DESALINATION

Desalination 191 (2006) 137–147

www.elsevier.com/locate/desal

Comparative studies of reverse osmosis membranes for wastewater reclamation

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Received 15 March 2005; accepted 18 August 2005

Abstract

Interest in wastewater reclamation and reuse has increased considerably over the past several years in Spain. However, the implementation of involving membrane-based advanced treatment and groundwater recharge schemes is still limited. The goal of this paper is to show part of the studies conducted using an experimental pilot plant (output: 100 m^3/d) in Chiclana de la Frontera, Province of Cadiz, southern Spain. The purpose pilot-plant study was to define the optimum conditions for physicochemical pretreatment of secondary effluents for successful reverse osmosis operation for groundwater recharge. The performance of cellulose acetate and two thin-film composite membranes was studied. Several pretreatment levels were used in order to optimise economic issues. Comparative analyses of the secondary effluent and the reclaimed wastewater for groundwater recharge were made in order to study the efficiency of the treatment sequence used and the feasibility of the processes studied. Membrane rejection characteristics are showed to be an important barrier to the presence of pollutants and micro-pollutants in reclaimed wastewater. Finally, the high quality of reclaimed wastewater allows it to be used with safety in groundwater recharge and other reuse applications without restrictions.

Keywords: Reverse osmosis; Reclamation; Fouling; Biofouling; Polyamide membrane; Cellulose acetate membrane

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1. Introduction

Wastewater reclamation and reuse is an intrinsic component of the water cycle and has become an integral part of water resources management in arid and semi-arid regions of the world. Several factors have contributed to this trend: the lack of adequate water in many regions of the world, the increasing water demand of modern societies, etc.

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Presented at the International Congress on Membranes and Membrane Processes (ICOM), Seoul, Korea, 21–26 August 2005.

doi:10.1016/j.desal.2005.08.013

Consequently, wastewater reclamation and reuse is often the only dependable water resource to counteract hydraulic deficits in many regions of the world. Thus, in those regions where droughts are frequent and have a significant impact on both socioeconomic and environmental arenas, new strategies for water resources management must be developed, for instance, indirect potable reuse. This approach should also alleviate the effluent disposal problems, given the high treatment level of reclaimed wastewater and the diversion of flows for beneficial uses. In addition, it represents a more practical and a viable means of implementing water conservation policies, and is evidently a more rational solution than the construction of large water-related facilities which, whilst useful, are unable to solve the short-term problem of increasing water demand in many different regions.

Direct reuse is of growing great interest in Spain, especially in those areas with a lack of water. For instance, in 2001 there were 140 wastewater reuse projects running, covering a water demand of 340 Hm^3/y. But in 2006 this amount will reach 640 Hm^3/y. This water will cover mainly agricultural irrigation, although groundwater recharge is an emerging application.

Planned, indirect potable reuse is the purposeful augmentation of surface or groundwater resources with highly treated reclaimed wastewater, which will ultimately serve as a source of drinking water. Thus, planned indirect potable reuse entails treatment and operational reliability and dilution with natural waters. In addition, public policy and public acceptance are the most challenging aspects of indirect potable reuse. Reclaimed wastewater in indirect potable reuse should be of the highest quality, and should meet, at least, the applicable drinking water standards. A few technological choices exist; amongst them, membrane technologies, in particular, reverse osmosis (RO), are of the utmost importance. Several advantages are listed below:

- high efficiency of the membranes in selective mineral rejection
- high permeability to the water
- decreased production costs
- fulfillment of the most stringent regulations for public health and environment protection
- separation process at room temperature without phase change
- no product accumulation inside the membranes, unlike processes such as ionic exchange
- separation does not require addition of chemicals, as may be the case in water clarification, by means of coagulation–flocculation processes
- development of highly effective and more resistant polymers.

In the case of direct injection of reclaimed wastewater for groundwater recharge, very high-quality water with low levels of TDS is needed. This allows recuperating salinized aquifers and the increasing of underground water resources [1]. To achieve these objectives reverse osmosis is an interesting treatment. The use of RO has been successful in all the projects in which it has been employed and which have been reported [2]. Nevertheless, there are two major problems associated with RO downstream of a secondary treatment, each of which needs to be closely monitored: membrane colonization by microorganisms and suspended solids deposition onto the membranes. Both phenomena foul the membrane's active surface and seriously impair the performance of the units, increasing the process costs. Microbial colonization is particularly harmful when cellulose acetate membranes are used since these may be irreversibly damaged [3]. In the case of polyamide membranes, no biodegradation occurs, but there is a greater tendency to fouling as a result of the surface morphology and high productivity of these membranes [4,5].

The use of RO in wastewater reclamation is gaining interest in Spain. However, the implementation of involving membrane-based advanced treatment and groundwater recharge schemes is still limited. In the La Barrosa municipal wastewater treatment plant (WTP) in Chiclana de la Frontera, Cádiz, a pilot plant was built in 1994 for domestic wastewater reuse using different advanced technologies as RO. This pilot plant was the pilot phase in an ambitious wastewater reclamation project in Campo de Dalías, Almería, actually in construction, with the main goal of reclaiming 14 Hm^3/y, using advanced treatment technologies.

In this pilot plant several studies were conducted using cellulose acetate (CA) membranes and polyamide (PA) membranes, made in Spain. Each kind of membrane tested poses different requirements and characteristics according to feed water composition and its applications. In these studies, secondary effluents were pre-treated, upstream to a RO unit, with different treatment levels: intense, moderate and minimum. The pre-treatment level directly influences membrane performance. An adequate pre-treatment in the feed water is of paramount importance to remove microorganisms and colloidal matter, whose presence decreases the efficient performance of membranes. If they work in well-controlled conditions, their useful life can be extended, rendering wastewater reclamation projects more economical.

2. Material and methods

The experimental plant (output = 100 m^3/d) is situated in the La Barrosa WTP in Chiclana de la Frontera, Cádiz, SW Spain. It was built with the main goal of carrying out optimization studies to get high-quality water, perfectly reusable, at reasonable costs, using advanced water treatment technologies and based on a membrane scheme. The final high-quality effluent is injected directly into the aquifer.

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 picture of the facility. Fig. 2 shows a schematic flow diagram of the pilot 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 consists of a 72-cm layer of coarse sand (2–0.2 mm). Average filtration velocity was 5.6 m^3/h. During the experiment, there was only one filter in operation; once silted, it was replaced by another 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 membranes employed in the trials were manufactured by Hydranautics (model 4040-MSY-CAB2) and were made of cellulose acetate. The PA membranes were two types: Permetec PAC-4040-BP for low-pressure operation (LP) and Permetec PAC-4040-MBP, for very low-pressure operations (VLP). Seven pressure vessels containing 42 membrane modules (40×40") were arranged in two stages: the first 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/d. CA membranes were first used in experiments due to the fact that they can be used under highly fouling conditions [6], and besides because their active surface is smooth [7]. PA membranes, although posing a higher trend for fouling, have pressure requirements that are lower with a higher productivity and salt rejection.

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, alkalinity, calcium, magnesium and total hardness levels and

Fig. 1. General view of the experimental pilot plant.

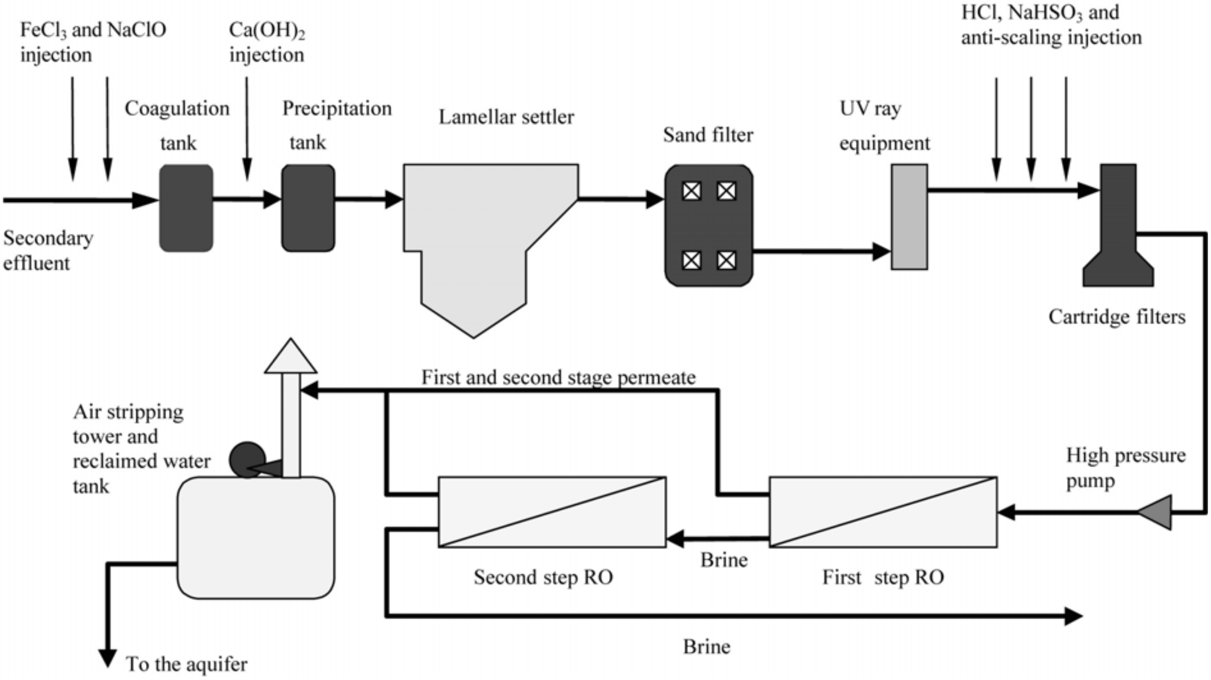

Fig. 2. Flow diagram of the experimental pilot plant.

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 [8] were used in the examination of the different parameters under study.

In order to examine the performance of the RO membranes with different water qualities, three levels of treatment were applied to the water fed into the RO unit, namely: intense, moderate and minimum. Preliminary jar testing proved extremely useful in determining the appropriate concentration levels to be employed in pilot-plant trials. This method was used to identify the most suitable pH value and, in addition, it was used to evaluate the optimum concentration levels of ferric chloride, anionic flocculant and sodium hypochlorite for subsequent application in plant experiments.

Below is a description of the operations involved in each of the three treatments performed.

1. Intense treatment: This treatment consisted of coagulation-flocculation-lamellar sedimentation (using calcium hydroxide for pH increase, ferric chloride and anionic flocculant: Pasafloct FI-35), sand filtration, disinfection (with sodium hypochlorite and ultraviolet radiation), anti-scaling (Osmoprot S-36 a polyacrilate solution), acidification (until pH 5.0 using hydrochloric acid), cartridge filtration (5 microns) and finally RO.

2. Moderate treatment: The same sequence as above was used but without the addition of lime. This omission had a series of significant repercussions, as reported in the Results and discussion section below.

3. Minimum treatment: This treatment used only the processes of settling, disinfection, sand filtration, cartridge filtration and RO. The aim of this method was to try to maintain the minimum conditions required for correct membrane operation.

In order to study the efficiency of the different treatments, several analyses were undertaken of the secondary effluent and of the reclaimed wastewater (pilot-plant effluent).

3. Results and discusion

3.1. Influence of secondary effluent characteristics

Secondary effluents have high organic matter contents compared with other RO applications (seawater desalination, brackish water, etc). Organic and colloidal matters are mainly responsible for fouling of RO membranes. The surface electric charge of colloidal particles in secondary effluents are negative. On the other hand, and although CA and PA membranes show anphoteric characteristics, due to the presence of acid and basic functional groups, the isoelectric point for CA and for PA membranes is, respectively, 3.5 and 5.2. Thus, both kinds of membranes show negative surface charge. That should decrease membrane fouling in the presence of negatively charged particles by repulsion forces. However, and as a consequence of operating conditions, colloids accumulate on the membrane surface, decreasing flow and permeate quality. The colloidal accumulation generates an hydraulic drag to the passage of the permeate, leading to flux decrease. Thus, physicochemical characteristics of feed water are of paramount importance for membrane performance. In Table 1 some analyses of secondary effluent quality during the experiments are shown. Feed water is homogeneous and of good quality. Organic matter contents, even low, should be seriously considered as Winfield [9] stated, since dissolved organic matter is more important in fouling processes than suspended solids. It is of paramount importance to develop an adequate pre-treatment upstream of the RO unit.

Table 1
Analyses conducted to secondary effluents and reclaimed wastewater from the different membranes. (Average value of five analyses)

	Cellulose acetate		PA, low pressure		PA, very low pressure		Drinking water standards	
Parameter	Secondary effluent	Reclaimed water	Secondary effluent	Reclaimed water	Secondary effluent	Reclaimed water	Guide level	Maximum admissible conc.
pH	8.1	7.0	7.9	7.4	7.8	7.2	6.5–8.5	9.5
Conductivity (µS/cm)	1568	66	1704	53	1655	52	400	—
TOC (mg C/L)	10.1	1.08	11.12	1.09	10.37	1.01	—	—
DBO_5 (mg O_2/L)	15	—	13	—	10	—	—	—
SS (mg/L)	19.2	0.0	21.3	0.0	23	0.0	Absence	—
Turbidity (NTU)	3.9	0.2	5.2	0.2	6.3	0.2	1[a]	6[a]
Sulphates (mg/L)	143.7	5.1	186.8	3.5	201.2	3.7	25	250
Nitrates (mg NO_3^-/L)	119.2	18.5	61.7	7.9	64.9	8.3	25	50
Chlorides (mg/L)	243	9	305	6	285	6	25	—
Phosphates (mg PO_4^{3-}/L)	5.65	0.03	11.02	0.12	8.08	0.08	400[b]	5000[b]
Nitrites (mg NO_2^-/L)	0.20	<0.02	1.6	0.03	1.3	0.02	—	0.1
Calcium (mg/L)	136.1	4.6	135.2	2.9	148.3	3.2	100	—
Magnesium (mg/L)	28.9	1.0	37.2	0.7	39.0	0.7	30	50
Total colif. UFC/100 mL	8×10^5	ND	7×10^5	ND	8×10^5	ND	—	0
Faecal colif. UFC/100 mL	1×10^5	ND	6×10^4	ND	4×10^4	ND	—	0
HPC (22°C) UFC/mL	9×10^6	ND	6×10^5	ND	7×10^5	ND	—	—

ND, not detected.
HPC, heterotrophic plate count.
[a] Nephelometric turbidity unit.
[b] Phosphorus (mgP_2O_3/L).

3.2. Influence of superficial membrane morphology

CA and PA membranes are different in their surfaces. In polyamide membranes due to the fact of their manufacturing process, their surface is extremely rough, showing peaks and valleys as a strongly mountainous landscape. On the other hand, the CA membrane surface is relatively smooth. Thus, these membranes are more resistant against fouling than PA membranes [7].

3.3. Influence of operating conditions

In the same way that polymer membrane characteristics show interactions with colloidal particles in feed water, operating conditions generate strong modifications in membrane performance. Data obtained in the experimental plant with different membranes are subsequently shown.

In Fig. 3, relationships among characteristics of membrane kind and influence on relative flow (ratio between normalized flow at any time and initial normalized flow) in the intense pre-treatment are given. Under these conditions, feed water quality is rather homogeneous due to the pre-treatment. Thus, interactions between membrane characteristics and organic matter present in feed water predominate. Fouling on the membranes leads to the decrease shown in the figure. Effects due to pressure and temperature are compensated for when normalized flows are used.

For CA membranes, practically there is no change in relative flow during this experiment, thanks to their lower trend to foul. But in PA membranes, due to the higher trend to foul as a consequence of their rough surface and also to their higher trend to permeate, colloid concentration on the surface is increased, which leads to a flux decrease. CA membranes rendered a flow of 4.3 m^3/h at 19 bars, while PA membranes had a BP of 5.66m^3/h at 16 bars and MBP of 6.0 m^3/h at 10 bars.

Fig. 4 shows the influence that the increase of recovery (from 75 to 90%) causes on BP (low pressure) membranes. The increase of recovery leads to a higher water cross through membranes; due to the fact that these are permeable surfaces, there is an approach of colloids and dissolved organic matter to membranes, overcoming the repulsion between negative charges of membrane surface and particles. Thus, polarization concentration increases. This leads to significant fouling, very difficult to remove even by strong wash. This trend is increased with the higher permeability characteristics. The colloidal deposition rate on a permeable surface is controlled by an

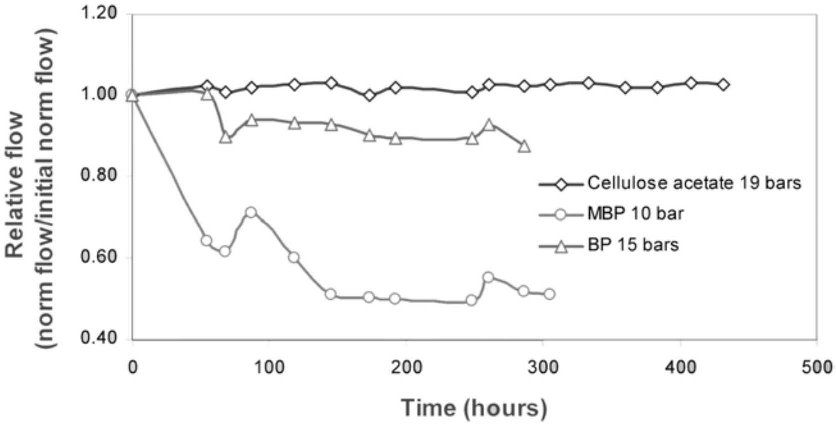

Fig. 3. Evolution of the relative flow along the time with the different membranes.

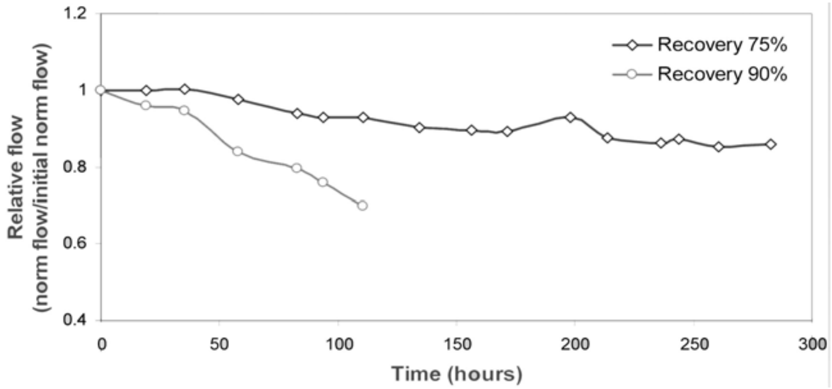

Fig. 4. Influence of the recovery increase on relative flow in intense pre-treatment conditions for BP membranes (pressure 16 bars).

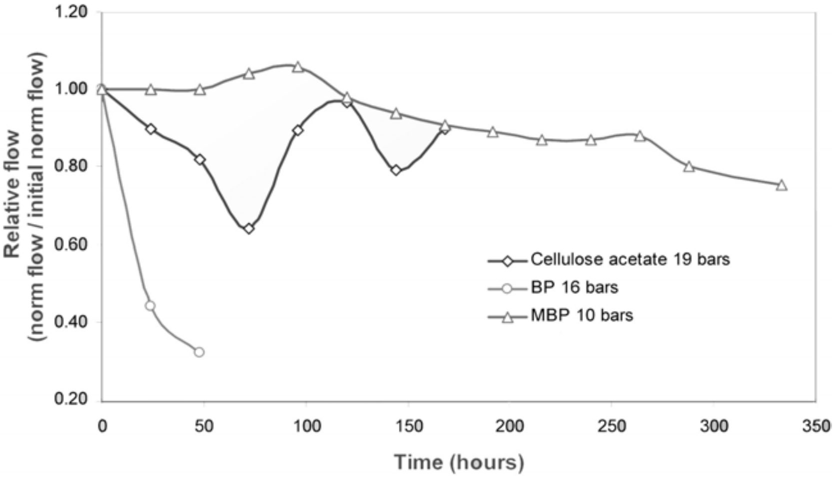

Fig. 5. Evolution of the relative flow along time with the different membranes in minimum pre-treatment conditions.

interaction between the repulsion force between the double electric layers (membrane-colloid) and a hydrodynamic force (permeation drag) resulting from the convective transport (the product of the recovery rate and the colloidal concentration) towards the membrane [7]. The permeation drag force is proportional to the permeate flow, and it acts perpendicularly to the membrane surface and in an opposing direction to the repulsion force of the double electric layers. Under typical operating conditions its value could be significant, overcoming the double layer repulsion, to result in a particle deposition and consequently in membrane fouling. Membrane fouling was also demonstrated, increasing with the recovery rate, because the convective transport towards the membrane also increases.

In Fig. 5 the influence of minimum pre-treatment on the relative flow is shown. Due to the absence of adequate pre-treatment, the presence of high organic matter contents have a notable influence on final fouling in all membranes, as a fast flow decrease is observed. High organic matter concentrations in feed water of RO membranes are an important influence, decreasing the life and membrane performance [10].

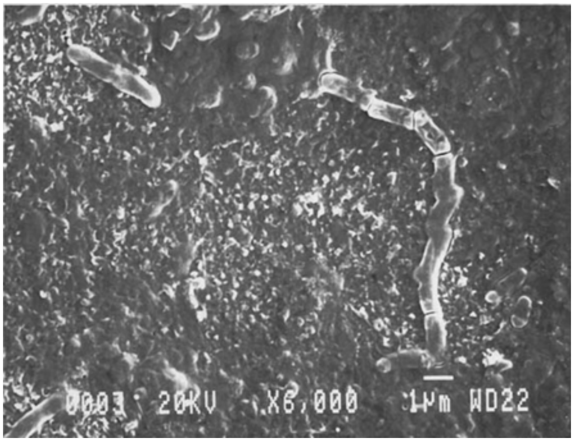

Fig. 6. SEM photomicrograph depicting biological and non-biological foulants on a BP membrane after its use under hard operating conditions (minimum pre-treatment and high recovery).

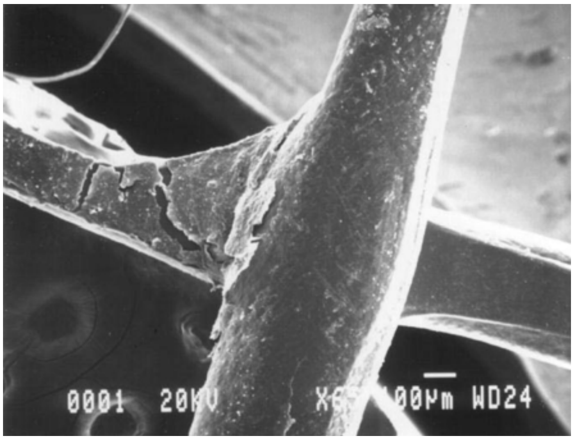

Fig. 7. Feed-channel spacer and fouling layer generated on an intersection of the plastic material.

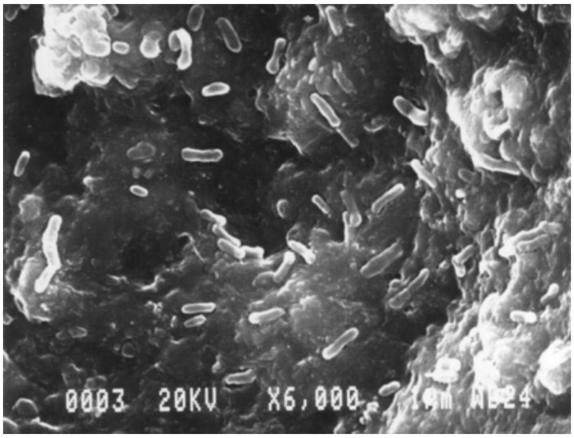

Fig. 8. Picture taken with increasing magnifications from the same place of Fig. 7. Note that in that area most of the bacteria cells are partially buried in the layer.

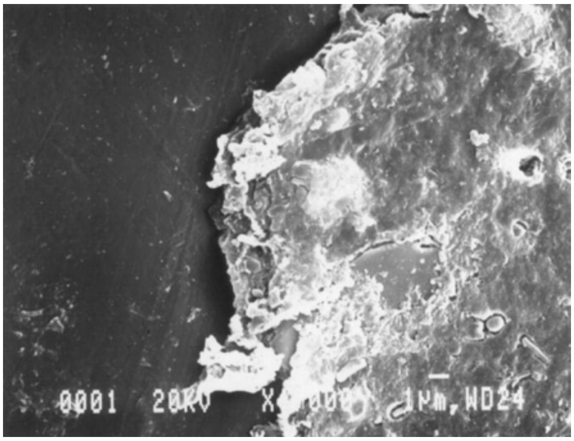

Fig. 9. Fouling layer of three microns of thickness on the plastic spacer.

After membrane operation, autopsies on some of them were done in order to establish the scope and nature of fouling in membranes. In Figs. 6–9 SEM photomicrographs taken of fouled PA membranes and feed-channel spacers are shown.

Fig. 6 shows a SEM photomicrograph depicting biological and non-biological foulants on a BP (low pressure) membrane after its use under hard operating conditions (minimum pre-treatment and high recovery). Fig. 7 shows a feed-channel spacer and the fouling layer generated on a intersection of the plastic material. Fig. 8 was taken at increasing magnifications from the same place of Fig. 7. In that area most of the bacteria cells are partially buried in the layer. In Fig. 9 the thickness of the fouling layer, 3 microns, on the plastic spacer can be measured.

3.4. Quality of the permeate

Comparative analyses of the secondary effluent and the reclaimed wastewater for groundwater recharge were conducted in order to study the efficiency of the reclamation process. Analytical parameters for reclaimed wastewater quality are shown in Table 1. Drinking water standards were also included as guide level and maximum admissible concentration. These drinking standards were widely exceeded by the reclaimed wastewater for the membranes tested using the multibarrier approach. The rejection characteristics of the membranes represent greatly reduced pollutants and micro-pollutants in the reclaimed waters; however, more analyses are needed and are part of future studies.

It is also noted that indicator microorganisms are absent from the effluent; this allows the reuse of water in a safe way, even for the irrigation of raw vegetables. 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, such as groundwater recharge. The low values achieved eliminate the problems of specific ionic toxicity that are customarily encountered with the use of non-desalinated reclaimed wastewater. In all cases, the high quality of reclaimed water allows it to be used with safety in groundwater recharge and other reuse applications without restrictions.

4. Conclusions

Studies conducted in the experimental pilot plant of Chiclana de la Frontera, Cádiz, reveal the following conclusions:

1. Membrane surface morphology plays a paramount role in colloidal deposition. In CA membranes, the cross flow can remove solids due to their smooth surface. On the contrary, this effect is strongly impeded by the presence of greatly superficial irregularities.

2. PA membranes have a higher permeability than CA membranes. Thus, there is a higher deposition of colloidal particles onto the membranes that alters the magnitude of the force of the repulsion between both negative charges, thus decreasing it, which is sometimes negligible, causing a fouling layer on the membrane. This phenomenon is jeopardized by the difficulty in the cross flow.

3. High recoveries lead to a fast and usually irreversible fouling in membranes, but if production must be increased by operational needs, an increase in membrane area is recommended using moderate recoveries.

4. An adequate pre-treatment is of utmost importance for correct membrane performance; even they there is fouling, it will be at a lower rate. An adequate washing system helps to maintain a RO unit operative for a long time. Both actions guarantee correct operation in wastewater reclamation projects using RO.

5. Water analyses conducted reveal that, for those parameters studied, the effluent quality obtained is high, thanks to the multibarrier approach carried out in this plant. Indirect potable reuse can be an alternative water resource in those regions with a lack of water, advanced technologies and high health standards.

Acknowledgements

The authors want to thank the collaboration of PRIDESA in this work, and specially Mr. Santiago Sahuquillo from the Research and Development Department.

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