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Gonzalez, Bayardo; Heijman, S. G.J.; Rietveld, L. C.; van Halem, D.

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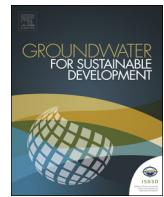
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Research paper

As(V) rejection by NF membranes using high temperature sources for drinking water production



Bayardo Gonzalez*, S.G.J. Heijman, L.C. Rietveld, D. van Halem

Delft University of Technology, Faculty of Civil Engineering and Geosciences, Stevinweg 1, 2628 CN Delft, the Netherlands

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ABSTRACT

In Nicaragua, a Central American country, geothermally influenced waters are frequently found to be contaminated with arsenic (as As(V)). This study investigated the effect of high-temperatures (25–50 °C), as found in geothermally influenced source waters, on the rejection of monovalent $H_2AsO_4^-$ and divalent $HAsO_4^{2-}$ species (at pH 6,7 and 8) during NF membrane filtration of a multi-component solution containing Cl^- and HCO_3^- . In this multi-component solution, As(V) rejection was found to be enhanced at higher temperatures, which was in contrast to the previous assumption that temperature increase would have a negative effect on As(V) rejection. Previous studies were conducted with deionized waters, where pore size expansion and decreased viscosity drove As(V) rejection; however, in the presence of other anions such as those utilized in this study, As(V) rejection was promoted at higher temperatures. The enhancement of As(V) rejection at high temperature was associated with the presence of HCO_3^- and Cl^- , which are considerably more permeable than both As(V) species. An additional advantage of the higher temperature was the lower feed pressure (down to 1.5 bar) needed to operate these NF membranes, compared to colder waters. The lower energy consumption in combination with the improvement in As(V) rejection at higher temperatures shows the potential application of this technology for efficient treatment of As(V) contaminated, geothermally influenced waters for decentralised, rural drinking water production, in As-affected countries such Nicaragua.

1. Introduction

Geothermal systems are known to be a source of arsenic (As) contamination since geothermal fluids are responsible for transporting As and heavy metals, contaminating both surface water and groundwater (Webster and Nordstrom, 2003). These geothermally influenced waters may have high As concentrations in combination with high temperatures (Ravenscroft et al., 2009; Smedley and Kinniburgh, 2002). The contamination of water sources by geothermal As has been reported around the world in locations such as Waikato River in New Zealand (McLaren and Kim, 1995) and Eastern Sierra Nevada in the USA (Wilkie and Hering, 1998).

In Latin America, geothermal As has been recognized mainly in the Pacific region and is usually associated with the active volcanism (Lopez et al., 2012) of the Pacific Ring of Fire. Geothermally influenced waters often present elevated temperatures (above the background) (Ravenscroft et al., 2009). In Nicaragua, a Central American country, drinking water sources with high temperatures and high As concentration has been identified in scattered rural communities in the municipality of Telica (Fig. 1 and Fig. 2) (OPS/OMS and Nuevas

Esperanzas, 2011), located in the Pacific region of the country where Quaternary volcanism is concentrated (McBirney and Williams, 1965).

The shallow alluvial aquifer of this area is influenced by the hot fluids associated with active geothermal fields located in the volcanic chain of “Los Maribios.” Consequently, the water source tends to be dominated by high temperature (up to 50 °C; Fig. 2) and high levels of As concentrations (> 350 µg/L) (OPS/OMS and Nuevas-Esperanzas, 2011). The range of concentrations of the major anions and cations is as follows: Ca^{2+} (40–77 mg/L), Mg^{2+} (9–58 mg/L), Na^+ (100–320 mg/L), K^+ (6–26 mg/L), HCO_3^- (240–495 mg/L), SO_4^{2-} (25–340 mg/L) and Cl^- (146–250 mg/L) (OPS/OMS and Nuevas-Esperanzas, 2011). Fig. 2 provides an overview of the percentage of wells with As concentrations > 10 µg/L (WHO, 2001), illustrating the correlation between As contamination and elevated temperatures in these geothermally influenced sources. Although As-safe wells with colder water are available in the surroundings of these rural communities, it is found that due to practical (e.g., walking distance) and social (e.g., private wells) factors, approximately one thousand people have been drinking water contaminated with As for the past two decades (OPS/OMS and Nuevas-Esperanzas, 2011).

* Corresponding author.

E-mail address: B.J.GonzalezRodriguez@tudelft.nl (B. Gonzalez).

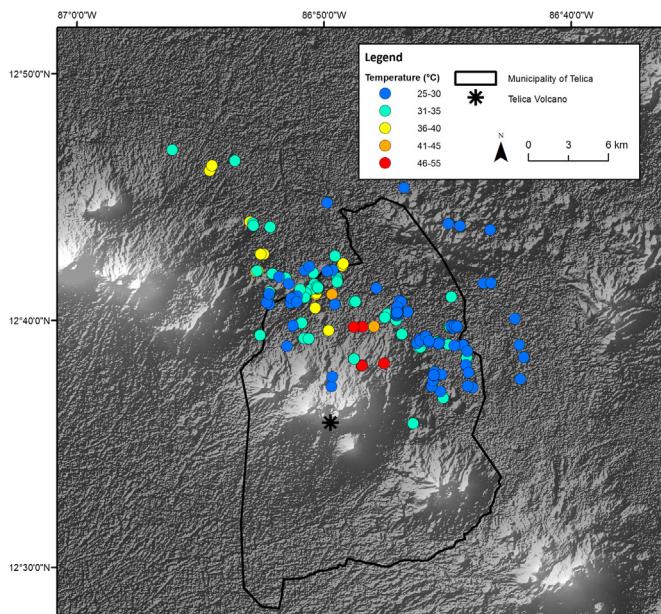


Fig. 1. Temperature of groundwater sources in the rural communities of Telica municipality. Adapted from OPS - OMS/Nicaragua - Nuevas Esperanzas (OPS/OMS and Nuevas-Esperanzas, 2011).

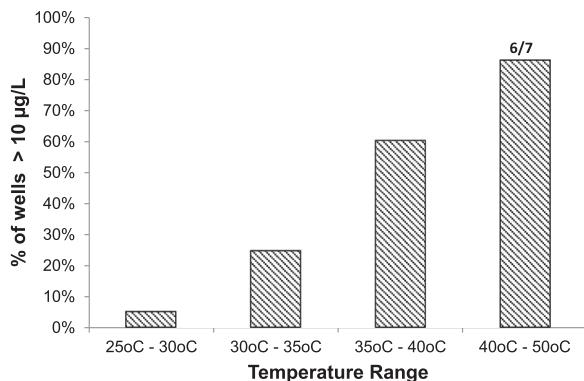


Fig. 2. Depicts the percentage of As contaminated wells $> 10 \mu\text{g/L}$ (WHO guideline) per temperature cohort. Adapted from OPS - OMS/Nicaragua - Nuevas Esperanzas (OPS/OMS and Nuevas-Esperanzas, 2011).

The As speciation in natural groundwater (pH 6.5–8.5) is mainly determined by redox potential (Eh) and pH (Smedley and Kinniburgh, 2002), leading either to As(III) or As(V) in the water. As(V) is a charged ion and is commonly found under oxidizing conditions. For a pH lower than 6.9, As(V) exists mainly as the monovalent H_2AsO_4^- species, and for a higher pH, the divalent HAsO_4^{2-} species is dominant (Smedley and Kinniburgh, 2002). On the other hand, As(III) is predominantly found under reducing conditions and as an uncharged ion when the pH is below 9.2 (Smedley and Kinniburgh, 2002). In geothermal fluids, the dominant species of As is the reduced form As(III). However, as geothermal water ascends to the surface and mixes with oxygenated water from shallow aquifers, it is oxidized to As(V) (Wilkie and Hering, 1998). Therefore, arsenic-contaminated drinking water sources in geothermally influenced waters are dominated by As(V) (Smedley and Kinniburgh, 2002; Van Halem et al., 2009).

For rural Nicaraguan communities exposed to geothermally influenced As contaminated drinking water sources, an As removal technology has to meet guidelines specific to resource-limited environments, such as restrictions regarding availability of electricity, spare parts and knowledgeable operators. To overcome the unavailability of electricity, this research paper examines the feasibility of treating hot

waters (with a temperature similar to those found in geothermally influenced waters $\sim 50^\circ\text{C}$) with a low pressure nanofiltration (NF) membrane, aiming to rely on the naturally available elevation in these volcanic areas for membrane pressure. Due to pore expansion and decreased viscosity, the high water temperature will be favorable for low-pressure operation; however, this might have a negative effect on the rejection of As(V) (Figoli et al., 2010). Polyamide negatively-charge NF systems have consistently demonstrated a high efficiency for the removal of As(V) from water with ambient temperatures (Harisha et al., 2010; Urase et al., 1998; Vrijenhoek and Waypa, 2000), and it is known from industrial applications that NF is capable of treating water at temperatures up to 65°C (Mänttäri et al., 2002). The influence of high temperatures has been identified as responsible for the deterioration of the NF rejection for different solutes such as trace organic contaminants (TrOCs) (Dang et al., 2014), Cl^- (Ben Amar et al., 2009) and As (Figoli et al., 2010). Scientific literature related to the use of NF membranes to remove As from high temperature waters is scarce. Figoli et al. (2010) worked with temperatures ranging from 15°C to 40°C , using distilled water spiked with As(V) ($100 \mu\text{g/L}$) and two types of membranes (NF90 and N30F). When temperature increased from 15°C to 40°C , the rejection efficiency diminished by 2.3% for NF90 and 11% for N30F membranes. This study attributes the decline in As(V) rejection as a consequence of the increase in the diffusive transport of As(V) across the membrane. Nevertheless, the mentioned research did not consider the influence of co-occurring ions. Furthermore, the influence of co-occurring ions on the rejection of As(V) species during nanofiltration have only been studied at 25°C . These earlier works (Nguyen et al., 2009; Vrijenhoek and Waypa, 2000) conducted at 25°C reported that in a multi-component solution (containing Cl^- , HCO_3^- and SO_4^{2-}), the rejection of As(V) species could be enhanced or decreased by the presence of co-occurring anions. Nevertheless, the influence of co-occurring ions on the rejection of As(V) during NF filtration of high temperature water has not been previously studied. With our research, we intend to fill this knowledge gap. Therefore, the objective of this study was to demonstrate the effect of high temperature (up to 50°C) waters on NF membrane filtration with regard to transmembrane pressure, pore size (molecular weight cut-off), rejection of major anions (Cl^- and SO_4^{2-}) and, specifically, the rejection of monovalent H_2AsO_4^- and divalent HAsO_4^{2-} species (at pH 6.7 and 8) during NF membrane filtration of a multi-component solution containing Cl^- and HCO_3^- . The research consisted of experimental research with a flat-sheet cross-flow module in order to identify proof-of-principle for future pilot-scale research in rural Nicaragua. With consideration of the intended implementation setting, membranes were operated at a lower recovery of 10%, as this would generate a concentrate flow with sufficiently low As content that could be used by local villagers for daily activities such as washing and bathing.

2. Material and methods

2.1. Experimental set-up

The experiments were conducted using a flat-sheet cross-flow module, as illustrated in Fig. 3. The experimental setup was operated as a closed circuit system with a feed water tank containing 50 L of solution. To avoid heat exchange with the environment, the feed tank was wrapped with heat insulation material (Aluminum Foil Air Bubble Heat Insulation Sheet). Prior to the start of the experiments, overhead stirrers (Heidolph RZR 2020, Heidolph Instruments GmbH & Co, Germany) were utilized for a period of 4 h to guarantee the homogeneity of the solution. During this time, the solution was heated to the desired temperature (25°C or 50°C). The temperature of the solution was controlled by a recirculating thermostatic bath (TC 16, Tamson Instruments B.V, NL), which was connected to a heat exchanger (coil) submerged in the solution. After this stage, the feed water was pumped, using a rotary (vane positive) displacement pump (Fluid-o-Tech s.r.l.,

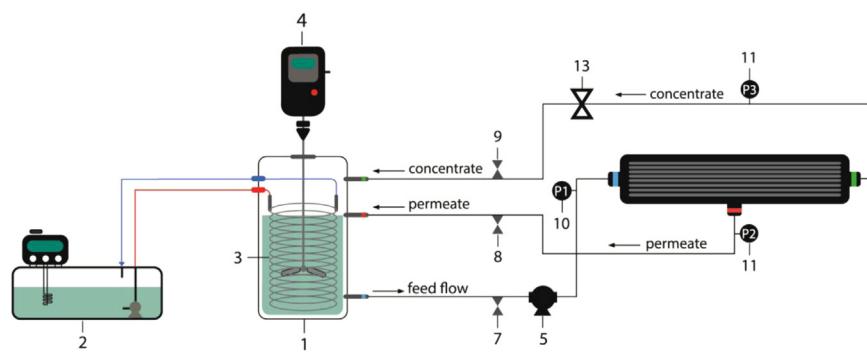


Fig. 3. Schematic representation of experimental setup. 1. Feed water tank, 2. Thermostatic bath, 3. Heat exchanger, 4. Overhead stirrer, 5. Pump, 6. Membrane module, 7. Sampling point – feed water, 8. Sampling point – permeate, 9. Sampling point – concentrate, 10. Pressure gauge – feed, 11. Pressure gauge – permeate, 12. Pressure gauge – concentrate, 13. Concentrate valve.

Italy), from the tank into stainless steel plates containing the NF membrane. The active area of the rectangular flat sheet NF membrane inside the metallic plates was 0.25 m^2 . The solution was filtered through the membrane for two hours to achieve stabilization of the rejection and to reach thermal equilibrium between the solution and flat-sheet cross-flow module. At the end of the preliminary filtration cycle, the rejection experiments began. The pressure in the feed, permeate, and concentrate line was monitored with a pressure gauge (En 837-1, Econosto, NL). Sampling of the feed, permeate, and concentrate was performed at both the middle and the end of each filtration cycle.

2.2. NF membranes and solutions

Two commercially available NF polyamide membranes were used. The specifications given by the respective manufacturers indicate that Dow NF270 (DOW FILMTEC™) has a molecular weight cut-off (MWCO) ranging between 200 and 400 Da and a recommended maximum operating temperature of $45\text{ }^\circ\text{C}$. Nevertheless, due the relatively short duration of the experiment, we decided to exceed the maximum recommended temperature. The second membrane from Alfa Laval NF (Alfa Laval) has a MWCO of 300 Da and a maximum operating temperature of $55\text{ }^\circ\text{C}$. In general, polyamide membranes are negatively charged for the tested pH range (between 6 and 8) (Bellona and Drewes, 2005; Boussu et al., 2006; Childress and Elimelech, 2000; Nguyen et al., 2009).

A standard stock solution of 1 g/L of As(V) was prepared using $\text{Na}_2\text{HAsO}_4\cdot 7\text{H}_2\text{O}$ (Sigma-Aldrich) dissolved in deionized water and acidified (pH 3) using 1.6 M HCl (Sigma-Aldrich). The solution, used in all As(V) rejection experiments, was kept in an aluminum foil-covered glass container and refrigerated ($5\text{--}8\text{ }^\circ\text{C}$). The individual salt rejection experiments were carried out with monovalent (NaCl ; VWR Chemical) and divalent (Na_2SO_4 ; Sigma-Aldrich) salts. To obtain the desired As(V) concentration of $300\text{ }\mu\text{g/L}$ ($0.004\text{ mM H}_2\text{AsO}_4^-/\text{HAsO}_4^{2-}$), the stock solution was diluted in demineralized water. To ensure the buffering capacity of the water matrix, NaHCO_3 (Sigma-Aldrich) was dosed. According to the requirements of the experiments, 1.6 M HCl (Sigma-Aldrich) or 0.1 M NaOH (Sigma-Aldrich) was employed for pH adjustment.

2.3. Effect of temperature on MWCO

The determination of MWCO for Dow NF270 and Alfa Laval membranes was carried out at $25\text{ }^\circ\text{C}$ and $50\text{ }^\circ\text{C}$. The solution used for the determination of MWCO was prepared using ethylene glycol (62 g/mol) and different polyethylene glycols (PEGs) with molecular weights ranging from 200 to 1000 g/mol (Sigma-Aldrich). The experiments were performed at constant flux ($30\text{ L/m}^2\text{ h}$) and a recovery of 15%. Samples of the feed permeate and concentrate were taken every 3 h. MWCO was measured by filtering the ethylene glycol /PEGs mixture and measuring the rejection with HPLC-GPC (Shimadzu) with RI-detection.

2.4. Transmembrane pressure (TMP) and temperature using demineralized water as feed solution

The relation between transmembrane pressure (TMP) and temperature ($25\text{ }^\circ\text{C}$ and $50\text{ }^\circ\text{C}$) was determined for Dow NF270 and Alfa Laval. Demineralized water was used as feed solution. The experiments were conducted at constant flux ($40\text{ L/m}^2\text{ h}$) (a cross-flow velocity of 0.15 m/s) and a recovery of 10%.

2.5. NF rejection experiments

Table 1 provides an overview of the experimental settings, membranes tested, and the water composition used for the NF rejection experiments. The rejection experiments were conducted at constant flux ($40\text{ L/m}^2\text{ h}$) (a cross-flow velocity of 0.15 m/s) and a recovery of 10%. All experiments were performed in duplicate and executed at both $25\text{ }^\circ\text{C}$ or $50\text{ }^\circ\text{C}$.

2.5.1. Rejection of Cl^- and SO_4^{2-}

Single solutions of monovalent (NaCl) and divalent (Na_2SO_4) salts were used to determine the individual rejection of Cl^- and SO_4^{2-} . The ionic strengths of the solutions were 1 mM for NaCl and 3 mM for Na_2SO_4 . Dow NF270 and Alfa Laval were used for these experiments.

2.5.2. Rejection of monovalent H_2AsO_4^- and divalent HAsO_4^{2-} species in the presence of NaHCO_3

Rejection of H_2AsO_4^- and HAsO_4^{2-} was evaluated by maintaining constant temperature ($25\text{ }^\circ\text{C}$ or $50\text{ }^\circ\text{C}$) and varying the pH (pH 8, 7 and 6) of the feed water. Samples were collected over 5 h of operation for each evaluated pH value. For each temperature, a series of three 5 h runs was executed, with the starting solution adjusted to pH 8 (0.1 M NaOH) and then corrected to pH 7 and pH 6 in the 2nd and 3rd run using HCl (1.62 M). Dow NF270 and Alfa Laval NF were used for these experiments.

2.6. Analysis of samples

Temperature, pH, and electrical conductivity of the feed water were measured using a multimeter (WTW GmbH, Germany). For the single solute rejection experiments of Cl^- and SO_4^{2-} , conductivity measurements of the feed and permeate were used to determine the rejection of both anions. The conductivity of the samples of the experiments carried out at $50\text{ }^\circ\text{C}$ was automatically converted into an equivalent conductivity at $25\text{ }^\circ\text{C}$. For the rejection experiments of $\text{H}_2\text{AsO}_4^-/\text{HAsO}_4^{2-}$, the concentrations of HCO_3^- and Cl^- were determined using titrimetric (702 SM Titrino, Metrohm) and ion chromatography analysis (IC - 883 Basic/Plus, Metrohm), respectively.

For the analysis of As(V), the samples from the feed, permeate, and concentrate were acidified using 1.7 ml of HNO_3 (22%) per 330 ml of sample. The concentration of As(V) in the samples was analyzed using inductively coupled plasma mass spectrometry (ICP-MS Thermo –

Table 1
Overview of NF rejection experiments.

Experimental settings	pH	NF tested	Water matrix composition
Rejection of Cl^- and SO_4^{2-}	6	Dow NF270 and Alfa Laval	Demineralized water + 1 mM NaCl/1 mM Na_2SO_4
Rejection of monovalent H_2AsO_4^- and divalent HAsO_4^{2-} species from buffered water	6,7 & 8	Dow NF270 and Alfa Laval	Demineralized water + 0.004 mM (300 $\mu\text{g/L}$) H_2AsO_4^- / HAsO_4^{2-} + 1 mM NaHCO_3 + HCl/ NaOH

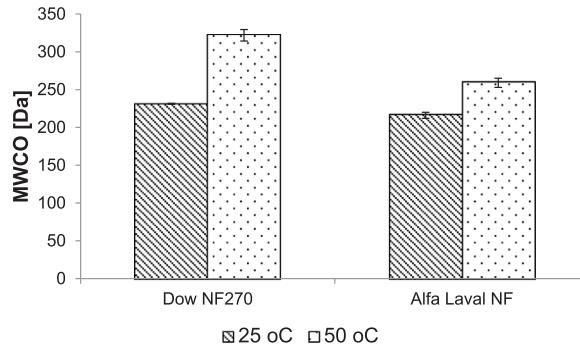


Fig. 4. Variation of the MWCO with temperature (25 °C and 50 °C) for Dow NF270 and Alfa Laval NF.

XSERIES II, Thermo Fisher Scientific). The method is equivalent to NEN-EN-ISO 172941-2 and can be applied to drinking, surface, process and groundwater.

3. Result and discussion

3.1. Effect of temperature on MWCO

Fig. 4 summarizes the effect of temperature increase on MWCO for Dow NF270 and Alfa Laval. An increase of 39% (from 231 Da to 322 Da) and 20% (from 217 Da to 260 Da) in MWCO was observed for Dow NF270 and Alfa Laval NF, respectively, as a result of temperature increase (from 25 °C to 50 °C). The larger increase in MWCO was found for Dow NF270 compared to Alfa Laval NF. The suggestion that pore size of the NF membranes is larger at 50 °C agrees with earlier findings that for mono-component solutions, rejection is lower at higher temperatures.

3.2. Transmembrane pressure (TMP) and temperature using demineralized water as feed solution

The relation between temperature (25 °C and 50 °C) and TMP is depicted in Fig. 5 for a constant flux of 40 L/m²h. Temperature and pressure had an inverse relationship, i.e. an increase in temperature

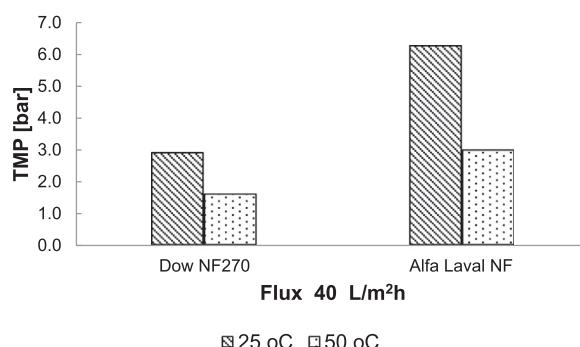


Fig. 5. TMP in bar evaluated as a function of a constant flux (40 L/m²h) and different temperatures (25 °C and 50 °C). Demineralized water was used as feed solution.

resulted in a lower transmembrane pressure. For both membranes, the transmembrane pressure at 50 °C was approximately 50% of the transmembrane pressure at 25 °C. For both temperatures, Dow NF270 needed lower transmembrane pressures than Alfa Laval NF to produce the same flux. The low operating pressure required by Dow NF270 at 50 °C (15 mwc) in combination with the elevated topography found in Nicaragua's volcanic region may make it feasible to operate the system without a pump (i.e. gravity-fed NF system).

For both membranes, the reduction in transmembrane pressure could be associated to both the decrease in water viscosity and the expansion of the effective pore diameter due to increased temperature. The difference between the two tested membranes could be associated with their different physical properties (i.e., pore size, thickness, tortuosity).

3.3. Rejection of Cl^- and SO_4^{2-}

Fig. 6 depicts the single solute rejection of Cl^- (left) and SO_4^{2-} (right) at 25 °C and 50 °C. The rejection of Cl^- (monovalent ion) was lower compared to SO_4^{2-} (divalent ion) at both temperatures. This order in rejection was valid for both NF membranes and is in line with expectations for negatively charged NF membranes (Peeters et al., 1998). A considerable decrease in rejection was noted for the monovalent anion (Cl^-) as a consequence of the temperature increase (26% for Dow NF270 and 68% for Alfa Laval NF). On the other hand, the rejection of the divalent anion (SO_4^{2-}) was found to be less sensitive to temperature changes.

With the temperature increase (from 25 °C to 50 °C), the reduction of Cl^- rejection can be ascribed to changes in its thermodynamic and physical properties (e.g., increase in diffusivity, decreases in hydration free energy and hydrated radius) as well as to the diminishing size exclusion mechanism due to thermal expansion of the pore (Sharma et al., 2003). As a consequence, there was an increase in the diffusive transport of Cl^- across the membrane layer resulting from increased temperature (Brandhuber and Amy, 2001; J. Waypa et al., 1997). This effect was more significant for Cl^- compared to SO_4^{2-} because of its higher diffusivity, lower charge, lower hydrated radius and lower hydration free energy (Nightingale, 1959; Tansel, 2012), offering an explanation for the large decrease of the Cl^- rejection and the unaffected rejection of SO_4^{2-} .

A lower rejection of Cl^- and SO_4^{2-} was observed for Alfa Laval NF when compared with the rejection for DOW NF270, while the average pore size (at 25 °C and 50 °C) of Alfa Laval NF is smaller than DOW NF270. This could imply that aside from the size exclusion, the membrane charge and membrane material had a significant effect on the rejection, particularly for monovalent ions (Cl^-).

Nguyen et al. (Nguyen et al., 2009) tested As(V) concentration ranging from 20 to 100 $\mu\text{g/L}$, reporting an improvement in the rejection of H_2AsO_4^- (3–6%) and HAsO_4^{2-} (1–3%) when using deionized water + 10 mM NaCl as a background solution compared to the rejection values obtained when only deionized water was used. The same study noted a decrease in the rejection of H_2AsO_4^- (1–1.7%) and HAsO_4^{2-} (< 0.6%) when deionized water + 10 mM Na_2SO_4 was used as a bulk solution compared to the rejection values obtained when only deionized water was used. Vrijenhoek and Waypa (Vrijenhoek and Waypa, 2000) compared the effect of two background solutions on the rejection

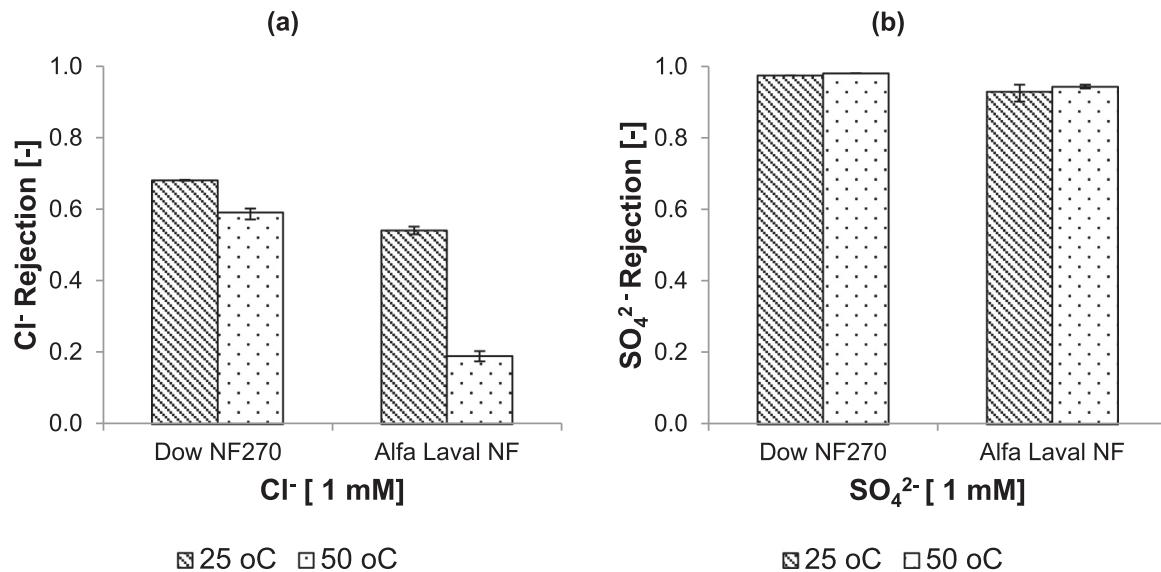


Fig. 6. Individual rejection of (a) monovalent anion (Cl^-) and (b) divalent anion (SO_4^{2-}) evaluated as a function of temperature (25 °C and 50 °C) at constant flux (40 L/m²h).

of a wide range of divalent arsenate concentrations (from 10 to 1000 $\mu\text{g/L}$). The first solution contained deionized water + 1 mM NaHCO_3 , and the second contained deionized water + 10 mM NaCl + 1 mM NaHCO_3 . In both cases, the rejection of HAsO_4^{2-} increased as a function of its concentration in the bulk solution. In general, a higher rejection was achieved during filtration of the solution containing NaCl and NaHCO_3 . This phenomenon has been ascribed to the relative “mobility or permeability” of the ions present in the bulk solution (Hodgson, 1970; Vrijenhoek and Waypa, 2000). The so-called “mobility or permeability” of the ion could be defined by the thermodynamic and physical properties (e.g., charge, diffusivity, hydrated radius and hydration free energy). For example, anions such as Cl^- and HCO_3^- (e.g., with smaller hydrated radius and smaller hydration free energy) compared to H_2AsO_4^- and HAsO_4^{2-} are considered more permeable (Binder and Zschörmig, 2002; Linde and Jönsson, 1995; Nightingale, 1959; Saitua et al., 2011; Stumm and Morgan, 2009; Tansel, 2012). The rejection of the more mobile anions is lower (e.g., Cl^- and HCO_3^-), and, because of the electro-neutrality that needs to be maintained in the feed solution, the rejection of the less permeable anions tends to be enhanced. In other words, the As(V) species tend to increase in the

presence of Cl^- and HCO_3^- .

3.4. Rejection of monovalent H_2AsO_4^- and divalent HAsO_4^{2-} species in presence of NaHCO_3

Fig. 7(a) shows that at 25 °C, the order of rejection of As(V) in the presence of NaHCO_3 for Dow NF270 was H_2AsO_4^- (pH 6) < HAsO_4^{2-} (pH 7 & 8), although there was only a slight difference (2%). At 50 °C, this rejection order was reversed, and the rejection of monovalent As(V) was equal or greater than that of the divalent As(V) at pH 7 and pH 8 ($\text{H}_2\text{AsO}_4^- \geq \text{HAsO}_4^{2-}$). However, the hierarchy in rejection of As(V) species for Alfa Laval NF was H_2AsO_4^- (pH 6) < HAsO_4^{2-} (pH 7 & 8) for both temperatures (Fig. 7(b)), i.e. divalent As(V) was better rejected than monovalent As(V). The degree of rejection for both As(V) species was higher at 50 °C than the rejection obtained at 25 °C for both membranes tested. Dow NF270 showed a rejection up to 0.97 and 0.93 for mono and divalent As(V), respectively, at 50 °C. At the same temperature, Alfa Laval presented a rejection of 0.86 for monovalent and 0.97 and 0.94 for divalent As(V).

At 25 °C, the As concentration in the permeate of both membranes

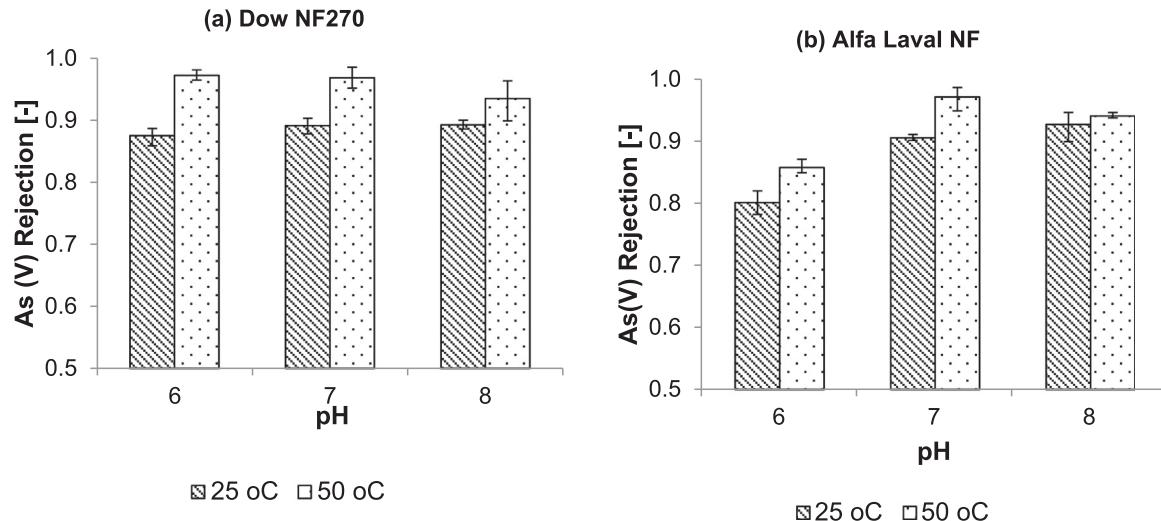


Fig. 7. Rejection efficiency of H_2AsO_4^- (pH 6) and HAsO_4^{2-} (pH 7 & pH 8) as a function of a constant temperature (25 °C or 50 °C). For (a) Dow NF270 and (b) Alfa Laval NF.

tested exceeded the WHO regulatory limit of arsenic in drinking water (10 µg/L). The As concentration in the permeate for Dow NF270 is close to 35 µg/L for the evaluated pH values, whereas the concentration in the permeate of Alfa Laval NF was around 57, 27 and 21 µg/L for pH 6, 7 and 8 respectively.

At 50 °C, the permeate quality is improved. Furthermore, for some of the evaluated pH values, the As concentration in the permeate was reduced to less than 10 µg/L for Dow NF270 (pH 6 and pH 7) and Alfa Laval NF (pH 7). Our results suggest that there is a restriction related with the maximum As(V) concentration that can be treated with NF, where NF systems seem most appropriate at As(V) concentrations below 300 µg/L.

An improvement in rejection of $H_2AsO_4^-$ and $HAsO_4^{2-}$ was achieved as the result of an increase in temperature. One would not expect this result based on the observed Cl^- and SO_4^{2-} rejection at higher temperatures, where a lower and an equal rejection were observed for these mono and divalent ions, respectively. Furthermore, previous work (Figoli et al., 2010) executed in deionized water showed a decline in the rejection of As(V) as a result of increased temperature. The difference between the cited research and our findings could be explained by the presence of HCO_3^- and Cl^- (used as a pH and ionic strength buffer in our study), which may have played a considerable role in the improvement of As(V) rejection. Earlier studies (Nguyen et al., 2009; Vrijenhoek and Waypa, 2000) conducted at 25 °C have shown that in a multi-component solution, the rejection of $H_2AsO_4^-$ and $HAsO_4^{2-}$ during nanofiltration could be influenced by the presence of co-occurring anions. Our results suggest that this phenomenon was temperature dependent, supporting the rejection of As(V) at higher temperatures. Anions such as Cl^- and HCO_3^- with an equal or lower valence, higher diffusivity, smaller hydrated radius and lower hydrated free energy are generally more permeable than $H_2AsO_4^-$ and $HAsO_4^{2-}$ (Nightingale, 1959; Padilla et al., 2010; Vrijenhoek and Waypa, 2000). As temperature increases, the permeability or mobility of Cl^- and HCO_3^- also increases. In addition, due to friction forces originating during nanofiltration, Cl^- and HCO_3^- (with lower hydration free energy) decrease their hydrated radius (Tansel, 2012). Because of the inverse relationship between the hydration free energy with temperature, the hydrated radius of Cl^- and HCO_3^- decrease as the temperature increases. This characteristic in combination with the enlargement of the pore size and the increase in the mass transfer across the membrane due to the temperature effect enhanced the permeation of Cl^- and HCO_3^- ; correspondingly, the rejection of the less permeable As(V) species increases because of electro-neutrality that needs to be maintained in the bulk solution. Therefore, Cl^- and HCO_3^- permeation had a beneficial effect on the rejection of As(V) species, and this effect was enhanced as temperature increased.

In natural waters, other anions will also interact with As(V) and thus may affect the rejection efficiency of the membranes. This study is a first step towards understanding As(V) rejection at higher temperatures, but further research will be required to elucidate the mechanism of As(V) rejection in the complex, natural water quality matrices in Nicaraguan geothermal waters.

4. Conclusions

At 50 °C, the transmembrane pressure required to operate the NF membranes was on average 50% lower than at 25 °C. This can be explained by the decreased viscosity of the water and the expansion of membrane pores (MWCO) at higher temperatures. The operational pressure for Dow NF270 at 50 °C was 1.5 bar (15 mwc), making it suitable for the use of natural elevation in volcanic areas, therefore not requiring electricity for operation. Depending on the pH tested, the As (V) concentration in the permeate was either slightly below (9 µg/L) or above (21 µg/L) the WHO regulatory limit in drinking water (10 µg/L), which indicates that there are restrictions related with the maximum As (V) concentration to be treated with NF.

It was found that at the higher temperature the rejection of both

monovalent $H_2AsO_4^-$ and divalent $HAsO_4^{2-}$ species increased. This finding differs from previous work where the As(V) rejection from deionized water showed a decline as a consequence of temperature increase. The presence of more permeable anions, HCO_3^- and Cl^- , may have been responsible for enhanced As(V) rejection. The interaction between ions (as will also be present in natural waters in Nicaragua) apparently counteracts the effect of increased pore size, resulting in enhanced As(V) rejection at higher temperatures.

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