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Is nanofiltration better than reverse osmosis for removal of fluoride from brackish waters to produce drinking water?

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ABSTRACT

In this paper, nanofiltration (NF) was investigated as a suitable technology for defluoridating brackish groundwater. A comparison between NF and reverse osmosis (RO) was performed to evaluate which method is the best for removing fluorine from groundwater to produce drinking water. Although NF employs a membrane that requires a low amount of energy, both NF and RO have advantages and limitations. NF and RO have similar costs for desalinating brackish water, and thus both the membranes can be used for this aim, but we believe that this will change with the next generation of NF membranes.

Keywords: Membrane; Groundwater; Economic assessment; Water cost; Desalination

1. Introduction

Using water with excessive fluoride for drinking water is a global problem. Over 200 million people worldwide consume drinking water with fluoride levels higher than the WHO guideline value (1.5 mg/L) [1]. Studies have reported that water with excessive fluoride in Morocco [2], Algerian [3], India [4], and Argentina [5]. Furthermore, Fawell et al. [6] and Shen and Schäfer [7] reported cases of water with excessive fluoride in Tanzania, Kenya, Turkey, the United States, Germany, Israel, Pakistan, and other countries. Excessive fluoride consumption is a health concern because it is associated with dental and skeletal fluorosis [6].

South America has a great transborder groundwater reservoir named the Guarani Aquifer System (GAS), which is located in Brazil, Argentina, Paraguay, and Uruguay. The area of the GAS is 1,194,000 km², with Southern Brazil comprising the largest area [8]. However, in confined regions, the water is brackish and has a fluoride concentration exceeding 1.5 mg/L, thus, is unfit for human consumption [8,9]. In some regions of Uruguay and Argentina, groundwater from the Guarani Aquifer contains 8,000 mg/L of total dissolved solids (TDS), 1,200 mg/L of sulfates, and 3.1 mg/L of fluorides and is used only for thermal baths owing to its excessive salt content [10]. In south Brazil, the fluoride concentration of the GAS is approximately 2 mg/L [8].

Reverse osmosis (RO) and nanofiltration (NF) have become important techniques for removing fluoride from brackish waters. RO is a desalination process that has spread worldwide and is a good alternative for removing fluoride from brackish waters, as shown in the studies performed by Richards et al. [11], Owusu-Agyeman et al. [1], Bejaoui et al. [2], and Shen and Schäfer [7], where fluoride removal was >95%. NF membranes are also capable of removing fluoride, as shown in the works published by Tahaikt et al. [12], Padilla and Saitua [5], Hoinkis et al. [13], Diawara [14], and Bejaoui et al. [15]. However, fluoride rejection via NF ranges broadly, that is, as low as 50% for loose membranes but 98% for tight membranes [12], depending on the membrane, the physicochemical proprieties of the water, and other characteristics of the process. Despite lower rejection, NF membranes produce higher permeate fluxes and require less energy compared

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with RO membranes [16,17]. Thus, both membrane types have advantages and disadvantages concerning brackish water defluoridation.

Complimentary information that helps in choosing between NF and RO is the economic feasibility of the processes. Economic evaluation can provide the necessary cost comparison between the two types of membranes and the financial information required to determine which type of membrane technology to invest in new desalination plants [18]. Thus, the higher permeate fluxes of NF must compensate for the possible lower rejection of the membrane in order for this technology to be an attractive investment.

Previous studies demonstrated that RO is a technical and economic alternative for desalinating the brackish waters from the Guarani Aquifer, which exceed the fluoride and sulfate standards for drinking water supply [8,19]. However, NF softening membranes can separate these inorganic salts as well. Thus, we decided to compare the advantages and disadvantages of both RO and NF in defluoridating the groundwater from the GAS to evaluate whether NF is a technical and economical alternative to RO for removing fluorine from brackish groundwater.

The aim of the work is to evaluate if NF is a technical and economical alternative to reverse osmosis (RO) to remove fluorine from brackish groundwater.

2. Materials and methods

This work is a follow-up to the studies by Brião et al. [8,19], in which RO was evaluated for the desalination of groundwater. Thus, the strategy of this research was divided into the three following steps.

- **Experimentation to evaluate NF rejection and permeate flux**: The aim of this part was to collect data to evaluate the fluoride separation and to design a NF facility.
- **Economic assessment of the NF facilities in six scenarios**: The aim here was to evaluate the sensitivity of the water cost by using low energy and to compare the effect of the groundwater fluoride concentration on the cost. First, an NF facility was designed for six scenarios: applying 1 or 2 MPa of pressure with each of three fluoride concentrations (2, 3, or 4 mg/L) in water from the Guarani Aquifer. Afterwards, economic assessments were made for all scenarios to evaluate the water cost.
- **Comparison between NF and RO results**: Our results (from this study and previous studies by our lab) and results from the literature were discussed in depth to compare the feasibilities of NF and RO for fluoride removal from brackish waters.

2.1. Experimentation to evaluate membrane rejection and permeate flux

2.1.1. Brackish water from the Guarani Aquifer

Three samples of groundwater were harvested from a well located at 27°30′10.3″S 51°54′6.3″W in the city of Marcelino Ramos, south Brazil. The water from this well is used by a tourist hotel for thermal baths. The well was drilled to 834 m depth, thus reaching the GAS. The physico-chemical characteristics of the water are shown in Table 1. The water temperature at the time of extraction was 37°C. The main cation present was Na^+, whereas the main anions present were SO_4^{2-}, Cl^-, bicarbonate, carbonate. Furthermore, Table 1 reveals that SO_4^{2-}, F^-, Na^+, and Fe^{3+} do not comply with the World Health Organization (WHO) guidelines [20] for potability. In fact, the water quality of GAS varies, with high salinity in confined zones [8].

2.1.2. Experimental

The experiments were carried out in a pilot module provided by WGM Systems (São Paulo, Brazil). Fig. 1 illustrates the RO pilot rig equipment, which consisted of two stainless steel tanks each with a 150 L capacity. The brackish water was fed to the tank and driven by a gear pump through the NF membrane, separating the permeate from the retentate, each of which was driven to one of the two tanks. The retentate passed through a shell heat exchanger on its way to the tank. Cold water (0°C–4°C) was recirculated with the aid of a thermostat bath (100 L capacity, Multi-Pão) to minimize the heat generated by the retentate due to recirculation during the batch operation in order to maintain the temperature in the range of 35°C ± 1°C (approximate temperature of the well). The equipment comprises transducers for temperature and pressure and flow meters, all connected to a control panel, and a computer for transferring the data via internet connection.

The NF membrane used belonged to a model 2538 SR3-VYV (Koch Membrane Systems, USA). This polyamide membrane had a spiral shape and 1.8 m² of filtration area. Hydraulic permeability of the membrane was 6.98 L/h/m²/bar, and its molecular weight cutoff (MWCO) was 200 g/mol.

Membrane rejection was calculated by relating the concentration of each compound in the permeate and retentate, as shown in Eq. (1).

$$R = 100\left(1 - \frac{C_P}{C_R}\right) \tag{1}$$

Here C_p indicates the permeate concentration, C_R represents the retentate concentration, and R is the membrane rejection.

2.1.3. Analytical methods

All analysis followed the American Public Health Association protocols [21]. All metals were measured via flame atomic absorption spectrometry. F^- and NO_3^- were quantified using an ion selective electrode, and NO_2 was measured with the colorimetric method. Ammonium was measured through the Kjeldahl method, and alkalinity was determined via acid titration. Sulfate was assessed using the turbidimetric method, and Cl^- was quantified through argentometric titration. Turbidity and color were measured spectrophotometrically (Merck-SQ118, Brazil), and conductivity and pH were determined using a benchtop meter (Tecnal, Brazil).

2.1.4. Data analysis

The independent variable was the pressure applied (1 or 2 MPa) to the NF membrane. The responses of the

Table 1
Physico–chemical characteristics of water harvested from the Guarani Aquifer System and of the nanofiltration permeate obtained at 1 and 2 MPa

	WHO recommendation	Brackish water	Permeate obtained at 1 MPa	Permeate obtained at 2 MPa
Total dissolved solids (mg/L)	1,000	922.6 ± 74.7	161.3 ± 11.4	140 ± 41.5
Suspended solids (mg/L)	–	ND	ND	ND
pH	6.5 ≤ pH ≤ 8.5	8.64 ± 0.06	7.86 ± 0.22	7.93 ± 0.07
Color (Hazen)	15	27.77 ± 2.12	4.3 ± 0.65	5.0 ± 1.13
Turbidity (NTU)	1	1.46 ± 0.06	0.21 ± 0.01	0.14 ± 0.04
Electrical conductivity (μS/cm)	–	981.6 ± 18.5	275.2 ± 18.7	279 ± 17.3
Zn (mg/L)	4	0.55 ± 0.01	0.38 ± 0.03	0.26 ± 0.01
Na^+ (mg/L)	**200**	275 ± 19	130.0 ± 18.3	165.0 ± 33.4
K^+ (mg/L)	–	1.24 ± 0.01	0.94 ± 0.01	0.94 ± 0.01
Ca^{2+} (mg/L)	–	1.96 ± 0.01	0.49 ± 0.01	0.29 ± 0.01
Mg^{2+} (mg/L)	–	0.45 ± 0.01	0.31 ± 0.01	0.12 ± 0.01
Mn (mg/L)	0.1	0.09 ± 0.01	0.04 ± 0.01	0.04 ± 0.01
Total Fe (mg/L)	**0.3**	1.41 ± 0.01	0.16 ± 0.06	0.18 ± 0.03
NH_4^+ (mg/L)	1.5	0.03 ± 0	0.01 ± 0.00	0.014 ± 0.0
NO_3^- (mg/L)	50	1.53 ± 0.07	0.24 ± 0.02	0.13 ± 0.07
Cl^- (mg/L)	250	181.2 ± 0.23	69.33 ± 0.47	58.37 ± 0.33
Alkalinity $CaCO_3$ (mg/L)	–	140.5 ± 0.57	19.67 ± 0.65	30.33 ± 0.65
Alkalinity HCO_3^- (mg/L)	–	413.33 ± 6.53	40.67 ± 0.65	73.33 ± 3.27
SO_4^{2-} (mg/L)	**250**	284.37 ± 0.24	100.0 ± 13.9	97.0 ± 22.3
F^- (mg/L)	**1.5**	4.5 ± 0.11	0.36 ± 0.06	0.19 ± 0.04

Values in bold exceed the limits for drinking water suggested by the World Health Organization (WHO).

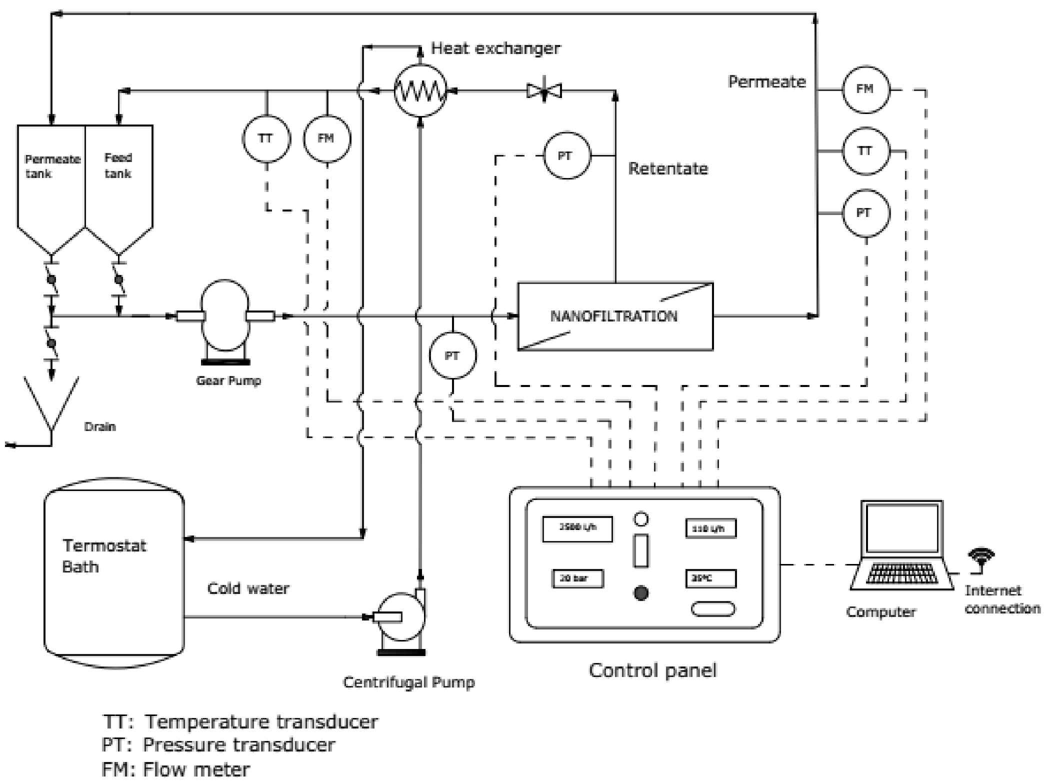

Fig. 1. Schematic drawing of the pilot-scale NF system.

system were the permeate flux and the membrane rejection. After the economic assessment, the water cost was the last response.

2.2. Economic assessment

2.2.1. NF facility design

We performed mass balance of six scenarios (two pressures: 1 or 2 MPa; three fluoride concentrations: 2, 3, or 4 mg/L) to predict the required volumes of raw water from the well, feed water to the NF system, and permeate to achieve a total rate of 3,200 m³/d. These volumes were enough for high capita demand (320 L/d) for 10,000 inhabitants. Furthermore, fluorine concentrations differ across the Guarani Aquifer. Thus, we predicted the flow rates of fluorine at different concentrations in feed water to check the sensitivity of NF in regard to this parameter. We kept the membrane rejection independent of fluorine concentration because variation of the latter lies in a narrow range (2–4 mg/L). Furthermore, we predicted the membrane area based upon the high permeate flux from Fig. 2. For this reason, there is threatening of long-term fouling occur and the membrane life was predicted as only 2 years.

We proposed a mix between feed water from the GAS and permeate to achieve higher recovery in the desalination plant. A fourfold volume reduction rate (VRR) was adopted, producing 75% permeate and 25% retentate.

We considered a constant power for the extraction of groundwater (100 HP). The required power for NF was calculated by Eq. (2):

$$P = \frac{Q \times \Delta P}{\eta} \tag{2}$$

where P is the required power (W), Q is the flow rate fed to NF process (m³/s), ΔP is the transmembrane pressure, and η is the pump efficiency (considered 0.88).

Membrane area was predicted by dividing the required volume of permeate and the permeate flux from Fig. 2 for each scenario.

2.2.2. Water costs of NF

We followed the procedure of Brião et al. [19] to predict capital and operation costs. We made actual budgets (in Brazilian real [R$]) for specialized companies to predict the water costs. The exchange rate used was US $1 = R$ 3.2.

We considered capital costs as building construction, well installation (including a 100 HP submerged pump), and NF and auxiliary equipment. A lifespan of 25 years was adopted with constant annual depreciation.

A small building (50 m² area) was sufficient to house the NF facility and cost R$ 2,444.5/m² (US $763.9).

Operation costs were associated with maintenance, membrane and cartridge filter replacement, labor, electricity, chemicals, and concentrate disposal.

The annual maintenance (and spare parts) cost was 2% of the capital cost.

Membrane replacement will be performed every 2 years. We adopted the same SR3 NF membrane (Koch Membrane Systems) used in the experiments, but with an area of 34.5 m². The unit cost is US $3000.

Cartridge filters (30 filters) will be replaced every 6 months, at a unit cost of R$ 100 (US $31.15).

Building maintenance was predicted as 5% of the construction investment per year.

The chemicals used are sodium hydroxide and citric acid (for cleaning), NaOCl (for disinfection), and 3 mg/L of Permacare from GE (for anti-scaling; unit cost: US $9.375/kg).

Annual equipment exploitation was estimated as 349 d/year (downtime of 1 d/month for cleaning and 4 d/year for maintenance).

Labor consists of five employees to supervise the system 24 h/d, 7 d/week and technically responsible chemist. A system-supervising employee's salary is R$ 1,300 per month (US $406.25), and the chemist's salary is R$ 3,000 per month (US $937.5).

Power was divided in two parts: that for intake (well) and that for NF. The cost of electricity is R$ 0.4/kWh (US $0.125/kWh).

Concentrate will be disposed of in the municipal sewer, where it will be diluted to a ratio of 1/20, as discussed by

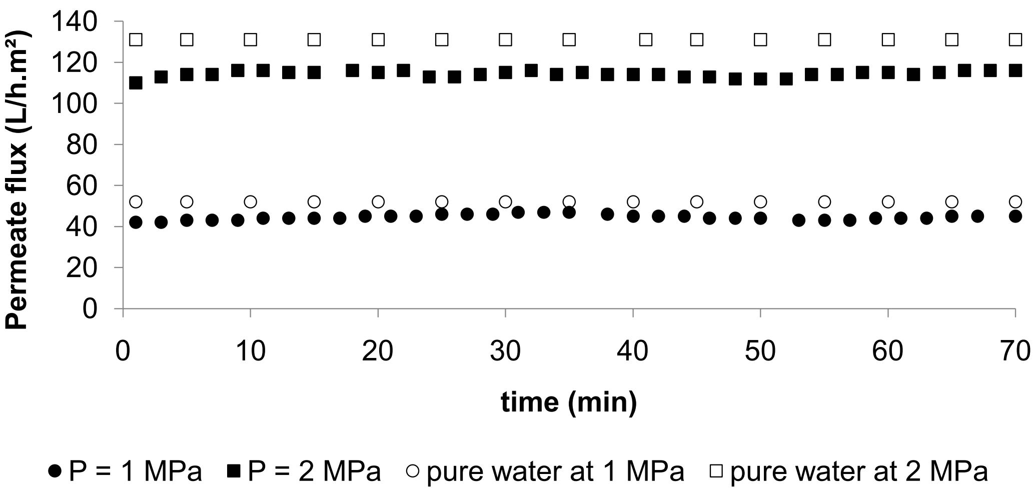

Fig. 2. Permeate flux during defluoridation via nanofiltration of brackish water from the Guarani Aquifer System.

Brião et al. [8]. Thus, this cost will be part of the municipal wastewater treatment and is R$ 3.43/m³ (US $1.07/m³).

3. Results and discussion

3.1. Experimentation to evaluate NF rejection and permeate flux

Table 1 shows the physical–chemical characterization of groundwater from the Guarani Aquifer and the characteristics of the NF permeate.

The brackish water from the GAS has exceeded the sodium, iron, sulfate, and fluoride (highlighted in bold in Table 1) concentrations suggested by the WHO guidelines for drinking water. High sodium and sulfate concentrations can cause unwanted taste in water. Iron could cause taste and deposits in distribution network pipes and cause long-term fouling. However, iron can be removed by oxidation and then removed by filter cartridges. A fluoride concentration higher than 1.5 mg/L is a health concern because it can lead to dental fluorosis and crippling skeletal fluorosis [7]. NF was able to adjust the water characteristics to drinking water quality standards under both transmembrane pressures tested, lowering concentrations of all parameters. To evaluate whether the pressure influenced membrane rejection, we performed an ANOVA test on the parameters that exceeded the WHO guidelines for drinking water [20], fluoride, sulfate, iron, and sodium. In addition, we performed statistical tests on permeate flux and TDS. Table 2 shows the ANOVA test results of these parameters.

Table 2 shows that doubling the pressure produces a permeate flux that is 2.5-fold higher. However, is the increase in energy worth it? Economic assessment will answer that question. As expected, high passage of Na^+ (pressure independent) through the membrane was observed and rejections of electrical conductivity and TDS both were approximately 80%. Iron rejection was near 90% for both pressures, but sulfate and fluoride rejections showed identical behavior, that is, the higher the pressure, the higher the rejection. In fact, the decrease in rejection with low pressure can be attributed to the so-called "dilution effect" [5]. The Langelier index was calculated as 0.024 and the water is classified as slightly scale forming and corrosive. This is of concern because the scale can occur in the membrane surface causing the long-term fouling. We will add anti-scaling to prevent fouling and the membrane replacement will be done in 2 years.

Despite high passage of Na^+ (rejection near 50%) through the membrane, NF was able to reduce sodium below the desired drinking quality (200 mg/L). The iron rejection of around 90% was enough to reduce the concentration to below 0.3 mg/L, reducing the risk of deposition of iron oxides in the water and pipes. The TDS of water from the GAS was in range of the maximum concentration (1,000 mg/L) suggested by the WHO guidelines for drinking water [20]. However, the TDS rejection of near 80% was sufficient to regulate the concentration to a safe value.

We observed a fluoride rejection between 94% and 97% in our experiments. This result was expected and in the range of fluoride rejections reported in the literature of 84%–91% [2], 98% [4], 97%–98% [13], and 50%–85% for a loose NF270 membrane and 98% for a tight NF90 membrane [12]. Furthermore, Table 1 shows that lower pressure leads to lower fluorine rejection. This effect was observed by other researchers. Chakrabortty et al. [4] demonstrated that the fluorine rejection of three NF membranes increased to a range between 95% and 98% with an increase in pressure from 10 to 16 bar. Bejaoui et al. [2] showed an increase from 93% to 97% in the pressure range of 2 to 9 bar. In fact, solute flux and solvent flux are uncoupled. Hence, with increasing pressure, pure water flux increases, whereas the solute flux (fluoride ion) remains constant, and owing to the low concentration of the solutes in the permeate side, the overall solute passage decreases. This implies that rejection of a solute of interest increases with an increase in transmembrane pressure. As mentioned above, the decrease in rejection can be attributed to the so-called "dilution effect" [5], and we found the same effect in the experiments performed.

The rejection by NF membranes is a consequence of the sieving effect, electrostatic and steric interactions (associated with charge shielding), Donnan exclusion, and ion hydration [22]. Thus, fluorine rejection in NF depends on several factors, such as MWCO, pH, ionic strength, water composition, and sieving.

Although fluoride is a small ion with an ionic radius of 0.13 nm, it is highly hydrated in water and thus has a relatively large hydrated radius of 0.352 nm [11,15]. The SR3 NF membrane has a pore radius of 0.38 nm [7] and MWCO of 200 g/L. Thus, the steric effect is important for fluoride separation in NF membranes and we observed in some studies [4,12] that loose NF membranes (MWCO > 250 g/mol) have lower F^- rejections. However, steric effects in NF are complicated because the sub-nanometer pore size of the membrane is not constant; rather a pore size distribution represents the pore radius. Thus, it is expected that the steric sieving of fluorine by the SR3 NF membrane can help the separation, but size exclusion itself does not fully explain the high fluorine rejection. The membrane has a relatively high zeta potential (–20 mV), as shown by Shen and Schäfer [23], and thus charge exclusion also plays an important role in fluoride separation. In addition, high pH and the presence of sulfates/alkalinity will aid in fluorine rejection.

Table 2
Nanofiltration membrane permeate flux and rejection when desalting brackish water from the Guarani Aquifer System

Pressure (MPa)	Permeate flux (L/h/m²)	F^-	SO_4^{2-}	Fe^{3+}	Na^+	Electrical conductivity	Total dissolved solids
1	45.33 ± 2.51$^{(a)}$	94.78 ± 0.87$^{(a)}$	81.60 ± 3.89$^{(a)}$	89.86 ± 2.58$^{(a)}$	54.82 ± 7.72$^{(a)}$	81.60 ± 3.89$^{(a)}$	88.66 ± 2.21$^{(a)}$
2	113.33 ± 7.57$^{(b)}$	97.54 ± 0.70$^{(b)}$	88.53 ± 2.76$^{(b)}$	89.58 ± 2.22$^{(a)}$	50.12 ± 5.00$^{(a)}$	82.66 ± 2.71$^{(a)}$	85.71 ± 3.38$^{(a)}$

*In the same column, identical indices stand for equal values in the statistical comparison of mean values. Cells with both indices in the same column indicate that their values are identical to the lowest and highest values.

High pH has a double effect in fluoride rejection, driving a higher rejection of F^-. The 8.6 pH of the brackish water from the GAS is in a good range for separation of negative ions because higher pH can keep the membrane charge of the carboxyl group of polyamide negatively charged, increasing the repulsion force to negative charges [4]. This is useful for separating sulfates and fluorides. Furthermore, in pH higher than 8, fluorine will be almost 100% in fluoride (F^-) form [1,11,23] and, thus, results in high charge exclusion by the membrane.

Sulfate helps fluorine separation because it provides a shielding effect on the membrane surface. Brackish water has an ionic strength higher than that of pure water, and the presence of SO_4^{2-}, CO_3^{2-}, and HCO_3^- are important because they improve the F^- rejection [5]. Dielectric exclusion is equivalent to a decrease in the electrolyte concentrations in solution, which is known to provoke an increase of electrostatic exclusion, and its effect is stronger in the presence of multivalent ions [15]. In electrical balance through the membrane, sulfates will be retained on the membrane surface (causing the shield effect), helping to repulse the F^-. In contrast, Na^+ will pass through the membrane into the permeate, as it searches for electrical balance on the other side of the membrane.

The complex effect of cation and anion passage through NF membranes was discussed by Galanakis et al. [24]. Cations shield negative surface charges and allow anions to pass through the membrane pores, whereas anions shield the inner amino residues and allow cations (Na^+ in the GAS water) to permeate first. The excess cations in the permeate generate an electrostatic force that increases anion transfer, particularly of Cl^-, because SO_4^{2-} anions are more hydrated and cannot cross the membrane. Finally, divalent cations (Ca^{2+}, Mg^{2+}) would pass with more difficulty in comparison with monovalent Na^+ because of the increased repulsion forces inside membrane pores. However, the water from the GAS has a high sodium content, and this electrical balance is made essentially by Na^+ on the permeate side and F^-, SO_4^{2-}, CO_3^{2-}, and HCO_3^- on the retentate side.

Now the advantages and disadvantages of NF and RO will be discussed, with the first point regarding membrane rejection. Our first work [8] shows that RO is capable of up to 100% retention of fluoride (in the current study: 97% via NF). We also observed higher fluoride rejection through RO than NF in others' research: 98% for RO and 90% for NF by Bejaoui et al. [2] and ~99% for RO and ~85% for NF by Owusu-Agyeman et al. [1]. Other papers have shown slightly higher rejection by RO, even when compared with the tight NF90 Filmtec™ membrane made by Dow (USA) [7,11]. At first view, this is a small difference; however, this higher rejection will make a difference when the permeate and feed water are mixed to produce drinking water, leading to similar recoveries between NF and RO. We will discuss these facts in sequence below.

Another advantage of RO is that the membrane is capable of keeping the permeate quality constant in a broad range of raw water F^- concentrations. This is useful for desalination plants with high recovery and when water has variable characteristics. As the fluoride concentration increases (above 22 mg/L), fluoride in the permeate of NF membranes increases to above 1.5 mg/L and the water cannot be used for drinking [23]. Pontie et al. [25] further compared the performances of NF and RO membranes and indicated that NF allows partial reduction of the total salinity and removes fluoride to meet WHO guidelines for feed fluoride concentrations only up to 15 mg/L. Furthermore, Walha et al. [26] showed that the permeate from NF is incapable of meeting the WHO guidelines for drinking water when saline waters with high TDS, Na^+, and Cl^- levels are fed to the membrane. Thus, as the fluorine concentration in feed water increases, NF is not able to efficiently adjust the water quality to a level acceptable for drinking water.

The permeate flux through the NF membrane during removal of fluoride from the brackish GAS water is shown in Fig. 2.

We extracted two pieces of information from Fig. 2 for use in further discussion: (a) the first point concerns the effect of pressure on the permeate flux: a twofold increase in pressure leads to a 2.5-fold increase in permeate flux and; (b) SR3 NF membranes produce a stable permeate flux even with an increase in VRR from 1 to 4 over a 70 min interval.

The main advantage of NF membranes over RO membranes is their permeability. This leads to a smaller required membrane area, and thus, a cheaper process than RO. In fact, for desalination of brackish waters from the GAS, Fig. 2 shows higher permeabilities (4.0–5.7 L/h/m²/bar) with NF than with RO (1.7–1.9 L/h/m²/bar), as found in our previous work [8]. Furthermore, we compared the permeabilities reported in several previous studies on desalination of brackish waters using NF and/or RO (Table 3). Table 3 shows we can expect a twofold or fourfold increase in permeate flux with NF, depending on the feed water.

The permeate flux is a based on a combination of pore size, hydrophobicity, and charge density. However, the work

Table 3
Permeabilities of reverse osmosis (RO) and nanofiltration (NF) membranes from several references

Reference	Water	RO (L/h/m²/bar)	NF (L/h/m²/bar)
Owusu-Agyeman et al. [1]	Synthetic water	1.5	6.1
Öner et al. [27]	Geothermal water in Turkey	0.6–4	–
Walha et al. [26]	Brackish water in Tunisia	–	5.5
Garg and Joshi [28]	Synthetic water	9	27
Elazhar et al. [29]	Groundwater in Morocco	–	21
Ang et al. [18]	Synthetic water	4.8–7.5	5.5–12.6
Hoinkis et al. [13]	Synthetic and tap water	–	11–13

of Ang et al. [18], who tested NF and RO membranes for desalination of model solutions. TS80 NF membranes (Trisep) presented flux as low as the standard BW30 RO membrane used for desalination of brackish water. Thus, the permeate flux of NF is higher than RO, but different waters can present various behaviors with the use of different membranes.

A second point to discuss is that the lower pressure (1 MPa) of NF produces the same permeate flux (~40 L/h/m²) as that of RO found by Brião et al. [8] at 2 MPa. The consequence is that the cost installation with membrane modules will be the same as that of RO, with half the power required for pumping feed water through the membrane. At first glance, this is interesting, but what if a higher pressure was used? Will it produce more than twice the amount of drinking water using the same facility? This hypothesis is also interesting. Hence, we designed the NF facility for both situations: low pressure with more membranes and high pressure with fewer membranes. The economic feasibility will help answer this question.

Fig. 2 shows a stable permeate flux after 70 min, even though the VRR was four. The salt concentration of the retentate was approximately 1.7 times that of the feed water; thus, the concentration polarization and back diffusion were not enough to reduce the permeate flux. Furthermore, the water from the GAS is slightly brackish (TDS = 922 mg/L) and TDS in the retentate was ~1,600 mg/L, thus we can observe from Fig. 2 that the osmotic pressure also did not rise enough to provoke the flux decline. Flux decline is still a concern in NF of brackish waters. Chakrabortty et al. [4] showed 20% flux decline over 200 h of operation of NF of brackish water and Tahaikt et al. [12] showed 30% flux decline with a VRR = 2.5 for the tight NF90 NF membrane. Thus, the permeate flux of the SR3 NF membranes used in our work presented a high permeate over the course of time and we used this high value to design the NF system. Other papers [4,18,28] also designed NF systems high permeate flux as 94, 158, 105 L/h/m², respectively.

It is remarkable that new NF membranes are emerging, membranes with higher permeability and hydrophilicity and narrow pore size distribution. The introduction of carbon-based nanomaterials (e.g., carbon nanotubes, graphene, nanocomposite membranes) will show improved permeability and mechanical/thermal stability [30]. Wang et al. [16] synthesized NF membranes with high permeability (350 L/h/m²/MPa) but the rejection with saline solutions was near that with traditional polyamide membranes. However, an efficient and convenient preparation method for orientation membranes should be developed and the membrane cross-linking density and stability should be further enhanced for satisfying application requirements. Thus, soon NF membranes will have higher permeability than, and rejections similar to, RO membranes. However, NF currently removes less fluoride than RO does, although Shen and Schäfer [23] and Tahaikt et al. [12] have classified the NF90 Filmtec™ membrane from Dow (USA) as having properties close to RO membranes for fluoride removal.

Thus, for brackish fluorinated waters with several water quality parameters above the allowed limits, a detailed study must be performed to conclude that NF can be used to adjust the salt concentrations to drinking water quality levels. Additionally, in general, RO permeate has to be remineralized, whereas the permeate from NF could have enough alkalinity to be used as drinking water. A mix of feed water and permeate could be a good solution for adding some salts to water and for achieving a higher production rate for the desalination plant. We approached this strategy to make the economic assessment.

3.2. Economic assessment

3.2.1. Design of NF facilities

Fig. 3 and Table 4 show the predicted flow rates at 2 MPa, and Fig. 4 and Table 5 show the flow rates at 1 MPa. From Fig. 2, it can be seen that the permeate flux at 1 MPa

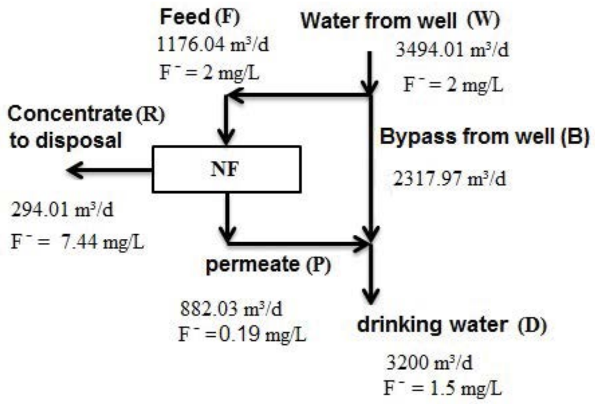

Fig. 3. Mass balance for nanofiltration treatment to produce drinking water when the feed water fluorine concentration is 2 mg/L and the pressure is 2 MPa.

Table 4
Mass balance of Fig. 3 with different fluoride concentrations in water from the Guarani Aquifer System (GAS) when pressure = 2 MPa

Fluoride (mg/L) in GAS water	2	3	4
Fluorine rejection (%)	97.5	97.5	97.5
F^- in permeate (mg/L)	0.19	0.28	0.37
F^- in concentrate (mg/L)	7.44	11.16	14.88
F^- in drinking water (mg/L)	1.5	1.5	1.5
Mixing ratio (B/P)	2.63	0.81	0.45
Recovery (%)	91.59	84.48	81.32
Permeate/groundwater (%)	33.66	62.09	74.72
Flow rates (m³/d)			
W (groundwater)	3,494.01	3,788.02	3,935.02
F (Feed)	1,176.04	2,352.08	2,940.10
R (Concentrate)	294.01	588.02	735.02
P (Permeate)	882.03	1,764.06	2,205.07
B (Bypass from well)	2,317.97	1,435.94	994.93
D (Drinking water)	3,200.00	3,200.00	3,200.00
Membranes			
Required area (m²)	316	633	792
Membrane area (m²)	34.5	34.5	34.5
Number of membranes	10	19	23

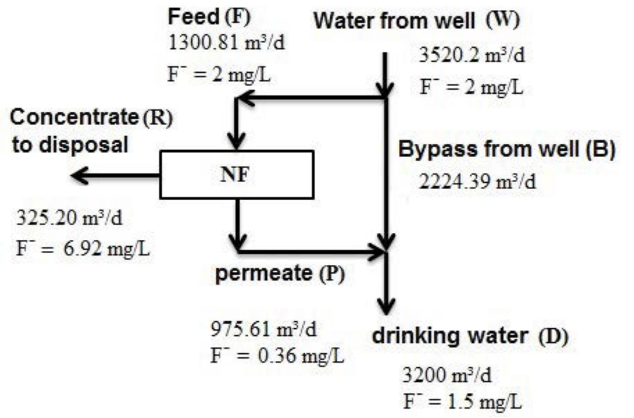

Fig. 4. Mass balance for nanofiltration treatment to produce drinking water when fluorine concentration of the feed water is 2 mg/L and the pressure is 1 MPa.

Table 5
Mass balance for Fig. 4 with different fluoride concentrations in water from the Guarani Aquifer System (GAS) when pressure = 1 MPa

Fluoride (mg/L) in GAS water	2	3	4
Fluoride rejection (%)	0.948	0.948	0.948
F^- in permeate (mg/L)	0.36	0.54	0.72
F^- in concentrate (mg/L)	6.92	10.38	13.84
F^- in drinking water (mg/L)	1.5	1.5	1.5
Mixing ratio (*B*/*P*)	2.28	0.64	0.31
Recovery (%)	90.77	83.11	79.74
Permeate/groundwater (%)	36.90	67.57	81.04
Flow rates (m³/d)			
W (Groundwater)	3,525.20	3,850.41	4,013.01
F (Feed)	1,300.81	2,601.63	3,252.03
R (Concentrate)	325.20	650.41	813.01
P (Permeate)	975.61	1,951.22	2,439.02
B (Bypass from well)	2,224.39	1,248.78	760.98
D (Drinking water)	3,200.00	3,200.00	3,200.00
Membranes			
Required area (m²)	1,204	2,409	3,011
Membrane area (m²)	34.5	34.5	34.5
Number of membranes	35	70	88

is 45 and 116 L/h/m² at 2 MPa. These values were used to calculate the required membrane area. Table 2 shows that higher pressures lead to higher rejection. Thus, the fluorine concentration in the permeate is lower at 2 MPa. In contrast, Table 1 shows the fluorine concentration in the permeate is much lower than the WHO recommendation (1.5 mg/L), hence we proposed a mix of feed water from the GAS and permeate to achieve higher recovery in the desalination plant.

Mixing permeate with groundwater seems to be a good strategy for reducing the membrane area. Furthermore, this mixture includes alkalinity from the concentrate and no post-treatment but chlorination is necessary. Elazhar et al. [29] suggested remineralization with lime, but this will add cost to the water treatment. Ghermandi and Messalem [31] also suggested this mixing of permeate and groundwater to produce water for irrigation, allowing the process to consume less energy. Tahaikt et al. [32] produced defluoridated water via NF and the mixing of permeate with feed water was the strategy to avoid remineralization in order to produce water with a satisfactory composition. Thus, mixing permeate with feed water seems to be a good alternative for achieving higher recovery, lower energy consumption, and lower cost.

The ratio of feed of NF/groundwater was in the range 33%–74%. Multiple consequences will arise with higher fluorine concentration: lower recovery; higher the permeate requirement for the mix; higher the membrane area; 2.5-fold increase in concentrate to dispose of. All these variables will affect the water cost.

The only pre-treatment is passage through a filter cartridge to remove possible suspended solids (SS). We proposed to dilute the concentrate in the municipal wastewater treatment system, as discussed by Brião et al. [8], at a dilution ratio of 1/20. The wastewater plant (hypothetically) has the capacity to treat the total volume of sewage of the city (approximately the same volume of drinking water ~3,200 m³/d).

The designed facility has two fiberglass buffering tanks, each with a volume of 25 m³ for the storage of raw water for a short time (approximately 20 min). Then, the produced drinking water is sent to the municipal reservoir.

A civil construction of 50 m² is large enough to house the RO system and a small laboratory and for possible expansion of the water treatment plant.

Small differences can be observed when Tables 4 and 5 are compared. However, the main effect of the lower rejection of the NF membrane at lower pressure (1 MPa) is approximately 10% higher permeate and concentrate that needs to be disposed of.

These flow rates were used predict the required membrane area. Pumping feed at 1 MPa (instead of 2 MPa) through NF membranes will require almost four times the number of membranes. This led us to think, "Why not use the full capability of the system and produce more water with the same facility?" We discuss this in the economic assessment.

3.2.2. Water cost

Tables 6 and 7 show the economic assessment of defluoridation of groundwater from the Guarani Aquifer by NF at a pressure of 2 and 1 MPa, respectively.

We considered that intake costs were the same in all the scenarios, but they did not exceed 27.9% of the total costs. However, if this cost for intake is removed from the account, the water cost will be US\$ 0.20/m³. This value is very near to the cost predicted by Elazhar et al. [29] of US \$0.21/m³. However, we are discussing the desalination of brackish water. Thus, we believe that the cost for intake must be considered. The NF facility cost increased linearly with membrane area [26] but did not exceed 2% of the total cost in the account. For 2 MPa, the increase in F^- concentration from 3 to 4 mg/L led to just four additional membranes. Thus, we considered the cost is same for both situations.

Table 6
Cost for defluoridating water from the Guarani Aquifer with different fluorine concentrations via nanofiltration and P = 2 MPa

	Life span	F^- = 2 mg/L			F^- = 3 mg/L			F^- = 4 mg/L		
Capital costs	(years)	Investment (US$)	Annual depreciation (US$)	% of total costs	Investment (US$)	Annual depreciation (US$)	% of total costs	Investment (US$)	Annual depreciation (US$)	% of total costs
Well facilities	25	289,250.0	11,570.0	3.4	289,250.0	11,570.0	2.3	289,250.0	11,570.0	2.0
Nanofiltration facilities	25	93,750.0	3,750.0	1.1	109,375.0	4,375.0	0.8	109,375.0	4,375.0	0.7
Investment	25	383,000.0	15,320.0	4.5	423,524.8	16,941.0	3.1	423,524.8	16,941.0	2.7
Operating costs	Time		Annual cost (US$)	% of total costs		Annual cost (US$)	% of total costs		Annual cost (US$)	% of total costs
Well maintenance	Annual	–	5,552.5	1.6	–	5,552.5	1.1	–	5,552.5	1.0
NF maintenance	Annual	–	1,875.0	0.5	–	2,187.5	0.5	–	2,187.5	0.4
Membrane replacement	Annual	–	15,034.2	4.4	–	28,565.0	5.7	–	34,758.7	5.9
Cartridge filter replacement	Annual	–	1,250.0	0.4	–	2,375.0	0.4	–	3,000.0	0.5
Civil construction maintenance	Annual	–	51.8	0.0	–	51.8	0.0	–	51.8	0.0
Chemical products	Annual	–	11,543.2	3.4	–	23,086.4	4.7	–	28,857.9	5.0
Operator Manpower	Annual	–	24,375.0	7.3	–	24,375.0	4.8	–	24,375.0	4.2
Chemist	Annual	–	11,250.0	3.3	–	11,250.0	2.3	–	11,250.0	1.9
Labor taxes	Annual	–	22,479.4	6.6	–	22,479.4	4.5	–	22,479.4	3.9
Electricity for intake	Annual	–	78,075.8	22.9	–	78,075.8	15.6	–	78,075.8	13.9
Electricity for NF	Annual	–	39,037.9	11.5	–	62,460.7	12.4	–	78,075.8	13.9
Concentrate disposal	Annual	–	109,984.4	32.4	–	219,968.8	43.8	–	274,961.0	47.0
Administrative costs		–	4,042.4	1.2	–	4,042.4	0.8	–	4,042.4	0.7
Total operating costs	Annual	–	324,551.6	95.5	–	484,470.2	96.9	–	567,667.8	98.3
Total (US$)		**–**	**339,871.6**	**100.0**	**–**	**501,411.2**	**100.0**	**–**	**584,608.8**	**100.0**
Water produced per year (m^3)			1,168,000			1,168,000			1,168,000	
Water cost (US$/$m^3$)			**0.29**			**0.43**			**0.50**	

Table 7
Cost for defluoridating water from the Guarani Aquifer with different fluorine concentrations via nanofiltration and $P = 1$ MPa

	Life span	$F^- = 2$ mg/L			$F^- = 3$ mg/L			$F^- = 4$ mg/L		
Capital costs	(years)	Investment (US$)	Annual depreciation (US$)	% of total costs	Investment (US$)	Annual depreciation (US$)	% of total costs	Investment (US$)	Annual depreciation (US$)	% of total costs
Well facilities	25	289,250.0	11,570.0	3.1	289,250.0	11,570.0	1.8	289,250.0	11,570.0	1.5
Nanofiltration facilities	25	125,000.0	5,000.0	1.4	140,625.0	5,625.0	0.9	156,250.0	6,250.0	0.8
Investment	25	414,250.0	16,570.0	4.5	459,904.3	17,195.0	2.7	475,529.3	17,820.0	2.4
Operating costs	Time		Annual cost (US$)	% of total costs		Annual cost (US$)	% of total costs		Annual cost (US$)	% of total costs
Well maintenance	Annual	–	5,552.5	1.5	–	5,552.5	1.0	–	5,552.5	0.7
NF maintenance	Annual	–	2,500.0	0.7	–	2,812.5	0.4	–	3,125.0	0.4
Membrane replacement	Annual	–	52,619.8	14.1	–	105,239.5	16.5	–	130,797.7	17.3
Cartridge filter replacement	Annual	–	1,250.0	0.3	–	2,375.0	0.4	–	3,000.0	0.4
Civil construction maintenance	Annual	–	62.1	0.0	–	62.1	0.0	–	62.1	0.0
Chemical products	Annual	–	12,760.3	3.4	–	81,697.4	12.8	–	102,145.3	13.5
Operator Manpower	Annual	–	24,375.0	6.6	–	24,375.0	3.8	–	24,375.0	3.2
Chemist	Annual	–	11,250.0	3.0	–	11,250.0	1.9	–	11,250.0	1.5
Labor taxes	Annual	–	22,479.4	6.0	–	22,479.4	3.5	–	22,479.4	3.0
Electricity for intake	Annual	–	77,490.3	20.8	–	77,490.3	12.1	–	77,490.3	10.3
Electricity for NF	Annual	–	19,372.6	5.2	–	39,037.9	6.1	–	46,845.5	6.3
Concentrate disposal	Annual	–	121,653.5	32.7	–	243,306.9	38.1	–	304,133.6	40.3
Administrative costs		–	4,042.4	1.1	–	4,042.4	0.6	–	4,042.4	0.5
Total operating costs	Annual	–	355,407.7	95.5	–	619,720.8	97.3	–	735,298.8	97.6
Total (US$)		–	**371,977.7**	**100.0**	–	**638,117.0**	**100.0**	–	**754,320.0**	**100.0**
Water produced per year (m^3)			1,168,000			1,168,000			1,168,000	
Water cost (US$/$m^3$)			**0.32**			**0.53**			**0.64**	

Capital costs were less than 5% in all scenarios. However, this is a small facility. Desalination plants of high capacity have higher capital costs than operation and maintenance costs. Afonso et al. [33] designed an RO desalination plant with 125,000 m² of membrane area and the capital cost was 54% of the annualized costs. However, in general, operation costs are predicted as the majority of the cost (79%) by Chakrabortty et al. [4] and Elazhar et al. (70%) [29].

Membrane replacement is stigmatized as a high cost of desalination. We predicted this replacement will be performed every 2 years, but the mixing promotes a dilution of the permeate, making this cost less than 18% in all scenarios. However, this is an important part of the total cost because NF membranes are the core of the treatment. This cost was predicted by Elazhar et al. [29] as only 4% and as 15% by Chakrabortty et al. [4]. Ari et al. [34] performed an interesting study to evaluate the costs of desalination in different situations and the comparison between NF and RO resulted in similar water cost for small desalination plants ($0.169/m³ for RO and $0.173/m³ for NF) for treatment of surface water to produce drinking water.

The chemical products used depend on the feed water quality. However, the water from the Guarani Aquifer is of medium salinity, thus the products for cleaning and disinfection will not represent a significant portion of the cost. As expected, there is a proportional rise in the chemical costs with an increase in fluoride concentration.

Labor (operator manpower + chemist manpower + labor taxes) costs are the same for all scenarios (US $58,104). This cost is up to 17% of the water cost, but we believe that five operators and a chemist can operate a higher capacity desalination plant and this cost could be diluted in the higher volume of produced water.

The comparison between this work and our previous work with RO for desalinating water from the Guarani Aquifer [19] demonstrates that for 1 MPa of pressure, a similar number of membranes (~30) is needed for the same water production rate (~1.1 Mm³/year). Thus, we expected similar costs in the installation, but with lower energy consumption for NF and a reflection of this in the total cost. However, this did not occur.

Specific energy consumption (SEC) is the great advantage of NF over RO. With 1 MPa of pressure and 2 mg/L of fluoride concentration, the SEC of NF was 0.458 kWh/m³. However, SEC is strongly dependent on VRR, feed water salinity, and desalination plant recovery. The values could be as low as 0.4 kWh/m³ [29] and as high as 0.76 kWh/m³ [31] or 9.35 kWh/m³ when using photovoltaic energy [28]. Electricity is an important part of desalination plant costs, and predicted costs of such range between 10% [4] and 18% [29].

RO showed a SEC of 0.837 kWh/m³ to defluoridate water from the Guarani Aquifer [19]. The SEC of NF is not half of that of RO because other pumps (i.e., for extraction of water from the well) are consuming energy. Yet, in general, the SEC of NF is nearly one half the SEC of RO, as shown by Ghermandi and Messalem [31], who found 1.49 kWh/m³ SEC for BW30 RO membranes and 0.89 kWh/m³ for NF90 (Dow Filmtec™, USA) membranes. However, the SECs of NF and RO can be similar owing to intensive fouling and convergence of the values near 0.5 kWh/m³, with a recovery rate of 80% [18]. In other cases, despite a lower SEC, NF was unable to adjust the brackish water to drinking water quality because there was a high passage of monovalent ions through the membrane, whilst RO presented a SEC in the range of 0.81–1,09 kWh/m³ [26]. Thus, NF is not always the best solution for desalinating fluorinated brackish water with high TDS.

A valuable comparative is to evaluate the water cost produced by applying 2 MPa (Table 6) and 1 MPa (Table 7) of pressure. With higher pressure, investment in NF equipment is lower (owing to fewer membranes required). This implies that membrane replacement and NF maintenance costs also will be lower. In addition, a lower volume of concentrate is sent for disposal (Table 4). In contrast, twice the amount of energy will be required. However, the energy needed for NF is only around 10% of the total cost. Nevertheless, the impact of this savings does not drive a higher reduction in the water cost because concentrate disposal, energy requirement for water extraction, and labor have a heavier impact on costs. The electricity needed for RO to defluoridate water from the Guarani Aquifer (applying 2 MPa) was almost identical to that for NF. Although the permeate flux of the NF membrane is higher, the water cost of NF (US $0.29/m³)was very similar to that of RO (US $0.25/m³). The same behavior was observed with the 3 mg/L fluorine concentration, where water cost from NF was US $0.43/m³ and US $0.39/m³ from RO. This occurs because the SEC for the operation of NF is 0.134 kWh/m³ (only NF equipment) and is 0.279 kWh/m³ for RO, but this is less than 13% of the total costs.

The high cost of concentrate disposal is remarkable. The alternative (send to wastewater treatment plant) is expensive. In this study and in our previous research on RO [8,19], we suggested this solution as a practical and real possibility, but other possibilities, such as deep injection wells, should be studied as well. However, disposal of the concentrate from inland desalination plants is a problem worldwide because the solutions for such are expensive. As the fluorine concentration increases, so does the volume of concentrate and with it, the cost. Operation with lower pressure (1 MPa, Table 7) generates higher volumes of concentrate because the fluorine rejection is lower with this pressure.

At last, is NF or RO better for defluoridating groundwater? Galanakis et al. [24] stated that NF provides more open pores, higher flux, low operating pressure as well as relatively low investment, operation and maintenance costs. However, this cost reduction is not that low. Ang et al. [18] performed experiments with synthetic water (without fluorine) and predicted the costs of NF and RO, with the authors stating that high permeability membrane does not necessarily reduce the energy consumption and total expenditure of a desalination plant because fouling could be more intense with NF membranes. In addition, "the use of high permeability membrane did not guarantee energy and cost savings as consistency of performance has larger impact on the desalination system and selection of membrane." Adding to this statement, the water cost to defluoridate water predicted by a theoretical model in the paper written by Chakrabortty et al. [4] was US $1.17/m³; thus, a close value to the water cost for desalination by RO. Our result confirms that the cost of NF to defluoridate groundwater is not lower than the cost of RO to do so, but we believe that the advances in nanotechnologies will bring a new generation of NF membranes with much higher permeabilities, allowing the water cost of NF to drop.

The cost, which varied between 0.29 and 0.64 US $m³, was higher than the water cost for producing drinking water by traditional surface water treatment (US $0.1/m³, according to Mierzwa et al. [35]) in Brazil. The water supply is a public health concern. Garg and Joshi [28] also predicted a high cost of desalinated water using NF/RO and suggested the water production cost could be further reduced after increasing subsidy (or tax reduction) by the government. We fully agree with this statement.

4. Conclusion

NF and RO are suitable technologies to remove fluoride from brackish groundwaters. NF has higher permeate flux and requires smaller membrane area, less frequent membrane replacement, and less power. In contrast, RO has higher rejection than NF, produces less concentrate for disposal, and requires less well water. Economically, the costs of NF (0.29–0.50 US\$/m³) and RO (0.25–0.39 US\$/m³) are similar. In the future, with recent advances in NF membranes in terms of their higher permeabilities, NF will surpass RO; however, currently both processes are similar regarding fluoride removal for adjusting the water quality to a potable level.

The SR3 NF membrane showed a 2.5-fold higher permeate flux (116 L/h/m²) than the RO membrane did. However, the membrane cost is lesser than 18% of total cost and the impact is not high on the water cost. Furthermore, in this case, lower pressure required by NF did not imply in lower water cost because a higher volume of concentrate is sent to disposal. In contrast, RO showed better rejection of fluorine than NF.

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