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Arsenic removal from geothermal influenced groundwater with low pressure NF pilot plant for drinking water production in Nicaraguan rural communities

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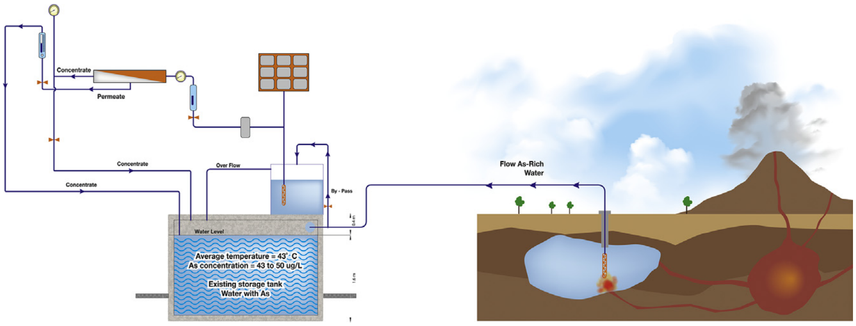
HIGHLIGHTS

- A NF pilot plant powered by solar panels was built and operated in rural community.
- As-rich (45 μg/L) water source due to geothermal influences was treated with NF.
- Low operating pressures (1.2 bar) produced high rejection of As (V) (0.87–0.9) at 43 °C.
- The permeate concentration (~5 μg/L) complied with the WHO guideline for drinking water.

GRAPHICAL ABSTRACT



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ABSTRACT

This research evaluated the effect of different fluxes (16, 23 & 30 L/m^2 h) and temperatures (31,35 & 43 °C) on the rejection of As(V) during nanofiltration (NF) of natural geothermal influenced groundwater in Nicaragua. A NF pilot plant powered by solar panels was built and operated in rural community Telica, exposed to As-rich drinking water sources due to geothermal influences. The results showed that even at high temperatures it is possible to obtain high rejection of As(V) (0.87–0.9) during NF filtration (recovery 10%; flux 16 L/m^2 h) of geothermal influenced groundwater, with the additional advantage of requiring low operating pressures (1.2 bar ~ 12mwc). The permeate concentration (~5 μg/L) complied with the WHO guideline for drinking water and the concentrate (~55 μg/L) could be used by local villagers for daily activities (e.g., laundry and bathing). For all investigated fluxes and temperatures the order of rejection of As(V) (as $HAsO_4^{2-}$), compared with the other anions, could be interpreted on the basis of its charge, hydrated radius and hydration free energy. At lower temperatures (31 and 35 °C) permeate quality improved slightly (~3 μg/L), but although an increased temperature had a negative effect on the As rejection, As concentrations in the permeate never exceeded 5 μg/L, while the required TMP dropped - depending on the flux - with 0.5 to 1 bar. This decrease in required pressure might be of huge benefit in deserted, rural locations where electricity is scarce, as with an overhead tank of 10–15 m a gravity-fed NF system would be feasible.

1. Introduction

Arsenic (As) rich drinking water sources have been identified in Nicaraguan rural communities in a geothermally active area near the

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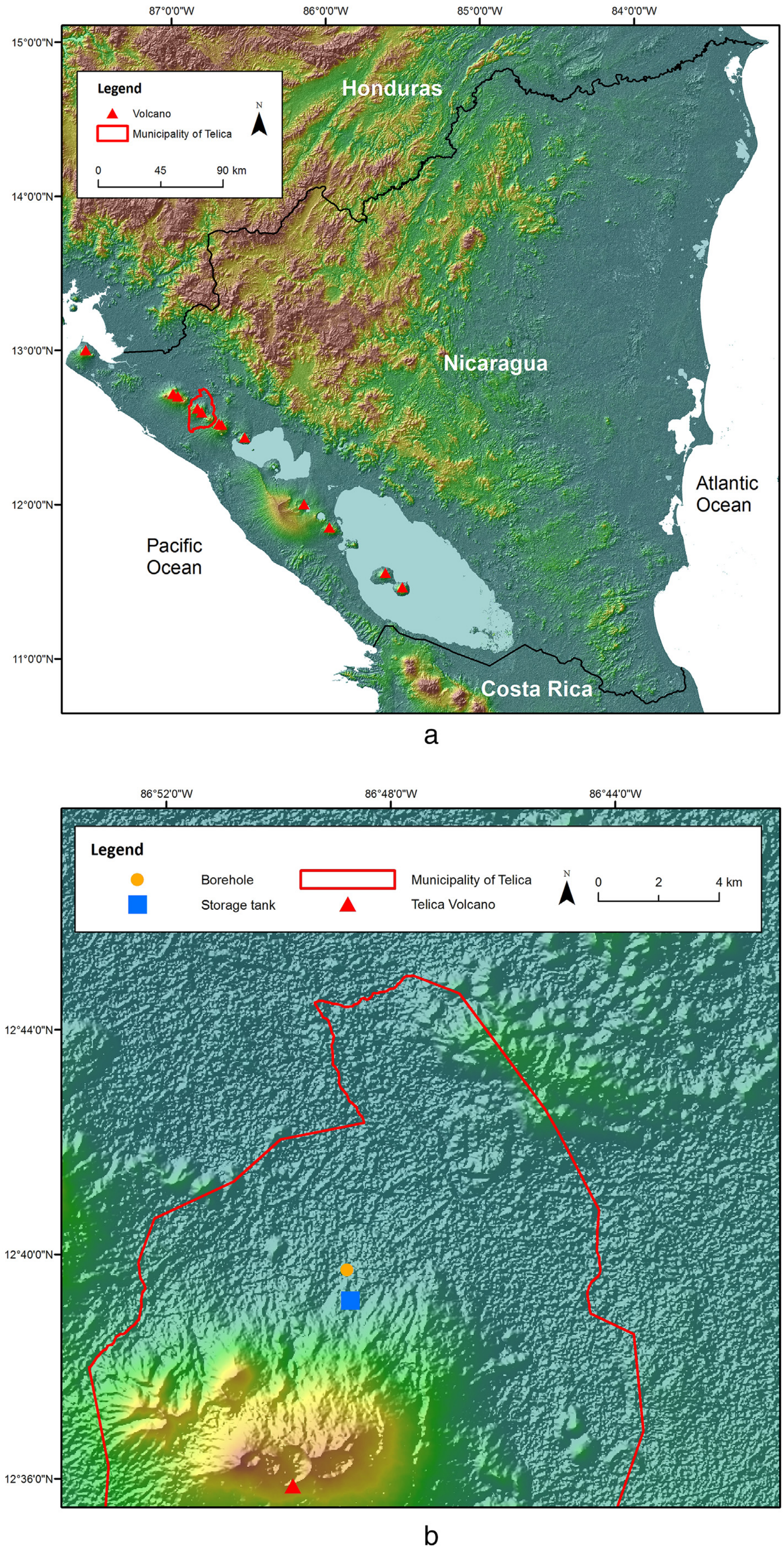


Fig. 1. (a) Location of the municipality of Telica. (b) Location of borehole and storage tank.

volcanic chain of "Los Maribios" (Longley, 2010). Hot, As-rich fluids flow from a geothermal zone mixed with the groundwater in the shallow alluvial aquifer causing locally variable well contamination (OPS/OMS and Nuevas-Esperanzas, 2011). The groundwater in this region has a temperature higher than 30 °C with some sources that can exceed 40 °C (Longley, 2010; OPS/OMS and Nuevas-Esperanzas, 2011). As-rich drinking water sources in geothermal influenced waters is likely to be dominated by charged As(V) species (Smedley and Kinniburgh, 2002).

Several arsenic removal technologies for drinking water production have been proposed for developing countries, i.e. precipitation, adsorption and membrane filtration (Jiang, 2001; Kabir and Chowdhury, 2017). Although adsorption technologies have shown high efficiencies (90 to 100%) in As removal for drinking water production (Kabir and Chowdhury, 2017), precipitation processes (e.g. through alum or iron coagulation) are not always appropriate to produce drinking water with As concentrations below the WHO guideline of 10 μg/L (Kabir and Chowdhury, 2017). Also, precipitation and adsorption processes are pH dependent and could be influenced by co-occurring contaminants (Jiang, 2001; Kabir and Chowdhury, 2017; Ng et al., 2004). Furthermore, both processes could lead to the production of As-containing wastes (Jiang, 2001; Kabir and Chowdhury, 2017; Ng et al., 2004). Among the membrane technologies, reverse osmosis (RO) and nanofiltration (NF) show the highest efficiency (90–99%) in arsenic removal (J. Waypa et al., 1997; Jiang, 2001; Ng et al., 2004; Padilla and Saitua, 2010). An important advantage of membrane technology is that the efficiency removal of arsenic does not depend on the composition of the water matrix or the pH (Ng et al., 2004; Sato et al., 2002).Furthermore operated at low recovery the waste streams could be used for daily activities (e.g. laundry and bathing). The lower operational pressure of the NF (<10 bar) compared with RO (>20 bar) (Jiang, 2001; Kabir and Chowdhury, 2017; Ng et al., 2004; Padilla and Saitua, 2010; Saitúa et al., 2005) make NF systems a better choice for arsenic removal in developing countries.

Nanofiltration (NF) systems have shown to have a high efficiency (above 90%) for As(V) removal, demonstrated in experimental research at bench scale (J. Waypa et al., 1997; Padilla and Saitua, 2010; Saitúa et al., 2005) and at on-site pilot plants (Oh et al., 2000; Saitua et al., 2011). These experiments have been conducted in a range of temperatures between 10 °C to 30 °C and with operating pressures ranging from 2 to 7 bar. As the temperature of the water source increases, a lower energy consumption is required during nanofiltration. This feature can be of great advantage in rural areas where there is no reliable energy supply system, but where the As-rich water sources have high temperatures.

The rejection efficiency of NF mainly relies on two mechanisms: size exclusion and Donnan exclusion. Size exclusion depends on the ratio between the ion size and the pore radius of the membrane, i.e. ions with a size larger than the pore size are more likely to be rejected by the membrane. On the other hand, the Donnan exclusion refers to the reciprocal action between the surface charge of the membrane and the charge of the ions present in the bulk solution (Bowen et al., 1997). In a negatively charged membrane, the Donnan exclusion mechanism determines the distribution of the co-ions (anions; same charge as the membrane) between the bulk and the membrane phase. Moreover, the concentration of the co-ions in the membrane usually shows a direct relationship with its rejection, i.e. the higher the concentration of the co-ions in the membrane, the lower their rejection (Peeters et al., 1998). The concentration of co-ions in the membrane phase depends on variables such as the valence and concentration of the co-ions and counter-ions (cations, different charge as the membrane), present in the solution, and the charge of the membrane (Peeters et al., 1998; Schaep et al., 1998).

Thus, the properties of the bulk solution, such as ionic strength and temperature, influence the permeability of the ions through the NF membrane. Furthermore, thermodynamic and physical properties of the ions namely hydrated radius and hydration free energy (Favre-Réguillon et al., 2008; Tansel, 2012), have been pointed out to play an

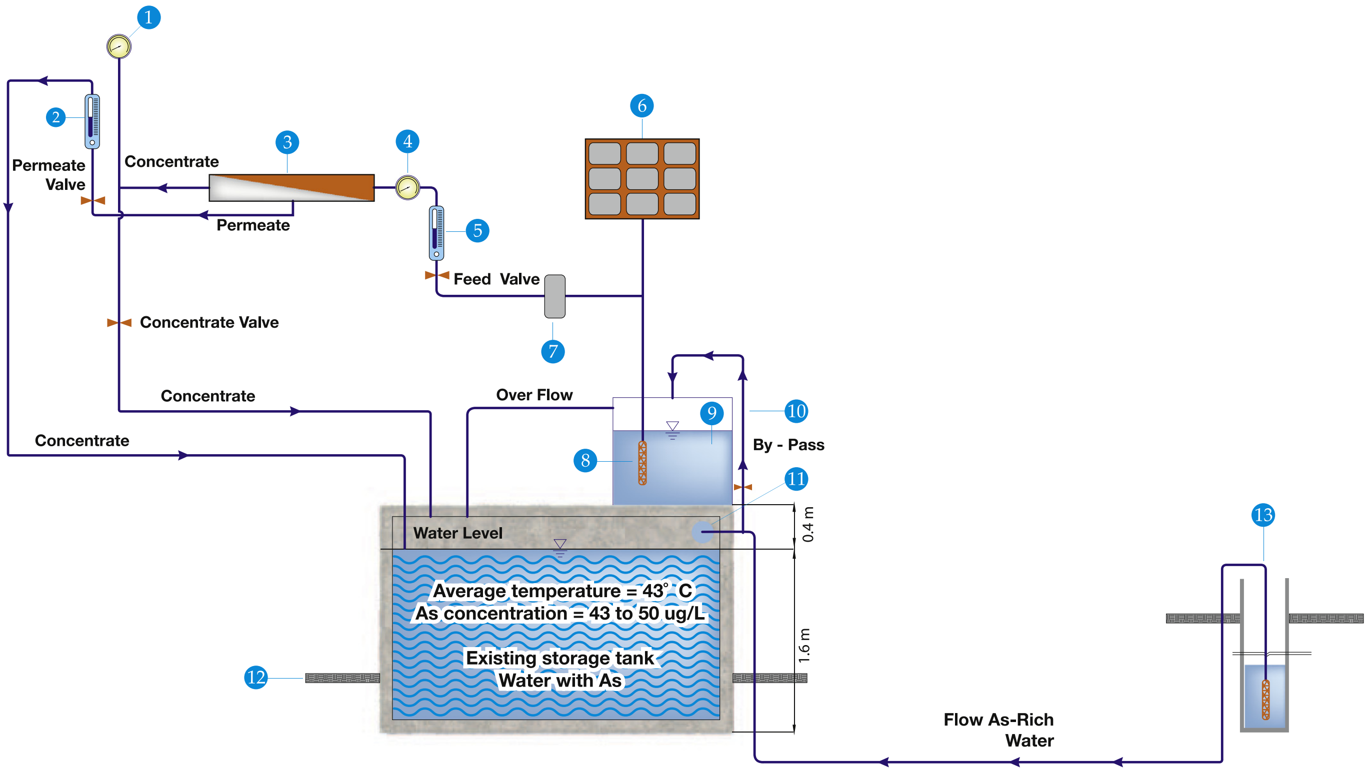


Fig. 2. Schematic representation of NF membrane filtration pilot unit. 1. Concentrate pressure meter, 2.Permeate flow meter, 3.Permeate valve, 4.Concentrate valve, 5.Membrane unit, 6. Feed pressure meter, 7. Feed flow meter, 8. Feed valve, 9. Solar pump, 10. Solar panels, 11. Buffer tank, 12. By-pass line, 13. Water entrance, 14.Existing As-rich well.

Table 1
Overview of pilot plant NF rejection experiments.

Experimental settings	Average temperature	Q feed (m^3/h)	Q permeate (L/min)	Flux (L/m^2h)	Recovery
Operation of NF pilot plant at a constant flux and temperature	43.6 °C	0.4	0.7	16	10%
Operation of NF pilot plant at different fluxes and temperatures	31 °C 35 °C 43 °C	0.4	0.7, 1 & 1.3	16, 23 & 30	10, 15 & 20%

important role in the rejection of the ions during NF filtration. As the temperature increases (in the bulk solution), a weakening of the size exclusion mechanism occurs due to thermal expansion of the pore (Dang et al., 2014; Gonzalez et al., 2019; Sharma et al., 2003), in addition to an increase in diffusive transport of the ions across the membrane layer (Brandhuber and Amy, 2001; J. Waypa et al., 1997), potentially leading to a lower As rejection.

Therefore, to determine the effect of the properties of geothermal influenced groundwater on As rejection, the objective of this paper is to investigate the performance of low-pressure NF membranes for various temperatures and fluxes. For this work, a NF pilot plant was built and operated in a Nicaraguan rural community exposed to As-rich drinking water sources due to geothermal influences. The NF pilot plant was operated during 6 to 7 h per day and was powered by solar panels in order to be able to be operated in remote areas. A low recovery of 10%, was chosen to operate the NF pilot plant, producing a concentrate flow with a relatively low As content that can be used by local villagers for other daily activities (e.g. laundry and bathing.) To the best of our knowledge, pilot studies regarding the NF application for As removal in natural geothermally influenced waters have not been reported earlier.

2. Material and methods

2.1. Location

The chosen rural community is located in the western part of the country (Fig. 1 (a)), north of the active Telica volcano (Longley, 2010). In 2007, it was discovered that well (Fig. 1 (b)) that supplies water to this community has an arsenic (As) concentration exceeding the WHO guideline of 10 μg/L (Longley, 2010). Since 10 years, a dual water system provides As free drinking water with communal taps through one piped system, and a second piped system supplies the As contaminated water to household connections for other household activities. Two different water sources are used and stored in different reservoirs, located in the higher part of the community. The As free drinking water system is gravity-fed starting in the surrounding mountains, but the capacity is insufficient to meet the water demand of the community and is therefore used for drinking water and cooking alone.

The As rich water is pumped from a drilled water well and As concentrations in this well range from 43 to 50 μg/L, while temperature ranges from 43 °C to 50 °C. This water is used for other household activities such as washing, cleaning and bathing; and was the water source for the pilot plant in this study.

2.2. NF membrane filtration pilot unit

A NF membrane filtration pilot unit powered by solar energy was built and operated on site. The NF system was installed on the roof slab of the reservoir that stores the As rich water. The storage tank (40 m^3) was fed during the day with water pumped from the drilled well located one kilometer away. Consequently, this implies that there was a variation in the temperature of the stored water, as the tank was filling up during the day. The operation of the NF pilot plant was synchronized with the operational hours of the community pump. To keep the temperature constant in the feed water of the pilot a by-pass system was installed. This system consisted of a 2 m^3 plastic tank (feed tank), constantly fed (pumping hours) by the main pipeline (water from the well). The plastic tank had an overflow, which allowed having a constant fresh water supply, as illustrated in Fig. 2. The feed water was pumped into the NF system using a submersible solar pump (PS2–1800 HR-23-4, LORENTZ, Germany). The solar pump was powered by three solar panel units (TSM-260-PC, Trina Solar, USA). In order to remove solid particulate material from the feed water, a 5 μm carbon pre-filter was installed (ELGA VEOLIA) before the NF system.

The flow, entering the system, was regulated manually with a feed valve and monitored with a feed flow meter (HRV-3MC). A feed flow of 0.4 m^3/h was used. All the experiments were conducted with a Dow NF270–2540 (DOW FILMTEC ™), a negatively charged NF polyamide membrane. The specifications given by the manufacturer indicate that this membrane has an active area of 2.6 m^2 and a maximum

Table 2
Average natural groundwater composition of geothermally-influenced drinking water well.

Parameter	Units	Average values			CAPRE normative	
		43.6 °C	35 °C	31 °C	Recommended value	Maximum admissible value
pH		6.9	7.1	7.0	6.5–8.5	NG
ORP	mV	113.6	116.7	129.6		NG
Dissolved oxygen	mg/L	1.3	NM	NM		NG
Conductivity	μS/cm	830.0	793.3	774.0	400.0	NG
Temperature	°C	43.6	35.3	35.3	18–30	NG
Na^+	mg/L	66.2	71.0	69.9	25.0	200.0
K^+	mg/L	13.1	13.5	13.5	NG	10.0
Mg^{2+}	mg/L	14.1	14.3	13.7	7.3	12.2
Ca^{2+}	mg/L	61.6	62.2	60.9	40.0	NG
Cl^-	mg/L	134.4	138.4	122.7	25.0	250.0
HCO_3^-	mg/L	195.7	200.6	193.2		
SO_4^{2-}	mg/L	27.9	28.3	26.6	25.0	250.0
NH_4^+	mg/L	ND	ND	ND		0.5
Fe (total)	mg/L	0.15	NM	NM		0.3
Mn	mg/L	0.0	0.0	0.0		0.5
F^-	mg/L	0.4	0.4	0.4		0.7–1.5
Al	mg/L	0.1	0.0	0.1		0.2
Zn	mg/L	0.0	0.0	0.0		3.0
As (total)	μg/L	42.6	42.1	43.2		10
As (V)	μg/L	40.0	NM	NM		
As (III)	μg/L	2.6	NM	NM		
Cd	mg/L	0.0	0.0	0.0		0.05
Cr	mg/L	0.0	0.0	0.0		0.05
Ni	mg/L	0.0	0.0	0.0		0.05
Pb	mg/L	0.0	0.0	0.0		0.01
Sb	mg/L	0.0	0.0	0.0		0.05
Se	mg/L	0.0	0.0	0.0		0.01
B	mg/L	1.5	1.4	1.4		NG
Si	mg/L	56.0	56.5	57.0		NG
Ti	μg/L	6.4	3.7	7.1		NG
V	μg/L	41.2	40.0	41.8		NG
Li	μg/L	71.8	71.3	69.9		NG
Be	μg/L	0.0	0.0	0.0		NG
Sr	μg/L	418.5	417.6	410.9		NG
Mo	μg/L	0.9	0.9	0.9		NG
Ba	μg/L	151.4	149.9	147.0		NG
Tl	μg/L	0.1	0.1	0.1		NG

NM = Not measured.
ND = Not detected.
NG = No guideline.

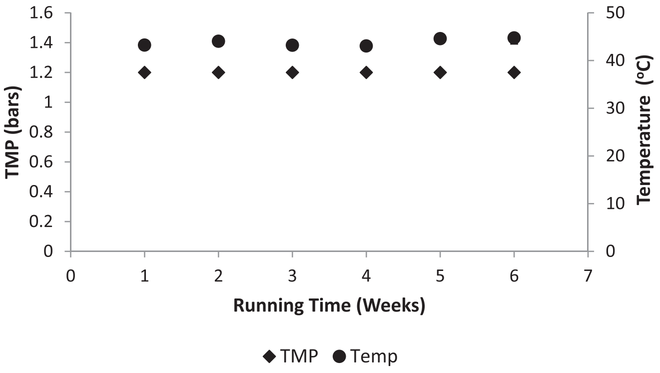


Fig. 3. Values of TMP and temperature.

operating temperature of 45 °C. A Wave cyber pressure vessel (Wave cyber, China) with 2.5″ diameter was used to contain the membrane. The pressures in the feed, permeate, and concentrate lines were monitored with a pressure gauge (MA-50-10-1/4, FESTO, NL). The permeate flow was controlled manually with the concentrate valve, monitoring the permeate flow meter (EK-5EA, Kytola Instruments).

2.3. NF rejection experiments

2.3.1. Overview of experiments

To investigate the effect of elevated temperatures on the performance of low-pressure NF membranes two sets of experiments were conducted. Table 1 provides a summary of the experimental conditions for the NF rejection experiments.

2.3.2. Operation of NF pilot plant at constant flux and temperature

The first set of experiments aimed to evaluate whether or not deterioration in the performance of the NF can occur during the operational run of the system. These experiments were conducted during a six-week period; fixed flux (16 L/m^2 h) and a fixed temperature (43.6 °C) were used. The NF pilot plant was operated during 6 to 7 h per day. Parameters such as pressure, feed flow, permeate flow, temperature and conductivity were continuously monitored (every 1.5 h).

Around 150 samples were collected from the feed and the permeate to measure As concentration and physical-chemical parameters. Chemical cleaning was not executed during these experiments, because there was no indication of the occurrence of either scaling or (bio)fouling.

2.3.3. Operation of NF pilot plant at different fluxes and temperatures

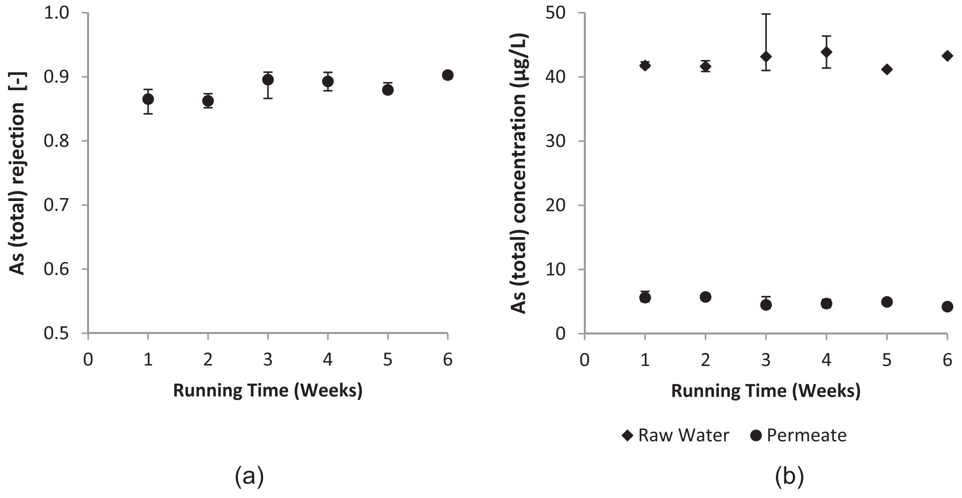
The second set of experiments consisted of the evaluation of the NF filtration cycles with fixed temperatures (31,35 & 43.6 °C) and varying fluxes (16,23 & 30 L/m^2 h). In order to investigate the effect of flux and temperature on As(V) rejection several rejection experiments with fixed temperatures and various fluxes were performed. For each of the evaluated temperatures (31,35 & 43.6 °C), a series of three 2-h runs were executed. In each run the fluxes recovery was increased (16, 23 & 30 L/m^2 h). For the 43.6 °C experiment, source water coming from the well was directly used. For the experiments conducted at the lower temperatures, 31 °C and 35 °C, it was necessary to collect the water in the feed tank and close the by–pass valve, waiting for the water to cool down: one day (for 35 °C) or two (for 31 °C) days. For both experiments with cooled water, the permeate and the concentrate returned to the feed tank. All the experiments were performed at least twice. Samples from feed and permeate sampling points were collected every two hours and their physical-chemical parameters were subsequently measured (around 20 samples per experimental condition). Parameters such as pressure, feed and permeate flow, temperature and conductivity were continuously monitored. Chemical cleaning was not applied during these experiments.

2.4. Analyses of samples

Temperature, pH, ORP (oxidation reduction potential) and electrical conductivity of the feed water were measured on-site, using a multimeter (HANNA Instrument).

For the analysis of As (total), Na^+, K^+, Mg^{2+}, Ca^{2+}, Fe (total) and some trace elements (e.g. boron), the samples from the feed, permeate, and concentrate were acidified using 150 μL of HNO_3 (69%) per 15 mL of sample. The concentration of these elements in the samples was analyzed using inductively coupled plasma mass spectrometry (ICP-MS Thermo – XSERIES ll, Thermo Fisher Scientific) at TU Delft water laboratory. NO_3^-, Cl^- and SO_4^{2-} were analyzed in a commercial Nicaraguan water laboratory using a Dionex Dx – 100 ion chromatograph. The concentrations of HCO_3^- were determined using a titrimetric method (702 SM Titrino, Metrohm).

For the As speciation, 200 mL of the raw water were filtered through a 100 mL syringe filled with 50 mL of Amberlite IRA-400 chloride form (anion-exchange resin). As in the raw water and the filtered water was measured using inductively coupled plasma mass spectrometry (ICP-MS Thermo – XSERIES ll, Thermo Fisher Scientific) at TU Delft water laboratory. The As concentration in the raw water represents the As total, while the As concentration in the filtered water represents



(a) (b)

Fig. 4. (a) As rejection and (b) As concentration in feed water and permeate for the evaluated period.

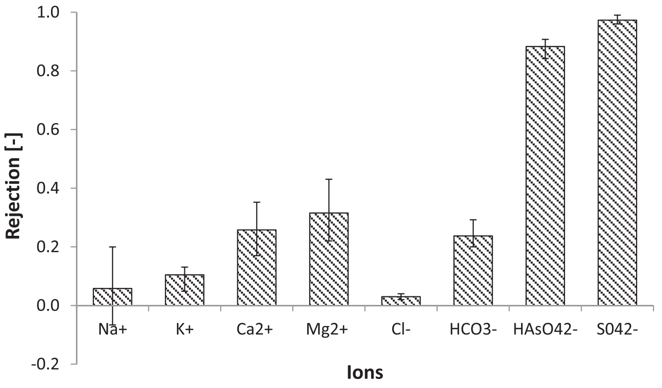


Fig. 5. Rejection of cations and anions (including arsenic) during the experimental period.

the concentration of As(III) (Clifford et al., 2005). The difference between these two is the concentration of As(V) in the raw water.

3. Results

3.1. Groundwater

In Nicaragua, the provisional guideline of the World Health Organization (WHO, 2001) has been adopted under the CAPRE normative (CAPRE, 1993) (Regional committee coordinator of potable water supply institutions and sanitation of Central America, Panamá, and Dominican Republic, 1994). Table 2 provides an overview of the water quality parameters of the feed water for each of the experimental temperatures. Fe concentrations were low (0.2 mg/L), NH_4 was not detected and ORP values were high (>100 mV), altogether indicating that the groundwater does not originate from a reduced (anoxic) aquifer. This is in-line with the measurement that As(V) is the dominant species (Clifford et al., 2005). And considering the values of pH and ORP is likely that the As(V) is mainly present as divalent arsenate ($HAsO_4^{2-}$). The presence of both fluoride and boron indicate - in combination with the elevated temperatures - that the source is geothermally influenced. Furthermore As-rich water sources influence by geothermal sources often present a positive correlation with Cl^- (Ravenscroft et al., 2009; Smedley and Kinniburgh, 2002).

3.2. Operation of NF pilot plant at a constant flux and temperature

3.2.1. Transmembrane pressure (TMP) and ionic rejection

At a flux of 16 L/m^2 h and a recovery of 10%, a stable transmembrane pressure (TMP) of 1.2 bar was observed during the evaluation period (Fig. 3), which may be considered a very low operating pressure for polymeric NF membranes. In this period the pilot plant produced an estimated 2.5 m^3 (260 l/day) of drinking water (permeate) and 84.5 m^3 of washing/laundry water (concentrate). Water was produced only during the sunny day hours (6–7 h/day), and based on daily water demand according to World Health Organization, this would be sufficient to supply drinking water for 2 families (8 to 10 peoples). The temperature of the feed water fluctuated between 43.2 and 44.7 °C. Even though operation was intermittent, it may be concluded that the pilot plant operated under stable conditions.

3.2.2. Rejection of As(V) at a constant flux and temperature

Fig. 4 depicts (a) the As (total) rejection at a constant flux (16 L/m^2 h) and constant temperature (43.6 °C) and (b) the concentration before (raw water) and after filtration (permeate). A steady (total) As rejection (0.87 to 0.9) was observed during the running period. The As concentration in the permeate was around 5 μg/L, which is below the WHO guideline.

3.2.3. Rejection of anion and cation at a constant flux and temperature

Fig. 5 depicts the average rejection of different monovalent and divalent ions during NF filtration observed during the six-weeks' period. The rejection of Cl^- (0.03), a monovalent anion, was considerably lower compared to SO_4^{2-} (0.97), a divalent anion. In addition the rejection of Na^+ (0.06), a monovalent cation, was also lower compared to Mg^{2+} (0.32). With the exception of Cl^- the rejection of the anions was higher compared to the rejection of the cations. The order of rejection for anions ($SO_4^{2-} > HAsO_4^{2-} > HCO_3^- > Cl^-$) and cations was ($Mg^{2+} > Ca^{2+} > K^+ > Na^+$). As a consequence of rejection of Mg^{2+} and Ca^{2+} the total hardness decreased with 30%. The HCO_3^- concentration decreased from 195 in the feed water to 149 mg/L in the permeate.

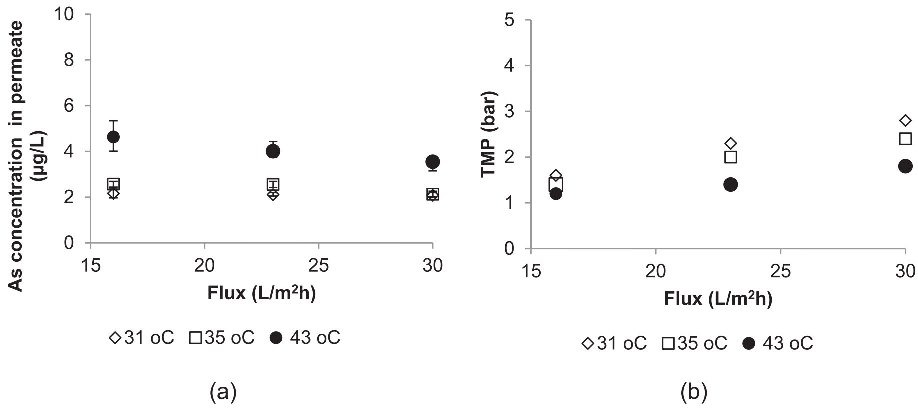
3.3. Operation of NF pilot plant at different fluxes and temperatures

3.3.1. Effect of flux and temperature on As(V) rejection

Fig. 6(a) depicts the As concentration in the permeate after NF filtration for various fluxes (16, 23 & 30 L/m^2 h) and temperatures (31,35 & 43 °C). When the flux increased and temperature decreased, a slight decrease in As concentration in the permeate was observed. However, at lower temperatures as well as higher fluxes, higher operating pressures were required (Fig. 6(b)). The As concentration in the permeate decreased from 4.6 to 2 μg/L when the flux increased from 16 to 30 L/m^2 h and the water temperature decreased from 43.6 to 31 °C, respectively. As a consequence the pressure increased from 1.2 to 2.8 bar (from 12 to 28 mwc).

3.3.2. Rejection of anions and cations at different flux and temperature

Table 3 presents the anions and cations rejection as function of flux and temperature. With the exception of SO_4^{2-}, both at lower



(a) (b)

Fig. 6. Effect of the flux and temperature for (a) concentration of the As(V) in the permeate and (b) TMP as function of flux and temperature.

temperatures and with higher fluxes the rejection was higher. For all the evaluated fluxes and temperatures there was no variation in the rejection order for all the anions ($SO_4^{2-} > HAsO_4^{2-} > HCO_3^- > Cl^-$). On the other hand, as temperature increases, there was a shift in the rejection order for the cations. For 31 °C and 35 °C ($Mg^{2+} > Ca^{2+} > Na^+ > K^+$) and for 43 °C ($Mg^{2+} > Ca^{2+} > K^+ > Na^+$).

Table 4 presents the water quality of the permeate for the for the tested conditions. At 31 °C the permeate could be considered moderately hard water (111 to 125 mg/L $CaCO_3$). At 43 °C the permeate could be recognized as hard water (130 to 150 mg/L $CaCO_3$). Nevertheless, the values of the hardness are in agreement with the values recommended by the CAPRE normative (400 mg/L $CaCO_3$)(CAPRE, 1993).For all the other ions the concentration are in the range recommended by the CAPRE normative, consequently there is no need for a remineralization step after NF filtration.

4. Discussion

4.1. Operation of the NF and water quality in the permeate

At a groundwater temperature of 43 °C and operating the NF pilot plant at different fluxes the system required an exceptionally low operational pressure (1.2 to 1.8 bar) and high As(V) rejection (0.89 to 0.95). Pilot studies regarding the NF application for As removal at these high temperatures have not been reported earlier, nevertheless previous studies reported similar rejection for experiments conducted in a range of temperatures between 10 °C to 30 °C and with operating pressures ranging from 2 to 7 bar (J. Waypa et al., 1997; Oh et al., 2000; Padilla and Saitua, 2010; Saitúa et al., 2005; Saitua et al., 2011). Also, the stability of the TMP indicates that scaling or particulate fouling did not occur in the pilot plant.

Although an increased temperature had a negative effect on the As rejection, As concentrations in the permeate never exceeded 5 μg/L, while the required TMP dropped - depending on the flux - with 0.5 to 1 bar. This decrease in required pressure might be of huge benefit in deserted, rural locations where electricity is scarce. Altogether it may be concluded that during the six-week trial, the pilot plant ran under stable conditions, even though there was only water production during daytime due to the use of a solar pump.

4.2. Effect of ion interaction on As rejection at constant flux and temperature

The order of rejection of $HAsO_4^{2-}$ compared with the other anions could be interpreted on the basis of its charge and hydration free energy. Which ultimately are related to the Donnan and size exclusion mechanism respectively, e.g., the lower rejection of $HAsO_4^{2-}$ with respect to the rejection of SO_4^{2-} observed in our results is in agreement with the order of their hydration free energy ($SO_4{}^{2-} > HAsO_4^{2-}$). Furthermore several studies have reported similar hierarchy in rejection between SO_4^{2-} and $HAsO_4^{2-}$.(Nguyen et al., 2009; Saitua et al., 2011; Vrijenhoek and Waypa, 2000).

Anions with lower charge and lower hydration free energy also present lower rejection (Saitua et al., 2011; Tansel, 2012). This could explain the higher rejection of $HAsO_4^{2-}$ compared with Cl^- and HCO_3^- observed in this study, which are in line with the order of their charge ($HAsO_4^{2-} > HCO_3^- = Cl^-$) and their hydration free energy ($HAsO_4^{2-} > HCO_3^- > Cl^-$). Table 5 shows a comparison between the rejection order and thermodynamic and physical properties of the ions, which ultimately are related with the NF rejection mechanisms.

The charge (valence) of the co-ions (anions; same charge as the membrane) could be associated with its concentration in the membrane phase (Peeters et al., 1998; Schaep et al., 1998). The concentration of the co-ions in the membrane (Donnan exclusion mechanism) usually shows a direct relationship with their rejection, i.e. the higher the concentration of the co-ions in the membrane, the lower their rejection (Peeters et al., 1998). Therefore, monovalent anions such as Cl^- and HCO_3^- will tend to have a lower rejection than divalent anions (SO_4^{2-} and $HAsO_4^{2-}$) as was also observed during our experiments. Furthermore, due to friction forces generated during filtration, anions with a low hydration free energy have the tendency to temporarily decrease the size of its hydrated radius due to the loss of water molecules that surround its ionic structure (Tansel, 2012). This characteristic allows the anions with less hydration free energy to pass through the membrane more easily (e.g., Cl^- and HCO_3^- compared with SO_4^{2-} and $HAsO_4^{2-}$).

Table 3
Comparison of ion rejection during NF filtration for different fluxes and temperatures.

Temp	Flux (L/m^{2}h)	Ion rejection [−]							
		Na^+	K^+	Ca^{2+}	Mg^{2+}	Cl^-	HCO_3^-	As(V)	SO_4^{2-}
31 °C	16	0.23	0.20	0.37	0.47	0.18	0.35	0.95	0.99
	23	0.28	0.26	0.44	0.54	0.20	0.46	0.95	0.99
	30	0.30	0.26	0.43	0.56	0.20	0.49	0.96	0.99
35 °C	16	0.21	0.20	0.34	0.46	0.10	0.36	0.94	0.99
	23	0.21	0.22	0.37	0.46	0.12	0.42	0.94	0.99
	30	0.29	0.24	0.42	0.55	0.14	0.46	0.95	0.99
43 °C	16	0.14	0.15	0.28	0.34	0.03	0.26	0.89	0.99
	23	0.14	0.17	0.29	0.38	0.04	0.31	0.91	0.99
	30	0.19	0.21	0.36	0.44	0.06	0.35	0.92	0.99

The rejection of cations on a negatively charged membrane is may be slightly decreased by their charge (higher charge, less rejection, e.g., Mg^{2+} and Ca^{2+}), but this is a minor effect. Most important is electro neutrality for the positive ions (Peeters et al., 1998; Saitua et al., 2011; Tansel, 2012). For the differences between positive ions the radius and hydration energy is responsible, e.g., divalent cations which have higher hydration free energy and large hydration radius are better rejected than the monovalent cations (Na^+ and K^+) as was observed during the experiments in this study.

The presented results showed that unlike the rejection of cations, the sequence of rejection of the anions does not have a strict relationship with their hydrated radius. This could be explained considering that, unlike cations, between anions there is only small variation in their hydration radius (Tansel, 2012).

4.3. Flux and temperature effect on As(V) rejection

As flux increased the As concentration in the permeate decreased, e.g., at 43.6 °C when the flux increased from 16 to 30 L/m^2 h the As concentration in the permeate decreased from 4.6 to 2 μg/L. The increase in As(V) rejection due to the increased flux can be ascribed to the so called “dilution effect” (J. Waypa et al., 1997) (Saitua et al., 2011). During filtration, permeate (solution) flow and As(V) (solute) flow are not totally coupled. Although the permeate flow increases, the As(V) flow remains constant. As a consequence, the As(V) concentration decreased.

The hydration-free energy keep an inverse relationship with the temperature, therefore as temperature increases, the hydration-free energy of the As(V) decreases. As a consequence, As(V) could

Table 4
Concentration of the major ions in permeate for different fluxes and temperatures.

Temp	Flux (L/m^{2}h)	Ions concentration in permeate [mg/L]						
		Na^+	K^+	Ca^{2+}	Mg^{2+}	Cl^-	HCO_3^-	SO_4^{2-}
31 °C	16	53.8	10.7	38.4	7.3	100.0	125.2	0.4
	23	50.3	9.9	34.3	6.2	97.7	104.5	0.4
	30	48.8	10.0	34.9	6.0	98.0	99.3	0.4
35 °C	16	55.8	10.9	41.2	7.8	124.7	128.8	0.4
	23	56.1	10.6	39.3	7.8	121.7	116.4	0.4
	30	50.5	10.2	36.0	6.5	118.6	109.0	0.4
43 °C	16	57.0	11.1	44.3	9.3	130.4	144.5	0.4
	23	56.7	10.9	43.7	8.7	129.1	135.9	0.4
	30	53.8	10.4	39.3	8.0	126.4	126.6	0.4

Table 5
Comparison between rejection order and some thermodynamic and physical properties of the ions.

Parameter	Cations	Anions	Reference
Rejection order	$(Mg^{2+} > Ca^{2+} > K^{+} > Na^{+})$	$(SO_4^{2-} > HAsO_4^{2-} > HCO_3^{-} > Cl^{-})$	[this study]
Charge	$(Mg^{2+} = Ca^{2+} > K^{+} = Na^{+})$	$(SO_4^{2-} = HAsO_4^{2-} > HCO_3^{-} = Cl^{-})$	[−]
Hydration free energy	$(Mg^{2+} > Ca^{2+} > Na^{+} > K^{+})$	$(SO_4^{2-} > HAsO_4^{2-} > HCO_3^{-} > Cl^{-})$	(Binder and Zschörnig, 2002; Stumm and Morgan, 2009)
Hydrated radius	$(Mg^{2+} > Ca^{2+} > Na^{+} > K^{+})$	$(SO_4^{2-} > Cl^{-} > HAsO_4^{2-} = HCO_3^{-})$	(Nightingale, 1959; Saitua et al., 2011)
Diffusivity of the ions in the bulk solution	$(Mg^{2+} < Ca^{2+} < Na^{+} < K^{+})$	$(HAsO_4^{2-} < SO_4^{2-} < HCO_3^{-} < Cl^{-})$	(Linde and Jönsson, 1995; Saitua et al., 2011)

decrease their hydrated radius more easily during filtration. This factor in combination with the thermal expansion of the membrane pores (Dang et al., 2014; Sharma et al., 2003), and the increase of the diffusive transport of the ions across the membrane layer (Brandhuber and Amy, 2001; J. Waypa et al., 1997) could be associated with the decrease of the As(V) rejection when temperature increase, as is observed during the experiments in this study, varying temperature and flux.

4.4. Gravity-driven NF for As mitigation in rural Nicaragua

The results showed that also at high temperatures it is possible to obtain high rejection of As(V) (0.87–0.9) during NF filtration of geothermal influenced groundwater, with the additional advantage of requiring low operating pressures (1.2 bar~12mwc). The research was executed with a solar pump, however, at the current pilot plant location with 43 °C, a gravity driven system could be a viable option as well. A 12 m overhead tank would suffice for reaching the required pressure to operate a gravity-fed NF system, and would as such not require a pump, nor electricity to be operated. In the case of a temperature drop to 31 °C one would require an additional 5–12 m of elevation head, so when designing a gravity-fed NF system it is therefore important to prevent loss of heat (e.g., due to long-term storage or pipelines without isolation). Having said this, the gravity-fed NF system might then not require a pump, depending on the local geohydrological situation it might still be necessary to install a groundwater pump for abstraction. Based on the presented research a gravity-fed NF system for As removal from high temperature source waters is feasible at low pressures and is therefore particularly interesting in regions with natural elevations, like the volcanic zones in Nicaragua.

5. Conclusions

At a groundwater temperature of 43 °C the NF pilot plant in rural Nicaragua could be operated under stable conditions of low recovery (10%) and low pressure (1.2 bar ~ 12mwc). In these conditions, the permeate of the NF system (~5 μg/L) complied with the WHO guideline for drinking water and the concentrate (~55 μg/L) could be used by local villagers for daily activities (e.g. washing and bathing.) For the same temperature and with an increase in operating pressure it is possible to run the NF system at higher fluxes and obtained a slight increase in the quality of the permeate. For a proper assessment of the effect of temperature in the life time of the membrane, the frequency of chemical cleanings and the effect of various fluxes and temperatures it would be necessary to investigate operation of the pilot plant for a longer period of time.

For all investigated fluxes and temperatures the order of rejection of As(V) (as $HAsO_4^{2-}$), compared with the other anions, could be interpreted on the basis of its charge, hydrated radius and hydration free energy. Altogether this study has illustrated that, although polymeric NF membranes have the image to be too expensive, high in maintenance and energy-demanding for low-income countries, NF membranes can be a sustainable barrier for As(V) in rural Nicaragua – especially at high water temperatures.

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