



Reverse osmosis for desalination of water from the Guarani Aquifer System to produce drinking water in southern Brazil



Vandré Barbosa Brião*, Jonas Magoga, Marcelo Hemkemeier, Edesnei Barbosa Brião, Laisa Girardelli, Luana Sbeghen, Danúbia Paula Cadore Favaretto

Universidade de Passo Fundo, Brazil

HIGHLIGHTS

- Water from the Guarani Aquifer revealed excess F^- , SO_4^{2-} and TDS.
- RO was used to desalinate this water varying cross-flow velocity and pressure.
- A mix between groundwater and permeate allowed for a recovery of 93%.
- There is a potential for the desalination of this water to supply small cities.

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ABSTRACT

Like other regions around the world, southern Brazil has experienced periods of drought, having to find alternative water resources for producing drinking water during these times. The deep wells drilled in the Guarani Aquifer could help with this water imbalance, but the water, in some places, is brackish. This work is an exploratory study of the use of the brackish water from the Guarani Aquifer as an alternative supply for drinking water, using reverse osmosis to reduce the content of F^- , SO_4^{2-} and TDS (Total Dissolved Solids). The desalinated water obtained from reverse osmosis at a pressure of 2 MPa and a cross-flow velocity of 1.61 m.s^{-1} showed rejections of approximately 94% for SO_4^{2-} , 97% for TDS and 100% for F^- . Blended water, produced by mixing groundwater and permeate, was proposed to optimize the produced drinking water with a recovery rate of 93%. Reverse osmosis is an excellent alternative for the supply of water in southern Brazil.

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1. Introduction

Brazil, contrary to what many people believe, is a country assailed by water shortage. Although the country has a large volume of superficial water, such water is poorly distributed across the Brazilian territory [1]. In southern Brazil, while some regions have abundant water, other microregions have endemic drought spells, and the rains are poorly distributed throughout the year. This indicates that inhabitants of Brazil must be prepared for dire water supply shortages. In addition to regulated, conservative use, other water sources must be sought as a preparation for drought conditions. An alternative would be the use of groundwater from the Guarani Aquifer.

The Guarani Aquifer System (GAS) is a cluster of hydrostratigraphic units, forming a large groundwater reservoir [2]. It is located in mid-eastern South America, as shown in Fig. 1. Its area corresponds to

1,194,000 km^2 [3] distributed across the territories of Brazil, Argentina, Uruguay, and Paraguay [4]. In Brazil, the southern region contains the largest area of the GAS [5].

The continental dimensions of the GAS have a large water storage potential; however, in most of its extension, the waters are classified as brackish [4]. A study coordinated by the Water Resources Agencies from Brazil, Uruguay, Paraguay and Argentina found that salinity is low/medium in the GAS, but the southern Brazilian region may have a higher salinity [6]. Thus, the GAS is a large groundwater reservoir, but the physicochemical quality is discontinuous, and in some areas the water is unfit for human consumption [6,7]. In some regions of Uruguay and Argentina, groundwater from the Guarani Aquifer has 8000 mg.L^{-1} of total dissolved solids, 1200 mg.L^{-1} of sulfates and 3.1 mg.L^{-1} of fluorides and is used only for thermal baths due to excess salt content [8].

Desalination of saline and brackish waters has expanded as an alternative technology for the production of water for human consumption and for industrial use [9]. Desalination by reverse osmosis is widely used for the production of drinking water [10] and is the main unconventional way to obtain drinking water in several countries, especially

* Corresponding author at: Universidade de Passo Fundo, Campus I, Faculdade de Engenharia e Arquitetura, Rodovia BR 285, Bairro São José, Passo Fundo/RS, CEP: 99052-900 – Caixa Postal 611, Brazil. Tel.: +55 54 3316 8269, +55 54 3316 8490.

E-mail addresses: vandre@upf.br, vandre.briao@gmail.com (V.B. Brião).



Fig. 1. Location of the Guarani Aquifer.

in those countries that suffer from a seasonal or continuous lack of natural fresh water resources [11]. Moreover, if fresh water must be pumped over long distances, it can become just as expensive as desalinated water, depending on the distances involved and on the amount of pumping required [12]. Thus, reverse osmosis is a possible solution for inland regions where there is no or inadequate superficial water available [13].

Reverse osmosis is a pressure-driven process whereby a semi-permeable membrane rejects dissolved constituents present in the feed solution. Size exclusion, charge exclusion and physicochemical interactions between solute, solvent, and membrane are the main mechanisms that facilitate the separation of permeate and reject in reverse osmosis [14].

We have seen many reports of desalination of brackish water by reverse osmosis in arid regions around the world, such as in the Middle East [15–29] and in Australia [30,31]. In addition, desalination has been largely used in the United States, which desalinates the third largest quantity of brackish or saline water of any country in the world [9]. In Brazil, desalination has gained momentum in the northeastern region, where there is a continuous shortage of superficial water, and where a large quantity of the supply is obtained from brackish groundwater [32]. In southern Brazil, however, desalination of groundwater has been used only for industrial applications, such as the production of boiler feed water. Nonetheless, desalination of water from the Guarani Aquifer could produce an alternative supply of water to the population, given that droughts have been far more frequent in this region.

The efficiency of reverse osmosis depends on operating parameters and on membrane and feed water properties [14]. Desalination of water by reverse osmosis should ideally occur under operating conditions that allow for the maximum rejection of salts by the membrane, yielding permeate with a lower salt content. The operating pressure has a direct impact on permeate flux, whereas cross-flow velocity minimizes the concentration polarization in the retentate stream, having an impact on

both permeate flux and on the efficiency of separation. Thus, cross-flow velocity and pressure can have a direct effect on membrane rejection and permeate flux in water desalination.

The aim of this work is to study the groundwater from the Guarani Aquifer as an alternative water resource, adjusting the physicochemical parameters of this water through reverse osmosis to produce drinking water.

2. Water characterization

The GAS is located in a sandstone formation (the Botucatu Formation) and is confined by basalt rock (the Serra Geral Formation) on the top side (Fig. 2). The overall recharge zones of GAS are associated with the outcrop areas [6], as shown in Fig. 2. The extraction of water from the aquifer requires wells with depths ranging from 200 m to 1000 m, depending on the location.

Fig. 3 shows a schematic of a groundwater well, which is 8 in. in diameter, and uses a 100 HP submersible pump to maintain a water extraction flow rate of approximately $100 \text{ m}^3 \cdot \text{h}^{-1}$. The well was drilled to a depth of 960 m in the Guarani Aquifer in the town of Tapejara (state of Rio Grande do Sul) in southern Brazil (coordinates $-28^\circ 3' 19''$, $-51^\circ 59' 49''$). Table 1 shows the physicochemical properties of the water from the Guarani Aquifer. The water temperature at time of extraction was approximately 42°C .

Previous studies performed in different regions of the GAS have demonstrated that, in general, the groundwater is good quality water, with a TDS concentration lower than $500 \text{ mg} \cdot \text{L}^{-1}$, low salinity and low hardness in shallower regions [6,33]. However, in deep wells drilled into confined regions of the GAS there is often higher salt concentrations. The hydrochemical evolution in the Guarani Aquifer is determinate by the flow direction, residence time and confinement conditions [54]. In fact, different water types can be found in the GAS due to the free or confined zones [57]. The temperature, pH, HCO_3^- concentration and EC have the tendency to rise in the flow direction and these parameters are higher in confined conditions. Sulfate is added in the water from GAS by meteoric waters or by dissolution of the basement of the Pirambóia formation. Fluoride is not common. Some evidences suggest that F^- is inserted by leaching of the basement formed before GAS, and in some deep confined zones from GAS this compound is found in higher concentrations (western region of the State of São Paulo and Santa Catarina) [54,55,57].

In the specific location where groundwater was extracted for this study, the water is slightly saline ($1000 < \text{TDS} < 3000 \text{ mg} \cdot \text{L}^{-1}$). An electrical balance including the major ions (sample 2) shows -1.1% , and, in general, analytical errors less than $\pm 5\%$ are acceptable.

The main cations (Sample 2) present are Na^+ and Ca^{2+} , while the main anions present are SO_4^{2-} , Cl^- and HCO_3^- . The high EC (and TDS) could indicate that the water was mineralized by the contact with soil/rocks. Beside, high TDS indicates that the water from GAS is in confined conditions [57]. The presence of sulfate, sodium and chloride as dominant species leads us to think that this water was extracted from a discharge area [56]. $\text{Na}^+ > \text{Ca}^{2+} > \text{Mg}^{2+}$ (sample 2) and the molar ratios $\text{Na}^+/\text{Ca}^{2+}$, $\text{Cl}^-/\text{HCO}_3^-$ and $\text{SO}_4^{2-}/\text{Cl}^-$ are higher than 1.0. This is typical for more confined water from the GAS [3]. In general, deep aquifers that are highly confined are old, and water quality is typically stable.

The Total Dissolved Solids (TDS) and the concentration of scaling substances (Ca, Si, Mg, Fe, and HCO_3^-) are not high; therefore, most common forms of fouling can be prevented by pH adjustment or the addition of an antiscalant or can be controlled by not exceeding the volume reduction rate (VRR) so that the TDS does not exceed $5 \text{ g} \cdot \text{L}^{-1}$. In addition, the total suspended solids concentration is below $10 \text{ mg} \cdot \text{L}^{-1}$ (sample 2), indicating a low level of suspended/colloidal matter.

However, Table 1 reveals that SO_4^{2-} , F^- and TDS do not comply with WHO [34] guidelines and Brazilian regulations [35] for potability. No

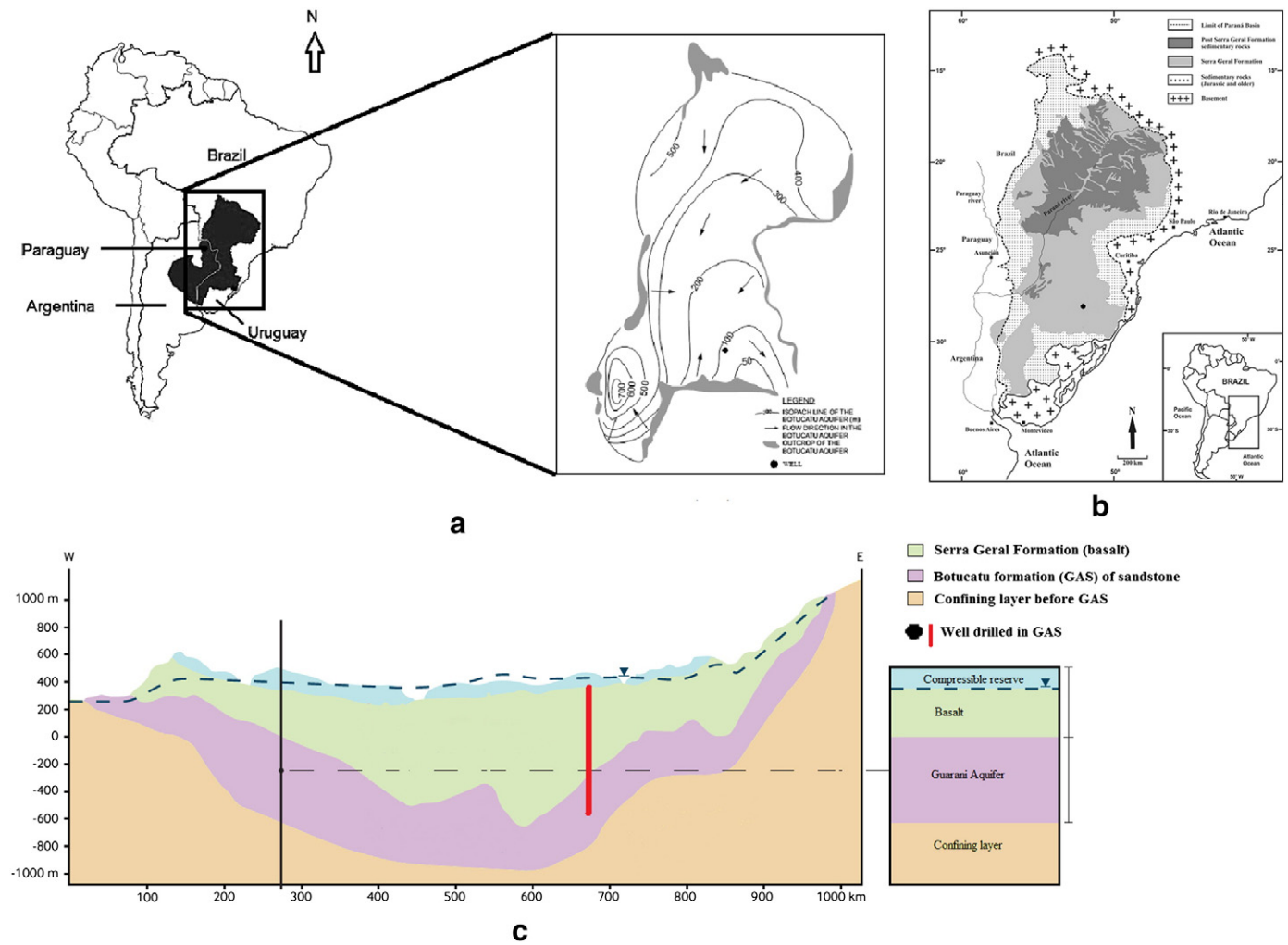


Fig. 2. Hydrogeological situation of the Guarani Aquifer System (adapted from [6,53]).

health-based guideline value has been developed for TDS and sulfate concentrations, but both chemical parameters can have effects on the acceptability of drinking water by consumers. The presence of sulfate in drinking water can cause a strong taste, and very high levels can have a laxative effect on unaccustomed consumers [34]. Water with high dissolved solids is of inferior palatability, and highly mineralized water has restricted industrial applications [36]. A TDS level of less than about $600 \text{ mg} \cdot \text{L}^{-1}$ is generally considered to be good; drinking water becomes increasingly unpalatable at TDS levels greater than approximately $1000 \text{ mg} \cdot \text{L}^{-1}$ [34]. High natural fluoride concentrations in groundwater can be found in many parts of the world, particularly in parts of India, China, Central Africa, and South America [34]. A fluoride concentration of approximately $1 \text{ mg} \cdot \text{L}^{-1}$ in drinking water may prevent dental cavities without harmful effects on health [36], but the regular consumption of fluoridated water with more than $1.5 \text{ mg} \cdot \text{L}^{-1}$ could seriously damage teeth or even skeletal structure [34,37–39].

3. Materials and methods

3.1. Research strategy

The research strategy followed three steps:

- Experiments were conducted to evaluate the effects of pressure and cross-flow velocity on the rejection of sulfate, fluoride, total solids dissolved and on the permeate flux.

- Experiments were conducted in the best operating conditions, aiming to concentrate the water at a volume reduction rate of four-fold to simulate an industrial-scale reverse osmosis equipment, which produces 75% permeate and 25% retentate;
- A mass balance was conducted in two ways to produce drinking water: first, all water volume is filtered through the reverse osmosis system, and a mixture of brine and permeate is made; second, a volume of groundwater is filtered, mixing permeate with the other part of groundwater. Fig. 4a shows the first strategy, and Fig. 4b shows the second strategy.

3.2. Effect of pressure and cross-flow velocity on membrane rejection and permeate flux

3.2.1. Experimental design

The use of two independent variables (pressure and cross-flow velocity) at two levels (2^2 factorial design) allowed for the evaluation of the effect of these variables as operating conditions. The response variables were the permeate flux and rejection of TDS, sulfate and fluoride. The experiments were performed in duplicate in random order. Table 2 shows the matrix of the experimental design.

These cross-flow velocities were obtained by adjusting the feed flow rates to $4 \text{ m}^3/\text{h}$ and $1 \text{ m}^3/\text{h}$. The flow rates recommended by the pilot-scale equipment manufacturer for 4 in diameter RO elements range between $1 \text{ m}^3 \cdot \text{h}^{-1}$ and $5 \text{ m}^3 \cdot \text{h}^{-1}$. The cross-flow velocities were

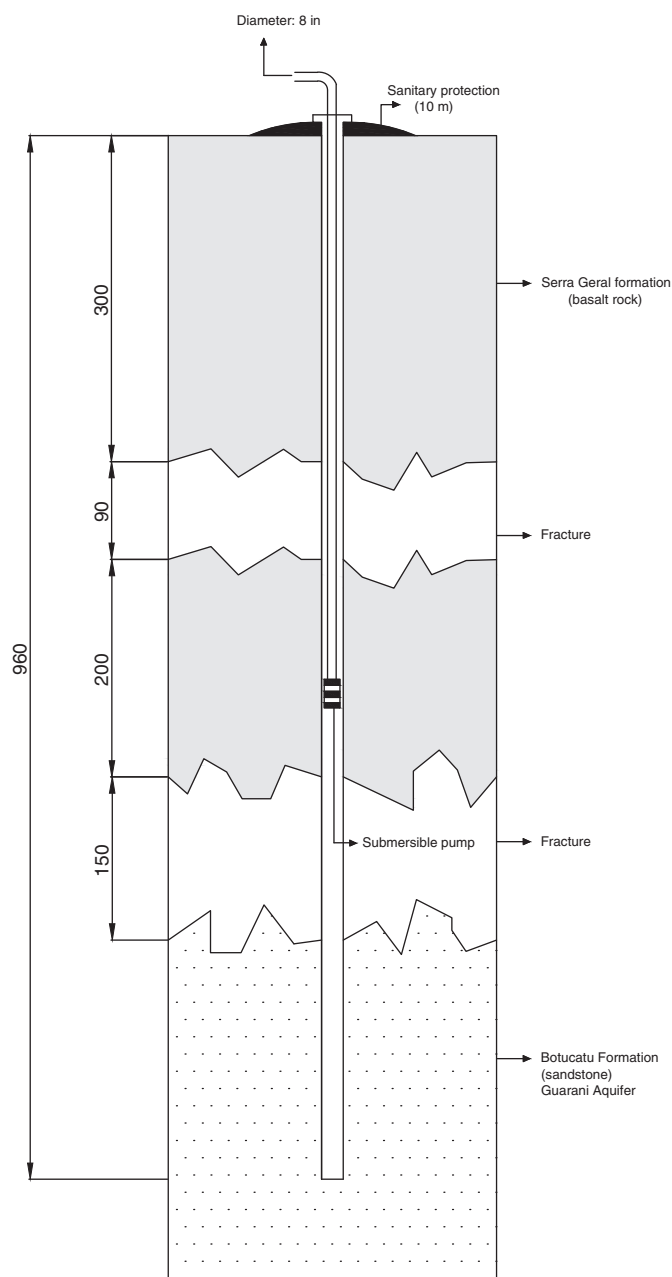


Fig. 3. Schematic drawing of the well drilled in the Guarani Aquifer.

calculated according to the suggestions by Clarke and Heath [40], dividing the flow rate by the free transversal area in the channel of the spiral membrane. The different cross-flow velocities resulted in Reynolds numbers of 1200 and 5000 and thus different turbulence regimes in the retentate channel.

3.2.2. Experimental procedure

The experiment was carried out in a pilot module provided by WGM Systems (São Paulo – Brazil). Fig. 5 illustrates the reverse osmosis pilot rig equipment. The equipment consisted of a stainless steel tank with 150 L capacity from which the brackish water was fed to and driven by a multi-stage centrifugal pump through the membrane, separating the permeate from the retentate. Permeate and retentate were recirculated back to the feed tank to keep a constant feed concentration. The equipment had a tubular heat exchanger in the feed line. Cold water (0 °C to 4 °C) was recirculated with the aid of a thermostat bath

(manufacturer: Multi-Pão, 100 L capacity) to minimize the heat generated by the reject stream due to recirculation during the batch operation in order to maintain the temperature in the range of 25 ± 1 °C.

The protocol was carried out as follows: a) the clean reverse osmosis membrane was installed on the equipment and the flux was measured with the permeate; b) the run was performed as described above; c) after each run, the reverse osmosis pilot rig equipment was flushed with permeate and a rinse was performed with the permeate; d) a new flux with permeate was measured to evaluate possible irreversible fouling; e) acid cleaning (HNO_3 , pH = 2.0) was performed, followed by a new flux with the permeate; and f) a new flux was measured to check the recovery of the original flux before the experiment.

3.2.3. Membrane

The reverse osmosis membrane used belonged to model 3838 HR-NYV (Koch Membrane Systems). The membrane had a spiral shape, 7.1 m² of filtration area, 9.6 cm (3.8 in.) in diameter and 96.5 cm in length, and was made of polyamide. Hydraulic permeability of the membrane was $1.9 \text{ L} \cdot \text{h}^{-1} \cdot \text{m}^{-2} \cdot \text{bar}^{-1}$ and its chloride rejection was 99.3% (measured with 2000 mg·L⁻¹ of NaCl solution at 15.5 bar).

3.2.4. Membrane rejection

Membrane rejection was calculated by relating the concentration of each compound in the permeate and in feed water as shown in Eq. (1) and reported as a dimensionless number.

$$R = \left[1 - \frac{C_p}{C_a} \right] \quad (1)$$

In Eq. (1), C_p indicates the permeate concentration, C_a represents the feed concentration and R is the coefficient of rejection.

3.2.5. Data analysis

The results were compared by analysis of variance at a 5% significance level, and the pressures and cross-flow velocities were determined for the best operating condition.

3.3. Concentration of water in the best operating conditions

A new experiment was performed with the best operating conditions. This new experiment aimed at concentrating the water from the Guarani Aquifer in a fourfold volume reduction rate (VRR). Typical VRR for brackish RO plants are in a range of 4–10 [41]. This way, we tried to simulate water desalination in a real condition, producing a 75%:25% permeate to concentrate ratio. Permeate and final brine were analyzed to determine membrane rejection and evaluate if the membrane would kept the rejection at a higher salt concentration.

3.4. Mass balance of the system upon adjusting the physicochemical parameters to improve the quality of drinking water

Afterwards, a mass balance of the system was conducted to find the appropriate permeate/brine ratio, to adjust the water quality according to WHO guidelines [34] and to evaluate system productivity. Two configurations were evaluated, as shown in Fig. 4. First, all water from the well was fed to the RO system. Permeate and brine were mixed to adjust the water quality, and a brine fraction was sent to disposal. Second, about one third of the water is fed to the RO system. The brine is sent to disposal, and permeate is mixed with water from the well. The main advantage of this configuration is that a lower membrane area is required.

3.5. Analysis

All analytical methods followed the American Public Health Association protocols [36]. All metals were measured by flame atomic absorption

Table 1
Physicochemical composition of water from the drilled well in the Guarani Aquifer.

	Sample 1	Sample 2	Sample 3	Sample 4	WHO recommendation	Brazilian standard ^a
TDS (mg·L ⁻¹)	1321	1410	1290	1059	1000	1000
TSS (mg·L ⁻¹)	NP	6	NP	NP	–	–
pH	8.71	8.79	8.82	8.53	6.5 ≤ pH ≤ 8.5	6.0 ≤ pH ≤ 9.5
Color (Hz)	0	0	0	0	15	15
Turbidity (NTU)	0	0	0	0	1.0	1.0
Electrical conductivity (μS·cm ⁻¹)	1842	1846	1726	1702	–	–
Zn (mg·L ⁻¹)	0.03	0.04	NP	NP	4	5
Na (mg·L ⁻¹)	159	192	NP	NP	200	200
K	NP	10	NP	NP	–	–
Hardness (CaCO ₃) (mg·L ⁻¹)	32	43	NP	NP	500	500
Ca ²⁺ (mg·L ⁻¹)	NP	29	NP	NP	–	–
Mg ²⁺ (mg·L ⁻¹)	NP	14	NP	NP	–	–
Mn (mg·L ⁻¹)	0.1	ND	NP	ND	0.1	0.1
Total Fe (mg·L ⁻¹)	0.09	0.1	NP	NP	0.3	0.3
Total Cr (mg·L ⁻¹)	ND	ND	NP	NP	0.05	0.05
Cu (mg·L ⁻¹)	ND	ND	NP	NP	2	20
Pb (mg·L ⁻¹)	ND	ND	NP	NP	–	0.01
Cd (μg·L ⁻¹)	ND	ND	NP	NP	3	5
Al (mg·L ⁻¹)	ND	ND	NP	NP	0.1	0.2
SiO ₂ (mg·L ⁻¹)	NP	14	NP	NP	–	–
Sr (mg·L ⁻¹)	NP	0.18	NP	NP	– ^b	–
NH ₄ ⁺ (mg·L ⁻¹)	ND	ND	NP	NP	1.5	1.5
NO ₂ ⁻ (mg·L ⁻¹)	ND	ND	NP	NP	3	1
NO ₃ ⁻ (mg·L ⁻¹)	0.65	0.52	NP	NP	50	10
Cl ⁻ (mg·L ⁻¹)	85	98	NP	NP	250	250
Alkalinity (CaCO ₃) (mg·L ⁻¹)	2.8	3.4	NP	NP	–	–
Alkalinity (HCO ₃ ⁻) (mg·L ⁻¹)	NP	68.3	NP	NP	–	–
SO ₄ ²⁻ (mg·L ⁻¹)	326.2	346.1	314.5	285.4	250	250
F ⁻ (mg·L ⁻¹)	2.14	2.25	2.01	1.91	1.5	1.5

ND: Not detected by the analytical method used.

NP: Not performed.

^a Ordinance 2914/2012 issued by the Brazilian Ministry of Health.

^b There are no guidelines for concentrations of strontium, but there is a radiation guidance level of 10 Bq/L of strontium⁹⁰.

spectrometry. F⁻ and NO₃⁻ were quantified by an ion selective electrode, pH was determined by the electrometric method and NO₂⁻ was measured by the colorimetric method. The ammonium was measured by the Kjeldahl method following titration, and carbonates were determined by acid titration. Water hardness was evaluated by the EDTA titrimetric method, SO₄²⁻ was assessed by the turbidimetric method and Cl⁻ was quantified by argentometric titration.

4. Results and discussion

4.1. Effect of pressure and cross-flow velocity on membrane rejection and permeate flux

Fig. 6 shows the behavior of permeate flux during desalination by reverse osmosis. The lines represent the fluxes obtained with permeate water measured before each experiment.

The permeate flux observed in our work is in line with that found by Afonso et al. [16] and Öner et al. [42]. Afonso et al. [16] desalinated brackish water at 20 bar and observed a permeate flux of about 30 L·m⁻²·h⁻¹ using a reverse osmosis membrane from FilmTec (FT30/SW30-2521), and Öner et al. [42] reported a great difference in four reverse osmosis membranes, with permeation rates between 10 L·m⁻²·h⁻¹ and 60 L·m⁻²·h⁻¹ at 20 bar.

Table 2
Matrix of the experimental design.

Run	Pressure (MPa)	Cross-flow velocity (m·s ⁻¹)
A	1.0	0.53
B	1.0	1.61
C	2.0	0.53
D	2.0	1.61

Note that the permeate flux remained constant during the 60 min of filtration in all tested operating conditions. This behavior was also verified by Öner et al. [42] and Afonso et al. [16], who also observed a constant flux in a short time of filtration. However, the elapsed time in our experiments was not enough to build up the long-term scale formation. Besides, the physicochemical quality of brackish water and the functional group present in the membrane surface are important factors that help form the scale layer on the membrane surface. This way, the TDS concentration of the water sample from the Guarani Aquifer and the low concentration of scale-forming constituents contributed towards less membrane fouling. On the other hand, depending on membrane characteristics and on feed water quality, there could be strong long-term fouling on the membrane surface, as reported in the work of Reddy et al. [10].

Fig. 6 shows that the flow of reverse osmosis membrane obtained from the well water sample collected from the GAS was, on average, 24% smaller than the values obtained from pure water (permeate). Stage (d) of the experimental protocol indicated total recovery of the flow, showing that there was no scale formation on the membrane. So, this reduction of approximately 24% results from the combination of the effect of osmotic pressure (decreasing the actual filtration pressure) and of concentration polarization, both considered to be reversible phenomena. Experiments performed by Sutzkover et al. [43] allowed identifying reductions in flux proportional to salt concentrations in solutions when different salts were added to the water to assess the effect of concentration polarization. Thus, even if desalination by reverse osmosis has low fouling, there will be lower flux compared to pure water due to the strong effect of osmotic pressure of the solution and of concentration polarization.

As shown in Fig. 6, the increase in cross-flow velocity did not produce an actual increase in permeate flux, and two flux levels were observed: around 17 L·m⁻²·h⁻¹ and around 35 L·m⁻²·h⁻¹, as a result of higher pressure. These values are discussed in further detail in

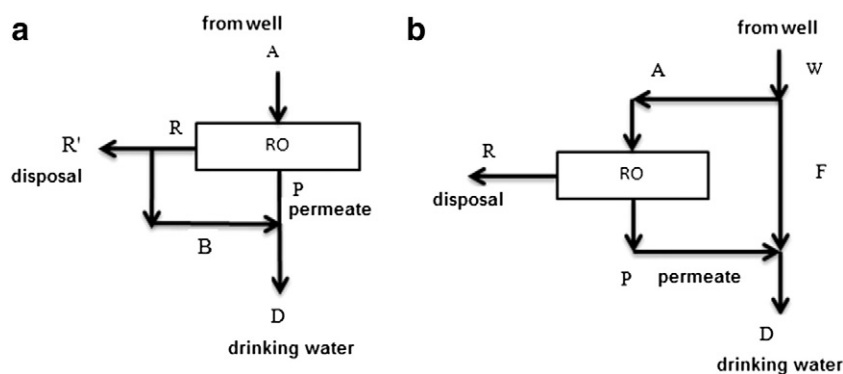


Fig. 4. Strategies of mixing to produce drinking water – (a) permeate and brine mixing and (b) permeate and fresh water mixing.

Table 3, which shows the membrane rejection at different pressures and cross-flow velocity.

The goal of desalination was to optimize the permeate flux and the membrane rejection rate of the three constituents for which the concentration exceeded the limits of WHO guidelines for drinking water.

Table 3 shows that 2 MPa of pressure produced higher flux. Still, at 2 MPa, there was no difference in the cross-flow velocity in fluoride and TDS rejection. However, there are doubts about the sulfate rejection because there is a minor value (0.873) and major value (0.944). The intermediate values are statistically equal to these higher and lower rejections. This issue will be discussed later in the text and is illustrated with Fig. 7.

From Table 3, a lower rejection of TDS, F^- , SO_4^{2-} and electrical conductivity was obtained at a pressure of 1 MPa and at a cross-flow velocity of $0.53 \text{ m} \cdot \text{s}^{-1}$. Thus, this experimental condition ($p = 1 \text{ MPa}$ and $v = 0.53 \text{ m} \cdot \text{s}^{-1}$) should be avoided.

Statistical analysis demonstrated that the difference in flux was not significant when larger cross-flow velocities were applied. Similar results were described by Öner et al. [42] and Afonso et al. [16], who reported that by elevating the cross-flow velocity in reverse osmosis desalination systems, fluxes increased slightly or were not significant. In contrast, increases in operating pressure produced proportional

increases in flux, which is similar to our findings, with a doubling of flux with a two-fold increase in pressure. Thus, both experimental conditions with a higher pressure produced a higher flux.

Table 4 shows the analysis of variance of the changes to permeate flux with pressure and cross-flow velocity increases. The qualitative aspects suggested in Fig. 6 are quantitatively shown in Table 4. Note that pressure strongly affected permeate flux (smaller p value), whereas cross-flow velocity did not greatly affect the permeate flux. Given that cross-flow velocity did not impact permeate flux, no interaction was observed between the two independent variables represented by product $p * v$.

The effects of pressure and cross-flow velocity on the response variables are shown in Table 5, which displays the p values from the ANOVA for all dependent variables, independent variables and their interactions ($p * v$).

The interactions between pressure and cross-flow velocity ($p * v$) in the membrane rejection of electrical conductivity, TDS, and fluorine are shown in Table 5, and these interactions are better visualized in Fig. 7. Sulfate rejection was improved in the same proportion when the pressure was raised for both cross-flow velocities, showing no interaction between the independent variables. In Table 3, this effect was not clear because there was a range of fluctuation between the higher

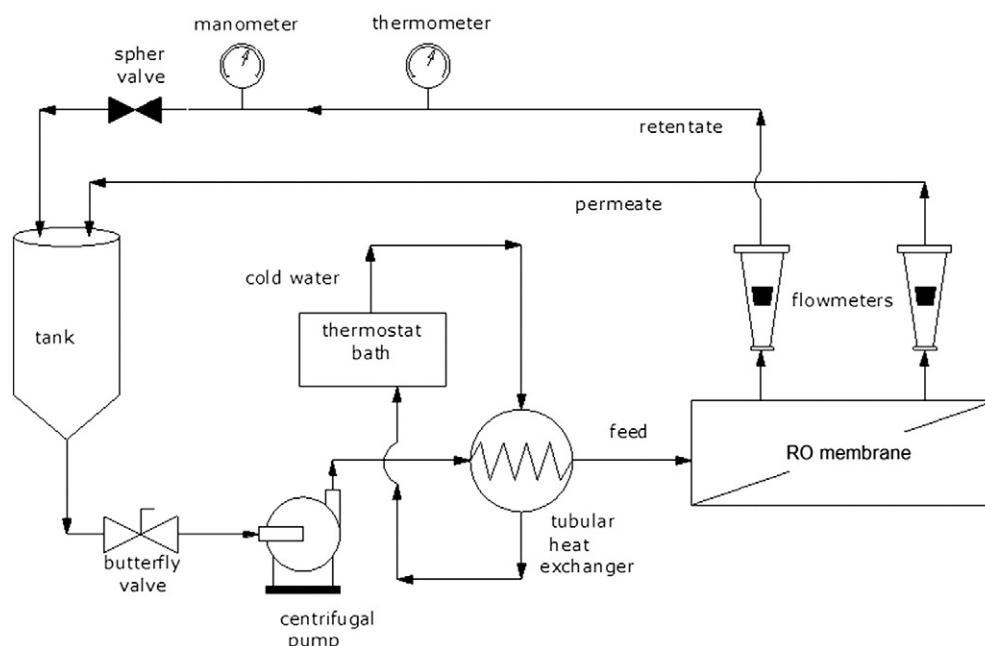


Fig. 5. Schematic drawing of the pilot-scale reverse osmosis system.

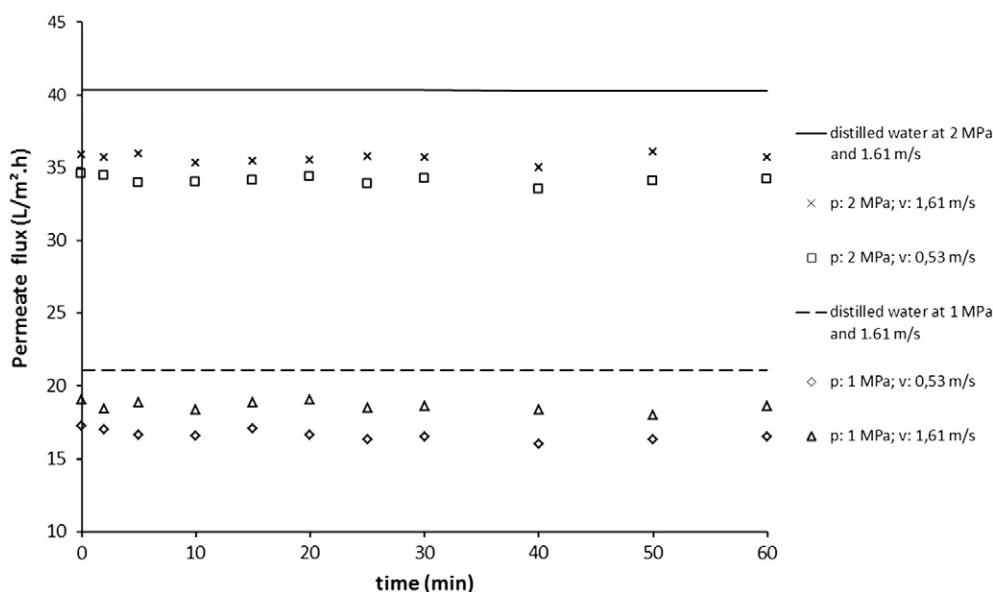


Fig. 6. Permeate fluxes for each experimental condition (the lines represent the permeate flux with distilled water).

sulfate rejection (0.944) and the lower sulfate rejection (0.873). However, Fig. 7A shows that the different cross-flow velocities produced higher sulfate rejection at both pressure levels. As seen in Table 5 and confirmed in Fig. 7, a higher “v” results in a higher sulfate rejection rate.

From Fig. 7B, however, it is possible to see the interaction between “p” and “v” in TDS rejection. This variable was not improved when the cross-flow velocity was increased by 2 MPa, whereas TDS rejection increased from 0.90 to 0.97 at 1 MPa.

The effect of pressure on the rejection of ions during the desalination of brackish water was reported by Öner et al. [42]. Herein, four RO membranes were tested, and no standard pattern was observed; some membranes had higher salt rejection rates at higher pressures, while others demonstrated consistent rejection regardless of the pressure. Using 2 MPa, Öner et al. [42] demonstrated salt rejection rates between 97% and 99% for different RO membranes. Furthermore, Öner et al. [42] and Afonso et al. [16] found that circulation velocity had no effect on permeate flux or on salt rejection, which is consistent with our results; at 2 MPa, the cross-flow velocity showed no effect on TDS rejection (Fig. 7b). However, at a lower pressure (1 MPa), the circulation velocity improved salt rejection, and TDS rejection increased from approximately 0.90 to 0.97. This result suggests that the concentration polarization and the Donnan effect near the membrane play an important role in separation efficiency, although cross-flow circulation showed no effect on permeate flux.

A sulfate rejection higher than 0.94 was expected because it is a covalent ion, but there are many factors acting in parallel (e.g., the pH of water, the net charge of the polyamide membrane, the Donnan effect, and charge exclusion). Sulfate rejection in other studies varied between 0.97 [31] for the AD membrane from GE Osmonics and over 0.99 for the BW-30/Filmtec RO membrane [42]. However, other studies reported

sulfate rejection rates of 0.95 [25] and 0.93 [28] for the desalination of brackish water by reverse osmosis.

Total fluoride rejection results were not surprising in the desalination process of the brackish water from the Guarani Aquifer. Fluoride was separated even in polyamide nanofiltration membranes [44,45], and RO in series (prior to nanofiltration) was shown to improve the rate of fluoride rejection, reaching 100%.

4.2. Concentration of the water in the best operating conditions

Fig. 8 shows the results of the RO treatment of water extracted from the aquifer at a VRR = 4, and with RO process parameters of 2 MPa and $1.61 \text{ m} \cdot \text{s}^{-1}$. It is clear that the RO membrane used here achieved the same rejection rates obtained by earlier experiments (approximately 98% for TDS, 97% for sulfate and 100% for fluoride). If the water from the Guarani Aquifer is fed into a real reverse osmosis system, regarding the critical constituents and their removal rates, the membrane rejection is kept and the permeate recovery ratio of 75% should be used. However, note that this is a lab experiment performed over a short time interval, and the long-term effects of the salts on the membrane (e.g., fouling) are not considered here. This will be the focus of future work, as a field experiment.

4.3. Mass balance of the system upon adjusting the physicochemical parameters to improve the quality of drinking water

The higher rejections shown in Table 3 reveal that the permeate has a superior quality as far as salinity and potability are concerned. Therefore, it is reasonable to mix permeate with a higher salinity water to reach the desired quality for drinking water. The critical constituent is

Table 3

Mean values and standard deviations of the permeated flux and rejection of electrical conductivity, sulfate, fluoride, and total solid dissolved for each experimental condition tested.

p (MPa)	v ($\text{m} \cdot \text{s}^{-1}$)	pH	Flux ($\text{L} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$)	Rejection			
				EC ($\mu\text{S} \cdot \text{cm}^{-1}$)	SO_4^{2-} ($\text{mg} \cdot \text{L}^{-1}$)	F^- ($\text{mg} \cdot \text{L}^{-1}$)	TDS ($\text{mg} \cdot \text{L}^{-1}$)
1	0.53	7.36 ^(a)	$17.02 \pm 0.69^{(a)}$	$0.911 \pm 0.008^{(a)}$	$0.873 \pm 0.004^{(a)}$	$0.905 \pm 0.028^{(a)}$	$0.905 \pm 0.001^{(a)}$
1	1.61	7.25 ^(a)	$17.91 \pm 0.98^{(a)}$	$0.978 \pm 0.005^{(b)}$	$0.906 \pm 0.021^{(a,b)}$	$1.000 \pm 0.000^{(b)}$	$0.971 \pm 0.001^{(b)}$
2	0.53	7.08 ^(b)	$34.97 \pm 1.03^{(b)}$	$0.974 \pm 0.006^{(b)}$	$0.922 \pm 0.007^{(a,b)}$	$1.000 \pm 0.000^{(b)}$	$0.973 \pm 0.015^{(b)}$
2	1.61	7.05 ^(b)	$36.24 \pm 2.33^{(b)}$	$0.980 \pm 0.011^{(b)}$	$0.944 \pm 0.011^{(b)}$	$1.000 \pm 0.000^{(b)}$	$0.970 \pm 0.007^{(b)}$

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 mean that their values are identical to the lowest and highest values.

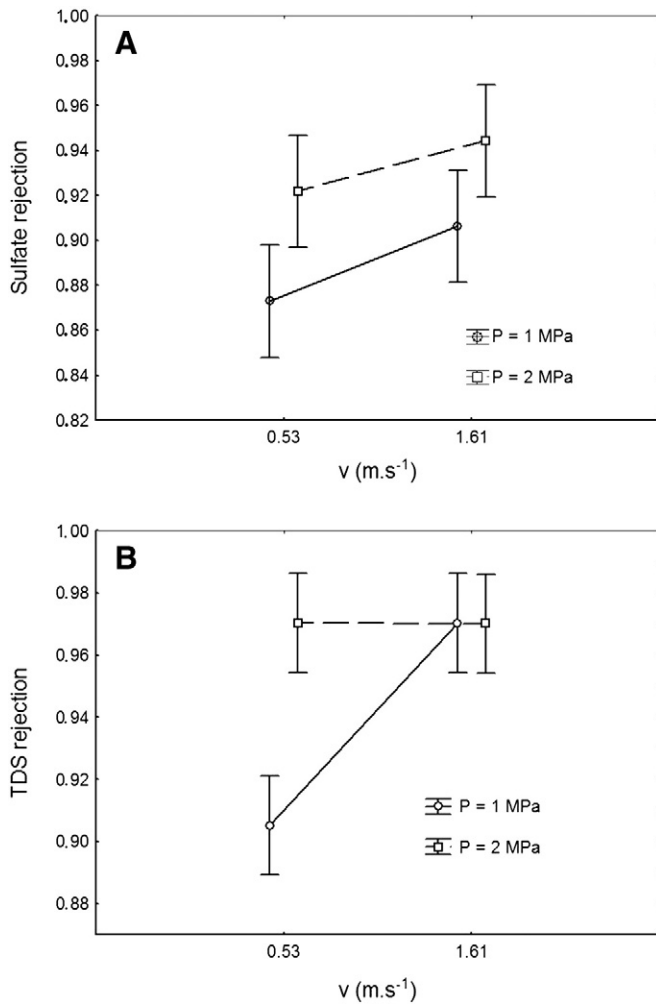


Fig. 7. Reverse osmosis rejection rates of sulfate (A) and TDS (B) for the desalination of brackish water from the Guarani Aquifer. Vertical bars denote 0.95 confidence intervals.

fluoride, so this anion was used as the reference to develop the mass balance in the system. Fig. 9 shows the mass balance with the concentration of F^- (at VRR = 4) just to show the strategies of mixing and Table 6 shows the mass balance related to both strategies adopted.

Table 6 shows the maximum recovery that could be achieved when scaling up the process because higher recovery values will exceed the limits for concentration for TDS and sulfate. The first strategy resulted in a higher recovery, but the second strategy seems the best way to desalinate the water extracted from the Guarani Aquifer. The strategy (b) has two great advantages:

- i) Only 31% of the pumped water from the Guarani Aquifer is sent to the RO system; thus, the required membrane area is lower and the equipment necessary will be smaller and cheaper.

Table 4
Analysis of variance for permeate flux in relation to pressure and cross-flow velocity independent variables.

Effect	SS	DF	MS	F	p
Pressure	657.9	1	657.9	330.7	0.000054
Cross-flow velocity	2.344	1	2.344	1.178	0.338776
Pressure * cross-flow velocity	0.070	1	0.070	0.035	0.860025
Error	7.957	4	1.989		

SS: sum of squares; DF: degrees of freedom; MS: mean square; F: Fisher's exact test value; p: probability.

Table 5
Summarized analysis of variance (p value) for each response variable relative to the independent variables.

Source	pH	EC	SO ₄ ²⁻	F ⁻	TDS	Flux
P	0.000 ^a	0.004 ^a	0.008 ^a	0.009 ^a	0.004 ^a	0.000 ^a
V	0.056	0.003 ^a	0.003 ^a	0.009 ^a	0.004 ^a	0.338
p ^a v	0.241	0.005 ^a	0.575	0.009 ^a	0.004 ^a	0.860

^a p value < 0.05 is statistically significant at $\alpha = 5\%$.

- ii) The concentrate volume is smaller; thus, the costs associated with the disposal of this concentrate will be smaller also.

The second strategy of mixing seems to be the better of the two options. The RO facility will be smaller and a lower volume of brine will be generated.

5. Concentrate disposal

There is great concern about the concentrate generated by desalination facilities. Finding an adequate treatment strategy and a final destination for this wastewater is a challenge for desalination plants around the world [46–48], and the high costs of desalination are increased further depending upon the strategy adopted for brine waste disposal [49]. There are many strategies for concentrate disposal, including surface water discharge, sewer discharge to a municipal wastewater treatment facility, evaporation ponds, deep well disposal, spray irrigation, zero liquid discharge technologies such as thermal evaporation, crystallization and spray drying [9,47,48,50–52] and other, emerging strategies [47].

Some assumptions must be done before to choose the correct disposal of RO concentrate:

- a) The low concentration of metals in the water extracted from GAS will result in metal concentrations below the Brazilian standard in the final brine being disposed.
- b) The disposal of fluoride has a maximum concentration limit of $10 \text{ mg} \cdot \text{L}^{-1}$, and the brine produced from desalination had a concentration of $7.4 \text{ mg} \cdot \text{L}^{-1}$;
- c) The high concentration of sulfate and TDS in the concentrate: Despite the fact that the Brazilian law does not have discharge standards for sulfate and TDS, surface waters cannot exceed $250 \text{ mg} \cdot \text{L}^{-1}$ of sulfate. A mass balance can show that the concentrate into the sewer will reach a dilution ratio of about 1/20. In practice, this dilution rate of 1/20 will reconstitute the initial concentration of the sulfate ($\sim 300 \text{ mg} \cdot \text{L}^{-1}$) of the water from the GAS, and this value is acceptable to feed conventional wastewater treatment.

Sulfate: 314 mg/L
TDS: 1290 mg/L
F: 2.01 mg/L

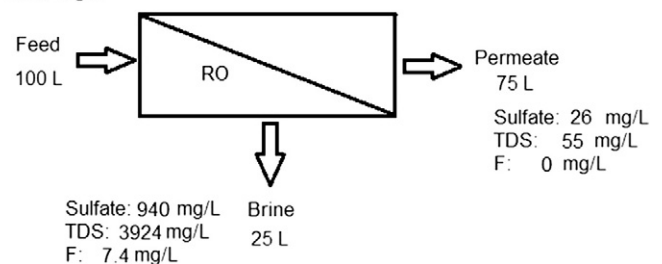


Fig. 8. TDS, F^- and SO_4^{2-} removal rates when concentrating extracted groundwater (VRR = 4) from GAS using RO at 2 MPa and $1.61 \text{ m} \cdot \text{s}^{-1}$.

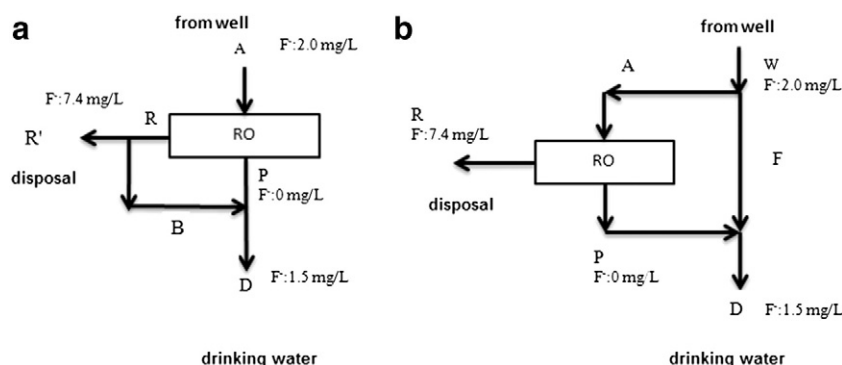


Fig. 9. Mass balance for the production of drinking water via RO product mixtures (a) permeate and brine mixing and (b) permeate and groundwater mixing.

Furthermore, some treatment can be done before the disposal to later treatment. There are studies regarding sulfate removal from industrial effluents. Precipitation [58–60] and biological sulfate removal [61] are some available techniques for reducing the sulfur levels before traditional wastewater treatment. The sludge generated by these processes can be used in soil remediation with acidic characteristics. This strategy could be used for the present case.

- d) Another strategy for the concentrate disposal is injection of this stream into recharge zones of the Guarani Aquifer System. This practice is not common in Brazil, but could be applied for this specific situation. The GAS contains deep zones with high TDS concentrations with sufficient permeability in such way the concentrate will not alter the characteristics of the groundwater.

It should be noted that all the strategies for concentrate disposal are subject to environmental licensing and disposal permit-specific limits.

6. Conclusions

This study gave a brief description of the water supply in southern Brazil, showing that the country should implement desalination to meet drinking water demand in drought-prone areas. The Guarani Aquifer is a potential source for water harvesting, but the total dissolved solids, sulfate and fluoride concentrations exceed the limits for drinking water without additional treatment.

Reverse osmosis has been shown to be an efficient method for improving the quality of brackish water from the Guarani Aquifer to the quality required for drinking water. A blend of fresh water and the permeate produced drinking water at a water recovery rate of approximately 93% (drinking water produced/fresh water).

Increased pressure applied to the RO membrane feed enhanced the permeated flux while the cross-flow velocity increased the rate of sulfate rejection. The operating condition of 2 MPa and $1.61 \text{ m} \cdot \text{s}^{-1}$ was the best strategy for the desalination of water from the Guarani Aquifer by reverse osmosis.

Table 6

Mass balance in the system for two strategies adopted to desalinate the water from the Guarani Aquifer.

Flow rate (m^3/h)	(a)	(b)
W	–	4
A	4	1.24
R	1	0.31
P	3	0.93
F	–	2.79
D	3.76	3.72
B	0.76	–
R'	0.24	–
Recovery (%)	94.00	93.00

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