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

J.C.J. Gude, L.C. Rietveld & D. van Halem

Department Water Management, Section Sanitary Engineering, Delft University of Technology, The Netherlands

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.

Figure 1. As(III) removal by Fe(II) and Fe(III) in presence and absence of MnO₂ and Mn(II) at pH 7 over 120 min. Concentrations were 20 µg L⁻¹ As(III), 2 mg L⁻¹ Fe, 2 mg L⁻¹ Mn and 100 mg L⁻¹ MnO₂ powder. (A) is As(III) removal by Fe(II) and (B) Fe(III) (Figure taken from Gude *et al.*, 2017).

Figure 2. As(III) and As(V) in the filtrate of As(III) preloaded (top) and virgin sand columns (bottom) over time. Filtration velocity 1 m h⁻¹ and bed height 0.5 m. Initial concentration of the groundwater: Fe 1.4 mg L⁻¹; As 13 µg L⁻¹ (as As(III)) also depicted <■>; PO₄ 0.45 mg L⁻¹; Mn 0.04 mg L⁻¹; NH₄ 0.62 mg L⁻¹. As concentration in the filtrate is depicted as the sum of the As(III) and As(V) species.

However, unlike Fe(II), the addition of Fe(III) did not hinder As(III) oxidation on the MnO₂ surface; resulting in subsequent effective As(V) removal by the flocculating hydrous ferric oxides. Mn(II) and Fe(II) are typically present in the pore volume of the top of the filter bed, therefore it can be concluded that just because MnO₂ is present in a filter bed, it does not necessarily mean that MnO₂ in the top of a sand filter is available to oxidise As(III).

3.2 Biological As(III) oxidation

Biological As(III) oxidation is a possible alternative for MnO₂ to catalyse the aerobic oxidation reaction of As(III) and O₂ in the top of the filter bed. This was investigated by ripening a sand filter with aerated natural groundwater water containing As(III) for 50 days. During rapid filtration of natural groundwater many biological processes take place, in this experiment it was tested whether As(III) present in low concentrations would be able to oxidise. Results shown in Figure 2 are averaged from triplicates and As in the filtrate is depicted as the sum of the As(III) and As(V) species.

As(III) was oxidized to As(V) gradually in the first 5 days (10%) and showed a steep increase in the next 5 days (>80%). This pattern follows a typical biological

process where after a slow lag phase, a rapid log phase follows. Mn(II) removal was not observed within the 50 day experiment and NH₄⁺ removal started after 15 days. Therefore it is concluded that independently of biological NH₄⁺ and Mn oxidation processes biological As(III) occurred in the sand filter.

The oxidation of As(III) was accompanied by a slight increase in As removal. During the ripening of the virgin filter sand 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.

4 CONCLUSIONS

As(III) oxidation in the top of the filter bed is crucial for efficient As removal in rapid sand filters. It was found with jar tests that the presence of Fe(II) and Mn(II) inhibited As(III) oxidation by MnO₂. Therefore it is concluded that just because MnO₂ is present in a filter bed, it does not necessarily mean that MnO₂ will be available to oxidise As(III).

In addition it was found that the ripening of a virgin sand filter As(III) oxidation was complete before Mn(II) and NH₄⁺ oxidation, strongly suggesting that As(III) oxidation 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.

ACKNOWLEDGEMENTS

This research is supported by the Dutch Technology Foundation STW, which is part of the Netherlands Organisation for Scientific Research (NWO), and which is partly funded by the Ministry of Economic Affairs.

REFERENCES

- Bissen, M. & Frimmel, F.H. 2003. Arsenic—a review. Part II: Oxidation of arsenic and its removal in water treatment. *Acta Hydrochim. Hydrobiol.* 31: 97–107.
- Gude, J.C.J., Rietveld, L.C. & van Halem, D. 2017. As(III) oxidation by MnO₂ during groundwater treatment. *Water Res.* 11:41–51.
- Gude, J.C.J., Rietveld, L.C. & van Halem, D. 2016. Fate of low arsenic concentrations during full-scale aeration and rapid filtration. *Water Res.* 88: 566–574.
- Huang, J.H. 2014. Impact of microorganisms on arsenic biogeochemistry: A review. *Water. Air. Soil Pollut.* 225(2): 1848.
- Kim, M.J. & Nriagu, J. 2000. Oxidation of arsenite in groundwater using ozone and oxygen. *Sci. Total Environ.* 247, 71–79.
- Manning, B.A., Fendorf, S.E., Bostick, B. & Suarez, D.L., 2002. Arsenic(III) oxidation and arsenic(V) adsorption reactions on synthetic birnessite. *Environ. Sci. Technol.* 36: 976–981.