Produced water treatment by nanofiltration

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Abstract

The problem about produced water (PW) is worst if we consider that, for a single gallon of petroleum, there are three gallons of produced water as byproduct. PW is composed of a wide range of salts, suspended solids, chemical products such as antifloculating and anticorrosive substances and some organic products, being a treatment necessary either to disposal to the environment as to reuse . For this, the membrane processes such as ultra, micro and nanofiltration is becoming an option. In this study, nanofiltration (NF) membrane was characterized in terms of hydraulic permeability (L_p) and rejection coefficient (f), to be used as membrane process for onshore PW treatment. A synthetic effluent, simulating PW from onshore platform, was treated by NF in different operational conditions, combining three values of feed flow rate (96, 192 and 240 $L.h^{-1}$) and pressures varying from 2 – 6 bars. Temperature and pH were practically constant, with few modifications during the assays. The optimal regime, ie. feed flow rate and applied pressure, was the combination of 192 $L.h^{-1}$ of feed flow rate and 6 bars of pressure, which was capable to remove more than 81% of ions present in the synthetic PW. Between all the assays, the NF membrane was washed until L_p reached at least 90% the initial value. This fact proves that NF is a very effective method in salts removing from PW, promoting water reuse, recycling and correct disposal.

Keywords: *membrane processes, nanofiltration, reuse and disposal, produced water treatment*

1. Introduction

Currently, scientists and researchers are engaged on finding solutions to water scarcity. This problem, allied with the news about petroleum leaks, bad wastewater treatment and waste disposal and even climate influence mainly in sea waters, culminate in a huge world problem. Besides, petroleum and gas activities result in large amounts of liquid wastes, mainly what is called "formation water", composed by produced water (PW) and small rock pieces from the petroleum wells perforation (Ahmadun et al., 2009; Bakke et al., 2013).

It is estimated that the crude oil demand is more than 83 million barrels per day (mbpd) resulting in nearly 260 mbpd of PW, what give us a proportion oil:PW of 1:3. In few decades, the production of crude oil should grow to 107 mbpd, ie. the amount of PW will be around 321 mbps in 2030 (BP, 2009; Da Motta *et al.,* 2013). All these data, with the oilfields maturation phenomenon and the secondary water recuperation processes, clearly indicate an increase of the production of oil industry effluents and, as consequence, a higher disposal in world's waters (Silva, 2000; Diya'uddeenet al., 2014).

There is a concern about the effluent disposal during oil production processes, once the water is discharged at the environment: from offshore platform to the ocean; from production onshore platforms to local; from refineries and oil terminals to coastal regions. These sorts of disposal commonly present high salinity and hydrocarbons. Because of this, there is an appeal about effluent treatment and the work of regulating agencies that could establish disposal limits. Countries that have productive oil fields are more interested in studies and research that could solve the contamination problems with low cost technologies associated to effective ways. There are big concerns mainly about PW, once its effects on the environment are less understood, when compared to the oil field perforation effects (Robinson, 2000; Bakke et al., 2013).

The PW is composed mainly by salts, oils, chemical products, heavy metals and some radioactive materials, and because of this, its disposal become even more complicated if the generated amount is analyzed. The proposed solutions are treating, recycling and reuse of PW, including its reinjection (that could enlarge oil production) and its use in other industrial activities like fire control and irrigation, for example (Silva, 2000; Ahmadun et al., 2009; Bakke et al., 2013).

As an alternative for PW treatment, the use of filtration membranes as separation method is becoming a promise that combine low cost and high performance due to its simplicity, use of low pressure, room temperature and no phase transition. Nanofiltration (NF) is highly recommended for salt removal due to its selective separation of sulphates and multi and monovalent ions (Baker, 2012). Besides, NF can be used to the treatment of water with a concentration nearly 2000 mg.L^{-1}, using a range of pressures from 2 until 25 bars (Alzahrani et al., 2013; Da Motta et al*.,* 2013; Giacobbo et al., 2013).

This work aims to evaluate the efficiency of the nanofiltration process in PW treatment for its reuse, mainly as reinjection water in the petroleum wells, increasing oil recuperation, or for the correct disposal, in cases of a large amount of PW that, even after treated, cannot be used for reinjection. For this, a synthetic PW simulating real PW from onshore platform was treated by NF evaluating productivity and selectivity.

2. Materials and methods

2.1 Membranes

For this study, a commercial flat-sheet membrane was used: Filmtec NF90, supplied by The Dow Chemical Company, São Paulo, SP (Brazil). Some of the performance characteristics of the membranes are shown in Table 1 (Figueredo et al., 2014).

Table 1. NF90 membrane performance range

pH	**Operating**	2 – 11
	Cleaning	1 – 13
Temperature	**Operating**	up to 25 ºC
	Cleaning	up to 45 ºC
maximum operating pressure	**Bars**	41
	Psi	600
permeate flow	**L.h^{-1}**	83 – 1,620
	GPD*	525 – 10,300

*Gallons Per Day

The FILMTEC membranes are thin films composite membranes formed by three layers: the base, that is a polyester web, with 120 µm thickness, acting like support; an interlayer (about 40 µm), made by microporous polysulfone; and the top surface, that is an ultra thin polyamide barrier layer, which have a thickness of about 0.2 µm.

2.1.1. Membrane Characterization

Membrane was first compacted through the circulation of deionized (DI) / distilled water (conductivity < 2μS.cm^{-1}). The transmembrane pressure used for this was 7 bars, during about 3.5h. This step is important to guarantee that other lower pressures values used during the experiment will not affect the membrane surface. The feed solution was 4L and feed flow rate was 192 L.h^{-1}.

The NF90 membrane was characterized in terms of water permeability and rejection coefficient to reference solutes: NaCl, $CaCl_2$ and Na_2SO_4. The pure water permeation flux (PWP) was measured at transmembrane pressures (ΔP) from 2 to 6 bars, increasing 1 bar at every run. The membrane permeability (L_p) was estimated by the slope of the line PWP x ΔP. The permeation of reference solutions for membranes characterization was performed at a transmembrane pressure of 6 bar, feed solution concentration of 2.0, 1.0, 0.5, 0.25, 0.10 and 0.05 mg.L^{-1} and at a feed flowrate of 192 L.h^{-1}. The rejection coefficient (f) is calculated as in (1):

$$f = \left(1 - \frac{C_{permeate}}{C_{feed}}\right) \times 100 \qquad (1),$$

where C_{feed} is the salt concentration in the feed tank and $C_{permeate}$ is the salt concentration in the permeate.

2.1.2. Onshore Synthetic PW

The PW was prepared using data from the Potiguar Basin onshore platform (Figueredo *et al.*, 2014) as a base for the effluent that would be treated by NF. Starting from the concentrations of each element, it was calculated the amount of soluble salts to simulate the onshore PW. For producing the synthetic PW, the salts were solubilized in deionized (DI) water at room temperature under magnetic agitation. The concentrations of each element and the amount of each salt are shown in Table 2.

Table 2. Characteristics of synthetic PW from Potiguar Basin onshore platform

Salts	Concentration (mg.L^{-1})	Salts	Concentration (mg.L^{-1})
NaCl	933.00	NaF	2.00
$CaCl_2.H_2O$	618.00	$FeCl_3.6H_2O$	1.00
$MgCl_2.6H_2O$	549.00	$BaCl_2.2H_2O$	1.00
KCl	89.50	$MnCl_2.4H_2O$	1.00
$Na_2B_4O_7.10H_2O$	26.70	NaBr	1.00
$AlCl_3.6H_2O$	3.00		

2.2. Permeation experiments

All the study were performed in laboratory, with one flat-cell unit like the ones previously used in similar experiments at the same laboratory and described before in other studies (Afonso e Pinho, 1990; Giacobbo *et al.*, 2013). Fig. 2 shows a scheme of the nanofiltration equipment, a simplified operation model.

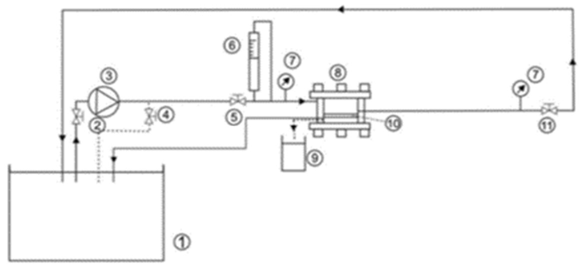

Fig. 2. Nanofiltration unit cell scheme. The arrows show the flow direction of the PW. 1-Feed tank; 2-Two way valve; 3-Pump; 4 and 5-Two way valves; 6-Rotameter; 7-Manometer; 8-Permeation cell; 9-Permeate sample; 10-NF90 membrane; 11-Pressure regulation valve (In: Giacobbo, Bernardes and De Pinho, 2013)

The NF90 membrane has 14.5 cm^2 of surface. The feed temperature was 28$\pm$ 2 °C during all the experiments. The assays were made in total recirculate mode, ie. the streams of permeate and concentrate PW were conducted back to the feed tank.

An evaluation of the synthetic PW was made before and after the NF membrane separation process and the different ions concentration under different values of pressure (from 2 – 6 bars, varying one by one) were compared. This part of the study aimed to define which used transmembrane pressure related with a certain feed flow rate could remove more salts and be considered as the optimal working regime.

Using the synthetic effluent previously mentioned in topic 1.1.3, three assays were carried out, varying the flow rate: 96 $L.h^{-1}$, 192 $L.h^{-1}$ and 240 $L.h^{-1}$. For each feed flow rate, pressure values varying from 2 – 6 bars were used. The common conditions were the room temperature (about 27 ºC) and the pH around 7.0. Membrane permeability was evaluated considering the synthetic effluent, and the salt coefficient rejection was calculated as previously mentioned, using the standard rejection curve. For this, samples from feed tank before the beginning of assays, and from the permeate, for each pressure, and in all used flow rates, were collected and compared. These samples were used to evaluate which was the optimal work regime, ie. the combination of flow rate and applied pressure that could best remove the ionic species in the solutions. The analysis of the salt content was made by ionic chromatography. Between the assays, the NF90 membrane was washed with pure DI water during periods of time that guaranteed that the L_p was at least 90% the initial value.

3. Results and discussion

3.1. Membrane characterization

Table 3 shows the hydraulic permeability L_p and salt rejection coefficients *f* to NaCl, $CaCl_2$ and Na_2SO_4 for 6 bars of pressure and 96 $L.h^{-1}$ of flow rate.

Table 3. Data of NF90 membrane characterization – hydraulic permeability and salt rejection coefficients

L_p ($L.h^{-1}.m^{-2}.bar^{-1}$)	f_{NaCl}	f_{CaCl2}	f_{Na2SO4}
9.19	95.79%	97.94%	99.07%

The values of salt rejection coefficients in Table 3 showed a typical behavior of NF membranes, that rejects divalent ions, such as Ca^{+2} and SO_4^{-2}, more effectively than monovalent ions, like Na^+ and Cl^-.

3.2. Permeation experiments

Fig. 3 shows the behavior of the permeate flux during the permeation experiments with pure water and with the synthetic PW at different feed flow rate conditions: 96, 192 and 240 $L.h^{-1}$. It is possible to notice that the permeate flux according to applied pressure for NF membrane presented a linear behavior for pure water and PW, which is a typical NF characteristic. The results are presented in order of the assays (192, 240 and 96 $L.h^{-1}$ successively).

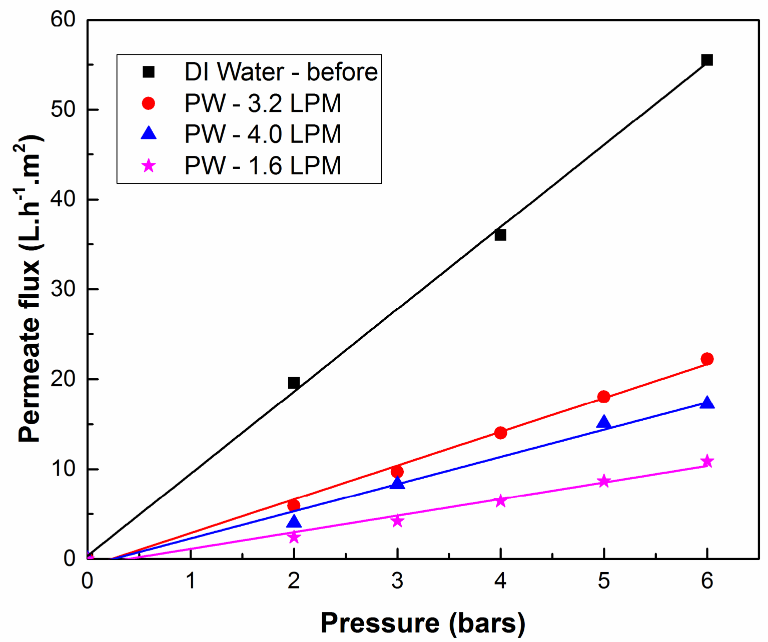

Fig. 3. Permeate flux with NF90 membrane as a function of pressure for pure water and synthetic PW at three feed flow rates: 96, 192 and 240 $L.h^{-1}$.

3.3. Separation membrane process with NF90

The assays with synthetic PW were made at same time as the permeability membrane studies. As previously mentioned, 3 different work conditions were used: with feed flow rates of 192, 240 and 96 $L.h^{-1}$ successively. This sequence of non-crescent flow rates is to verify if the equipment is able to change its work capacity without losing reproducibility. For each feed flow rate, different pressures were applied, varying from 2 to 6 bars. The combination of feed flow rate and applied pressure was called "work regime". After the membrane processes, the amount of each salt was verified by ionic chromatography and all the results were grouped in Figure 4.

The ideal work regime was chosen considering the highest *f* for 3 or more ions, showed in Table 4.

Table 4. Ions concentrations ($mg.L^{-1}$) before and after applied pressures (varying from 2 to 6 bars) according to the used flow rate (96, 192 or 240 $L.h^{-1}$). Green cells indicate best *f* values; yellow cells indicates worst *f* values; red borders are the chosen regimes for each feed flow rate.

96 $L.h^{-1}$											
	before	**2 bars**	***f* (%)**	**3 bars**	***f* (%)**	**4 bars**	***f* (%)**	**5 bars**	***f* (%)**	**6 bars**	***f* (%)**
Ca^{+2}	104.57	9.61	90.81	9.19	91.22	8.23	92.13	6.48	93.81	5.84	94.42
K^{+}	53.46	7.91	47.79	24.79	53.64	19.06	64.35	14.16	73.51	13.80	74.19
Mg^{+2}	127.08	3.78	97.03	6.35	95.00	5.21	95.90	5.00	96.06	3.88	96.95
Na^{+}	375.48	144.92	61.40	117.18	68.79	96.28	74.36	76.97	79.50	60.50	83.89
Cl^{-}	1.492.44	270.44	81.88	221.09	85.19	173.96	88.34	139.32	90.66	108.61	92.72
F^{-}	1.92	< 0,02	> 98	0.40	79.28	0.73	62.26	< 0,02	> 98	0.22	88.39
SO_4^{-2}	4651.13	2.81	99.94	3.59	99.92	5.75	99.88	1.45	99.97	6.17	99.87
192 $L.h^{-1}$											
	before	**2 bars**	***f* (%)**	**3 bars**	***f* (%)**	**4 bars**	***f* (%)**	**5 bars**	***f* (%)**	**6 bars**	***f* (%)**
Ca^{+2}	139.19	8.17	94.13	11.06	92.05	7.29	94.76	6.16	95.58	4.69	96.63
K^{+}	42.32	11.93	71.8	20.1	52.49	10.41	75.41	9.1	78.49	7.81	81.55
Mg^{+2}	70.33	1.68	97.61	3.55	94.95	2.97	95.78	2.07	97.06	1	98.58
Na^{+}	437.79	91.78	79.03	134.84	69.2	79.56	81.83	67.22	84.65	59.01	86.52
Cl^{-}	894.11	122.84	86.26	174.93	80.44	97.88	89.05	89.44	90	79.15	91.15
F^{-}	1.49	< 0,02	> 98	0.22	85.49	< 0,02	> 98	< 0,02	> 98	< 0,02	> 98
SO_4^{-2}	10.85	0.87	92.02	0.64	94.12	0.52	95.19	1.24	88.56	0.68	93.73
240 $L.h^{-1}$											
	before	**2 bars**	***f* (%)**	**3 bars**	***f* (%)**	**4 bars**	***f* (%)**	**5 bars**	***f* (%)**	**6 bars**	***f* (%)**
Ca^{+2}	148.47	9.37	93.69	7.94	94.65	7.51	94.94	9.01	93.93	8.08	94.56
K^{+}	45.68	10.6	76.79	11.36	75.12	9.42	79.37	14.49	68.27	8.1	82.27
Mg^{+2}	69.8	1.88	97.31	3.14	95.5	2.26	96.76	2.89	95.86	2.78	96.02
Na^{+}	476.68	84.86	82.2	86.77	81.8	73.64	84.55	82.75	82.64	72.15	84.86
Cl^{-}	940.54	108.67	88.45	108	88.52	95.48	89.85	109.55	88.35	97.86	89.59
F^{-}	2.1	0.49	76.52	0.35	83.43	0.18	91.25	0.22	89.34	0.29	86.12
SO_4^{-2}	5.23	< 0,04	> 99	1.08	79.34	< 0,04	> 99	0.48	90.75	0.63	88.02

Using 96 $L.h^{-1}$ of feed flow rate, we can clearly notice a considerable decrease of Cl^{-} and Na^{+} concentration (about 93% and 84%, respectively) when using 6 bars of pressure. However, for the other ions, the differences between *f* values were too small to notice in Fig. 4 (in the order of decimal places), but higher than 88%. For example, for Mg^{+2} *f* for 2 bars was 97.03% and for 6 bars was

96.95%. Considering that Ca^{+2} and K^{+} had suffered higher amount decreases for 6 bars, the best work regime in 96 L.h-1 was that one that used 6 bars of pressure.

In the case of 192 $L.h^{-1}$, it is possible to notice that all ions decrease for 2 and 3 bars, but as in previous case, the bigger difference of *f* values appeared for 4 to 6 bars (about 6% for K^{+}, corresponding to 2.6 $mg.L^{-1}$). For the other ions, *f* values in 6 bars of pressure were higher than 86% and because of this, the best work regime using 192 $L.h^{-1}$ was, as in 96 $L.h^{-1}$, the one that used 6 bars of pressure.

Finally, the regime that used 240 $L.h^{-1}$ of feed flow rate presented *f* values even closer between each other than the other two work regimes. Fig. 4 shows a notable decrease of all salts concentration, but it is difficult to notice for which pressure *f* was higher than the others. In this case, it was considered not only the best values of *f*, but the work regimes that had not worst *f* values too. So, between 4 – 6 bars, the regime submitted to 4 bars presented higher *f* values (for Cl^{-}, F^{-} and SO_4^{-2}, 90%, 91% and more than 99%, respectively) than when using 6 bars. Because of this, the best work regime for 240 $L.h^{-1}$ was that one that used 4 bars of pressure.

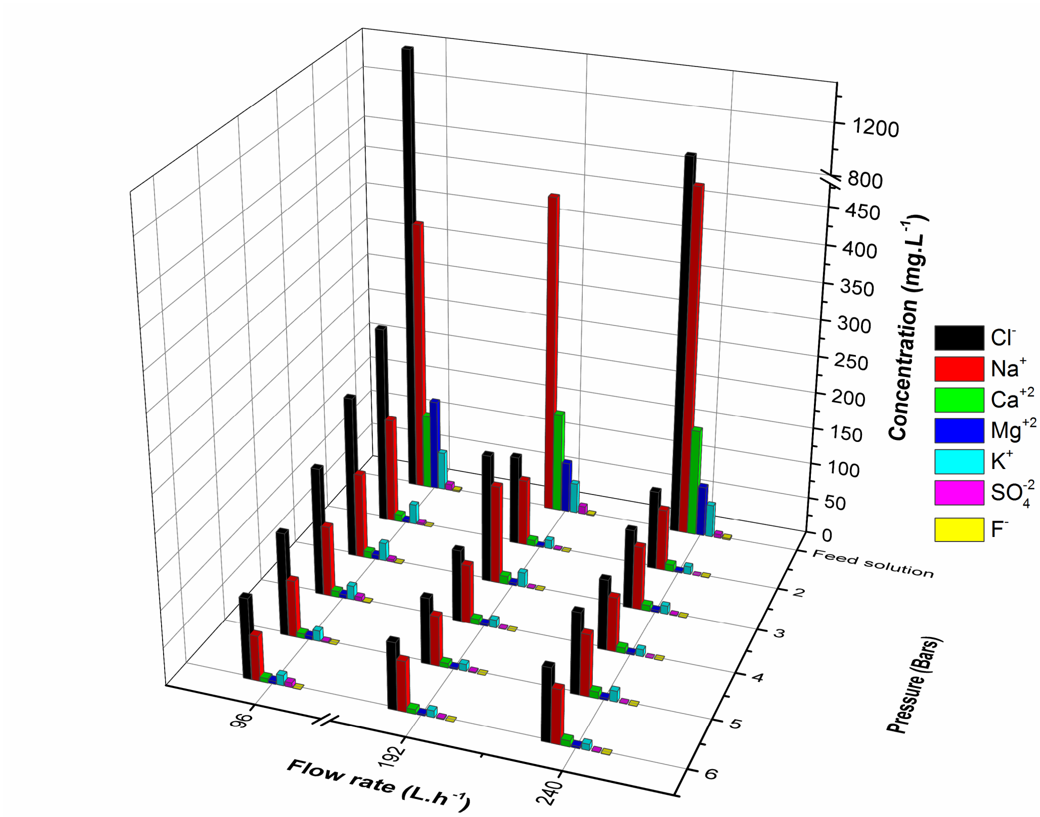

Fig. 4. Ionic concentration depending on flow rate and applied pressures. Each combination of flow rate and pressures was called as "work regime" and the best work regime was chosen considering the rejection indexes for each ion present in PW

When analyzing applied pressures, there is a rejection tendency clearly observed in Fig. 4: bivalent ions are stronger rejected than monovalent ions. Divalent cations, like Ca^{+2} and Mg^{+2}, suffered more than 90% of rejection in all work regimes. Monovalent cations, such as Na^{+} and K^{+} were rejected between 45 – 85%. Cl^{-} and F^{-} presented an irregular behaviour of rejection indexes and sulfate was rejected more than 98% in most of the cases, probably for being a bigger ion. To higher pressures, *f* values were, as a rule, bigger than to lower pressures. Observing feed flow rate, 96 and 192 $L.h^{-1}$, treatment behaviors were more regular than for 240 $L.h^{-1}$. Following previously mentioned rule, better rejection values were found when 6 bars of pressure was applied. Intermediate flow rate presented even a more constant behavior from 4 bars. Comparing work regimes in Fig. 4, beginning from 4 bars, it is possible to predict that the chosen regime is that one using an intermediate feed flow rate and the higher pressure, since these presented the highest values of ions rejection, what indicates a more effective treatment.

After analyzing all the combinations of feed flow rate-applied pressures, and choosing the best work regimes, the calculated *f* values are given in Table 5.

Table 5. Comparison of rejection coefficients (*f*) between chosen best work regimes

	Regime \ Ions	Cl^-	Na^+	Ca^{+2}	Mg^{+2}	K^+	SO_4^{-2}	F^-
***f*(%)**	96 $L.h^{-1}$ 6 bars	92.72	83.89	94.42	96.95	74.19	99.87	88.39
	192 $L.h^{-1}$ 6 bars	91.15	86.52	96.63	98.58	81.55	93.73	> 98
	240 $L.h^{-1}$ 4 bars	89.85	84.55	94.94	96.76	79.39	> 99	91.25

To choose the optimal regime, it was considered the highest *f* values for, at least 3 ions. Is possible to notice that the work regime of 192 $L.h^{-1}$ with 6 bars presented best *f* values for Na^+, Ca^{+2}, Mg^{+2}, K^+ and F^-. Observing data of Cl^- and SO_4^{-2}, *f* values were higher than 91%, what represent good rejection rates, being considered the optimal work regime.

These results corroborate the idea of NF treatment applied to PW. In this case, like previously mentioned, the treatment by NF enables the reuse of PW in different steps of petroleum production, like in the reinjection of treated PW to improve oil recuperation and its use to refrigerate the drill that perforate the rock that contains the oil. In both cases, this reuse means both financial and natural resources savings.

Finally, if the treated PW can not be totally applied in the oil industry reuse, there is the recycling option: treated PW could be used in irrigation (agriculture, soccer fields and landscaping, for example). In addition, in case of exceeding PW, the treated water can be stored with no concern about container corrosion, because NF process generate a clear neutral pH water (nearly 7.0), with a low salts content.

4. Conclusions

Following manufacturer's recommendations, it is possible to achieve a high salts rejection (almost 100%) using the NF90 membrane. In all conditions, the permeation fluxes with the synthetic PW were lower than the ones achieved with pure water, what can be attributed to the high produced water salinity. Between a range of combination of flow rate and applied pressures, it was possible to choose an optimal work regime, which provided us high rejection coefficient values. The use of 192 liters per hour of flow rate and 6 bars of pressure were capable to remove more than 80% of ions in the water.

Observing this great rejection capability, the use of NF90 membrane to remove salts in sense to reuse/recycle/dispose produced water has an enormous industrial potential, avoiding the need to use clean and/or even potable water to injection in petroleum wells.

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