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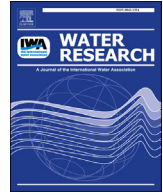
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# As(III) removal in rapid filters: Effect of pH, Fe(II)/Fe(III), filtration velocity and media size

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## ABSTRACT

In the top layer of aerated rapid sand filtration systems, uncharged As(III) is biologically converted to charged As(V). Subsequently, the main removal mechanism for As(V) is adsorption onto oxidised, flocculated Fe(III) (hydrated ferric hydroxides; HFO). The aim of this research was to understand the interactions between As and Fe in biologically active rapid filter columns and investigate the effect of different operational modes on Fe removal to subsequently promote As removal. For this purpose, different filter media column experiments were performed using natural, aerated groundwater containing 3.4 µg/l As(III). Results show that independent of the filter media size, complete (biological) conversion of As(III), manganese, ammonium and nitrite was achieved in approximately 70 days. After ripening, enhanced As removal was achieved with a top layer of coarse media or by dosing additional Fe(III). Addition of Fe(II) did not have the same effect on As removal, potentially due to heterogeneous Fe(II) oxidation in the upper layer of the filter, attaching rapidly to the filter grain surface and thereby preventing HFO flocs to penetrate deeper into the bed. Increasing the flow rate from 1 to 4 m/h did not improve As removal and lowering the pH from 8 to 7.4, resulted in an 55% increased removal of dissolved As. Altogether it is concluded that As removal in biologically active rapid sand filters can be improved by applying coarser filter media on top, in combination with dosing Fe(III) and/or pH correction.

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## 1. Introduction

Arsenic (As) removal is increasingly important when treating groundwater for drinking water production. The World Health Organization (WHO) put in effect a provisional guideline of <10 µg/L on As since 1993. However, As is toxic and can cause adverse health effects even at concentrations below 10 µg/L (Roh et al., 2017; van Halem et al., 2009; WHO, 2011). Hence, drinking water companies in the Netherlands have decided to investigate the practical implications of distributing drinking water with As concentrations <1.0 µg/L. In practice, requiring a reduction in the range of 1–4 µg/L to below 1 µg/L (Vitens, 2014) in commonly applied aeration - rapid sand filtration systems. At these low concentrations, the challenge for effective As removal is rapid oxidation of As(III) to As(V) before iron (Fe) removal occurs, since As(V) is more effectively adsorbed onto flocculating hydrous ferric oxides (HFO) than As(III) (Bissen and Frimmel, 2003; Gude et al., 2016, 2017, 2018). Both reduced As(III) and Fe(II), react with O<sub>2</sub> to As(V) and

Fe(III), respectively. These are the species present at thermodynamic equilibrium in an oxic environment at alkaline pH (Stumm and Morgan, 1996). Unlike Fe(II) oxidation, homogeneous As(III) oxidation by oxygen (O<sub>2</sub>) is sluggish (Driehaus et al., 1995). Kim and Nriagu (2000) observed that in 5 days only 54% of 48 µg/L As(III) in groundwater (pH between 7.6 and 8.5) was oxidised when exposed to air. This oxidation pathway is therefore not relevant for centralised groundwater treatment plants with limited residence times (Gude et al., 2016). Strong oxidants like chlorine, permanganate and ozone gas can instantly oxidise As(III) together with most other reduced constituents in groundwater (Ghurye and Clifford, 2004). However, as an alternative, also biological oxidation of As(III) can be employed. The existence of bacteria that are capable of oxidizing As(III) with oxygen (O<sub>2</sub>) has been well documented (Cavalca et al., 2013; Huang, 2014; Oremland and Stolz, 2003; Quéméneur et al., 2008), and their presence in rapid sand filters has been observed (Bai et al., 2016; Corsini et al., 2015; Gude et al., 2018). Despite their usefulness, no extensive research is available on how these As(III) oxidising bacteria in rapid sand filters can be optimally exploited for enhanced As removal.

For Fe(II) oxidation with O<sub>2</sub> in aeration-filtration systems a

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subdivision is generally made between homogeneous, heterogeneous and biological oxidation (van Beek et al., 2015; Vries et al., 2017). Homogeneous oxidation rate is mainly influenced by pH and O<sub>2</sub> concentration (Stumm and Lee, 1961) and occurs predominantly during aeration and supernatant water storage. Heterogeneous and biological Fe(II) oxidation occur on the surface of filter media in the rapid filter. During heterogeneous Fe(II) oxidation, Fe(II) is adsorbed to Fe oxides (such as HFO) prior to oxidation (Sharma et al., 1999; Wolthoorn et al., 2004). This oxidation rate is similarly governed by pH and O<sub>2</sub> but much faster, since it is catalysed by Fe oxides (Jones et al., 2014; Tamura et al., 1976). Additionally biological oxidation can occur in the filter bed, becoming more predominant when homogeneous and heterogeneous oxidation are hampered (de Vet et al., 2011; Katsoyiannis and Zouboulis, 2004b).

The aim of this research was to understand the interactions between As and Fe in biologically active rapid filter columns and investigate the effect of different modes of Fe removal to subsequently promote As removal. Filter media size, filtration velocity, supernatant level and pH can greatly affect Fe(II) and HFO removal pathways in rapid sand filters e.g. Sharma et al. (2001) and van Beek et al. (2015). However, to the best of our knowledge, the influence of these design and operational conditions on As removal has not been investigated yet. As(III) in the native groundwater is oxidized in the top layer of biologically active filters (Gude et al., 2016), so As(V) is mainly present in the deeper layers of the filter bed. It is therefore hypothesized that stimulating HFO penetration deeper into the filter bed, with applicable operational and design conditions, will result in more effective As adsorption in filters. Therefore experiments were performed to compare various filter media sizes, Fe(II) and Fe(III) additions, filtration velocity and pH in natural groundwater containing, on average, 3.4 µg/l As(III).

## 2. Materials and methods

### 2.1. Groundwater quality

The research was performed at drinking water production plant Wageningenseberg (Vitens N.V.). The tested water has a relative high pH (pH 8.0), contains low concentrations of As (3.4 µg/L), Fe (0.31 mg/L) and ammonium (NH<sub>4</sub><sup>+</sup>) (0.04 mg/L). The manganese (Mn) concentrations were 0.14 mg/L. The groundwater, used for these experiments, was the same as used for regular drinking water production. Therefore, depending on production demand, the number of groundwater wells in operation varied multiple times per day, leading to minor water quality changes as depicted in Table 1.

**Table 1**  
Groundwater quality water production plant Wageningenseberg (Vitens N.V.).

Water quality parameters	Units	average	min	max
Temperature	°C	10.7	10.7	10.7
O <sub>2</sub>	mg/L	0.02	0.01	0.02
ORP	mV	-172	-180	-165
Conductivity	µS/cm	185	185	185
pH	[-]	8.01	7.82	8.08
HCO <sub>3</sub> <sup>-</sup>	mg/L	94.5	85.8	99.7
As	µg/L	3.43	3.08	3.78
Fe	mg/L	0.31	0.25	0.34
Mn	mg/L	0.14	0.13	0.15
Ca	mg/L	29.4	27.5	31.0
Mg	mg/L	2.28	1.89	2.45
NH <sub>4</sub> <sup>+</sup>	mg/L	0.04	0.03	0.06
NO <sub>2</sub> <sup>-</sup>	mg/L	<0.01	<0.01	<0.01
PO <sub>4</sub> <sup>3+</sup>	mg/L	0.13	0.12	0.14
SiO <sub>2</sub>	mg Si/L	5.93	5.56	8.81

### 2.2. Experimental column set-up

The experimental set-up consisted of eight columns, with a diameter of 90 mm and a height of 1 m. Four pairs were made by filling duplicate columns with either fine sand, coarse sand, anthracite or pumice at a filter bed height of 50 cm, mainly simulating the upper part of a rapid filter. All variable settings were tested on one of the duplicate columns, whereas the other acted as the reference (Fig. 2). A fixed pressure of 6 m was obtained by a feed pump in the raw water (Wilo, Yonos PARA 3–45W). To ensure a constant, steady flow throughout the experiment the pressure was reduced just before the individual columns. Before starting the experiment, the columns were >30 min backwashed at ±30% expansion (15 cm). Backwashing was done with tap water without air scouring.

Aeration of the anaerobic groundwater was achieved by application of a small spray aeration device and cascading the water from 30 cm directly into the supernatant water; resulting in an O<sub>2</sub> concentration of 5–6 mg/L. This is half of the O<sub>2</sub> equilibrium concentration at 10 °C (±11.8 mg/L O<sub>2</sub>). However, the cumulative O<sub>2</sub> demand for the oxidation reactions of As(III), Fe(II), Mn(II) and NH<sub>4</sub><sup>+</sup> was below 0.5 mg/l O<sub>2</sub>. The supernatant water height was set at 1 cm by adjusting the height of the filtrate overflow, directly after backwashing. The default filtration velocity was 1 m/h (6.4 L/h per column). Due to filter clogging the supernatant water in the fine sand columns rose to ±10 cm in three to four days; for the other columns no rise in supernatant level was observed in this time-frame. After clogging of the fine sand columns, all columns were backwashed. Throughout the nine months of experiments, the columns were continuously fed with aerated groundwater and were situated at a location deprived from sun and artificial light.

### 2.3. Experimental settings

All collected data contributed to the assessment of five experiments: (1) biological filter ripening, (2) influence of filter media on Fe and As removal, (3) Fe(II) or Fe(III) addition in the supernatant water, (4) influence of filtration velocity on Fe and As removal and (5) adjusting the pH in the range of 7.4–8.0, thereby varying the time to homogeneously oxidise 90% of the Fe(II) from ±20 min to ±1.5 min (calculated in PHREEQC with wateq4f.dat), thus greatly affecting the mode of Fe removal within the practical pH-range of groundwater treatment. In experiment 1, the column pairs were operated in the same manner and therefore acted as real duplicates. In experiments 3–5, the duplicate filter media columns were operated as single columns. One was used to impose the various settings, while the other column acted as reference to account for the small water quality changes in the raw water. In this set-up, the reference column and the setting column were measured twice in the time span of 3h and averaged. The results could therefore be subjected to the paired *t*-test for statistical analysis to evaluate whether a significant difference was measured between the reference and the setting columns. Experiment 1, the biological ripening phase, was performed to observe the changing water quality as a result of the accumulation of biomass. As(III), NH<sub>4</sub><sup>+</sup> and Mn(II) were analysed in the filtrate twice a week at a filtration rate of 1 m/h (±10%). After the ripening period (72 days) and an additional 70 days stable operation was observed in all filter columns. Mn, NH<sub>4</sub><sup>+</sup> and nitrite (NO<sub>2</sub><sup>-</sup>) were converted or removed completely. At this point the other experiments (2–5) were performed. For experiment 2, the influence of filter media on As removal, all measurements of the reference filters were used. 18 measurements over 4 months with the same settings were averaged (n = 18). When running the other experimental settings (3–5), a stabilisation period of at least two days per setting was used before taking samples (Gude et al., 2016;

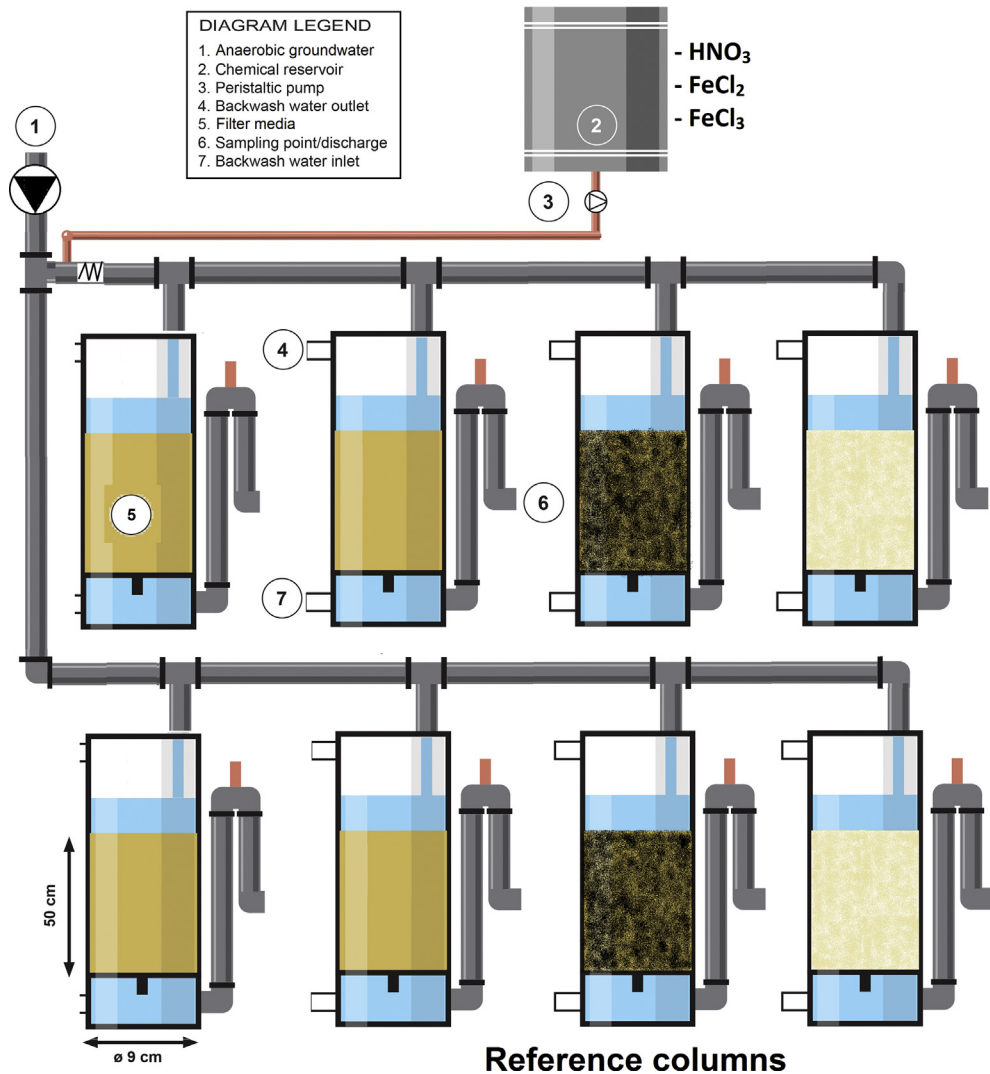


Fig. 1. Schematic overview of the filter column set-up, with duplicate columns for fine sand, coarse sand, anthracite and pumice.

Jessen et al., 2005), and before every setting the columns were backwashed. After 48 h runtime, the filtrate of all columns was sampled and analysed.

For experiment 3, on top of the naturally occurring 0.3 mg/L Fe(II), 0.3 and 0.6 mg/L Fe(II) or Fe(III) was added to the feed water of the four columns containing fine sand, coarse sand, anthracite and pumice. In experiment 4, different pH values, between 7.4 and 8.0, were tested by acidifying the raw groundwater with HNO<sub>3</sub>. Finally, for experiment 5, the filtration velocity was increased to 4 m/h and compared to their reference filters that were kept at a velocity of 1 m/h. To ensure that the biomass was adjusted to the higher flow rate, the filter columns were ripened for an additional 32 days. Duplicates for all settings were obtained by sampling all columns twice within a period of 2 h.

#### 2.4. Filter media

Four types of filter media were compared on their ability to remove As; the filter media and their properties are depicted Table 2.

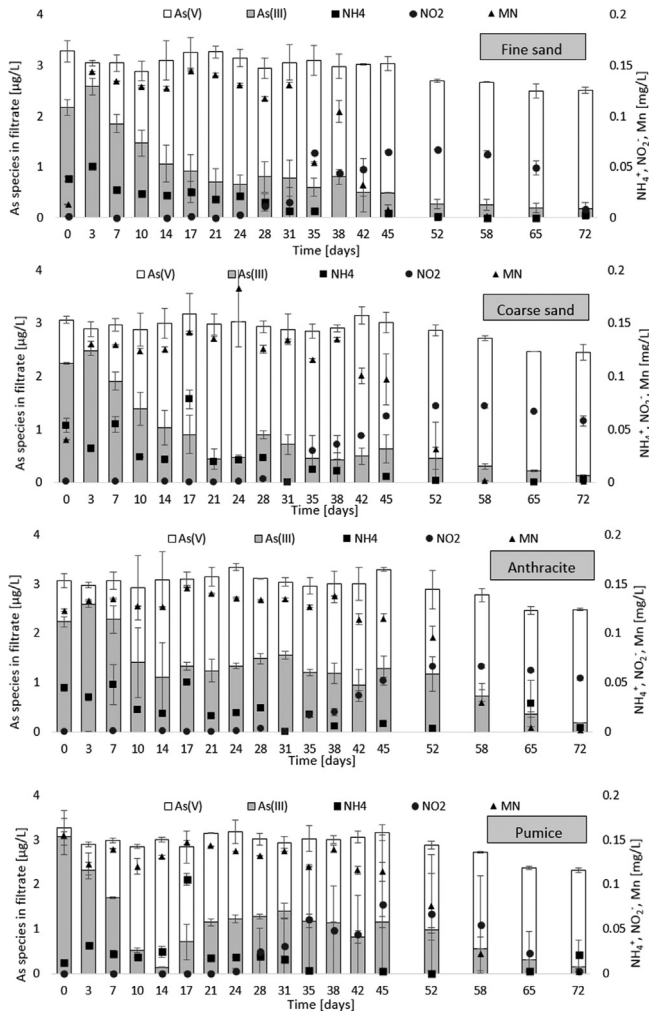
Filter media were obtained from Aqua-techniek B.V., fine and coarse sand were of 100% natural silica and type 1 according to EN 12904. Anthracite was type III and the pumice was Aqua-Volcano

according to EN 12906. Sand and anthracite are non-porous, pumice is (initially) porous (Technical datasheet).

#### 2.5. Chemicals, sampling and analytical methods

Fe was obtained from Sigma Aldrich: FeCl<sub>2</sub> • 4H<sub>2</sub>O (99.99%) and FeCl<sub>3</sub> • 6H<sub>2</sub>O (99%). Reagents grade 5M HNO<sub>3</sub> was used to adjust the pH of the columns and to stabilize the Fe(II) and Fe(III) dosing solutions by decreasing the pH to 3. The chemical concentration was adjusted in the reservoir, see Fig. 1, to obtain the various desired concentrations; the peristaltic pump continuously pumped the chemicals into the supernatant water at a flow rate of 0.9 ml/min (only pH 7.7 was achieved by increasing the pump speed to 1.8 ml/min).

Filtrate was collected in 2L jars that were continuously fed after the overflow to prevent changing the filtration rate while sampling. From these jars, filtered samples (0.45 μm), and unfiltered samples were taken and analysed. After 0.45 μm filtration total Fe concentrations in all samples were <0.02 mg/L, so the As in these samples can be considered as dissolved As. pH, electrical conductivity (EC) and O<sub>2</sub> were measured with WTW electrodes (SenTix 940, TerraCon 925 and FDO925, respectively). As, Fe and Mn were analysed with Inductively Coupled Plasma Mass Spectrometry (ICP-MS; Thermo X2-series), NH<sub>4</sub><sup>+</sup>, NO<sub>2</sub><sup>-</sup> and NO<sub>3</sub><sup>-</sup> were analysed by a



**Fig. 2.** As(III) oxidation,  $\text{NH}_4^+$  and Mn removal over time on quarts sand 0.4–0.8 mm; quarts sand 1.4–2.0 mm; anthracite 2.0–4.0 mm (Type N/III); pumice 2.3–3.4 mm. Filtration velocity of 1 m/h and water temperature of 10.7 °C. Error bars represent min and max values of duplicates.

spectrophotometer (Aquakem 250, company: Thermo Scientific). As speciation was done according the Clifford (2006) method. Here, 150 mL sample was passed through an anionic resin (80 mL Amberlite® IRA-400,  $\text{Cl}^-$ ) in a 100-mL syringe. The first 50 mL was always discarded, the remaining 100 mL was collected and analysed using ICP-MS. The charged As(V) species are retained by the resin, and the filtrate from the resin is considered to be only As(III). An additional measurement, without using resin, was done to determine the total As concentration, and the As(V) concentration was determined by subtracting the As(III) concentration from the total As concentration. However, at neutral pH the resin unavoidably retains on average 14% of As(III) (min = 7%, max = 23%; n = 24) (Gude et al., 2018).

**Table 2**

Properties of filter material used in the column experiments: fine sand, coarse sand, anthracite and pumice. Data obtained from product sheets supplier: Aqua-Techniek B.V.

	SIZE	EFFECTIVE SIZE ( $D_{10}$ )	HYDRAULIC SIZE	MASS DENSITY	POROSITY
	mm	mm	mm	$\text{Kg/m}^3$	[-]
FINE SAND	0.4–0.8	0.47	0.59	2.57	0.35
COARSE SAND	1.4–2.0	1.51	1.66	2.58	0.39
ANTHRACITE	2.0–4.0	2.4	2.8	1.36	0.46
PUMICE	2.3–3.4	2.51	2.83	2.40	0.80

### 3. Results and discussion

#### 3.1. Ripening of the filters

In rapid sand filters that treat aerated groundwater without application of strong oxidants like permanganate and chlorine, As(III) is biologically oxidised (Gude et al., 2018; Katsoyiannis and Zouboulis, 2004a; Oremland and Stolz, 2003), Mn(II) starts biologically (Bruins et al., 2015) and  $\text{NH}_4^+$  oxidation is a biological process (Lee et al., 2014). The processes start to become effective when sufficient biomass has accumulated on the filter media grains during a period of several weeks. Previous work showed that biological As(III) oxidation develops first, followed by  $\text{NH}_4^+$  and Mn(II) (Gude et al., 2018). In the current study, the ripening of the different filter media was monitored for a period of 72 days. The filtrate concentrations of dissolved As(III), As(V),  $\text{NH}_4^+$ ,  $\text{NO}_2^-$  and Mn are depicted in Fig. 2 for each of the filter media.

The biological oxidation processes of As(III),  $\text{NH}_4^+$  and Mn(II) developed sequentially over time. In all columns As(III) oxidation developed first, followed by  $\text{NH}_4^+$  oxidation and thereafter Mn(II) oxidation. Nevertheless, a differentiation between the various filter media can be made on the rate of start-up of the various processes. The biological ripening time was shortest for the fine sand columns and after 72 days all As(III),  $\text{NH}_4^+$ ,  $\text{NO}_2^-$  and Mn was completely converted or removed. On the coarse sand and anthracite, which have a larger grain size and therefore a smaller specific surface area than fine sand, Mn oxidation and removal started about 1–3 weeks later, while nitrification (i.e.  $\text{NO}_2^-$  production) started about 2 weeks later. Measurements (not shown in Fig. 2) indicated that all columns completely removed and converted all As(III),  $\text{NH}_4^+$ ,  $\text{NO}_2^-$  and Mn after 86 days.

Pumice, with the largest grain size, but with a very high internal porosity, was quickest to establish a biomass to convert As(III) to As(V). However, after 14 days, the steep decline in As(III) concentration was reversed and As(III) concentrations in the filtrate increased again. We visually observed, using a microscope, that in time, pumice becomes covered with mineral deposits, possibly hindering the transport of As(III) to the internal biomass. While not shown in Fig. 2, the Fe removal (initial concentration 0.3 mg/L) was instantaneous in all columns and Fe oxides may thus well be responsible for blockage of the internal pores of pumice.

Overall, the filter media with their different sizes, surface areas and shapes had a minor impact on the start-up time of As(III),  $\text{NH}_4^+$  and Mn oxidation. This may be related to the relatively low concentrations of Mn,  $\text{NH}_4^+$  and As(III) in the groundwater, for which only a limited amount of surface would suffice to accommodate the required biomass. This is confirmed by Lee et al. (2014) in Denmark, where Fe, Mn, and  $\text{NH}_4^+$  at similar concentrations were completely removed in the first 50 cm of a sand filter in a pilot experiment. It is expected that when the filter loading increases more surface area is required for the biomass. In addition, the accompanying effect due to frequent backwashing to remove the higher (Fe) solids load can disrupt immature biofilms and flush loosely attached biomass out of the system (Liu et al., 2012).

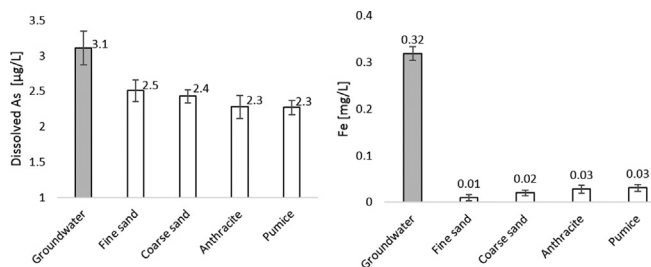
### 3.2. Influence of ripened filter media on As removal

The major part of removed As in a rapid sand filter is achieved by adsorption of As(V) to HFO (Gude et al., 2016). The HFO originates from naturally present Fe(II) by either homogeneous oxidation in the supernatant or in the pore volume of the filter material, or heterogeneous/biological oxidation on the surface of the filter grains. The homogeneously formed HFO flocs are subsequently retained in the filter, while, at least part of, the heterogeneous oxidised Fe(II) attaches itself to the filter media grains (de Vet et al., 2011; van Beek et al., 2015; Vries et al., 2017). In this respect, it was hypothesised that different (ripened) filter media sizes (i.e. different surface area and hydraulic pore channel size) perform differently concerning Fe removal and the accompanied As adsorption. Both dissolved As (left) and total Fe (right) concentrations in the filtrate of the columns are depicted in Fig. 3. The variations per filter media, which are depicted by the error bars, were mostly due to water quality changes during the measuring period of four months.

The removal of Mn,  $\text{NH}_4^+$  and  $\text{NO}_2^-$  was, after ripening, complete and consistent in all columns, As on the other hand varied as a result of the applied filter media. The removal of As was highest for the filter materials with the largest grain sizes. 27%, 27%, 22% and 19% As removal for pumice, anthracite, coarse sand and fine sand respectively. For Fe the opposite was observed, Fe removal was less effective in the columns with larger size filter media grains. The remaining Fe in the filtrate for pumice, anthracite, coarse sand and fine sand was 31, 28, 20 and 10  $\mu\text{g/L}$ , respectively. Consequently less HFO was present in the coarser filter media, however an increased As adsorption was observed. In Table 3 the accumulated As and the accumulated Fe present in the filter bed at the moment of sampling are depicted.

Not only the dissolved As concentrations were lower in the filtrate of the anthracite and pumice columns, but also the total As was lower. In 48h the accumulated As was highest in the anthracite and pumice columns while the least HFO was retained. Hence it is concluded that not only the amount of HFO is important in rapid filtration, but also the location where the HFO is retained in the filter bed, i.e., height over the filter, is of importance for effective As removal.

The application of different size filter media influences As and Fe removal. A smaller grain diameter results in high available surface area for chemical and biological processes, while a larger diameter results in more deep-bed filtration and subsequently a less effective particle retention (Moel et al., 2006). Apparently, the positive effect on biological activity by an increased surface area in the fine sand columns is out-competed by the positive effect of deep-bed



**Fig. 3.** Average dissolved As (left) and total Fe (right) concentration in the groundwater influent and filtrate of the various ripened filter media in filtration mode. Filtration velocity of 1 m/h, water temperature of 10.7 °C and samples taken after  $\pm$ 48h runtime. Error bars represent standard deviation ( $n = 18$ ). Using the paired  $t$ -test on the As values, chances of being in the same group are  $p < 0.025$  (being significantly different), with exception of comparing anthracite and pumice, they score  $p = 0.85$  (being very similar).

**Table 3**

Accumulated As and Fe after 48h runtime in the fine sand, coarse sand, anthracite and pumice columns ( $n = 18$ ). Filtration velocity 1 m/h, pH 8 and water temperature of 10.7 °C.

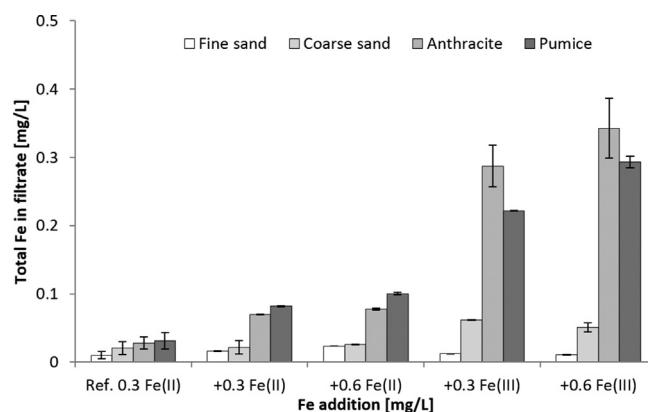
	As [mg]	Fe [mg]	As/Fe [-]
Fine sand	0.190	94.7	2.01E-03
Coarse sand	0.190	91.6	2.08E-03
Anthracite	0.252	89.2	2.82E-03
Pumice	0.249	88.2	2.82E-03

filtration of Fe in the coarser media columns. The proposed mechanism that larger grain sizes resulted in more effective As removal is that they permit less effective sieving/filtering of formed HFO and the larger hydraulic pore channels of the coarse filter media allows more homogeneous HFO production. Since homogeneous Fe(II) oxidation it is not surface related, it is assumed that the subsequently formed HFO can penetrate deeper in the filter bed.

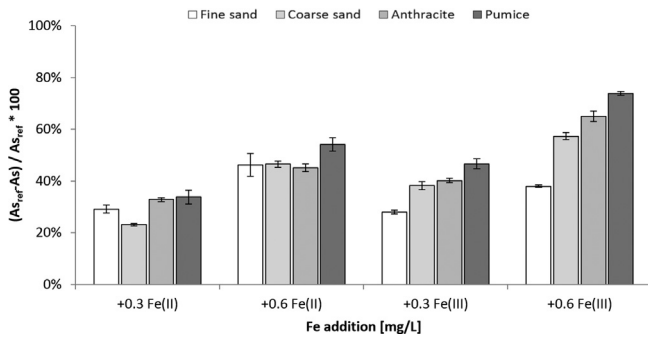
### 3.3. Effect oxidation state of Fe entering the filter bed on As removal

It was shown that by applying filter media with larger grains, more Fe ended up in the filtrate, indicating that HFO penetrated deeper into the filter bed and subsequently adsorbed more As. This positive effect was hypothesised to be related to a higher ratio homogeneous Fe oxidation and flocculation, compared to heterogeneous (surface-related) oxidation within the larger hydraulic pore channels of the coarser material. To investigate the role of Fe oxidation state in the filter bed, different Fe(II) and Fe(III) concentrations were dosed to the influent. Total Fe concentrations in the filtrate of the fine sand, coarse sand, anthracite and pumice columns, after dosing additional Fe, are depicted in Fig. 4, for 0.3 and 0.6 mg/l Fe(II) and 0.3 and 0.6 mg/L Fe(III) additions.

Addition of either Fe(II) or Fe(III) at the same concentrations resulted in different Fe concentrations in the filtrate. Fe(II) was more effectively retained than Fe(III) in the coarse sand, anthracite and pumice filter columns. Fine sand, on the other hand, removed the additional Fe(III) slightly more effectively than Fe(II). The dosing of 0.3 and 0.6 mg/L Fe(II) resulted in filtrate concentrations of 16 and 23  $\mu\text{g/L}$  versus 12 and 11  $\mu\text{g/L}$  for Fe(III). Apparently, confirmed by the strongest increase in pressure drop, the Fe(III) blocked the pores in the top layer of the fine sand column,



**Fig. 4.** Fe concentrations in filtrate [mg/L] as a result of Fe(II) and Fe(III) additions on top of 0.3 mg/L Fe(II) naturally present in the groundwater. Filtration velocity of 1 m/h, water temperature of 10.7 °C and samples taken after  $\pm$ 48h runtime. Error bars represent min and max values of duplicates.



**Fig. 5.** Effect of 0.3 and 0.6 mg/L Fe(II) and Fe(III) additions on dissolved As concentration in filtrate. Results depicted as percentage of additional dissolved As removal with respect to their reference column. Filtration velocity of 1 m/h, water temperature of 10.7 °C and samples taken after  $\pm$ 48h runtime. Error bars represent min and max values of duplicates.

increasing Fe(III) removal efficiency also observed by Sharma et al. (2001) where 4 times more head loss was occurred in fine media compared to coarse media during Fe floc filtration. The other media did not remove Fe(III) better than Fe(II). Clearly the larger hydraulic pore channels in the coarse filter media retained less HFO flocs (originating from the Fe(III)), ending up deeper in the filter bed and ultimately in the filtrate. Similarly for Fe(II), the grain size determined the Fe removal efficiency, however, the removal efficiencies were more in the same range. Apparently Fe(II) is more efficiency removed in coarse filters than Fe(III), probably due to the surface related heterogeneous Fe(II) oxidation which does not occur when Fe(III) is dosed. Sharma et al. (2001) also observed decreased Fe concentrations in the filtrate when comparing adsorptive Fe(II) removal compared to floc filtration. Altogether is concluded that heterogeneously oxidised Fe(II), especially in media with larger grain size, was more effectively removed than homogeneous Fe(II) oxidation prior to filtration (simulated by Fe(III) addition in the feed water).

Fig. 5 depicts the decrease of dissolved As in the filtrate as a result of Fe(II) and Fe(III) additions; this decrease was calculated by using the dissolved As values:  $(As_{ref} - As)/As_{ref} * 100$ .

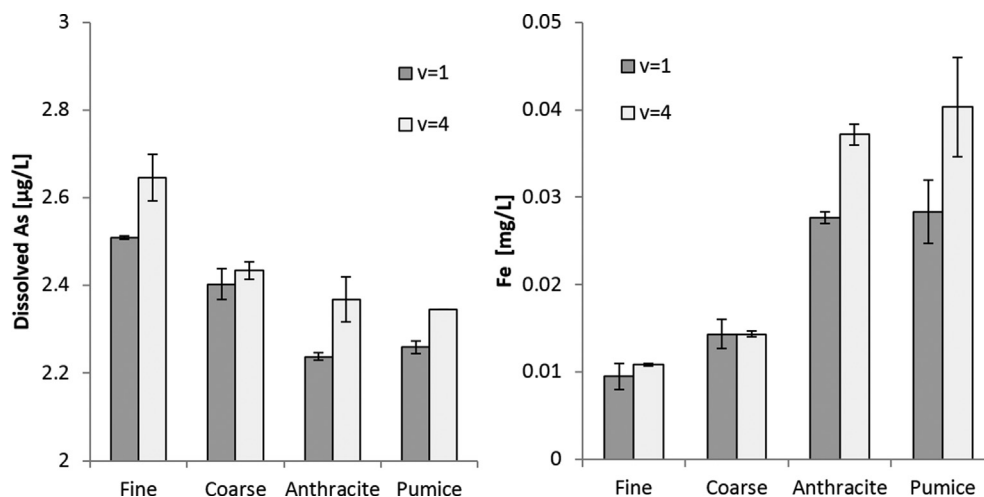
As a result of adding 0.3 mg/L Fe(III), dissolved As was decreased by 28% 38% 40% and 46% for fine sand, coarse sand, anthracite and pumice respectively. Addition of 0.6 mg/L Fe(III) resulted even in

higher adsorption of dissolved As: 28%, 57%, 65% and 74% also fine sand, coarse sand, anthracite and pumice respectively. For Fe(II), dissolved As adsorption was lower: 29%, 23%, 33% and 34% for fine sand, coarse sand, anthracite and pumice respectively, when adding 0.3 mg/L Fe(II) and 46%, 47%, 45% and 54% when adding 0.6 Fe(II). For all filter media, except fine sand, the addition of Fe(III) thus resulted in a larger decrease in dissolved As than the addition of Fe(II). Confirming the hypothesis that more As is adsorbed in rapid filters when Fe(II) is oxidised prior to filtration or in the pore channels. In addition, the better retention of Fe(II), compared to Fe(III), resulted in more HFO accumulation during a filter run. However, this did not attribute to increased As removal. Calculating the As/HFO ratio that was retained in the filter during the run time, it was found that with both the Fe(II) and Fe(III) additions, the As/Fe ratio in the filter bed increased with the filter media size (fine sand < coarse sand < anthracite < pumice). Indicating that the filter media that retained the least amount of HFO, most effectively adsorbed As. The data suggest that application of a dual layer filter with coarse media in the top, to effectively adsorb As to HFO, and fine media in the bottom, to retain the As-HFO flocs, would result in maximum As removal.

Possible explanations for the lower effectivity of reducing the dissolved As concentrations by Fe(II), compared to Fe(III), are, (1) Fe(II) oxidises (partly) on the grain surface and is removed rapidly in the top layer of the filter bed (Mettler et al., 2009; Tamura et al., 1976; Vries et al., 2017), preventing it to reach deeper layers for As(V) adsorption (Sharma et al., 2001; van Beek et al., 2015), and/or (2) heterogeneous oxidation results in less available sites for surface complexation, lowering the adsorption capacity of the HFO – comparable to HFO formed through Fe(II) oxidation by MnO<sub>2</sub> (Gude et al., 2017) and/or (3) that the Fe minerals form a mineral layer on top of As-oxidizing biofilm or taking available surface, hindering As(III) oxidation.

### 3.4. Influence of filtration velocity on As removal

Increasing the filtration velocity can be an alternative method to force HFO deeper into the filter bed, as it, among other mechanisms, increases the hydraulic shear forces within the pore channels. On the other hand biological As(III) oxidation may occur deeper in the filter bed as well. Fig. 6 depicts the total Fe and dissolved As concentration in the filtrate of the fine sand, coarse sand, anthracite



**Fig. 6.** Average dissolved As concentrations in the filtrate after 0.45  $\mu$ m filtration (left) and total Fe concentration in the filtrate (right) at 1 m/h and 4 m/h in the fine sand, coarse sand, anthracite and pumice columns. Water temperature of 10.7 °C and samples taken after  $\pm$ 48h runtime. Error bars represent min and max values of duplicates. The paired t-test results ranging from 0.1 > p > 0.3 indicating no significant change (p > 0.05) in As concentrations for the two filtration velocities.

and pumice columns at 1 m/h and 4 m/h.

There were basically no changes in Fe concentrations in the filtrate of the fine and coarse sand filters, when increasing the filtration velocity from 1 m/h to 4 m/h. Only in the anthracite and pumice columns an increase of 10  $\mu\text{g/L}$  Fe was observed in the filtrate, and instead of improving the As removal, the concentration in the filtrate went up. Modestly however, with 5%, 1%, 6% and 4% for fine sand, coarse sand, anthracite and pumice respectively. These results show that by increasing filtration velocity, As adsorption to HFO is slightly decreased. However, the removal was not significantly reduced in the columns with increased filtration velocity ( $t$ -test  $p > 0.05$ ).

It seems that the strictly surface-related biological As(III) oxidation was differently affected by increased filtration velocity than HFO formation. Together this resulted in a negative effect on As removal, which is in line with the finding that Fe(II) oxidation prior to filtration is beneficial for As removal (Fig. 5). At increased filter loading, the residence time in the supernatant level is shortened which should result in increased Fe(II) in the filter bed and a subsequent negative effect on As removal. Additionally, the increased filtration velocity resulted in a factor 4 higher Reynold numbers (e.g. pumice from 1.2 to 4.7; Tchobanoglous et al., 2003). More turbulence within the hydraulic pore channels may have accelerated the transport of Fe(II) to the grain surface and increased the chance for heterogeneous oxidation at the grain surface. In addition, the surface related mineral formation may have competed with biological As(III) oxidation for the available surface. This surface limitation hypothesis is, for example, building on observations by Lee et al. (2014), where increased loading of  $\text{NH}_4^+$  on a rapid sand filter did not result in additional oxidation of  $\text{NH}_4^+$ .

The complexity and number of processes involved make it difficult to draw a general conclusion on the observations shown in Fig. 6. However, it is clear that simply increasing the filtration velocity to bring HFO deeper into the filter bed will increase As removal is not true.

### 3.5. Influence of pH on As removal

Lowering the pH decreases the rate of Fe(II) oxidation, both homogeneous (Stumm and Lee, 1961) and heterogeneous (Tamura et al., 1976), and could potentially cause Fe to penetrate deeper in the filter bed. Additionally, HFO has a higher adsorption capacity for As(V) at lower pH (Dixit and Hering, 2003; Dzombak and Morel, 1990; Gude et al., 2016), suggesting that As(V) adsorption can be

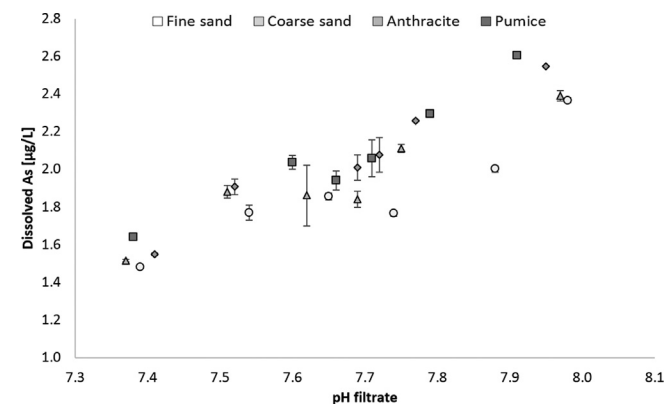


Fig. 7. Effect of pH on dissolved As in the filtrate of fine sand, coarse sand, anthracite and pumice columns. Filtration velocity of 1 m/h, water temperature of 10.7 °C and samples taken after  $\pm 48$ h runtime. Error bars represent min and max values of duplicates.

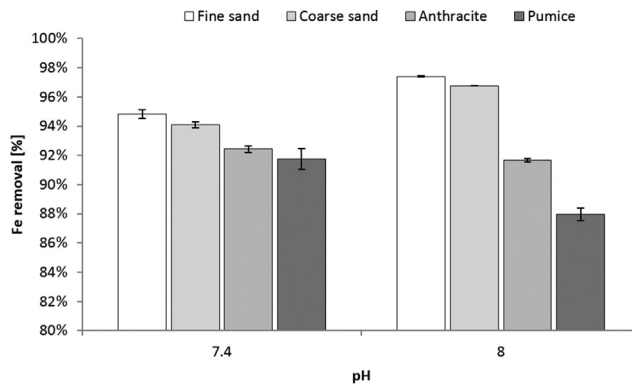


Fig. 8. Fe removal efficiency shown for pH 7.4 and 8 in fine sand, coarse sand, anthracite and pumice filtrate. Filtration velocity of 1 m/h. Error bars represent min and max values of duplicates.

increased at lower pH values after As(III) is oxidised. Influence of pH was investigated at a pH range of 7.4–8.0 which is not an uncommon pH for groundwater treatment. The dissolved As concentration in the filtrate as a function of pH for the investigated filter media is depicted in Fig. 7.

The results show that in the investigated pH range, the dissolved As in the filtrate decreased as the pH decreased for all filter media. Dissolved As concentrations decreased from 2.40 to 2.60  $\mu\text{g/L}$  at pH 8.0 to 1.50–1.65  $\mu\text{g/L}$  at pH 7.4, respectively. This corresponds to a decrease in dissolved As of 15%–55%. The exceptional As removal performance by pumice at the measurement intervals  $> \text{pH } 7.7$  was probably caused by a greater ‘pool’ of retained HFO in the filter bed from previous runs, which provided (temporarily) additional sorption sites while lowering the pH, analogue to observations in Gude et al. (2016), where HFO showed increased sorption capacity at lower pH. Fig. 8 depicts the corresponding Fe removal percentage in the fine sand, coarse sand, anthracite and pumice for pH 7.4 and 8.0.

Anthracite and pumice, the coarsest filter media, showed improved Fe removal: from 91% to 88% at pH 8–93%–92% at pH 7.4, respectively. While for the fine and coarse sand filters, Fe removal efficiency dropped from about 97 to 94%. Given that flocculation is not so effective while using large grain sizes the increased removal can perhaps be explained by a switch to adsorptive removal which was also observed by (Sharma et al., 2001). In itself, this shift to surface-related, heterogeneous oxidation was observed not to be beneficial for As removal – as observed in the prior experiments with Fe(II) additions – however, when reducing the pH also heterogeneous Fe oxidation rate is reduced (Jones et al., 2014; Tamura et al., 1980). Additionally, substantial increase in adsorption capacity of HFO for As(V) was found at lower pH (Dixit and Hering, 2003; Gude et al., 2016; Mercer and Tobiason, 2008; Qiao et al., 2012). Hence, HFO formation may have occurred deeper in the filter bed where biological As(III) oxidation was complete and the adsorption capacity would have been increased due to favourable charge conditions.

## 4. Conclusions

The research aimed at promoting As removal by understanding its interaction with Fe(II) and HFO in the filter bed. For this purpose the effect of filter media size, pH, Fe(II) and Fe(III) additions and filtration velocity were investigated in natural groundwater filter columns. Based on the presented research it may be concluded that biological As(III) oxidation developed in filter columns, independent of the applied filter media (fine sand, coarse sand, anthracite



or pumice), with a slightly faster ripening for media with a finer grain size or larger internal porosity (pumice). After ripening, enhanced As removal was achieved with a layer of coarser media or by dosing additional Fe(III), promoting HFO flocs to penetrate deeper into the bed, which was observed by higher Fe concentrations in the filtrate. Apparently, Fe(II) oxidation prior to rapid filtration is beneficial to As(III) removal. This was confirmed by increasing the flow rate from 1 to 4 m/h, where As removal was not improved, although HFO flocs were 'pushed' deeper in the filter bed. Lowering the pH in the range of 7.4–8.0 resulted in a positive effect on As removal. Possibly due to slowing the Fe removal rate and the advantageous adsorption capacity of HFO at lower pH. Altogether it is concluded that As removal in biologically active rapid sand filters can be improved by applying coarser filter media, in the top of the filter bed, in combination with dosing of Fe(III) and/or pH correction.

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