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

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ABSTRACT: Geothermally influenced waters are frequently found to be contaminated with arsenic (as As(V)). This study investigated the effect of high-temperatures (50°C), as found in geothermal source waters, on the rejection of monovalent H_2AsO_4^- and divalent HASO_4^{2-} species (at pH 6 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, whereas so far it was assumed that temperature rise had a negative effect on As(V) rejection. Previous studies were conducted with ultrapure waters, where pore size expansion dominated As(V) rejection, however, in the presence of other anions – like in natural water – As(V) rejection is 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. Additional advantage of the higher temperature was the lower feed pressure (down to 3 bar) needed to operate these NF membranes, compared to colder waters. Temperatures shows the potential application of this technology for efficient treatment of As(V) contaminated, geothermally influenced waters.

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. These geothermally influenced waters may thus have high As concentrations in combination with high temperatures. The contamination of water sources by geothermal As has been reported around the world in locations such as Waikato River in New Zealand, Eastern Sierra Nevada in USA, and Telica in Nicaragua (Johnson, 1965; Polhill, 1982).

The As speciation in natural groundwater (pH 6.5–8.5) is mainly determined by redox potential (Eh) and pH. Depending on the conditions, As is present as arsenate (As(V)) or arsenite (As(III)). 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. On the other hand, As(III) is predominantly found under reducing conditions and as an uncharged ion when the pH is below 9.2. In geothermal fluids, the dominant species of As primarily consists of 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). Therefore, arsenic-contaminated drinking water sources in geothermally influenced waters are dominated by As(V).

The objective of this paper is to demonstrate the effect of high-temperature (50°C) waters, such as

geothermally influenced waters, on the rejection of monovalent H_2AsO_4^- and divalent HASO_4^{2-} species during NF membrane filtration of a multi-component solution containing Cl^- and HCO_3^- .

2 METHODS/EXPERIMENTAL

Dow NF270 and Alfa Laval were used to assess the As(V) species rejection. Rejection of H_2AsO_4^- and HASO_4^{2-} was evaluated by maintaining the temperature constant (25°C or 50°C) and varying the pH (pH 8 and pH 6) of the feed water. The rejection experiments were conducted using feed flow of 100 L h^{-1} (velocity = 0.15 m s^{-1}), a flux of $40 \text{ L m}^{-2} \text{ h}^{-1}$ and a recovery of 10%. All experiments were executed either at 25°C or 50°C. The concentration of arsenic in the samples were analyzed using an inductively coupled plasma mass spectrometry (ICP-MS MS Thermo – XSERIES II, Thermo Fisher Scientific, USA).

3 RESULTS AND DISCUSSION

An improvement in rejection for H_2AsO_4^- and HASO_4^{2-} was achieved as the effect of increasing temperature (Fig. 1). The rise of rejection of As(V) species could attribute to the presence of other anions (Cl^- and HCO_3^-) in the water matrix composition, used for pH and ionic strength buffer. Hodgson (1970) defined the terms less and more permeable ions, to describe the difference in behavior between co-ions (ions with same charge of the membrane). Anions such as Cl^- and

Figure 1. Removal efficiency of As(V) ($300 \mu\text{g L}^{-1}$) for (a) Dow NF270 and (b) Alfa Laval NF as a function of a constant Temperature (25°C or 50°C) and variable pH.

HCO_3^- with an equal or lower valence and higher diffusivity are more permeable than H_2AsO_4^- and HAsO_4^{2-} . Therefore Cl^- and HCO_3^- will have a beneficial effect on the rejection of As(V) species (less permeable). The enhanced rejection of As(V) at 25°C , due to the presence of other -more permeable- co-ions has been reported by other researchers (Nguyen et al., 2009; Vrijenhoek & Waypa, 2000).

Additionally, to explain the improvement in As rejection, Vrijenhoek & Waypa (2000) pointed out the importance of the relatively small concentration of As compared with the concentration of the others co-ions present in the solution. The so-called more permeable ions can penetrate through the membrane more easily. Because of the electroneutrality condition need to keep in the bulk solution, the rejection of less permeable ions increases. The deterioration of the size exclusion mechanism and the increase in diffusion transport

across the membrane due to temperature effect will enhance the permeation of the more permeable ions and as a consequence will improve the rejection of H_2AsO_4^- and HAsO_4^{2-} which are less permeable. The results in Figure 1 indicate that this phenomenon is temperature dependent and aiding in the rejection of As(V) at higher temperatures.

4 CONCLUSIONS

The presented study assessed the effect of high-temperature (50°C) waters, like geothermally influenced waters, on the rejection of monovalent H_2AsO_4^- and divalent HAsO_4^{2-} species during NF membrane filtration of a multi-component solution where Na^+ , Cl^- , and HCO_3^- were present. It can be concluded that the higher the temperature, the better the rejection achieved for both As(V) species, with the added advantage that less transmembrane pressure was required to operate these NF membranes at higher temperatures.

Our findings differ from previous work where the As(V) rejection showed a decline as the consequence of temperature increase. This difference can be explained by the presence of HCO_3^- and Cl^- in our study. The experiments indicate that the enhancement of As(V) rejection was directly related to the presence of HCO_3^- and Cl^- , which are considerably more permeable than both As(V) species. The enlargement of the pore size and the increase of the mass transfer across the membrane due to temperature effect enhanced the permeation of these more permeable ions and, as a consequence, improved the rejection of H_2AsO_4^- and HAsO_4^{2-} , which are less permeable. In particular, HCO_3^- played a vital role in As(V) retention during NF membrane filtration at higher temperatures.

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As(III) oxidation during full-scale aeration and rapid filtration

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ABSTRACT: Arsenic (As) oxidation during full-scale aeration and rapid filtration was investigated. In the supernatant water, As(III) showed no apparent oxidation and meagre adsorption to HFO was observed. However, in the top of the filter bed rapid As(III) oxidation occurred and the subsequently formed As(V) was efficiently adsorbed. Although MnO₂ could potentially oxidise As(III) it was found that As(III) oxidation was inhibited in the presence of Mn(II) and Fe(II). During ripening of virgin sand filters, As(III) oxidation was complete after 21 days of operation, before Mn(II) and NH₄⁺ oxidation. Therefore, it may be concluded that formation of MnO₂ could not have been responsible for As(III) oxidation, strongly suggesting that this is a microbial process. This process could develop amongst common groundwater bacteria and mineral precipitates, directly leading to an increased As removal in the filter bed.

1 INTRODUCTION

In the Netherlands, groundwater treatment commonly consists of aeration, with subsequent sand filtration without using chemical oxidants like chlorine. Oxidation of As(III) is imperative for efficient removal in this process (Bissen & Frimmel, 2003; Gude *et al.*, 2017), but the oxidation reaction between As(III) and O₂ is sluggish and takes days (Kim & Nriagu, 2000). However, As(III) oxidation was observed in the top layer of rapid sand filters without the use of chemicals (Gude *et al.*, 2016). It was hypothesised that As(III) oxidation was caused by bacteria and/or MnO₂. Both are present in the filter bed and could be capable of (catalysing) the oxidation reaction (Huang, 2014; Manning *et al.*, 2002). However conclusive evidence whether bacteria and MnO₂ are actually oxidising As(III) in rapid sand filters is scarce. For the purpose of identifying contributors to natural As(III) oxidation, jar tests with MnO₂ grains and pilot plant research using sand filter columns were conducted.

2 MATERIALS AND METHODS

2.1 MnO₂ jar tests

Jar tests experiments were executed in 1.8 L, buffered, demineralised water. 20 µg L⁻¹ As(III), 2 mg L⁻¹ Fe(II), 2 mg L⁻¹ Fe(III), 2 mg L⁻¹ Mn(II) and 100 mg L⁻¹ pure MnO₂ power were used to investigate As(III) redox and As sorption behaviour. The jars were constantly kept at pH 7 and magnetically stirred. Samples were taken after 2, 5, 10, 20, 30, 60 and 120 minutes contact time. Sample preparation consisted of immediately filtering through 0.45 µm and acidifying to pH 1 until analysis by ICP-MS.

2.2 Biological ripening experiment

For this experiment 3 sand columns were loaded/ripened with aerated, natural groundwater containing

Table 1. Water quality natural groundwater

Parameter	Unit	Value
As	µg L ⁻¹	13
Fe	mg L ⁻¹	1.4
Mn	mg L ⁻¹	0.04
PO ₄	mg L ⁻¹	0.45
NH ₄	mg L ⁻¹	0.62
pH		7.54
HCO ₃	mg L ⁻¹	246
Temperature	°C	12.4

As(III) for 50 days. The remaining As in the filtrate was speciated to follow As(III) oxidation in the filter bed. Filtration rate was set to 1 m h⁻¹ and supernatant level between 5 and 20 cm. Principal water quality parameters are depicted in Table 1.

3 RESULTS AND DISCUSSION

3.1 MnO₂ jar tests

In order to investigate whether MnO₂ could be responsible for As(III) oxidation in the top of the filter bed, As(III) was exposed to MnO₂ grains with possible competing substances: Mn(II) and Fe(II)/Fe(III). These results are depicted in Figure 1. Fig. 1 left shows As(III) in combination with Fe(II) only, Fe(II) and MnO₂ and Fe(II)-MnO₂-Mn(II). The same experiments were executed for Fe(III) and are depicted in Fig. 1 right.

Fig. 1 left shows that As(III) removal is similar for Fe(II) with and without MnO₂ grains with As(III) removal of 60% after 120 min. On the other hand Fe(III) and MnO₂ removed 98% of As(III) in 120 min (Fig. 1B). It was observed that the presence of Fe(II) and Mn(II) inhibited As(III) oxidation on MnO₂. At pH 7, Fe(II) and Mn(II) adsorption and oxidation were preferred over As(III) on the MnO₂ surface.