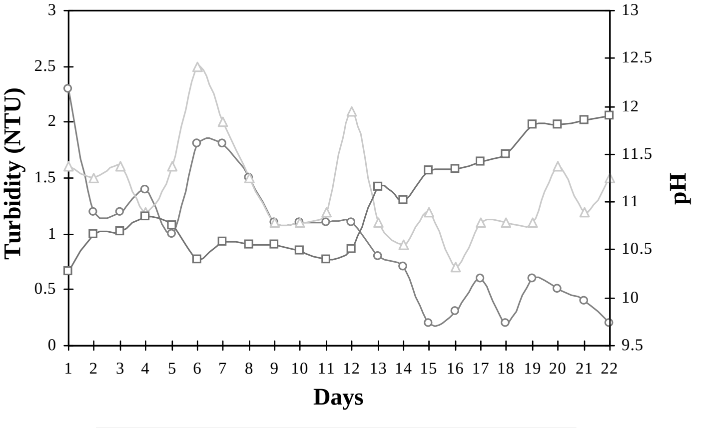

Fig. 2. Turbidity of the secondary effluent and turbidity and pH of the clarified water.

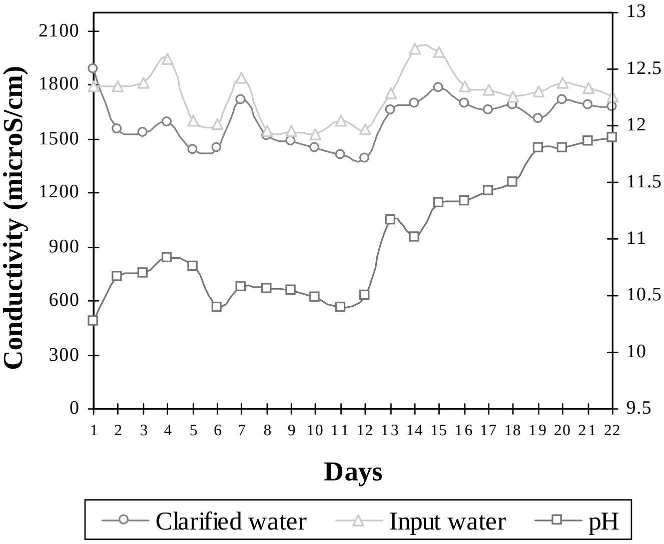

Fig. 3. Conductivity of the secondary effluent and conductivity and pH of the clarified water.

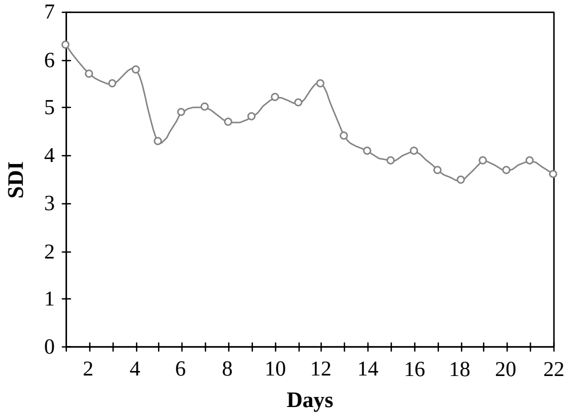

Fig. 4. Change in SDI values of clarified water during the experiment.

sparingly soluble salts on the membranes and quality of permeate improves as a result of lower content of salts in feed water. Besides, given the nature of this water, a poor calcium removal leads to react this one with organic matter onto the membranes of the RO unit fouling them. Due to that it promotes a destabilisation in organic material making it more markedly hydrophobic, and consequently, less stable in solution. Wiessner and Chellam [5] have observed that this effect occurs particularly in hard, rather than soft waters, and despite the fact that each may have an identical SDI value. Fig. 4 shows SDI values of the clarified water from the sedimentation unit. It can be seen that the results improve from first days to the end of the experiment, coinciding with the increase in pH and solids removal. Such removal of solids is corroborated by reduction in turbidity as shown in Fig. 2.

### 3.2.2. *Filtration*

During the period over which the experiment was conducted, two sand filters were put into operation as shown in Table 1. The first filter was in operation the first 12 days, the second one until the end of the experiment. It was observed that the turbidity of filtered water showed an increase along the time, even to the extent of exceeding the turbidity of the input water. At this point, the operating cycle of the filter was considered finished and it was subjected to washing. The working of the second filter is analogous to that of the first. The resulting low values for SDI can be explained by the combination both of a good removal of suspended solids in the lamellar settler due to lime clarification, and a good performance of sand filters.

### 3.2.3. *Reverse osmosis*

Table 2 shows the data for the key operating parameters of the RO unit corresponding to the days during which the experiment was conducted. The unit operated in a two-stage configuration (75% recovery) due to the need of a high recovery but without sparingly salts precipitation risk on the membranes.

Table 2 shows the input, product, and the normalised flow rate. The normalised flow rate is the one referenced to the certain fixed conditions of pressure and temperature, i.e., 15 bar and 25°C, respectively. It can be observed that there is not only no falling off in the product water flow rate, but also an increase in the production. The solids removal achieved in sedimentation with increased pH was effective. In addition,

Table 1
Operating parameters of the sand filters during the experiment

| Filter | Days | Turbidity of clarified water (NTU) | Turbidity of filtered water (NTU) | SDI |
|---|---|---|---|---|
| 1 | 1 | 2.31 | 0.27 | 0.1 |
| 1 | 2 | 1.22 | 0.28 | 0.1 |
| 1 | 3 | 1.25 | 0.32 | 0.1 |
| 1 | 4 | 1.43 | 0.32 | 0.1 |
| 1 | 5 | 1.04 | 0.36 | 0.1 |
| 1 | 6 | 1.84 | 0.41 | 0.2 |
| 1 | 7 | 1.83 | 0.48 | 0.2 |
| 1 | 8 | 1.52 | 0.52 | 0.7 |
| 1 | 9 | 1.13 | 0.57 | 0.8 |
| 1 | 10 | 1.15 | 0.68 | 1.1 |
| 1 | 11 | 1.11 | 0.88 | 1.2 |
| 1 | 12 | 1.14 | 1.03 | 1.5 |
| 2 | 13 | 0.82 | 0.26 | 0.1 |
| 2 | 14 | 0.71 | 0.31 | 0.1 |
| 2 | 15 | 0.22 | 0.25 | 0.1 |
| 2 | 16 | 0.33 | 0.29 | 0.2 |
| 2 | 17 | 0.59 | 0.51 | 0.2 |
| 2 | 18 | 0.25 | 0.33 | 0.2 |
| 2 | 19 | 0.61 | 0.46 | 0.4 |
| 2 | 20 | 0.53 | 0.52 | 0.5 |
| 2 | 21 | 0.44 | 0.55 | 0.8 |
| 2 | 22 | 0.23 | 0.64 | 0.9 |

the normalised flow rate practically coincided with the product water flow rate, which confirms the good pretreatment applied to the water, since no loss of flow was recorded.

The recovery rate reported in Table 2 shows an increasing trend, due to the slight increase in temperature that leads to a better permeability of the membranes, and therefore, higher production rate in the system. However, as the increase of temperature was moderate (0.8°C) in the experiment, there was no increase membrane fouling. Zhu and Elimelech [2] reported that an increase of recovery leads to a severe fouling rate.

Table 2 also shows the pressure of input water to the RO unit, its temperature and the pressure of rejected water. While the pressure remained constant throughout the experiment, the temperature increased slightly during the first 10 days, but remained constant later. The result of this was that more water permeated through the membranes, increasing the production.

The pressure loss between the input and output of the RO unit showed values between 1.0 and 1.1 bar during the first 10 days. After this, a value of 1.1 bar is maintained until the end of the experiment. Fouling can be discounted as a factor, given that the low SDI values are obtained. In fact, the flow rate of product water and the pressure loss showed the same trend.

Fig. 5 shows conductivity values in feed water and permeate of RO unit. The feed water showed relatively constant conductivity throughout the period of the experiment. The analogous behaviour of the permeate was evident that no damage to the membranes has been produced. The overall rejection of the membranes showed a constant trend and thus reflected no loss of rejection capacity by the membranes.

The other operation parameters measured (Table 2) do not indicate the existence of any problems in the unit. Thanks to the previously suspended and colloidal solids removal the behaviour of RO unit has been successful. A free chlorine concentration of 0.5 mg/L, recommended by the membrane manufacturer, was maintained during the experiment for biofouling control. Finally, the conductivity differences between the water obtained directly from the membranes (permeate) and that destined for aquifer direct injection (reclaimed water) is due to the operation of the air-stripping unit that removes from water especially volatile compounds and carbon dioxide.

### 3.2.4. *Quality of reclaimed water*

A comparative analysis of the secondary effluent and the reclaimed water for groundwater recharge was realised in order to study the efficiency of the treatment method used, see Table 3. The operating conditions selected for the analysis and the sample-taking were as follows: ferric chloride: 25 mg/L; pH: 10.5; anionic flocculant: 0.5 mg/L; sodium hypochlorite: 8 mg/L; anti-scaling 3 mg/L; feed pressure: 19 bar; recovery: 75%; inlet flow rate: 5.6 $m^3/h$. The rejection characteristics of the membranes represent greatly reduced pollutants and micropollutants in the reclaimed waters. It is also noted that indicator microorganisms are absent from the effluent. The low-saline content of this water makes it very useful for a number of applications where the presence of salts could have undesirable effects, like groundwater recharge. The low values achieved eliminate the problems of specific ionic toxicity that are customarily encountered with the use of non-desalinated reclaimed water. Finally, the high quality of reclaimed water allows it to be used with safety in this and another reuse applications without restrictions.

## 4. Conclusions

The following conclusions are drawn from the experimental results obtained.

### 4.1. *Laboratory tests*

Jar tests are a suitable and extremely valuable tool for optimising reagent concentrations; by means of a series of simple laboratory experiments, the subsequent studies

Table 2
Key operating parameters of the RO unit during the experiment

| | Days | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 |
| Feed pressure (bar) | 19.0 | 19.0 | 19.0 | 19.0 | 19.0 | 19.0 | 19.0 | 19.0 | 19.0 | 19.0 | 19.0 | 19.0 | 19.0 | 19.0 | 19.0 | 19.0 | 19.0 | 19.0 |
| Brine pressure (bar) | 18.0 | 17.9 | 18.0 | 18.0 | 17.9 | 18.0 | 18.0 | 17.9 | 17.9 | 17.9 | 17.9 | 17.9 | 17.9 | 17.9 | 17.9 | 17.9 | 17.9 | 17.9 |
| Pressure loss (bar) | 1.0 | 1.1 | 1.0 | 1.0 | 1.1 | 1.0 | 1.1 | 1.0 | 1.0 | 1.1 | 1.1 | 1.1 | 1.1 | 1.1 | 1.1 | 1.1 | 1.1 | 1.1 |
| Temperature (°C) | 17.4 | 17.4 | 17.2 | 17.5 | 16.5 | 17.2 | 17.4 | 16.8 | 17.2 | 17.8 | 18.0 | 18.1 | 18.0 | 17.9 | 18.2 | 18.2 | 17.9 | 18.0 |
| Inlet flow rate ($m^3$/h) | 5.7 | 5.7 | 5.6 | 5.7 | 5.7 | 5.7 | 5.7 | 5.7 | 5.6 | 5.7 | 5.7 | 5.7 | 5.7 | 5.7 | 5.7 | 5.7 | 5.7 | 5.7 |
| Permeate flow rate 1st stage ($m^3$/h) | 2.44 | 2.52 | 2.46 | 2.51 | 2.50 | 2.52 | 2.48 | 2.49 | 2.45 | 2.54 | 2.57 | 2.58 | 2.56 | 2.57 | 2.57 | 2.57 | 2.58 | 2.57 |
| Permeate flow rate 2nd stage ($m^3$/h) | 1.86 | 1.89 | 1.85 | 1.91 | 1.90 | 1.88 | 1.85 | 1.86 | 1.86 | 1.70 | 1.92 | 1.92 | 1.92 | 1.93 | 1.92 | 1.92 | 1.92 | 1.91 |
| Total recovery (%) | 75.4 | 77.4 | 77.0 | 77.5 | 76.7 | 77.2 | 76.0 | 76.3 | 77.0 | 77.9 | 78.8 | 78.6 | 78.6 | 78.9 | 78.7 | 78.7 | 78.9 | 78.6 |
| Permeate conductivity 1st stage (μS/cm) | 57 | 57 | 56 | 55 | 57 | 55 | 52 | 56 | 56 | 50 | 50 | 52 | 54 | 50 | 56 | 49 | 52 | 50 |
| Permeate conductivity 2nd stage (μS/cm) | 97 | 98 | 102 | 92 | 99 | 101 | 90 | 97 | 101 | 88 | 86 | 88 | 88 | 82 | 90 | 82 | 87 | 84 |
| Overall permeate conductivity (μS/cm) | 80 | 82 | 77 | 75 | 78 | 77 | 70 | 75 | 77 | 72 | 68 | 68 | 70 | 66 | 78 | 66 | 69 | 66 |
| Reclaimed water conductivity (μS/cm) | 74 | 77 | 71 | 69 | 72 | 70 | 65 | 68 | 67 | 67 | 63 | 61 | 60 | 59 | 71 | 60 | 62 | 59 |
| Overall salt rejection (%) | 95.0 | 95.0 | 95.2 | 95.4 | 95.3 | 95.2 | 95.8 | 95.3 | 95.2 | 95.7 | 95.8 | 95.7 | 95.6 | 95.7 | 94.8 | 95.6 | 95.4 | 95.6 |

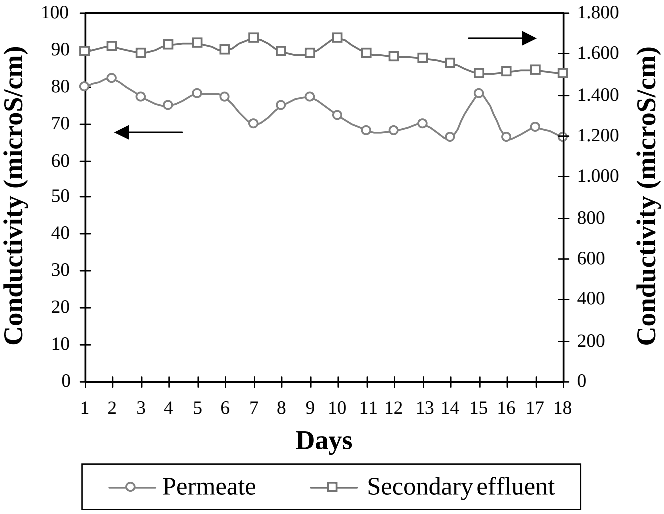

Fig. 5. Change in the values of conductivity in feed water and permeate of the RO unit.

Table 3
Analyses conducted on the input water to experimental plant (secondary effluent) and the product water for injection into aquifer (reclaimed water) using operation optimum conditions

| Parameter | Input water | Product water |
|---|---|---|
| pH | 8.03 | 6.98 |
| Conductivity (μS/cm) | 1.507 | 66 |
| COD (mg $O_2$/L) | 34 | 4 |
| $BOD_5$ (mg $O_2$/L) | 16 | — |
| SS (mg/L) | 22 | 0 |
| Turbidity (NTU) | 1.71 | 0.35 |
| Sulphates (mg/L) | 127 | <10 |
| Nitrates (mg $NO_3^-$/L) | 13.5 | 1.8 |
| Chlorides (mg/L) | 226 | 9 |
| Phosphates (mg $PO_4^{3-}$/L) | 6.05 | 0.03 |
| Nitrites (mg $NO_2^-$/L) | 0.22 | <0.02 |
| Alkalinity (mg $Ca(HCO_3)_2$/L) | 330 | 20 |
| Calcium (mg/L) | 109 | 4 |
| Magnesium (mg/L) | 39 | 1 |
| Total Coliforms/100 mL | $10 \times 10^6$ | Not detected |
| Faecal Coliforms/100 mL | $1.5 \times 10^6$ | Not detected |
| Aerobes (22°C)/mL | $3 \times 10^5$ | Not detected |

that have to be conducted at the actual plant-operating scale are considerably facilitated.

### 4.2. Sedimentation

In the tests with 25 mg/L of ferric chloride and pH values between 10.3 and 11.9, it is observed that the best results in the elimination of calcium, conductivity and bicarbonates are produced when working with pH values 10.5. It was also observed that the consumption of hydrochloric acid under these conditions was the lowest of all experiments carried out since a higher elimination of bicarbonates is produced. However, the elimination of suspended solids does not reach the levels of other developed experiments.

### 4.3. Filtration

The performance of the sand filters and cartridge filters under the various operating conditions tested in the experiments was satisfactory in all cases; the main reason for this is the generally good quality of water from the sedimentation unit.

### 4.4. Reverse osmosis

The behaviour of the membranes was excellent in all the experiments: no microbiological problems were experienced, nor of fouling, given that no losses of flow rates nor of pressure were observed in the system. Moreover, the effluent quality is high in all cases tested, as demonstrated by the low-conductivity values obtained.

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