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Experimental investigation on arsenic removal with a nanofiltration pilot plant from naturally contaminated groundwater

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ABSTRACT

In this research, the efficiency and the arsenic removal mechanism with a Nanofiltration (NF) pilot plant from naturally contaminated groundwater have been evaluated. The process integral evaluation at 7 bar shows an arsenate (HAsO_4^{2-}) rejection over 95% and a total sulfate (SO_4^{2-}) rejection. Divalent ions calcium and magnesium (Ca^{2+} and Mg^{2+}) rejection produced an 81% reduction of the total hardness. The total dissolved solids TDS concentration decreased to 53%. Monovalent ions moderated rejections contributed to the membrane hydraulics stability. The arsenate (HAsO_4^{2-}) rejection from an electrolytes solution (SO_4^{2-} , HCO_3^- , F^- , Cl^- , NO_3^- , Ca^{2+} , Mg^{2+} , K^+ and Na^+) was prevalently ruled by Donnan exclusion combined with the preferential passage of more permeable ions. Results show the importance of ionic composition on ion transmission and rejection in the studied membrane. Ion rejection in multicomponent solutions showed to be significantly different to that in individual salt solutions. Whereas monovalent anion rejections remarkably decreased, divalent cation rejections were three times superior. In arsenate rejection (HAsO_4^{2-}) from artificially contaminated natural groundwater, the membrane showed the same selectivity.

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1. Introduction

Arsenic high contents in groundwater destined to human consume constitute one of the most important problems related to population

health in many countries in the world. Among affected countries, are Argentina, Bangladesh, Canada, Chile, China, Hungary, India (West Bengal), Mexico, Pakistan, Romania, Taiwan, Vietnam and USA [1,2]. The Central region in Argentina is one of the most extensively

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contaminated areas in the world, with a 1 million km² surface and an affected population of 4 million people [1].

At the beginning, exposure to arsenic by potable water causes skin diseases such as pigmentation (dark and light stains on the skin) and arsenicosis (skin hardening in feet and hands). Afterwards, bioaccumulation might produce skin, lung, kidney and bladder cancer. For this reason, World Health Organization (WHO) and the Environment Protection Association (EPA) have classified arsenic as cancerous, and established a maximum guide value of 10 µg/L [3–6].

The new legal system propelled the development of more efficient technologies, from which reverse osmosis (RO) happened to be one of the best for arsenic removal; however economical studies showed that it was too expensive. Since operating pressures in NF are lower than RO, separation occurs at low energy consumption (21% less than RO) and higher water fluxes can be achieved at lower transmembrane pressures. This is the reason why nanofiltration has become of interest in the whole world [7]. A general revision about nanofiltration application in water treatment has been recently published [8].

In general, commercial NF membranes have negative charges and a pore size close to 1 nm [9]. Behavior followed by NF membranes to reject ions is known enough. Essentially, these membranes have a high multivalent ion rejection due to the combination of electrostatic interactions with the membrane charge and exclusion due to the hydrated ion size. Monovalent ions tend to have lower rejection unless they are retained to maintain electroneutrality with multivalent counter-ions. Thus, for pure salt solutions the extended Nernst-Planck equation has been used successfully to explain rejection [10].

An increase in the ionic concentration produces a decrease in the rejection, probably due to a membrane charge screening which reduces the electrostatic repulsion. On the other hand, solution properties such as pH and the composition have significant effects over the membrane charge, solute speciation and solute–solute and solute–membrane interactions [11–14].

Due to all these effects and to the different properties commercial membranes have, predictive models use is complicated. As mentioned above, the most direct method to evaluate a NF membrane behavior in the presence of a specific solution is the gathering of experimental data [15].

In the specialized literature different studies destined to As removal from water by nanofiltration can be found [16–33]. However, most of them have been performed at a laboratory or bench scale, and using synthetic or natural (superficial or groundwater) water contaminated with arsenic. Recently, Košutić et al. (2005) and Sen et al. (2010) studied arsenic separation from groundwater naturally contaminated at laboratory scale [24,32]. Nevertheless, there are a few studies performed at pilot-plant scale; however, all of them have been performed in artificially contaminated waters [17,23,29,33].

Considering that the studies reveal that the efficiency in arsenic removal by Nanofiltration may substantially vary with membrane properties and with feed water composition, new researches from naturally contaminated water and few studied membranes are a matter of interest in arsenic elimination strategies.

Indistinctly, groundwater with arsenic problems can be found in reducing and oxidizing environments as well as in humid/mild or arid climates. Considering the environment, the world distribution of waters contaminated with As, may be ordered as follows: a) reducing environments (West Bengal, Bangladesh, Taiwan, Northern China, and Vietnam), b) oxidizing arid environments (Argentina, Chile, México, Peru, and Bolivia), c) mixed oxidizing and reducing environments (South-western USA) [1].

Groundwater in Argentina are type b), predominantly oxidized, with high alkalinity and salinity, and a pH range of 7–8.7. Arsenic is as As(V) and its average concentration varies between 145 and 255 µL depending on the region [1].

In this work arsenic removal from naturally contaminated groundwater using an NF pilot plant will be studied. Firstly, the membrane

rejection capacity in individual salt solutions of the ten groundwater components will be studied in order to have a reference line. Secondly, the rejection of every groundwater component will be studied and the influence of pressure will be analyzed. Afterwards, results will be compared; ion coexistence effects will be observed and the mechanisms involved in rejection will be explained. Finally, As(V) removal from artificially contaminated natural groundwater was studied and the results were compared.

2. Materials and methods

2.1. Membrane

The spiral wound membrane used in this research was a NF-300 membrane (Osmonics Inc. USA), a TFC polyamide membrane. According to the manufacturer, this membrane has a nominal MWCO of 180 Da, with a 3 to 10 operational pH range. The NF membrane module is enclosed in OSMO 19E-HR 500-ECN membrane housing. Each element is 2 × 39 in. and has a 1.5 m² active membrane surface. The membrane was already characterized in a previous work as a negatively charged one [31].

2.2. Individual salt solutions

Individual salt solutions were freshly prepared using NaCl, KCl, CaCl₂, MgCl₂ · 6H₂O, Na₂SO₄, NaHCO₃ and Na₂HAsO₄ · 7 H₂O analytical grade supplied by Sigma-Aldrich.

2.3. Groundwater

Groundwater samples were taken from the distribution system of a city localized in La Pampa province. Studied water is only submitted to a chlorination process before entering the distribution system. Groundwater composition is showed in Table 1. It is alkaline water with high salt contents. Electrical conductivity (E.C) was 2.57 mS/cm, total dissolved solids (TDS) were 1290 mg/L, total organic carbon (TOC) was 0.26 mg/L, silt density index (SDI) was <1 and pH was 8.5. In order to value the obtained results in a chemical analysis, it was performed as an ionic balance. The difference between the anionic mEq/L (27.33) and the cationic mEq/L (27.94) was 2.22%. Ionic strength was 0.0336 mol/L.

2.4. Permeation experiment

The experiences were carried out in an NF pilot plant described in a previous work [33]. The operating temperature was 293 K. The operating pressure varied in a 2 to 10 bar range except for the experiments with individual salts which were performed at 7 bar. The feed flow was fixed at 417 L/h (cross flow velocity was kept in 18.11 cm/s) high enough to prevent concentration polarization [34]. The cross flow velocity of 18.11 cm/s, corresponds to the Reynolds number of 275

Table 1
Naturally contaminated groundwater composition (95% confidence interval; n = 3).

Component	ppm	WHO standard	mM	mEq/L	Equivalent fraction of anions
HCO ₃ ⁻	728	75–150	11.93	11.93	0.437
Cl ⁻	269	250	7.58	7.58	0.277
NO ₃ ⁻	0.9	50	0.0145	0.0145	–
F ⁻	5.52	1.5	0.29	0.29	0.011
SO ₄ ²⁻	360	400	3.75	7.50	0.274
HAsO ₄ ²⁻	0.428	0.010	0.003	0.006	–
Na ⁺	521	200	22.60	22.60	0.810
K ⁺	33	–	0.84	0.84	0.030
Mg ²⁺	36	–	1.5	3.00	0.107
Ca ²⁺	30	–	0.75	1.50	0.054

typical in spiral-wound modules [35,36]. Technically, this is the laminar flow region, but the additional turbulence contributed by the spacers, which can be substantial should also be taken into account [36,37]. The state of turbulence can be determined by the nature of the relationship between pressure drop (ΔP) and flow rate (Q) in the feed channel. The general relationship between these two quantities is:

$$\Delta P = f(Q)^n$$

with $n=1$ for laminar flow and $n=1.5$ – 1.9 for turbulent flow [36]. Saitúa et al. [33] working with the same membrane, determined the turbulence state by using a number of experiences with pure water for cross flow velocity between 8.40 and 18.11 cm/s (at 2 bar and 293 K). Data were well fitted by the following correlation:

$$\Delta P = 4.73(Q)^{1.62}$$

The value $n=1.62$ indicates that the system is working in the turbulent flow region. On another hand, and despite the low organic matter content in groundwater, the potential fouling of the membrane working at different cross flow velocity was investigated. Rejections weren't affected by changes in the cross flow velocity; therefore, it can be assured that the polarization concentration effect isn't significant.

Samples of permeate and feed were collected and a mean value was calculated for each determination. pH was determined for the feed and permeate. The observed parameter was rejection (R%) derived from the following relation:

$$R\% = [1 - (C_p / C_o)] \cdot 100$$

where C_p and C_o are respectively the concentration or conductivity in permeate and in the feed solution depending on the performance test.

Individual NaCl, KCl, CaCl₂, MgCl₂, Na₂SO₄, and NaHCO₃ salt rejections were obtained from experiences realized in a 1 to 10 mM concentration range. NaF rejection was obtained from measures realized between 0.1 and 0.5 mM (2 to 10 ppm). NaNO₃ rejection was achieved in a 0.5 to 5 mM range. Arsenic rejection was obtained from a 1 mM NaHCO₃ solution (pH=8) contaminated with Na₂HAsO₄·7 H₂O in a 30 to 400 µg/L As(V) concentration range.

2.5. Analytical methods

Individual NaCl, KCl, CaCl₂, MgCl₂, Na₂SO₄, NaNO₃ salt solution rejections were determined using an electrical conductivity meter (Cole-Parmer). Fluoride concentrations were determined using a fluoride ion-selective electrode (Orion Research). Bicarbonate concentrations were calculated through potentiometric titration. Arsenic concentrations were measured by HG-ICP-OES using a sequential inductively coupled plasma spectrometer (Baird ICP 2070) connected to a hydride generator (PS Analytical LTD). Sodium and potassium concentrations were carried out by Flame Emission Spectroscopy (FES) using a spectrometer (Metrolab 315). Calcium and magnesium concentrations were determined by EDTA titration. Nitrate was determined by Cadmium reduction method. Chloride was determined by the Mohr method. Sulfate concentrations were determined by turbidimetric method.

3. Results and discussion

3.1. Ions rejection in individual salts

Considering the experiences performed with individual salts, the selected rejections were those obtained at similar concentrations to those presented by different ions in groundwater. Fig. 1 showed salt rejections at 7 bar and 293 K, corresponding to concentrations indicated in each case: Na₂SO₄ 5 mM, NaHCO₃, NaCl and KCl 10 mM,

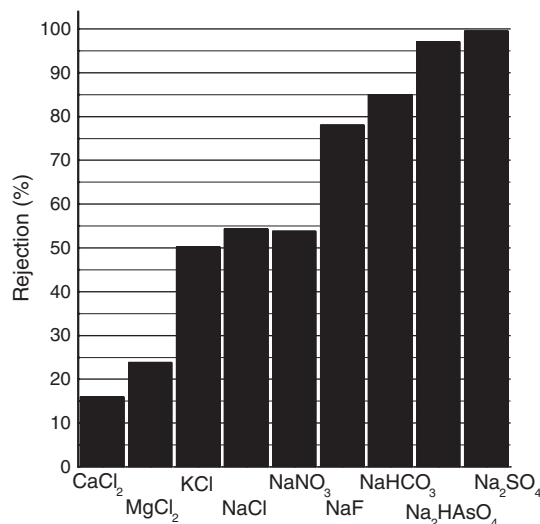


Fig. 1. Individual salt rejections corresponding to concentrations indicated in each case: Na₂SO₄ 5 mM; NaHCO₃, NaCl and KCl 10 mM; MgCl₂ and CaCl₂ 1 mM; NaNO₃ 0.5 mM; NaF 0.2 mM and As(V) 400 µg/L as Na₂HAsO₄ in 1 mM of NaHCO₃ solution. Conditions: T = 293 K; ΔP , 7 bar; flow rate, 417 L/h.

MgCl₂ and CaCl₂ 1 mM, NaNO₃ 0.5 mM; NaF 0.2 mM (5 ppm) and As (V) 400 µg/L as Na₂HAsO₄ in 1 mM of NaHCO₃ solution. All studied ion characteristics are listed in Table 2.

3.1.1. Anions separation

Given all anion rejections as sodium salts, the following sequence is established: Na₂SO₄ > Na₂HAsO₄ > NaHCO₃ > NaF > NaNO₃ > NaCl. Divalent anions (SO₄²⁻ and HAsO₄²⁻) high rejections are related to steric and electrical effects. On one hand, they present a higher hydration radius than monovalent anions, therefore a more effective exclusion for size. On the other hand, they are much more affected for electrical repulsion or Donnan exclusion, due to their higher charge density. Monovalent anions revealed high and moderated rejections. The major bicarbonate rejection could be related to a higher charge density due to its little hydrated radius, besides, bicarbonate presents the lowest diffusivity.

3.1.2. Cations separation

Cation rejections were obtained from chloride salts. As can be observed in Fig. 1, the sequence is NaCl > KCl > MgCl₂ > CaCl₂. Donnan exclusion indicates a strong electrostatic attraction among divalent counter-ions (Ca²⁺ and Mg²⁺) and negatively charged membranes, compared to monovalent counter-ions (Na⁺ and K⁺), that produces a screening of the membrane charge and a lower anion rejection, and in consequence, lower CaCl₂ and MgCl₂ rejections. Higher rejections of NaCl and KCl, in spite of their less hydrated radii and their major

Table 2
Characteristics of studied ions.

Ions	Diffusion coefficient (10 ⁻⁵ cm ² /s)	Hydrated radii (Å)	Hydration free energy (kJ/mol)
Cl ⁻	2.032 [20] [41]	3.32 [38]	376 [42] 384 [40] 340 [39]
HCO ₃ ⁻	1.185 [45]	2.0–2.2 [48]	–
NO ₃ ⁻	1.902 [52] 1.7 [45]	3.35 [38]	329 [42] 314 [44]
F ⁻	1.45 [46]	3.52 [38]	515 [43] 494 [39] 494.6 [40]
SO ₄ ²⁻	1.065 [20] [41]	3.79 [38]	561 [43] 1138 [42]
HAsO ₄ ²⁻	0.323 [20]	>2.0–2.2 [48]	–
Na ⁺	1.33 [47]	3.58 [38]	365 [39] 343 [40] 407 [42]
K ⁺	1.96 [47]	3.31 [38]	295 [39] 270 [40]
Mg ²⁺	0.71 [47]	4.28 [38]	1828 [39] 1768 [40]
Ca ²⁺	0.79 [47] 0.92 [20]	4.12 [38]	1504 [39] 1446 [40]

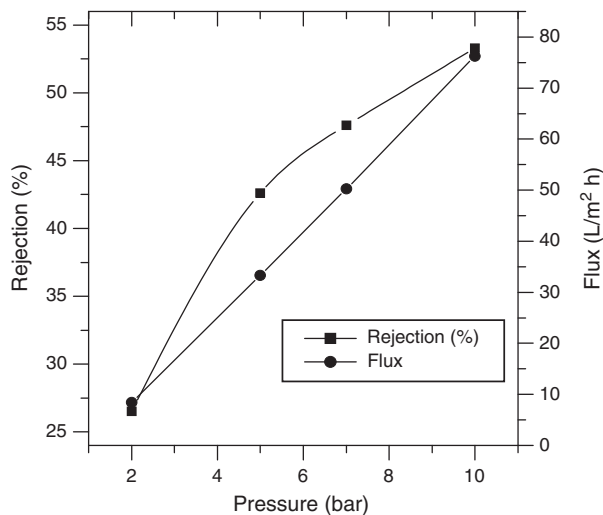


Fig. 2. Total ionic rejection and permeate flux as a function of the operating pressure for groundwater. Conditions: $T = 293$ K; flow rate, 417 L/h.

diffusivity, could indicate that electrostatic effects slightly predominate over steric effects in membrane selectivity [10]. The sequence $\text{NaCl} > \text{KCl}$ and $\text{MgCl}_2 > \text{CaCl}_2$ is associated to ions diffusivity and hydrated radius.

3.2. Ions rejection in groundwater

In a polyelectrolyte system with high ionic strength, steric impediment has influence over ion distribution in the membrane-solution interface and the ions hydrated radii become important.

In Fig. 2 the operating pressure effect over permeate volumetric flux and the total ionic rejection is shown, calculated on conductivity measures. As it can be seen, permeate volumetric flux linearly increases with the pressure. At the time, rejection duplicates with the pressure in a 2 to 10 bar range.

Fig. 3 showed all ion rejection in groundwater, according to pressure. It can also be observed that in general, all ion rejections

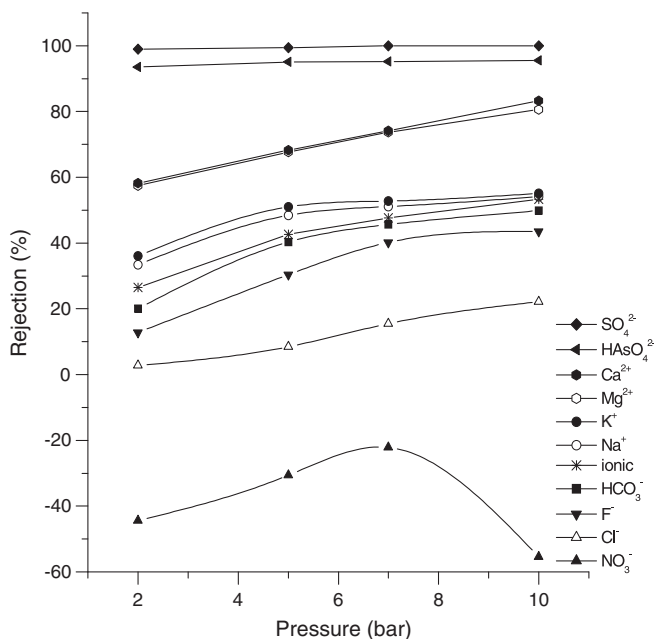


Fig. 3. Total ionic rejection calculated on conductivity measures and individual ions rejection as a function of the operating pressure for groundwater. Conditions: $T = 293$ K; flow rate, 417 L/h.

increase with pressure. This is associated to “dilution effect”, which means, as the pressure increases, it increases the water flow in permeate, meanwhile solute flow remains practically constant. This causes a lower solute concentration in permeate and therefore a major rejection. From 7 bar on, most ion rejections approximate to their respective maximum values, which are called reflection coefficient considered in the Spiegler–Kedem analysis [49]. Nevertheless, the Ca^{2+} and Mg^{2+} ion tendency was different, since its rejection didn't approximate to a maximum. This described behavior could be related to high Ca^{2+} and Mg^{2+} hydration free energies. This means that at high pressures, ions with weak attraction strengths because of water molecules can lose the hydration shells and pass through the membrane pores tending to a constant value in their rejection. At the time, ions which strongly retain more water molecules in their hydration shells, aren't able to get rid of them easily and they are retained in the membrane [50]. In case of nitrate which presents negatives rejections, it increased until 7 bar and then decreased. For all the studied pressure ranges, anion rejections expose the following sequence $\text{SO}_4^{2-} > \text{HAsO}_4^{2-} > \text{HCO}_3^- > \text{F}^- > \text{Cl}^- > \text{NO}_3^-$. For cations, the rejection sequence is: $\text{Ca}^{2+} > \text{Mg}^{2+} > \text{K}^+ > \text{Na}^+$.

3.3. Comparison between individual salts and groundwater

Table 3 compares each ion rejection in groundwater, to ion rejections in individual salts at a 7 bar pressure and similar concentrations. Results show a strong monovalent anion rejection decrease in groundwater. All monovalent ion rejections decreased over 45%; this might be a consequence of two synergic effects: ionic strength increase and the multivalent anion pump effect over univalent in electrolyte solutions. The increase of salt concentration screens the membrane charge and decreases the electrostatic repulsion among the membrane and univalent anions, decreasing its rejection. On the other hand, multivalent anions with higher charge densities are strongly rejected by the membrane and push monovalent anions to pass through the membrane to fulfill the electroneutrality requirements, decreasing its rejection as well [51]. This last mechanism would also explain high multivalent anion rejections, similar to those obtained in experiences with individual salts. In fact, in spite of its low concentration and the environment highest ionic strength, arsenate (HAsO_4^{2-}) slightly decreases its rejection (97 to 95.2%). This phenomenon can be related to the presence of more permeable ions such as monovalent ions, which not only increases arsenate rejection, but also reverses sulfate effect [21].

In the case of monovalent anions, in individual salts the rejection sequence obtained is $R(\text{NaNO}_3) > R(\text{NaCl})$ whereas in groundwater it is $R(\text{Cl}^-) > R(\text{NO}_3^-)$. Wang et al. [52] and Paugam et al. [43] achieved the same results and they awarded higher chloride rejection to its higher hydration free energy respect to nitrate.

Nitrate rejection dramatically decreased with respect to individual salts in groundwater. Under all pressures, rejections were negative.

Table 3

Comparison of ion rejections in individual salt solutions and groundwater at 7 bar and 293 K. Ionic equivalents in groundwater feed and permeate (95% confidence interval; $n = 3$).

Component	R% (individual salt)	R% (groundwater)	mEq/L feed	mEq/L permeate (7 bar)
HCO_3^-	85	45.6	11.93	6.49
Cl^-	54.3	15.47	7.58	6.41
NO_3^-	53.8	-22.2	0.0145	0.02
F^-	78	40.21	0.29	0.17
SO_4^{2-}	99.5	100	6.56	-
HAsO_4^{2-}	97	95.2	0.003	-
Na^+	54.3	51.1	22.7	11.1
K^+	53.2	52.8	0.846	0.40
Mg^{2+}	23.8	73.7	3.0	0.79
Ca^{2+}	16.1	74.2	1.5	0.39

Other researches have obtained nitrate negative rejections in the presence of sulfate [45,52–54]. This is a classical behavior in nanofiltration when multivalent ions push more permeable univalent ions to pass through the membrane. This behavior can be explained by the Donnan effect, which predicts a higher impulse and even negative rejections when permeant/non permeant species relation is small (i.e. $\text{NO}_3^-/\text{SO}_4^{2-}$) as showed in Table 1 [10].

Multivalent cation rejections in groundwater are much stronger than monovalent cations, the inverse happened in individual salt solutions. In fact, in a high ionic strength environment, the ion's hydration radius and their free hydration energies earn importance. As a consequence, multivalent ions push more permeable monovalents to pass through the membrane in order to maintain electroneutrality in permeate. Nevertheless, in Table 3 it is showed that monovalent cation rejections slightly decreased with respect to the individual salt obtained values; this is so because of a high monovalent/divalent relationship, therefore this is not favorable for monovalent cation impulses. The described behavior reveals the ionic composition importance over ion rejection and transmission in the studied membrane. In fact, if it is observed, permeate ionic composition in mEq/L (Table 3), it shall be seen that the cation which has prominently passed through the membrane is sodium, representing the 95% of permeate cationic composition, and then magnesium which presents a 4.4%. At the same time, anions which have been carried the most through the membrane are bicarbonate and chloride in a 49.6 and a 48.9% respectively, in relation to anionic composition.

3.4. Comparison between arsenic rejection in naturally contaminated groundwater (Gw1) and artificially contaminated natural groundwater (Gw2)

The studied system revealed the importance of the ionic composition over the membrane ion rejections. In order to investigate the possibility to reproduce the obtained results, natural groundwater was contaminated with 409 $\mu\text{g/L}$ As(V).

Table 4 shows the arsenic rejection from Gw2. Basically Gw2 presents a lower ionic strength and a minor relative equivalent fraction of sulfate with respect to other present ions than Gw1. Efficiency in HAsO_4^{2-} rejection in Gw2 was slightly superior to rejection in Gw1. The major rejection can be associated on one hand, to a membrane higher density, and therefore a major Donnan exclusion; and on the other hand, it can be related to a lower sulfate (SO_4^{2-}) ions concentration.

4. Conclusions

The purpose of this research has been to study As(V) removal from naturally contaminated groundwater with an NF pilot plant operating in cross flow mode, and using a negatively charged membrane.

The integral evaluation of the NF process in one single stage at 10 bar and at 293 K shows a HAsO_4^{2-} rejection over 95% and a total SO_4^{2-} rejection. Divalent Ca^{2+} and Mg^{2+} ion rejections happened to be an 81% reduction from total hardness. Total dissolved solids (TDS) concentration decreased to 53%. Permeate composition mostly impli-

Table 4

Artificially contaminated natural groundwater composition, ion rejections (at 7 bar and 293 K) and anion equivalent fractions in feed. E.C. was 441 $\mu\text{S/cm}$, TDS were 298 mg/L, TOC was 0.18 mg/L, SDI <1 and pH was 8.5 (95% confidence interval; n = 3).

Component	ppm	R% (Gw2)	Equivalent fraction of anions
HCO_3^-	198	61.2	0.786
Cl^-	15.44	18.3	0.105
NO_3^-	1.7	-23.2	-
F^-	1.1	53.2	0.015
SO_4^{2-}	17	100	0.087
HAsO_4^{2-}	0.409	96.0	-

cates sodium, chloride and bicarbonate in concentrations which don't produce any problem. Moderate monovalent ion rejections contributed to membrane hydraulics stability.

Arsenic rejection as HAsO_4^{2-} in aqueous environments containing nine coexistent ions (SO_4^{2-} , HCO_3^- , F^- , Cl^- , NO_3^- , Ca^{2+} , Mg^{2+} , K^+ , and Na^+) was ruled by Donnan exclusion combined with preferential passage of the most permeable ion. In spite of its low concentration, HAsO_4^{2-} separation increases in presence of more mobile ions such as HCO_3^- , F^- , Cl^- and NO_3^- which compensates the decrease exerted on its rejection by a less movable ion such as SO_4^{2-} .

From the comparison between ion rejections in individual salt solutions and in a multicomponent mixture such as groundwater, for the studied system it is concluded that:

- i) Multivalent co-ions maintain their rejections. Electrostatic repulsion decrease due to a membrane charge screening by a higher ionic strength is compensated by a more permeable monovalent co-ions preferential passage through the membrane. The effect magnitude depends on permeable/non permeable species relationship.
- ii) Monovalent co-ions decrease their rejection due to an electrostatic repulsion diminution by a higher ionic strength. Hydrated radius and specially ion hydration layer strength, increase their influence and determine the rejection; monovalent/multivalent relationship influence, although small, isn't worthless.
- iii) Multivalent counter-ions increase their rejection due to monovalent counter-ions preferential passage, in order to fulfill electroneutrality requirements in permeate. Hydration radius and hydration free energy influence acquire predominance in a high ionic strength environment. Monovalent counter-ion rejection diminution will depend on permeable/non permeable relationship respect to multivalent ions.
- iv) Monovalent ion composition in permeate is related to its composition in feed.
- v) In multicomponent solutions, membrane rejection can be significantly different to those cases where only an individual salt is present; so the complexity of making predictions a priori on selectivity is demonstrated.

In arsenic removal from artificially contaminated groundwater and constituted by the same components than naturally contaminated groundwater, membrane showed the same selectivity.

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