Arsenic removal to $<1 \mu\text{g L}^{-1}$ by coprecipitation with in-situ generated Fe(III) precipitates with and without advanced pre-oxidation

A. Ahmad^{1,3,4}, J. van Mook², B. Schaaf² & A. van der Wal^{2,3}

¹*KWR Water Cycle Research Institute, Nieuwegein, The Netherlands*

²*Evides Water Company N.V. Rotterdam, The Netherlands*

³*Department of Environmental Technology, Wageningen University and Research (WUR), Wageningen, The Netherlands*

⁴*KTH-International Groundwater Arsenic Research Group, Department of Sustainable Development, Environmental Science and Engineering, KTH Royal Institute of Technology, Stockholm, Sweden*

ABSTRACT: The aim of this study is to investigate removal of low As concentrations from groundwater at a Drinking Water Treatment Plant (DWTP) in The Netherlands in order to achieve $<1 \mu\text{g L}^{-1}$ As in produced drinking water. Two iron based emerging technologies, both relying on in-situ generated Fe(III) precipitates for As adsorption, were investigated. These include: 1) Advanced Oxidation-Coprecipitation-Filtration (AOCF) and 2) Coprecipitation prior to ultrafiltration (C-UF). We show that most of the As removal occurs in the top half of a Rapid Sand Filter (RSF) bed. In this part we also observe the conversion of As(III) into As(V). The mechanism of As(III) oxidation to As(V) in the RSF is still not understood, however we hypothesize that either the manganese oxides or the biological activity in the filter bed may be responsible for this conversion. In agreement with this observation, we also notice that drinking water only contains As(V) and that the levels of As(III) are negligible. The experiments have shown that both AOCF and C-UF are promising emerging technologies to reduce arsenic levels to below $1 \mu\text{g L}^{-1}$ which is the agreed target in The Netherlands between the Dutch water companies.

1 INTRODUCTION

Arsenic (As) is a highly toxic metalloid which occurs naturally in the earth's crust. It is frequently encountered in natural (ground) waters around the world. According to the World Health Organization (WHO), long term exposure to As from drinking water and food can cause cancer and skin lesions. The WHO guideline for As in drinking water is provisionally set at $10 \mu\text{g L}^{-1}$, however lower levels are recommended technically and economically feasible (WHO, 2011). In 2016, the drinking water sector in The Netherlands agreed to aim for drinking water production whereby As $<1 \mu\text{g L}^{-1}$. The aim of this study was to investigate removal of low As concentrations from groundwater at a drinking water treatment plant (DWTP) in The Netherlands to achieve $<1 \mu\text{g L}^{-1}$ As in produced drinking water. Two emerging technologies, both relying on in-situ generated Fe(III) precipitates for As adsorption, were investigated. These include: 1) Advanced Oxidation-Coprecipitation-Filtration (AOCF) and 2) Coprecipitation prior to ultrafiltration (C-UF). The study includes sampling campaigns at the full-scale treatment trains of the DWTP, as well as batch and pilot experiments using actual process water of the treatment facility.

2 MATERIALS AND METHODS

The study was carried out at DWTP Ouddorp which uses infiltrated dune water as its source. The treatment

consists of the following steps: 1) rapid sand filtration (RSF), 2) granular activated carbon filtration (GAC) and 3) ultrafiltration (UF). Firstly, multiple sampling campaigns were carried out at the full-scale treatment trains to understand the mobility and fate of As and its species. Subsequently, batch experiments were carried out using the actual process water samples collected at different points along the treatment train. The water samples that contained As(III) were pre-treated with KMnO_4 to oxidize As(III) to As(V). This may be called as the advanced oxidation process. The samples that contained As(V) only were directly dosed with FeCl_3 to produce Fe(III) precipitates for As(V) adsorption. Eventually, the As laced Fe(III) precipitates were removed from water using a $0.45 \mu\text{m}$ syringe filter. After gaining preliminary indications of As removal efficiency by different coprecipitation approaches, pilot experiments were carried out to investigate the issues of practical concern and long-term treatment efficiency. Samples were preserved by acidifying with concentrated nitric acid. As(III) and As(V) were measured using ion chromatography coupled to ICP-MS detection, whereby the samples were stabilized with EDTA.

3 RESULTS AND DISCUSSION

The levels of total dissolved As as well as the As(III) and As(V) species in the raw (ground) water are given in Table 1. Most ($>65\%$) of the dissolved As in the raw water is available as As(III), which is more difficult to

Table 1. Average dissolved arsenic levels ($\mu\text{g L}^{-1}$) in the raw water for the DWTP (>38 samples, 2014–2016).

Total As	As(III)	As(V)
9.10 ± 1.67	6.00 ± 1.61	2.99 ± 0.99

Figure 1. Arsenic profile, including its species in the rapid sand filter (top) as well as arsenic speciation in produced drinking water (bottom).

remove than As(V), due to its charge neutrality below pH 9.2. Figure 1 (top) shows the profile of As and its species over the height of the RSF bed. Most of the As removal occurs in the top half, i.e. in the top 800 mm of the filter bed. In the bottom half of the filter bed, only very low concentration of As, probably co-precipitated with Fe(III) precipitates, is being removed. Moreover, Figure 1 shows that most of the transformation of dissolved As(III) into As(V) takes place in the top half of the filter bed. Figure 1 (bottom) shows that the drinking water contains only As(V) and no As(III), which is consistent with the previous observation that As, while passing through the filter bed, is effectively removed and that the dissolved As(III) becomes oxidized into As(V) (Gude *et al.*, 2016). This has also been observed at other drinking water production locations in The Netherlands (Ahmad *et al.*, 2014). Nevertheless, this observation is remarkable, considering that oxidation of As(III) by atmospheric oxygen/air is known to be a slow process (Bissen and Frimmel, 2003). So far, the mechanism of oxidation of As(III) into As(V) in the RSF is not fully understood.

We hypothesized that by oxidizing As(III) into As(V) in the influent water of the RSF, more of the capacity of the RSF becomes available for As removal, which should lead to an increased As removal efficiency. In order to validate this, jar tests were performed with the raw (ground)water, whereby As(III) was converted to As(V) by dosing KMnO_4 as an oxidant, prior to filtration. Figure 2 (top) shows the

Figure 2. Residual arsenic levels in raw (ground) water in AOCF jar test (top) and C-UF lab test (bottom).

reduction in As levels to below $1 \mu\text{g L}^{-1}$ by dosing FeCl_3 at levels higher than 1.3 mg L^{-1} in the RSF influent, in which KMnO_4 (0.6 and 0.9 mg L^{-1}) is also present. The same result could also be obtained by dosing FeCl_3 into UF influent, which is shown in Figure 2 (bottom).

4 CONCLUSIONS AND OUTLOOK

It has been shown that most of As removal from groundwater occurs in the top half of a Rapid Sand Filter bed. In this part we also observed the conversion of As(III) into As(V). The mechanism of oxidation of As(III) into As(V) in the RSF is still not understood, however we hypothesize that either the manganese oxides or the biological activity in the filter bed may be responsible for this conversion. In agreement with this observation, we have also observed that drinking water only contains As(V) whereas the levels of As(III) are negligible. The experiments have shown that both AOCF and C-UF are promising emerging technologies to reduce arsenic levels to below $1 \mu\text{g L}^{-1}$.

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