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Use of reverse osmosis for the removal of coliform bacteria from brackish water in the dairy industry

Habib Bouzid*, Mouffok Redouane Ghezzar

Laboratoire des Sciences et Techniques de l'environnement et de la Valorisation, Département de Génie des Procédés, Faculté des Sciences et de la Technologie, Université de Mostaganem, BP 227 Route de Bel-Hacel, 27000 Mostaganem, Algeria, Tel. +213 (0)45 43 45 03; Fax: +213 (0)45 43 43 54; emails: habib.bouzid@univ-mosta.dz/habib_bouzid@yahoo.fr (H. Bouzid), ghezzar_redouane@yahoo.fr (M.R. Ghezzar)

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ABSTRACT

A limiting recovery rate strategy has been established for completely eliminating pathogenic bacteria as total coliforms by reverse osmosis (RO) spiral membrane during hard and non-organic brackish water treatment for the manufacture of reconstituted powder-based milk in the dairy industry. The physicochemical quality of brackish water showed that the total hardness and conductivity, around 600 mg L^{-1} as $CaCO_3$ and 2,300 µS cm^{-1} respectively, were significantly higher than World Health Organization (WHO) and European directive drinking water standards. Similarly, the microbiological quality did not meet regulatory standards because of the high number of pathogenic microorganisms as total coliforms present in the feed water of the RO process. $CaCO_3$ scale has been found to be the major constituent of brackish water highlighting the absence of organic compounds, which weakens the thickness of the membrane fouling layer and therefore the limiting flux cannot be reached. So, the limiting recovery rate has been found as an alternative solution to the limiting flux in which the limiting conditions of RO filtration were conserved. Indeed, it was found that the retention is more efficient at the limiting recovery rate revealing the limiting transmembrane pressure ($TMP_{limiting}$). Furthermore, the pH of permeate water decreased with the increase of TMP until a constant value (pH5.6) was achieved at the limiting recovery rate corresponding to the $TMP_{limiting}$ (11 bar). Total retention (100%) of total hardness and total coliforms from 11 bar was achieved for a limiting recovery rate value of about 72%. The remaining bacteria are non-pathogenic as aerobic mesophiles (total bacteria) which can be removed or reduced by pasteurization of reconstituted milk.

Keywords: Reverse osmosis; Brackish water; Coliform bacteria; Retention; Limiting recovery rate; Dairy industry

1. Introduction

Desalination of brackish water, by reverse osmosis (RO), to produce freshwater is an important commercial use [1]. The advantage of RO compared to other separation processes such as distillation is to operate at ambient temperature without phase change. Moreover, RO can provide a very high degree of water purity while still maintaining reasonable flow rates [2]. However, membrane fouling management remains a real challenge in the RO process [3]. Cleaning-in-place (CIP) remains an efficient solution to reduce fouling and restore the membrane performances by changing the morphology and/or the surface chemistry of the fouling layer [4]. Nevertheless, the consumption of chemical agents to carry out periodic CIP of the membranes weakens the advantages of membrane filtration. Therefore, the critical flux has been proposed by Field et al. [5] as a new concept in cross-flow membrane filtration. This flux was proposed as a sustainable production instead of filtration at limiting flux [5,6]. The critical flux ($J_{critical}$) is the maximum flux below which only a reversible deposit fouled the membrane during

* Corresponding author.

filtration, while the limiting flux ($J_{limiting}$) is the maximum flux available during filtration and for which a strongly irreversible deposit is formed on the membrane [5–10].

To the best of our knowledge, the critical and limiting fluxes have been studied for suspensions containing mineral and/or organic substances [11–14]. While in this study, there was an elimination of microorganisms contained in hard and non-organic brackish water. In this case, the membrane fouling will be totally inorganic and thus the limiting flux cannot be reached. For this reason, the limiting recovery rate was studied for the first time as an alternative strategy to the limiting flux for the total removal of coliform bacteria. In addition, this study combined engineering and microbiology regarding the microbiological treatment of brackish water in the dairy industry.

There are a few methods [15,16] in the literature that address water disinfection in the membrane process. These methods are reliable; however, their application could not be performed in the present work. Among them, the conventional methods such as chlorine, O_3, UV, and UV/chlorine disinfection after pretreatment stages [16] were time-consuming and harmful to the polyamide membrane. Other novel methods have also proven insufficient to completely remove bacteria [15]. Moreover, Stoica et al. [17] found that the RO permeate streams still contained viable microorganisms of which only 90% retention was achieved which required a final UV rays treatment.

The relevant dairy industry is that of Sidi Saada city (in the north-west of Algeria) which uses the RO of brackish water to produce water of excellent quality intended for the manufacturing of dairy products mainly the reconstituted powdered milk. In this industry, the RO process is the final step in the brackish water pretreatment chain namely sand filtration to remove suspended solids, the addition of scale inhibitor to reduce the amount of total hardness of water, and microfiltration (MF) to remove fine suspended solids, ferric oxides, and colloids.

Besides the pretreatment solution, some new trends, such as intermittent operation with membrane rinsing with permeate water, were investigated [18]. So, the membrane permeability can be improved with a permeate water rinse before the extended shutdown period. Besides, the intermittent operation was more advantageous than continuous operation in terms of removing fouling and improving permeability [18].

Since it is a food industry, then it is not only the salinity of the produced water which is essential but also its bacteriological quality. Therefore, to comply with regulatory standards [19–21] for the microbiological quality of drinking water to produce reconstituted milk, total coliforms must be completely eliminated. The above-mentioned brackish water pretreatment chain may contain a chlorine disinfection step, but its residual concentration negatively affects the RO membrane by the deterioration of its polymer [2,22]. Hence, filtration through activated carbon can also be inserted to remove residual chlorine before passing through the RO modules. But if it will be the case, the cost of installation and operation will be increased. In addition, the by-products from the activated carbon regeneration process may result in environmentally harmful effluent. It should be noted that iron and suspended solids or turbidity must be removed, in pretreating feed step, before the water enters the RO unit [2–23]. In addition, the feed water of the RO unit should be free from emulsified or unemulsified oil and grease [23]. To prevent plugging the water passages or coating the membrane, the scale inhibitor, which inhibits the precipitation of compounds such as carbonates and sulfates salts of calcium and magnesium, must be injected into the feedwater [2–23], but an increased residence time should be avoided since it would diminish the scale suppression capability of the antiscalant as reported by Hasson et al. [24]. Besides, the silt density index (SDI), during water microfiltration as a pretreatment step, must be less than 3 for the RO system to start [22,25].

The research was undertaken to investigate the sustainability of the process of coliform removal from brackish water in the dairy industry. The aim was to find the conditions for completely eliminating pathogenic bacteria as total coliforms without adding any chemical disinfection reagent and thereby avoid contamination of reconstituted milk contaminated with coliforms which would cause a danger to a humans health.

2. Materials and methods

2.1. Physicochemical and microbiological composition of pretreated brackish water

Brackish groundwater from drilling in Sidi Saada city is pretreated before entering the RO process in the dairy industry.

The physicochemical and microbiological quality of pretreated brackish groundwater is shown in Tables 1 and 2, respectively.

As shown, in Table 1, the conductivity is significantly higher than that (250 μS cm^{-1}) recommended by WHO and European directive for drinking water [19], which

Table 1
Physicochemical analyses of pretreated brackish groundwater

Parameter	Physicochemical quality of pretreated brackish groundwater
pH	7.4
Total hardness (mg L^{-1} as $CaCO_3$)	598
Ca^{2+} (mg L^{-1} as $CaCO_3$)	509
Mg^{2+} (mg L^{-1} as $CaCO_3$)	89
Alkalinity (mg L^{-1} as $CaCO_3$)	0
Total alkalinity (mg L^{-1} as $CaCO_3$)	187
Cl^- (mg L^{-1})	635.5
SO_4^{-2} (mg L^{-1})	121
NO_3^- (mg L^{-1})	22.9
Na^+ (mg L^{-1})	19.7
Fe (mg L^{-1})	0.211
Conductivity (μS cm^{-1})	2,344
BOD_5 (mg O_2 L^{-1})	0.57
COD (mg O_2 L^{-1})	0.98
Turbidity (NTU)	3.91

Table 2
Microbiological analyses of pretreated brackish groundwater

Parameter	Microbiological quality of pretreated brackish groundwater	WHO standards	European Directive Standards
Total bacteria (CFU/100 mL)	746	10^4 CFU/100 mL	10^4 CFU/100 mL
Total coliform bacteria (CFU/100 mL)	77	0 CFU/100 mL	0 CFU/100 mL
Escherichia coli (CFU/100 mL)	0	0 CFU/100 mL	0 CFU/100 mL

shows the poor quality of raw water feeding this industry. In addition, the total hardness recorded a significantly high value, consisting mainly of calcium hardness, showing that the water in question is very hard, according to WHO drinking water standards (200 mg L^{-1} as $CaCO_3$) [20]. Therefore, reconstituted milk will be of poor quality unless further treatment of water is implemented. On the other hand, chemical oxygen demand (COD) and biochemical oxygen demand (BOD_5) have very low values, reflecting the lack of organic compounds in this brackish water.

The count of bacteria is carried out in a liquid medium (Bromocresol Purple Broth with Lactose) by the technique of Most Probable Number (MPN) [26–28].

It can be seen that total bacteria meet the standards required by WHO and European directive, which is limited to 10^4 CFU/100 mL (100 CFU/1 mL) [20,21]. However, pathogenic germs such as total coliforms exceed the regulatory standards set to 0 CFU in 100 mL by WHO and European directive [20,21], which requires further treatment before being used for the manufacture of reconstituted milk. It should be noted that pretreated brackish water is free of Escherichia coli which is recommended (0 CFU in 100 mL) by WHO and European directive [20,21].

2.2. RO on industrial scale: set-up and filtration conditions

This dairy industry uses three modules (OSMOPAC HH20000, USA) (Fig. 1), each consisting of five spiral wound elements, so the set uses 15 spiral wound elements to treat an overall feed flow rate of 23 m^3 h^{-1}. The module located at the top is fed by the retentates of the other modules at the bottom, with the overall feed flow rate (already passed through sand filtration, the addition of scale inhibitor, and microfiltration (MF) but without UV disinfection) with TH (total hardness) of 600 mg L^{-1} as $CaCO_3$, and an overall permeate flow rate of 17 m^3 h^{-1} (issued from 15 spiral wound elements) with TH of 0 mg L^{-1} as $CaCO_3$ at 20°C and TMP initially set to 14 bar when the membranes were new. After mixing the overall permeate flow rate (17 m^3 h^{-1}) with 1.5 m^3 h^{-1} (TH of 600 mg L^{-1} as $CaCO_3$) of sand filtered UV disinfected water (without the addition of scale inhibitor and MF), the

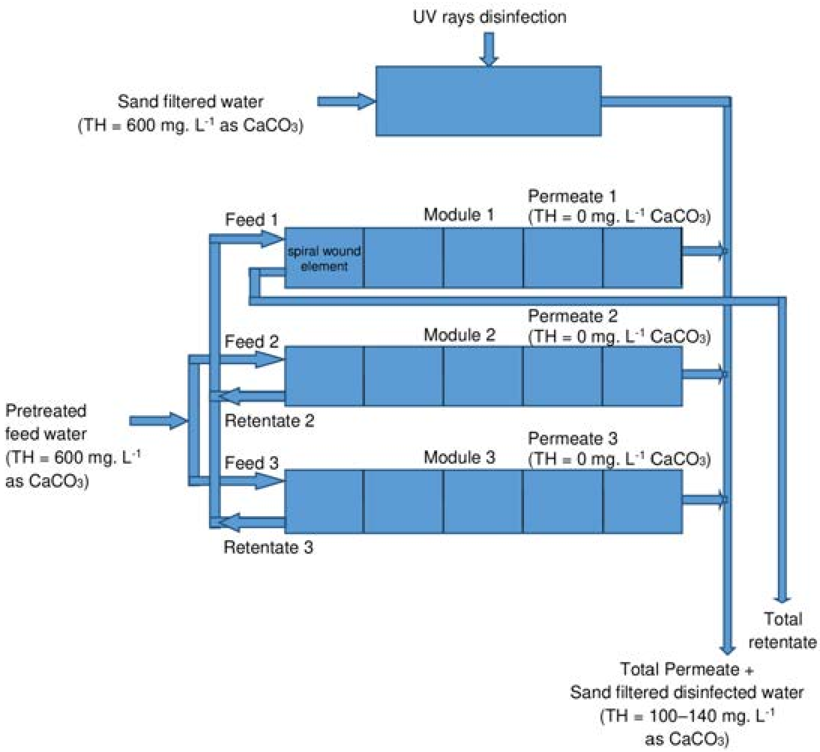

Fig. 1. Final brackish water treatment by RO installation in the dairy industry of Sidi Saada.

resulting water of 18.5 $m^3 h^{-1}$ will have a TH about 100–140 mg L^{-1} as $CaCO_3$ (Fig. 1). Reconstituted milk prepared from water with a hardness of 0 mg L^{-1} as $CaCO_3$ (after RO process) or 600 mg L^{-1} as $CaCO_3$ (before RO process) cannot be consumed because of the total lack of minerals (0 mg L^{-1} as $CaCO_3$) or excessive mineralization (600 mg L^{-1} as $CaCO_3$) where in both cases are not recommended for consumption as it may cause a hazard to human health. On the other hand, the water hardness between 100 and 140 mg L^{-1} as $CaCO_3$ is considered to be favorable for the preparation of reconstituted milk which is below WHO drinking water standards [20]. The RO spiral membrane (11.2 m^2) is a polyamide thin-film composite from Filmtec (USA).

The modules are currently operating at TMP 13 bar to reduce membrane fouling, with a water recovery rate of 70% and salt retention of 97% from brackish water around 1,600 mg L^{-1} of salinity (around 2,300 µS cm^{-1}) at 20°C [22]. The feed (*F*), permeate (*P*), and retentate (*R*) flow rates are measured at different TMP (5, 6, 7, 9, 11, 13, and 15 bar). It should be noted that 15 bar is the maximum achieved value corresponding to the total opening of the pump in the RO process. To switch from one TMP to another, it is necessary to wait 10 min for the system to stabilize.

The recovery rate is given by Eq. (1):

$$\text{Recovery rate } (\%) = \frac{Q_P}{Q_F} \times 100 \quad (1)$$

where Q_P is permeate flow rate and Q_F is feed flow rate.

The permeate flux is given by Eq. (2):

$$J_P = \frac{Q_P}{A} \quad (2)$$

where J_P is the volumetric flux of permeate and A is membrane area.

The performance of RO is expressed as observed retention (rejection) (*R*) of salt or bacteria according to Eq. (3) [9,29,30]:

$$R\ (\%) = \frac{1 - C_P}{C_F} \times 100 \quad (3)$$

where C_F and C_P are the concentration in the feed and permeate, respectively.

2.3. Limiting and critical flux determination

The increase in the permeate flux (J_p), in the RO process, is caused by the increase in TMP (Fig. 2). The flux increases linearly with the TMP up to a critical point ($J_{critical}$, $TMP_{critical}$) where this straight line begins to diverge from the linearity, delimiting the critical filtration conditions. Then, the permeate flux increases slightly until reaching a plateau where the first performed TMP that appears is called limiting pressure ($TMP_{limiting}$). Beyond this $TMP_{limiting}$, the permeate flux no longer increases and reaches a constant maximum value called limiting flux ($J_{limiting}$). The way of determining the critical and limiting fluxes is shown in the given example of Fig. 2. The flux values presented are made with a precision of 5%, for the given example of filtration of a dairy effluent [9], by increasing step by step the TMP [7–9].

In order to better understand the chemical nature of brackish water used in this dairy industry, analyses by Fluorescence X, and scanning electron microscopy (SEM) were carried out on a fouled RO spiral membrane already used by this dairy industry.

2.4. X-ray fluorescence

X-ray fluorescence analysis was performed using an X-ray fluorescence spectrometer ZSX Primus II Rigadu.

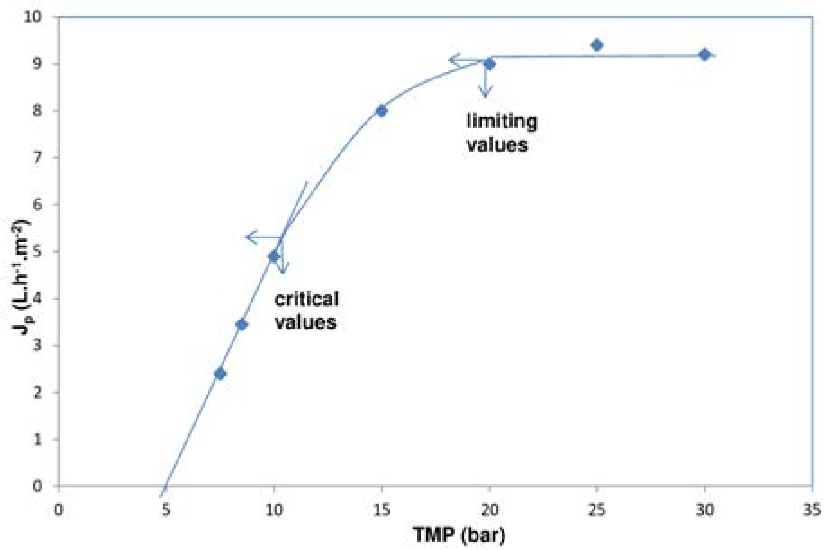

Fig. 2. Limiting and critical flux determination, in RO process, for skimmed milk vs. TMP at pH 6.7 and 25°C [9].

The analysis was carried out on a 3 cm diameter pellet of a fouled RO spiral membrane sample already used by the dairy industry.

2.5. Scanning electron microscopy

The same membrane sample was observed by SEM Quanta 250 from the FEI Company (Tokyo, Japan). Several image acquisitions were made on the surface of the sample highlighting its geometric topography with different magnifications.

3. Results and discussion

3.1. Feed, permeate, and retentate flow rates

The permeate (Q_P), retentate (Q_R), and feed (Q_F) flow rates indicated values (Tables 3–5, respectively) are averages calculated from the measurements carried out in triplicate (n = 3) with precision or relative standard deviation (RSD), defined as the ratio of standard deviation (SD) to the mean value, varied in the range from 0% to 2.3% by increasing step by step the TMP with pretreated brackish water. The feed flow rate was determined from the sum of the permeate and retentate flow rates.

The CIP between the measurements is performed, every 2 weeks, with citric acid (2%) (Weifang Ensign Industry Co., Ltd., China) (8 kg citric acid in 400 L of permeate water) at 45°C. The cleaning solution (400 L) is placed in an external back with a pump operating at a maximum pressure of 3.5 bar and is connected with the RO module, forming a closed hydraulic circuit, to circulate the cleaning solution through the membrane for 30 min. Then there will be a 15 min stop with the membranes remaining submerged in the solution, and then restart the pump to circulate the cleaning solution for 30 min again [22]. When CIP is finished, the closed hydraulic circuit is disconnected then the backwash is carried out with permeate water at TMP 13 bar, letting the permeate water pipe run down the drain for 10 min. Then, a disinfection solution based on hydrogen peroxide (Analysys, France) 0.5% (2 L of commercial solution in 400 L of permeate water) circulates in the RO installation, in a closed hydraulic circuit, at 3.5 bar for 10 min. Finally, a second backwash with permeate water at TMP 13 bar is applied for 10 min.

It should be noted that the change in flow rates will occur, even slightly, since this is an industrial scale dominated by dynamic conditions. The total permeates flux (J_P) shown in Table 3 is calculated according to Eq. (2), which is obtained from the mean of total permeate flow rate (Q_P) passing through (divided by) the membrane area of 15 spiral wound elements (A × 15).

It can be seen in Table 5, for a given TMP, that minimal changes in flow rate measurements has been recorded generating very low RSD values. This is a result of the constant hourly total flow rate that is set in the dairy industry. The flow rate measurements were made with a precision whose values meet the International Union of Pure and Applied Chemistry (IUPAC) quality control criteria, RSD% lower than 10% shows the high-level precision of the method [31]. Thus, the fluctuation of the permeate flow rates shown in Fig. 3, for TMP 13 bar usually set during the RO water treatment stage, gives rise to a minimum change in the measurements.

Table 3
Permeate flow rate measurements

TMP (bar)	5	6	7	9	11	13	15
Q_p (m^3 h^{-1})	Q_{P5}	Q_{P6}	Q_{P7}	Q_{P9}	Q_{P11}	Q_{P13}	Q_{P15}
	4	6.5	8	10.3	12.85	14.9	17
	3.95	6.4	8.05	10.25	12.75	14.8	16.8
	4.05	6.4	7.95	10.2	12.8	14.85	16.85
SD	0.05	0.06	0.05	0.05	0.05	0.05	0.1
Mean	4	6.43	8	10.25	12.8	14.85	16.88
J_p (L h^{-1} m^{-2})	24	38	47	61	76	88	101
RSD (%) = (SD/mean) × 100	1.3	0.9	0.6	0.5	0.4	0.3	0.6

Table 4
Retentate flow rate measurements

TMP (bar)	5	6	7	9	11	13	15
Q_R (m^3 h^{-1})	Q_{R5}	Q_{R6}	Q_{R7}	Q_{R9}	Q_{R11}	Q_{R13}	Q_{R15}
	4	4.5	4.65	5	5.15	5.8	6.35
	4.15	4.5	4.65	4.95	5.2	5.8	6.65
	4.15	4.4	4.65	4.9	5.1	5.75	6.55
SD	0.09	0.06	0	0.05	0.05	0.03	0.15
Mean	4.1	4.47	4.65	4.95	5.15	5.78	6.52
RSD (%) = (SD/mean) × 100	2.1	1.3	0	1	1	0.5	2.3

Table 5
Feed flow rate measurements

TMP (bar)	5	6	7	9	11	13	15
Q_F (m^3 h^{-1})	Q_{F5}	Q_{F6}	Q_{F7}	Q_{F9}	Q_{F11}	Q_{F13}	Q_{F15}
	8	11	12.65	15.3	18	20.7	23.35
	8.1	10.9	12.7	15.2	17.95	20.6	23.45
	8.2	10.8	12.6	15.1	17.9	20.6	23.4
SD	0.1	0.1	0.05	0.1	0.05	0.06	0.05
Mean	8.1	10.9	12.65	15.2	17.95	20.63	23.4
RSD (%) = (SD/mean) × 100	1.2	0.9	0.4	0.7	0.3	0.3	0.2

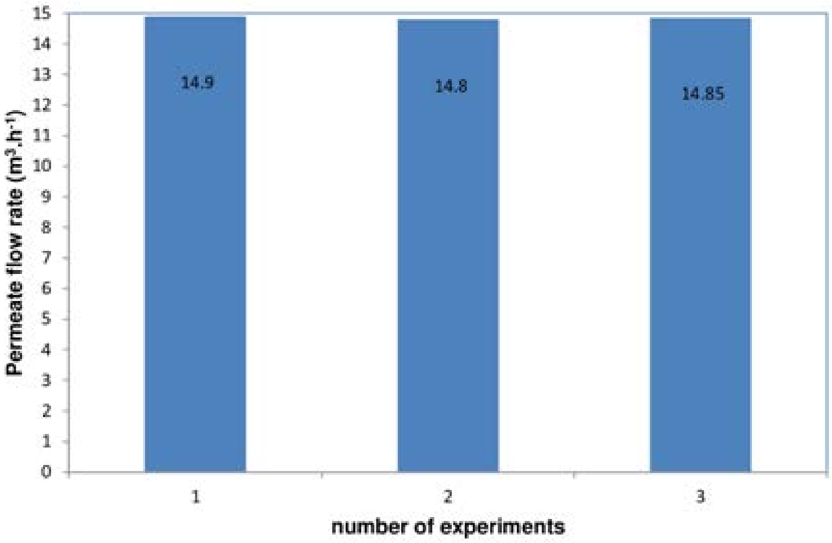

Fig. 3. Change in permeate flow rate during RO filtration for n = 1, 2, and 3 with TMP 13 bar set by the dairy industry for RO brackish water treatment.

According to the permeate flux values shown in Table 4 and plotted in the curve of Fig. 4, the plateau indicating the limiting values is not reached. This is very probably due to the absence of macromolecules, in the studied brackish water, which if present might have constituted a gel giving reversible and irreversible fouling. Such fouling causes additional hydraulic resistance [9].

In order to confirm that there are no organic matters in the chemical composition of the used brackish water, the X-ray fluorescence, and SEM analysis performed, on a fouled RO spiral membrane already used by this dairy industry, led to the following results.

3.2. X-ray fluorescence result

X-ray fluorescence analysis of a fouled RO spiral membrane sample, in contact with the brackish water for 3 y, indicated the existence of a considerable amount of calcium (Ca^{2+}) combined with carbonate (CO_3^{2-}) since both had high proportions in the sample (Table 6) which were 35.9 and 37.54 wt%, respectively. The other elements recorded low proportions thus insignificant quantities should be in the sample. In fact, it has not been detected any track of organic matter in the sample, which can be stated that the entire fouling was of mineral origin mostly found as $CaCO_3$ scale.

3.3. SEM result

The image of the SEM analysis sample showed the existence of a $CaCO_3$ scale deposit (Fig. 5a–d) at the membrane interface with the appearance of aragonite [32–34] shown in the red circle (Fig. 5a and b). In addition, it has been seen congestion of particles already identified on the membrane, which showed its strong fouling.

The absence of organics in the fouled RO spiral membrane confirms their lack previously found in the feed brackish water of the RO process. As a result, the entire fouling is of mineral origin ($CaCO_3$ scale). So, the absence of a fouling gel, formed by organic substances, prevents the achievement of the limiting flux while increasing the TMP during the RO process.

To identify and determine the limiting conditions in the RO process and therefore apply the strategy of the limiting recovery rate, the RO feed water should be free from organics and contain a large amount of hardness.

From calculated averages of feed and permeate flow rates, for each TMP, given in Tables 3 and 5, the water

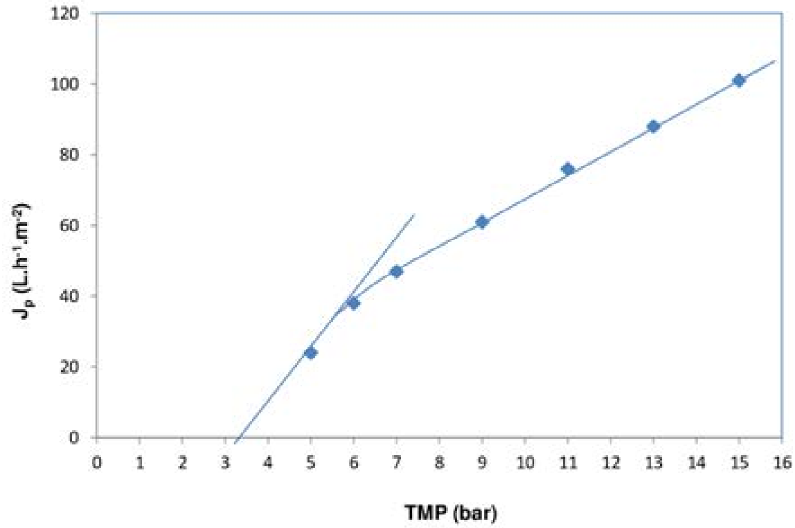

Fig. 4. Brackish water permeates flux vs. TMP.

Table 6
Result of X-ray fluorescence analysis of the fouled spiral RO membrane sample

N°	Component	Result (wt%)	Oxide	Result (wt%)
1	B	1.83	B_2O_3	5.878
2	C	10.2	CO_3	37.5437
3	Na	0.212	Na_2O	0.2861
4	Mg	0.311	MgO	0.5164
5	Si	0.606	SiO_2	1.2954
6	P	0.005	P_2O_5	0.0114
7	S	1.27	SO_3	3.1796
8	Cl	0.142	/	/
9	K	0.006	K_2O	0.0072
10	Ca	35.9	CaO	50.1987
11	Ti	0.021	TiO_2	0.0351
12	Cr	0.0078	Cr_2O_3	0.0114
13	Fe	0.0978	Fe_2O_3	0.1398
14	Cu	0.0031	CuO	0.0039
15	Zn	0.563	ZnO	0.7003
16	Sr	0.0427	SrO	0.0505

recovery rate is calculated; however, it can also be calculated in triplicate (n = 3) for each feed and permeate flow rates corresponding to each TMP. Then, an average will be calculated from the three recovery rate values found as shown in Table 7 and plotted as a function of TMP (Fig. 6).

3.4. Physicochemical analyses of pretreated brackish water before and after reverse osmosis process

To be limited to regulatory standards, a final treatment of brackish water will occur by the RO process. To better understand the efficiency of this process on the quality of the water produced, samples of feed (F) and permeate (P) water were analyzed in triplicate (n = 3) at different TMP (Table 8). The retentions (rejection) of conductivity and total hardness were calculated and their mean values were plotted as a function of TMP as shown in Fig. 7.

It should be observed that the conductivity of the permeate water at different TMP complies with the drinking water standard (less than 250 µS cm^{-1}) issued by WHO and European directive [19]. The best-achieved retentions correspond to the TMP of 11, 13, and 15 bar indicating the appearance of the limiting filtration conditions. Likewise, the total hardness was completely removed from the TMP 11 bar revealing the limiting filtration conditions. Therefore, it is preferable not to filter at conditions giving a TMP beyond 11 bar to further reduce membrane fouling. But a slight increase in the amount of hardness will occur after mixing the overall permeate flux with the pretreated brackish water for the better quality of the milk produced as previously mentioned in Fig. 1.

For recovery rates, a plateau was also formed in the same TMP interval previously found with the aforementioned parameters.

Indeed, the water hardness form a thicker and faster scale layer on the membrane than with other minerals, demonstrating an increase in the permeate flux (or permeate flow rate) decay when the TMP increases in agreement with the work of Greenberg et al. [35], but at the same time, is thinner and slower to form compared to that of organics allowing the membrane to achieve premature fouling, which is clearly reflected in the constancy of the permeate flux at high TMP which increase the resistance and thickness of the fouling layer as previously shown in Fig. 2. While in the absence of organics as in our case, the fouling layer is less developed and therefore the loss of the permeate flow rate at high TMP is relative to the feed flow rate. So, even if the permeate flow rate increases slightly, its rate related to the membrane feed water is almost constant at high TMP when the $CaCO_3$ scale layer accumulates more quickly generating a large diffusion in the opposite direction of the convective permeate flow rate, which results in a constant overall permeate flow

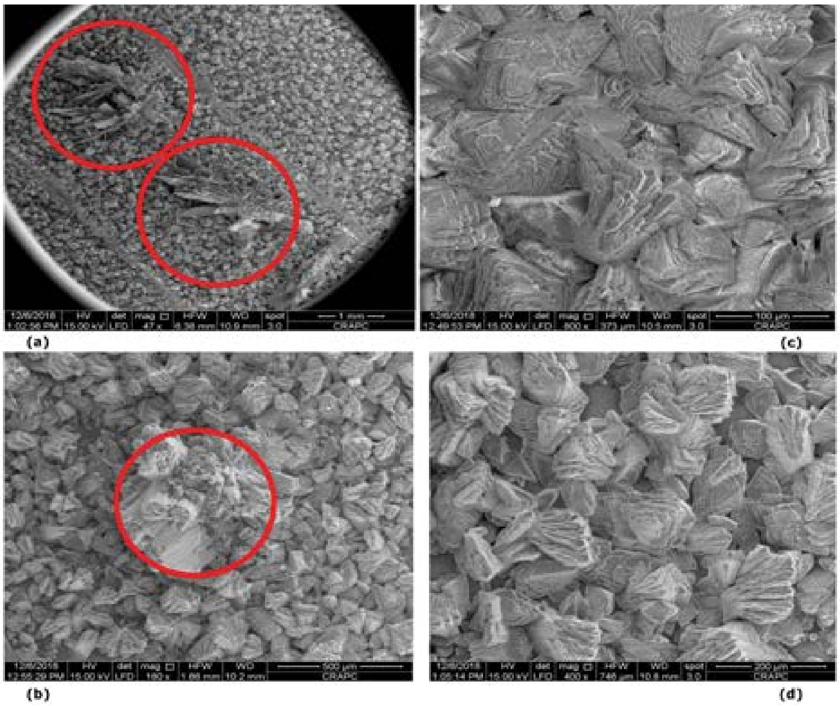

Fig. 5. (a–d) SEM analysis on fouled RO spiral membrane sample, in contact with brackish water for 3 y, with different magnifications.

Table 7
Water recovery rate values of RO spiral membrane

TMP (bar)	Recovery rate 1 (%)	Recovery rate 2 (%)	Recovery rate 3 (%)	Mean recovery rate (%)	SD	RSD (%)
5	50	48.8	49.4	49.4	0.006	1.2
6	59.1	58.7	59.3	59	0.003	0.5
7	63.2	63.4	63.1	63.2	0.001	0.2
9	67.3	67.4	67.5	67.4	0.001	0.1
11	71.4	71	71.5	71.3	0.002	0.3
13	72	71.8	72.1	72	0.001	0.1
15	72.8	71.6	72	72.1	0.006	0.8

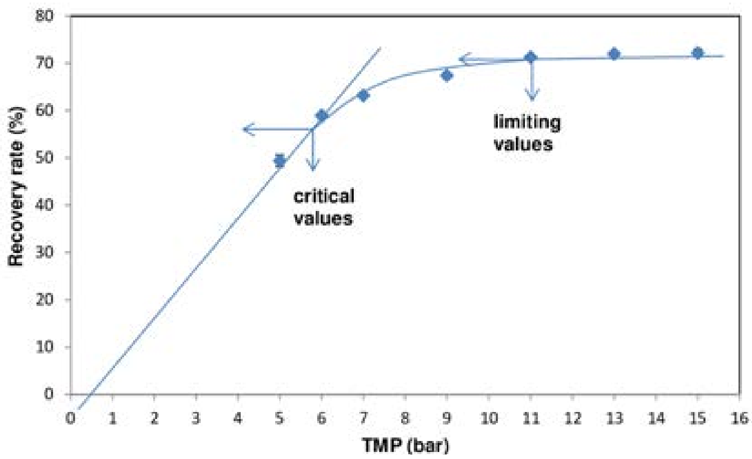

Fig. 6. Limiting and critical recovery rate values vs. TMP during reverse osmosis of pretreated brackish water.

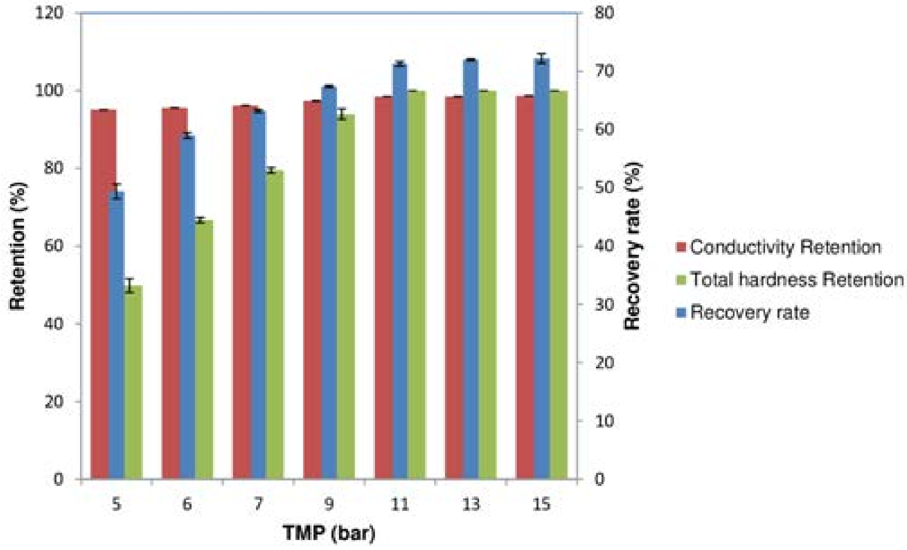

Fig. 7. Relationship between the retentions of conductivity and total hardness with the water recovery rate as a function of TMP during reverse osmosis of pretreated brackish water.

Table 8
Physicochemical analyses as conductivity and total hardness of pretreated brackish water before and after reverse osmosis process at different TMP

TMP (bar)	Water samples at different TMP	Conductivity (µS cm^{-1})			Average retention of conductivity (%)	RSD (%)	Total hardness as $CaCO_3$ (mg L^{-1})			Average retention of total hardness (%)	RSD (%)
5	5F	2,290	2,280	2,300	95.1	0.02	606	630	610	80.4	1.76
	5P	112.3	112	112			110	124	128		
6	6F	2,280	2,310	2,310	95.6	0.02	616	626	604	83.9	0.67
	6P	101	101.5	101.5			98	106	94		
7	7F	2,320	2,310	2,330	96.2	0.05	622	628	630	86.9	0.67
	7P	89	89.4	88			84	78	84		
9	9F	2,390	2,370	1,260	97.4	0.09	630	626	620	94.5	1.36
	9P	61	59	63			44	32	28		
11	11F	2,410	2,410	2,390	98.5	8.8E-03	614	622	626	100	0
	11P	35	35.4	34.8			0	0	0		
13	13F	2,420	2,420	2,410	98.5	0.04	592	624	612	100	0
	13P	36	37	35			0	0	0		
15	15F	2,320	2,310	2,290	98.7	0.02	610	620	614	100	0
	15P	31	30.9	31.2			0	0	0		

rate (convective flow rate – diffusive flow rate) compared to the membrane feed flow rate, means a constant rate of water recovery.

To better visualize the evolution of conductivity retention as a function of TMP, the values were revealed in Table 9 and plotted in comparison with NaCl retention (Fig. 8).

According to Fig. 8, it seems that the conductivity retention follows the same behavior of total hardness in which the retention became constant from the TMP 11 bar, despite the fact that the retention increased in a slight way from the low TMP. While NaCl retention increases linearly but very slightly with TMP. This may be due to the Donnan effect in which the monovalent chloride ions (Cl^-) pass into the permeate, making retention almost constant over the entire TMP range, except at high TMP (15 bar) where a slight increase in retention has occurred, most likely due to the formation of a very high hydraulic resistance which prevents these ions from passing into the permeate.

The highest achieved value (80.6%) for NaCl retention is lower than that achieved on the plateau (98.7%) for conductivity retention. This makes the latter the most complete with the exception of the total hardness which is entirely retained because of its bivalent ions (Ca^{2+} and Mg^{2+}) better retained as a scale layer, causing a high resistance on the membrane.

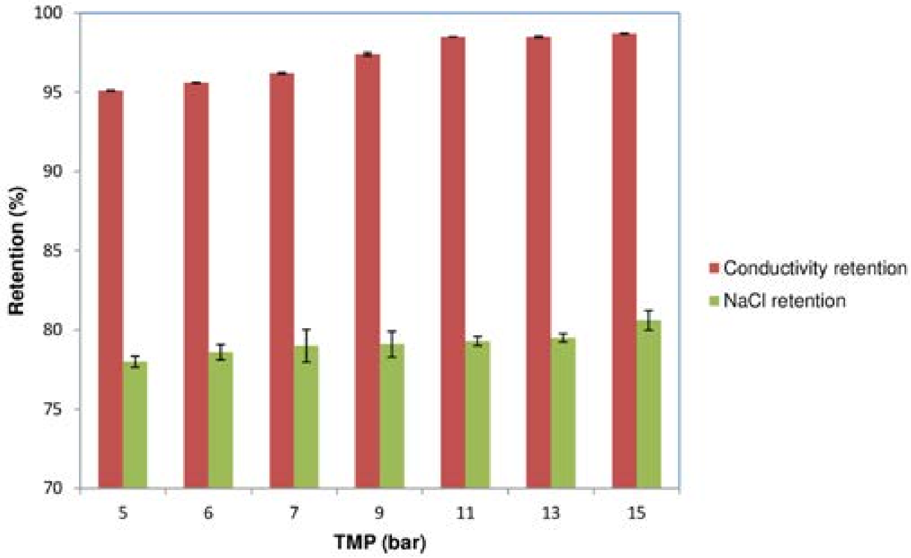

Fig. 8. Evolution of the retentions of conductivity and NaCl as a function of TMP during reverse.

Table 9
Physicochemical analyses as conductivity and NaCl of pretreated brackish water before and after reverse osmosis process at different TMP

TMP (bar)	Water samples at different TMP	Conductivity ($\mu S\ cm^{-1}$)			Average retention of conductivity (%)	RSD (%)	NaCl ($mg\ L^{-1}$)			Average retention of NaCl (%)	RSD (%)
5	5F	2,290	2,280	2,300	95.1	0.02	1,053	1,079.4	1,023.8	78	0.35
	5P	112.3	112	112			234	234	225.1		
6	6F	2,280	2,310	2,310	95.6	0.02	1,047.2	1,053	1,053	78.6	0.48
	6P	101	101.5	101.5			215.9	225.1	234		
7	7F	2,320	2,310	2,330	96.2	0.05	1,053	1,053	1,047.2	79	1.03
	7P	89	89.4	88			225.1	234	225.1		
9	9F	2,390	2,370	1,260	97.4	0.09	1,047.2	1,053	1,047.2	79.1	0.81
	9P	61	59	63			215.9	215.9	225.1		
11	11F	2,410	2,410	2,390	98.5	8.8E-03	1,047.2	1,057.9	1,057.9	79.3	0.29
	11P	35	35.4	34.8			225.1	225.1	225.1		
13	13F	2,420	2,420	2,410	98.5	0.04	1,053	1,064.9	1,064.9	79.5	0.26
	13P	36	37	35			215.9	225.1	234		
15	15F	2,320	2,310	2,290	98.7	0.02	1,065.5	1,057.9	1,065.5	80.6	0.62
	15P	31	30.9	31.2			210.9	210.9	225.1		

3.5. Microbiological analyses of pretreated brackish water before and after reverse osmosis process

In order to better understand the influence of the RO process on the elimination of non-pathogenic (aerobic mesophyles) and/or pathogenic (total coliforms) bacteria, bacteriological analyses were carried out on the feed and permeate water samples. The retentions of total bacteria and total coliforms are shown in Table 10 and Fig. 9.

It can be seen that the total coliforms are completely eliminated from the TMP 11 bar indicating a limiting TMP during RO process. It seems that at low TMP the total bacteria retention is insignificant but improved with the TMP increase in agreement with the work reported by Chong et al. [36]. The higher operational flux corresponding to higher TMP produces greater amounts of the bacterial population involved in biofilm formation on the membrane. As a result, the retention of bacteria increases with the TMP until the pressure drop occurs, at the limiting recovery rate, due to the formation of the fouling layer creating a constant hydraulic resistance from 11 bar.

In addition, it can be stated that both polyamide RO membrane and total coliforms are hydrophobic and have a negative charge [37]. But, cell surface charge becomes less negative when the ionic strength increases (high salinity of brackish groundwater) as reported by Chun

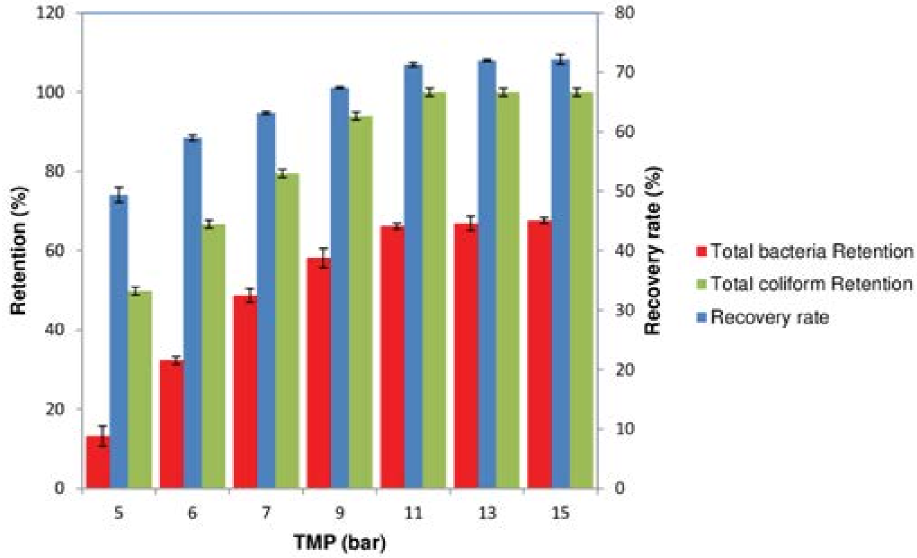

Fig. 9. Relationship between the retentions of total bacteria and total coliforms with the water recovery rate as a function of TMP during reverse osmosis of pretreated brackish water.

Table 10
Bacteriological analyses of pretreated brackish water before and after reverse osmosis process at different TMP

TMP (bar)	Water samples at different TMP	Total bacteria (CFU/100 mL)			Average retention of total bacteria (%)	RSD (%)	Total coliforms (CFU/100 mL)			Average retention of total coliforms (%)	RSD (%)
5	5F	812	804	816	13.2	2.57	80	86	75	49.8	0.77
	5P	702	700	710			40	43	38		
6	6F	890	902	894	32.3	0.99	71	77	74	66.7	4.27
	6P	602	614	603			22	25	27		
7	7F	976	971	984	48.7	1.72	70	66	73	79.5	3.26
	7P	508	500	496			14	12	17		
9	9F	728	731	737	58.2	2.4	83	74	78	94	2.27
	9P	304	316	298			5	6	3		
11	11F	589	594	580	66.2	0.72	79	74	73	100	0
	11P	198	204	194			0	0	0		
13	13F	626	614	621	66.9	1.82	83	81	86	100	0
	13P	200	211	204			0	0	0		
15	15F	600	609	602	67.6	0.71	73	76	81	100	0
	15P	195	200	192			0	0	0		

et al. [37], causing cell aggregation, and thus an irreversible adhesion could be formed on the membrane. Besides, the presence of high content of divalent cations such as Ca^{2+} and Mg^{2+} and the increase of pH (7.4) would result in greater membrane surface charge in which became more electron donor rich, more wetting, and therefore lead to increased adsorption of counterions or coulombic interactions [38]. So, it is believed that total hardness (Ca^{2+} and Mg^{2+}) would be adsorbed on the membrane surface, at first, by reducing its negative charge, then total coliforms could be adsorbed on the $CaCO_3$ scale layer. While, total bacteria as aerobic mesophyles were less rejected meaning that this kind of bacteria are more negative than total coliforms since their number is higher, generating a high electrostatic repulsion toward the membrane surface, and as a result, less retention has been noticed.

Furthermore, the biofouling layer is not only controlled by electrostatic interactions and the membrane-bacteria hydrophobicity, but also by the increase in permeate flux [37], where the TMP seems to play a major role in the retention mechanism. It is believed that beyond a limiting TMP, corresponding to a limiting recovery rate, and in the presence of divalent ions (Ca^{2+} and Mg^{2+}) forming a $CaCO_3$ scale layer generating a strong resistance on the membrane from which total retention of the total coliforms occurred, which is very probably due to the bacterial attachment on the $CaCO_3$ scale layer by forming biofouling.

Therefore, it should be said that the treated water quality in terms of total coliforms meets the recommended drinking water standards (0 CFU in 100 mL) by WHO [20] and European directive [21]. On the other hand, the total bacteria could not be totally eliminated by the RO process despite their number reaching the plateau of limiting TMP. However, the values obtained on this plateau are significantly lower than those recommended by WHO and European directive (10^4 CFU in 100 mL) [20,21]. In addition, the pasteurization process for reconstituted milk could destroy or reduce all these non-pathogenic residual microorganisms, after mixing the treated water with the milk powder.

It should be noted that the retention of total coliforms and total bacteria reaches a maximum when the recovery rate is at its maximum. To completely eliminate the pathogenic bacteria as total coliforms and to significantly reduce the non-pathogenic bacteria as total bacteria from the brackish water operation at too lower flux should be avoided.

3.6. Effect of TMP on permeate pH

To determine the effect of TMP on the pH of permeate water, measurements were carried out on water treated by the RO process. The values found are shown in Table 11 and Fig. 10.

It should be noted that the pH of permeate water decreased with the increase in TMP then stabilized at a limiting TMP of 11 bar corresponding to the limiting recovery rate. The pH decrease can be explained by the decrease in the temporary or carbonate hardness (total alkalinity)

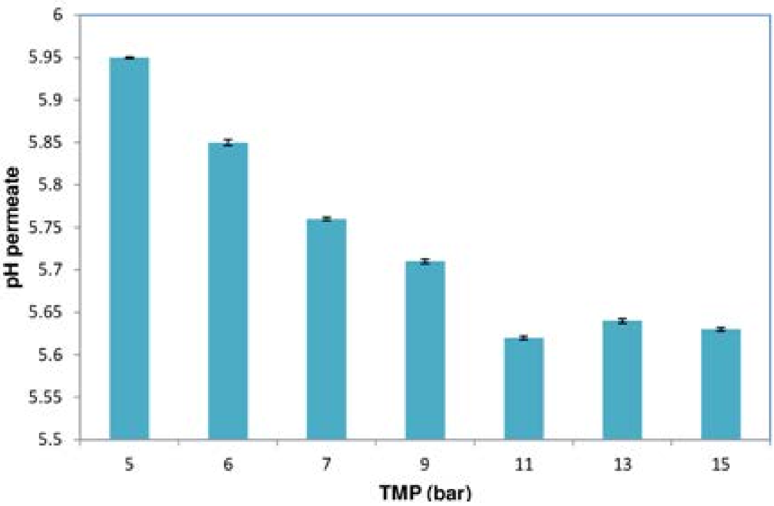

Fig. 10. Effect of TMP on permeate pH.

Table 11
pH of pretreated brackish groundwater before and after reverse osmosis process at different TMP

TMP (bar)	Water samples at different TMP	pH			Average feed pH	RSD (%)	Average permeate pH	RSD (%)
5	5F	7.43	7.43	7.42	7.43	0.08	5.95	0.10
	5P	5.96	5.95	5.95				
6	6F	7.43	7.41	7.42	7.42	0.13	5.85	0.34
	6P	5.85	5.83	5.87				
7	7F	7.44	7.42	7.417	7.42	0.21	5.76	0.20
	7P	5.77	5.77	5.75				
9	9F	7.42	7.42	7.44	7.43	0.16	5.72	0.27
	9P	5.73	5.7	5.72				
11	11F	7.45	7.44	7.43	7.44	0.13	5.62	0.21
	11P	5.61	5.63	5.63				
13	13F	7.44	7.42	7.42	7.43	0.16	5.64	0.17
	13P	5.62	5.65	5.64				
15	15F	7.43	7.44	7.43	7.43	0.08	5.63	0.21
	15P	5.62	5.64	5.62				

due to retention under the TMP effect. This is justified by the dependence of pH on the total alkalinity; that is, $[OH^-] + [CO_3^{-2}] + [HCO_3^-]$ (hydroxide, carbonate, and bicarbonate, respectively) [28]. Since the carbonate hardness is a fraction of the total hardness; that is, [total hardness] = [carbonate hardness] + [permanent hardness], thus the total removal of carbonate hardness will occur in the same TMP range from 11 bar as the removal of total hardness, where its removal contribute in the pH decrease as already explained above, confirming that the limiting recovery rate will occur from TMP 11 ($TMP_{limiting}$) meaning that the limiting conditions of filtration are retained from this $TMP_{limiting}$, where an elevation of TMP above 11 bar does not contribute to any improvement in the quality of the treated water and thus will only contribute to fouling of the membranes.

4. Conclusions

The limiting recovery rate strategy was found to be a useful indicator to identify the limiting conditions of RO filtration when the limiting flux cannot be reached due to totally inorganic fouling of the membrane. It was found that under these conditions that pathogenic bacteria as total coliforms and hardness are completely eliminated from brackish water in the dairy industry, thereby allowing the consumption of reconstituted milk without any risk to human health.

It was found that the retention has the highest value at the limiting recovery rate defining the limiting TMP. In addition, the pH of permeate water decreased with the increase of TMP until a stable value (pH 5.6) which corresponds to the limiting recovery rate.

So, the retention (100%) of total coliforms and total hardness has been reached when a recovery rate remains constant, around 72%, for high TMP from 11 bar. It can be stated that the limiting conditions of filtration were conserved from 11 bar ($TMP_{limiting}$) where an increase of TMP above $TMP_{limiting}$ did not contribute to any improvement in the physicochemical or microbiological quality of the treated water and therefore will only lead to excessive fouling of the membranes. To completely eliminate the pathogenic bacteria as total coliforms, and to significantly reduce the non-pathogenic bacteria as total bacteria, operation at too lower flux should be avoided. The constancy of the recovery rate at the limiting TMP did not result in total removal of conductivity and/or total bacteria. However, there was a significant increase, of 67.6% and 98.7%, in the retention of non-pathogenic bacteria as total bacteria and conductivity respectively, leading to a total bacteria concentration of approximately 30 CFU/100 mL and 200 μS cm^{-1} of conductivity which is in compliance with the WHO and European directive drinking water standards.

It can be concluded that the limiting recovery rate can completely remove the coliform bacteria and hardness of the RO system feed water, showing that the limiting recovery rate as engineering is a sustainable strategy for treating and disinfecting raw water for manufacturing in the dairy industry.

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