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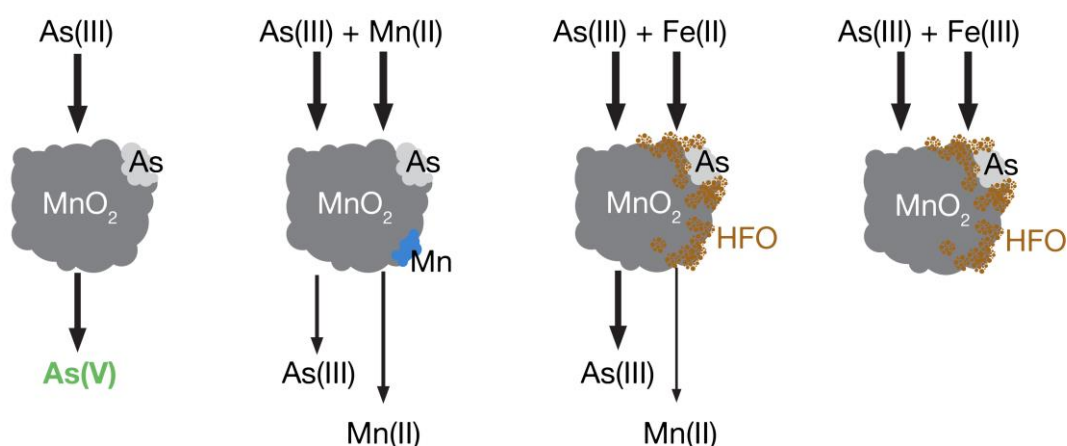
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As(III) oxidation by MnO₂ during groundwater treatment

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Graphical abstract



Highlights

- MnO₂ rapidly oxidises As(III) in demineralised water;
- MnO₂, in absence of bacteria, did not enhance As(III) removal in natural groundwater;
- Fe(II) and Mn(II) prevented As(III) oxidation by MnO₂;
- Fe(III) did not hinder As(III) oxidation on MnO₂; resulting in subsequent effective As(V) removal by the flocculating HFO.

Abstract

The top layer of natural rapid sand filtration was found to effectively oxidise arsenite (As(III)) in groundwater treatment. However, the oxidation pathway has not yet been identified. The aim of this study was to investigate whether naturally formed manganese oxide (MnO₂), present on filter grains, could abiotically be responsible for As(III) oxidation in the top of a rapid sand filter. For this purpose

As(III) oxidation with two MnO₂ containing powders was investigated in aerobic water containing manganese(II) (Mn(II)), iron(II) (Fe(II)) and/or iron(III) (Fe(III)). The first MnO₂ powder was a very pure - commercially available - natural MnO₂ powder. The second originated from a filter sand coating, produced over 22 years in a rapid filter during aeration and filtration. Jar test experiments showed that both powders oxidised As(III). However, when applying the MnO₂ in aerated, raw groundwater, As(III) removal was not enhanced compared to aeration alone. . It was found that the presence of Fe(II) and Mn(II) inhibited As(III) oxidation, as Fe(II) and Mn(II) adsorption and oxidation were preferred over As(III) on the MnO₂ surface (at pH 7). 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). 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.

Keywords: Natural groundwater treatment; As(III) oxidation; As removal; MnO₂; HFO

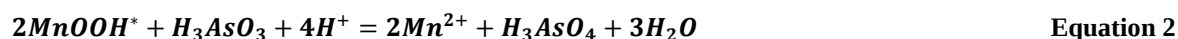
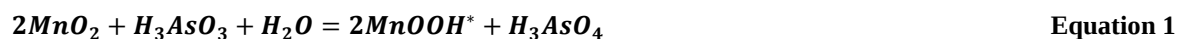
Introduction

Conventional groundwater treatment plants consisting of aeration and rapid sand filtration, are merely designed and optimised for iron (Fe), manganese (Mn) and ammonium (NH₄⁺) removal (Moel et al., 2006). However, due to ever decreasing detection limits and more insight into the toxicity of other inorganic parameters such as arsenic (As), chromium and nickel (van Halem et al., 2009; WHO, 2011), drinking water companies in the Netherlands are considering to bring the current national As standard of 10 µg/L down to a new guideline of 1 µg/L. The benefits of aeration and rapid filtration, apart from being economically attractive, are that (i) no chemicals are required, (ii) dense, possibly valuable, iron (Fe) rich waste streams are generated and (iii) biologically stable drinking water is produced. The latter is crucial for the Netherlands, as (post) chlorination is not applied and biologically stable drinking water (low in nutrients) is required to assure the microbial safety in the distribution network (Smeets et al., 2009).

The filter bed plays a crucial role in efficient As removal (Gude et al., 2016) due to the rapid oxidation of As(III) to As(V). In the filter bed, Fe(II) is removed by homogeneous, heterogeneous and biological

oxidation (van Beek et al., 2015; de Vet et al., 2011). The accumulated Fe in the filter bed is easily removed from the filter during the periodic backwash procedure, and only a small part is retained in a filter coating as hydrous ferric oxides (HFO). Mn, on the other hand, is not oxidised in absence of bacteria and surface catalysts (Diem and Stumm, 1984) and has therefore mainly been found to be retained in the filter coating (Gude et al., 2016), predominantly as poorly crystalline MnO₂ identified as Birnessite (Bruins et al., 2014). NH₄⁺ is removed in the rapid sand filter bed by biotic oxidation in a two-step oxidation process from NO₂⁻ to NO₃⁻ (Katsoyiannis et al., 2008; Lee et al., 2014). The fate of As(III) in the rapid sand filter bed is still unrevealed. Oscarson et al. (1981) found that As(III) oxidises on a MnO₂ surface, but HFO was inactive with regard to As(III) oxidation. Therefore, Gude et al. (2016) suggested that the cause of accelerated As oxidation in the filter bed was either biotic or by, the highly reactive, biogenic MnO₂ (Spiro et al., 2010) present on the filter grains.

In this reaction, MnO₂ is the electron acceptor for As(III) oxidation, resulting in the reduction of MnO₂ to Mn(II). The reduction of MnO₂ by As(III) entails a two-step reaction where both the initial MnO₂ and the intermediate product, MnOOH, can oxidise As(III) (Manning et al., 2002; Nesbitt et al., 1998):



During this oxidation process, depending on pH, As can either adsorb onto MnO₂ surface (Manning et al., 2002) or remain in solution. Apart from As(III), Fe(II) can also react on the MnO₂ mineral surface, resulting in formation of HFO and mobilization of Mn(II) (Postma, 1985; Postma and Appelo, 2000).



Wu et al. (2015) studied the redox and sorption interactions between MnO₂, As(III) and Fe(II) in anaerobic water. Similar to the reactions described by Nesbitt et al. (1998), the As(III) oxidation showed a two-phase trend with a fast initial oxidation followed by a decreased oxidation rate. Furthermore, observations concerning Fe(II) addition were analogue to Equation 3. The Fe(II) was oxidised at the MnO₂ surface, mobilising Mn(II), and thereby inhibiting As(III) oxidation, but overall increasing As removal by adsorbing As on the formed HFO. Also Mn(II) was found to be able to inhibit As(III) oxidation and pacify a MnO₂ surface. Using X-ray absorption spectroscopy (XAS) and

X-ray diffraction (XRD) among other techniques, Lafferty et al. (2010) showed increased Mn(III) content in a MnO_2 mineral as a results of Mn(II) sorption. The interactions of As(III), Fe(II) and Mn(II) individually on MnO_2 are schematically depicted in Figure 1.

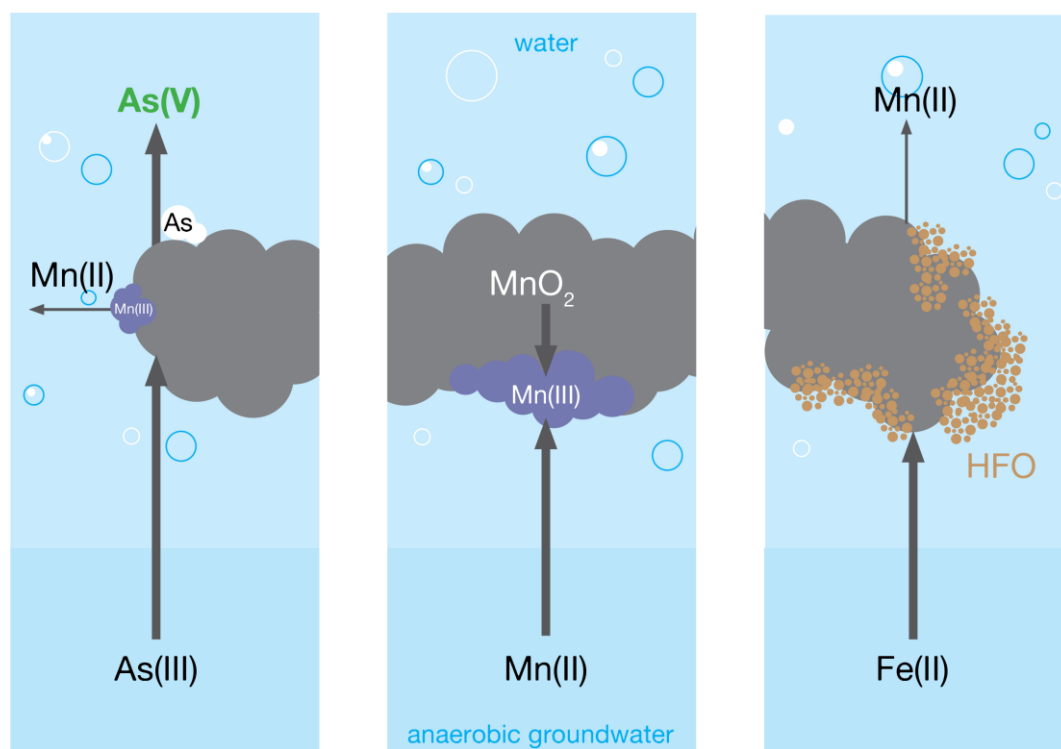


Figure 1 Schematics of As(III), Fe(II) and Mn(II) interaction with MnO_2 derived from literature (Lafferty et al., 2010; Manning et al., 2002; Postma, 1985).

As(III) and As(V) adsorption onto HFO has been thoroughly investigated. Adsorption of As(III), the reduced uncharged As state, is stable at the neutral pH range of 7 to 8 (Dixit and Hering, 2003). As(V), being the oxidised and negatively charged state form, shows a decrease in sorption onto HFO with increasing pH (Dixit and Hering, 2003; Manning et al., 1998). At low As to Fe molar ratios (≈ 0.01) and limited contact times, As(V) is easier to remove by adsorption on HFO than As(III) (Bissen and Frimmel, 2003a). However in aerobic Fe(II) and As(III) systems; As(III) has been shown to catalytically oxidise by intermediate Fe(IV) species, either during homogeneous Fe(II) oxidation (Hug and Du, 2003; Johnston and Singer, 2007), but also during heterogeneous oxidation, where Fe(II) oxidises on a Fe oxide (Amstaetter et al., 2010; Wang et al., 2015). Therefore, a beneficial effect

concerning As(III) removal can be expected from HFO originating from Fe(II) at near neutral pH. This beneficial effect is reported by Roberts et al. (2004) by using Fe(II) and Fe(III) for the removal of high As(III) concentrations in simulated groundwater.

Rapid As(III) oxidation has been found to occur in the top layer of natural groundwater filters (Gude et al., 2016). In addition, MnO₂ has been found to accumulate on the sand grain surface in these filters. Although it is known that MnO₂ is capable of oxidising As(III), it is unknown whether naturally grown MnO₂ on filter sand grains are able to oxidise As(III). Additionally, it is unclear whether MnO₂ in a sand filter remains capable to oxidise As(III) in competition with other reduced constituents in natural groundwater like commonly co-occurring Fe(II) and Mn(II). Basically, the effect of MnO₂ on As(III) in the complexity of the natural groundwater matrix remains a knowledge gap. Therefore, it was the aim of this study to investigate whether MnO₂ – in the absence of bacteria – could be responsible for the observed As(III) oxidation in the top layer of natural rapid sand filters.

For this purpose, abiotic oxidation of low As(III) concentrations (20 µg/L) by MnO₂, obtained from both a commercial supplier and from a filter sand coating, was studied in oxygenated, buffered, demineralised water at pH 7. Additionally, As(III) and MnO₂ interactions were investigated in the presence of Mn(II) and Fe(II) both in demineralised water and natural aerated groundwater.

Materials and methods

Jar test procedure

Jar test experiments were executed to simulate As(III) oxidation and removal in the presence of MnO₂, Fe(II), Fe(III) and/or Mn(II). Additionally, As(III) adsorption experiments with HFO, originating from either Fe(II) or Fe(III), were executed to differentiate between the effect of HFO alone and the added effect of MnO₂. The origin of the HFO and its influence on As(V) adsorption was further scrutinised by a comparison between HFO originating from Fe(II) + O₂, Fe(II) + Cl₂ and Fe(III).

The general procedure for the jar tests with synthetic water was: 20 µg/L As(III) or 100 µg/L As(V) and 2 mM NaHCO₃, acting as a pH buffer, were added to 1.8 L demineralised water. The solution was

fully saturated with O₂ and brought to pH 7 or to 7.7 by addition of HNO₃. Figure 2 depicts the experimental settings schematically.

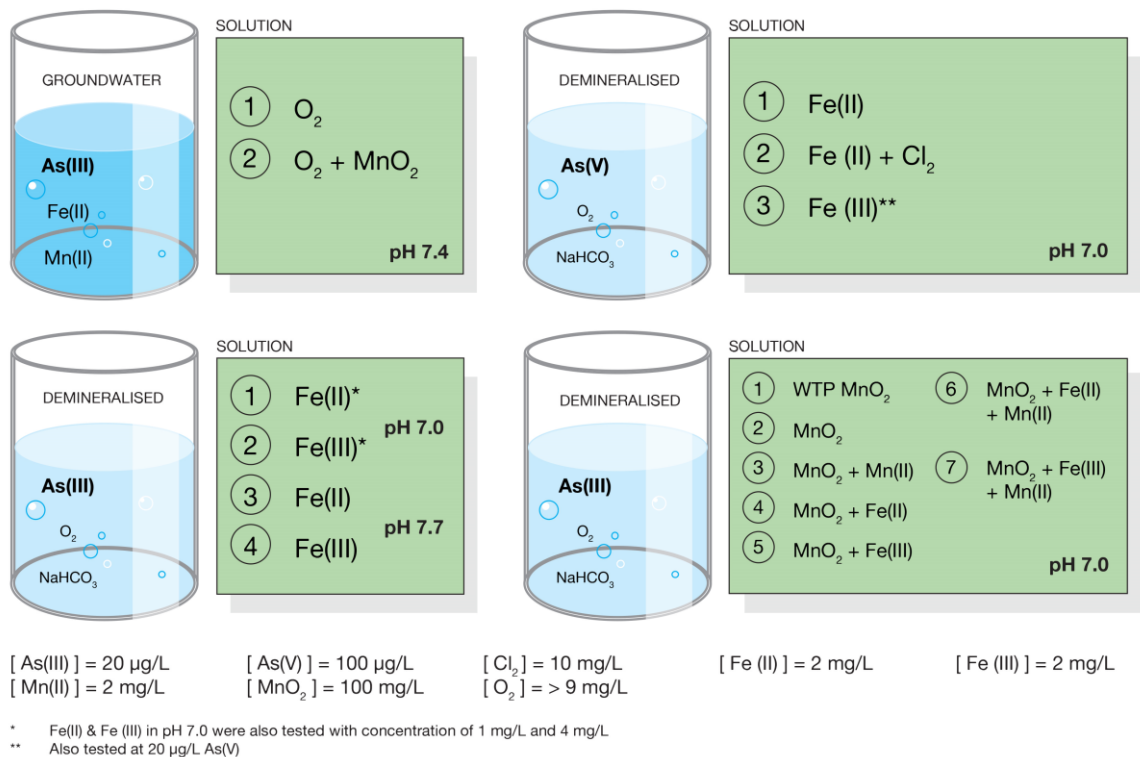


Figure 2 Schematic overview of experimental settings. Experiments were performed in duplicate.

To start the experiment using As and demineralised water, 0.1 g/L MnO₂ powder, 2 mg/L Fe(II,III) and/or 2 mg/L Mn(II) were added to the jar. Independent of the used chemicals, the dosing sequence remained the same. The chemicals sequence was: NaHCO₃, As(III)/As(V), Cl₂ (only used in combination with As(V)), Mn(II), Fe(II,III) and MnO₂ as the final additive. For the natural groundwater tests 0.28 g/L MnO₂ powder was used because more Fe(II) and competing ions were present. Before addition to the natural groundwater and the demineralised water, the MnO₂ powder was brought into suspension using 20 mL demi water; 1.8 mL NaOH 10 mM was added to the MnO₂ suspension when used with Fe(II) and Fe(III) to compensate for the pH drop. For all experiments, fresh, dry MnO₂ was used and reaction time was kept under 2 h to exclude the effect of homogeneous As(III) oxidation and the role of manganese oxidising bacteria. The sample intervals for the natural

groundwater experiments were 10, 20 and 60 min. The experiment was done in duplicate and the samples were taken from the same jar over time. The sample intervals for the experiments using demineralised water were 2, 5, 10, 20, 30, 60 and 120 min and were also performed in duplicate. For each measurement 120 mL sample water was taken from the same jar, leaving approximately 1.0 L of test water at the end of each run. The reaction was stopped by directly filtering the sample over 0.45 μm and acidifying to pH 5 by adding HNO_3 to prevent further Fe(II) oxidation during As speciation. 50 mL was used for analysis of total As, Fe and Mn, and 70 mL was used for As speciation. The jars were stirred by a magnetic stirrer (Labinco model LD-746) at 40% power, maintaining the MnO_2 powder in suspension. The jars were continuously analysed for pH and temperature. At the start of the demineralised water experiments, the pH drop, caused by Fe(II) and Fe(III) addition, was compensated within 1 min to the initial pH using NaOH. During the 120 min experiment, the solution pH was kept constant by adding diluted HNO_3 intermittently.

Chemicals and preparation

As(III), NaAsO_2 , 0.05M, Company (Fluka Analytical) and As(V) $\text{HAsNa}_2\text{O}_4 \cdot 7\text{H}_2\text{O}$, $\geq 98\%$, (Sigma-Aldrich) were prepared into a stock solution of 1 mg/L on a daily basis. To stabilise pH during the experiment, 2 mM NaHCO_3 (J.T. Baker) was used, which is a common concentration in Dutch groundwater. For Fe(II), Fe(III) and Mn(II), stock solutions were prepared with $\text{Cl}_2\text{Fe} \cdot 4\text{H}_2\text{O}$ (99.99%, Sigma-Aldrich), $\text{Cl}_3\text{Fe} \cdot 8\text{H}_2\text{O}$ ($\geq 98\%$, Sigma-Aldrich) and $\text{Cl}_2\text{Mn} \cdot 4\text{H}_2\text{O}$ (99.99%, Sigma-Aldrich), respectively. The chemicals were dissolved in demineralised water to 2 g/L and acidified with HCl; the same stock solutions were used for all experiments. The Cl_2 used for instantaneous oxidation of Fe(II) was diluted from a stock solution of 15% Cl (Brenntag) sodium hypochlorite to 20 mg/L Cl_2 in the test water. At the start of an experiment, the stock solutions were dosed to the ambient air saturated ($> 9 \text{ mg/L O}_2$) demineralised water (21-23°C) with a calibrated ThermoFisher Finn timer F1 (0.5 – 5.0 ml).

Natural aerated groundwater

On-site experiments were executed at a water treatment plant in Loosdrecht (Vitens Water Supply). The groundwater composition at this plant was: temperature 11 °C, pH 7.39; HCO₃ 115 mg/L, electrical conductivity (EC) 250 µS/cm, oxidation reduction potential (ORP) -139 mV, As 26.1 µg/L, As(III) 22.4 µg/L, Fe 4.33 mg/L, Mn 0.178 mg/L, NH₄⁺ 0.29 mg/L-N, phosphate (PO₄) 0.19 µg /L-P, total organic carbon 2.56 mg/L and sulphate 7.72 mg/L.

MnO₂ grains

Two types of MnO₂ powders were used. The first was the commercially available Mangalox-K-45 (Sibelco; d₁₀ 2.2 µm, d₅₀ 9.4 µm, d₉₀ 36.1 µm), hereafter 'MnO₂'. The second originated from a filter coating produced in 22 years during a filtration process in the Netherlands (WTP 1 in Gude et al. (2016)), hereafter 'WTP MnO₂'. The coating was easily, manually peeled off the extracted filter sand grains (coating thickness was approximately 2 mm) and dried at 80 °C for 24 h. The dried filter sand coating was ground into a fine powder.

For analytic purposes, the powdered MnO₂ was dissolved in a solution of 0.05 M sulphuric acid and 0.04 M oxalic acid (Artamonova et al., 2013). For the solution, 278 µl of w(H₂SO₄)=96% and 0.36 g H₂C₂O₄ in powder were added to sample containers with 100 mL demineralised water. 0.1g of the two MnO₂ powders remained in the containers for at least 11 d before ICP-MS analysis. X-ray diffraction (XRD) was performed in a Bruker D8 Advance diffractometer for both powders, X-ray fluorescence (XRF) was performed in a Panalytical Axios Max WD-XRF spectrometer and particle sizes of the MnO₂ powder were measured with a Malvern Mastersizer 2000. The relevant properties of both MnO₂ powders are summarised in Table 1.

Table 1 Properties of MnO₂ and WTP MnO₂

Parameter	Unit	MnO ₂	WTP MnO ₂
Mn	mg/g	548	301
Fe	mg/g	20	126
Ca	mg/g	2	38

XRD ¹	compound	Vernadite (Mn(OH) ₄) Ramsdellite (MnO ₂) Bixbyite (MnFeO ₃) Pyrochroite (Mn(OH) ₂) Quartz (SiO ₂)	Birnessite ((MnO ₂)(H ₂ O) _{1.784}) Quartz (SiO ₂)
XRF	compound	MnO ₂ (82%) Al ₂ O ₃ (6%) SiO ₂ (5%) Fe ₂ O ₃ (4%) Rest (<3%)	MnO ₂ (63%) Fe ₂ O ₃ (24%) CaO (8%) SiO ₂ (4%) Rest (<1%)

¹Not all peaks were identified

Analyses

pH, EC, ORP, O₂ and temperature were measured with WTW electrodes (SenTix940, SenTix ORP 900, TerraCon 925 and FDO925). During the on-site groundwater experiments, water samples of 50 mL were analysed for Fe, As, Mn, P, both unfiltered and filtered over a polyethersulfone 0.45 µm filter (25 mm, VWR). For the demineralised water experiments, a cellulose acetate 0.45 µm membrane 47mm (Whatman) with a vacuum system was used. Both filtered and unfiltered samples were acidified with 0.6 mL 5M HNO₃ and analysed with Inductively Coupled Plasma Mass Spectrometry (ICP-MS).

As speciation

As(III) was measured by filtering 70 mL of water through a syringe of 60 mL filled with 40 mL Amberlite® IRA-400 chlorite form anion ion-exchange resin. The first 20 mL was discarded, and the last 50 mL was collected and analysed for As by ICP-MS. The measured As after contact with the resin was considered to be the uncharged As(III) (Clifford et al., 2005). As(V) was calculated by subtracting As(III) from the concentration of total As. However, the resin was found to retain 15.1%, just after preparation of test water, and 14.8 % As(III), after 120 min aeration of the test water (n=6).

194 Indicating that (1) no measureable As(III) oxidation occurred within the 2 h experiment and (2) some
195 unwanted As(III) removal by the resin cannot be excluded with this method. An additional check was
196 performed by exposing 100 µg/L As(III) to aerated drinking water for 24 h. It was found that only 6%
197 of the As(III) was oxidised, thereby excluding homogeneous As(III) oxidation by O₂ as an oxidation
198 pathway within the timeframe of our experiments (max. 120 min).

199

Results and discussion

1. As(III) oxidation by MnO₂ containing powder

As(III) was put into contact with MnO₂ powder and WTP MnO₂ powder in demineralised water at pH 7. The oxidation of As(III) and formation of As(V) over time on both MnO₂ powders in oxygenated, buffered, demineralised water is depicted in Figure 3.

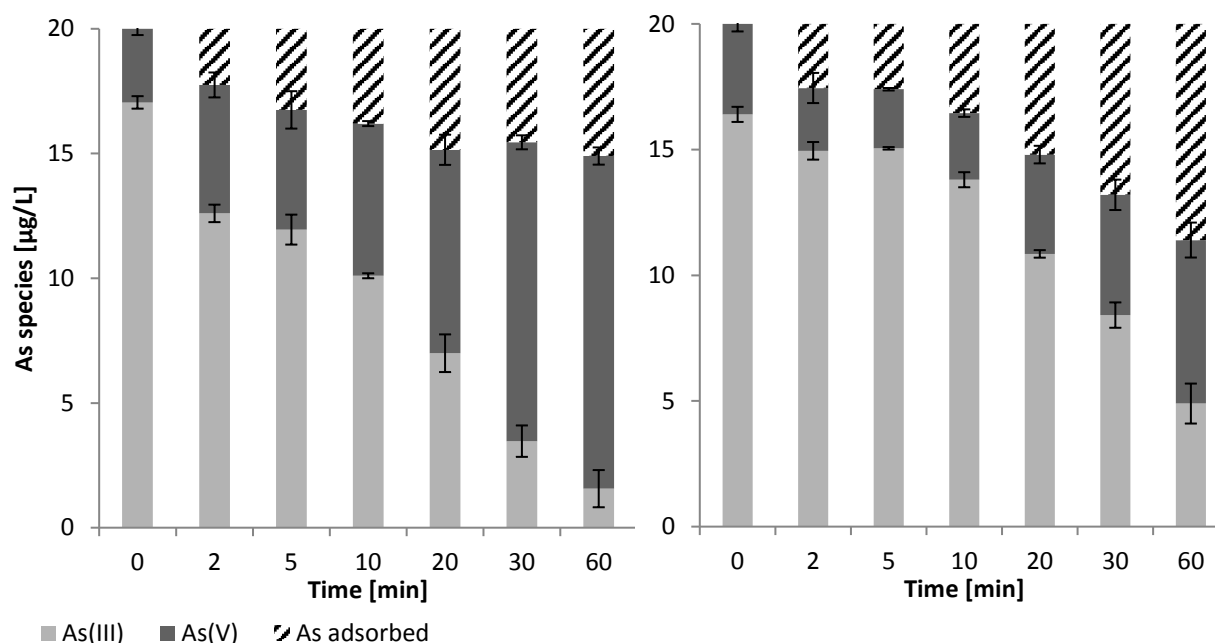


Figure 3 Oxidation of As(III) in 60 min by MnO₂ (left) and WTP MnO₂ (right); oxygenated, buffered demineralised water with 20 µg/L As(III) and 0.1 g/L MnO₂ containing powder at pH 7.

Addition of both MnO₂ powders resulted in As(III) oxidation, as As(III) concentrations decreased and As(V) concentrations increased over time. At the end of the 60 min experiment, the jars containing MnO₂ powder contained 2 µg/L As(III) and 13 µg/L As(V), 5 µg/L of the initial As(III) was adsorbed. The jars containing WTP MnO₂ powder resulted in 5 µg/L As(III), 7 µg/L As(V) and adsorbing 9 µg/L of the initial As(III). The MnO₂ powder, containing mainly MnO₂, decreased the concentration of mobile As(III) more effectively, whereas the WTP MnO₂ powder, also containing HFO (12%w Fe), resulted in a lower total As concentration. Therefore it is concluded that the As(III) was oxidised by the MnO₂ present in the powder, and the HFO, mainly present in the WTP MnO₂, resulted in adsorbing As. This is in line with Oscarson et al. (1981) who found MnO₂ to oxidise As(III) and Fe

oxides do not. Furthermore, limited As adsorption can be expected on the MnO₂ (Manning et al., 2002) where on the other hand As is effectively adsorbed to HFO at pH 7 (Dixit and Hering, 2003). The production of As(V) over time by WTP MnO₂ shows that the MnO₂ present in rapid sand filters can potentially oxidise As(III), also in absence of bacteria.

2. MnO₂ addition to natural aerated groundwater

It is generally accepted that for efficient As(III) removal with HFO, an oxidation step to As(V) is imperative (Bissen and Frimmel, 2003b; Gude et al., 2016). Since MnO₂ rapidly oxidises As(III) (Figure 3), it may be expected that the HFO-MnO₂ system removes As(III) more efficiently than HFO alone. Therefore, the MnO₂ powder was brought into contact with aerated groundwater containing As(III) as well as other typical groundwater constituents such as Fe, Mn, PO₄ and NH₄⁺ at a drinking water treatment plant. Table 2 shows the results after 60 min of aeration, both with and without addition of MnO₂ powder.

Table 2 Comparison of As(III), Fe, Mn and PO₄ during aeration of natural groundwater, with and without addition of 0.28 g/L MnO₂ powder at pH 7.4, O₂ 9.6 mg/L and 11 °C. ORP (t=60) aeration and aeration + MnO₂ -41 mV and 216 mV respectively. Results shown are averaged from duplicates.

	Time	As ¹		Fe		Mn		PO ₄	
	[min]	µg/L	Removal %	mg/L	Removal %	mg/L	Removal %	mg/L	Removal %
Groundwater	t=0	26.1		4.3		0.18		0.18	
Aeration	t=60	17.3	34%	1.2	72%	0.19	-3%	0.03	84%
Aeration + MnO ₂	t=60	17.3	34%	0.5	88%	0.85	-68%	0.07	60%

¹As≈As(III), all mobile As was analysed to be As(III) within 60 min.

Aeration alone and aeration aided by an addition of 0.28 g/L MnO₂ powder resulted both in 34% As removal from the natural groundwater and, additionally, it was measured that, after the 60 min experiment, the remaining mobile As of both experiments was in the reduced As(III) form. Hence it

was concluded that adding 0.28 g/L MnO₂ powder in aerated groundwater, did not increase the As(III) removal efficiency compared to aeration alone, so less As(III) was oxidised in natural groundwater – containing Fe(II) and Mn(II) – than in demineralised water. Although the As(III) removal was not enhanced, the MnO₂ addition resulted in an increased Fe(II) removal of 0.7 mg/L Fe as compared to aeration alone.

Soluble Fe concentrations decreased over time, as expected, since the HFO formed by Fe(II) oxidation are retained by 0.45 µm filters. On the other hand, mobile Mn concentrations increased during the experiment after filtration over 0.45 µm. The increased Mn concentrations were most likely the result of Fe oxidation on the MnO₂ surface, thereby reducing the MnO₂ (and MnOOH) to soluble Mn(II) (equation 3). The Mn concentration quadrupled during the 60 min experiment and increased over all measured time intervals while Fe(II) decreased. Figure 4 depicts the Fe and Mn concentrations at intervals 0, 10, 20 and 60 min contact time.

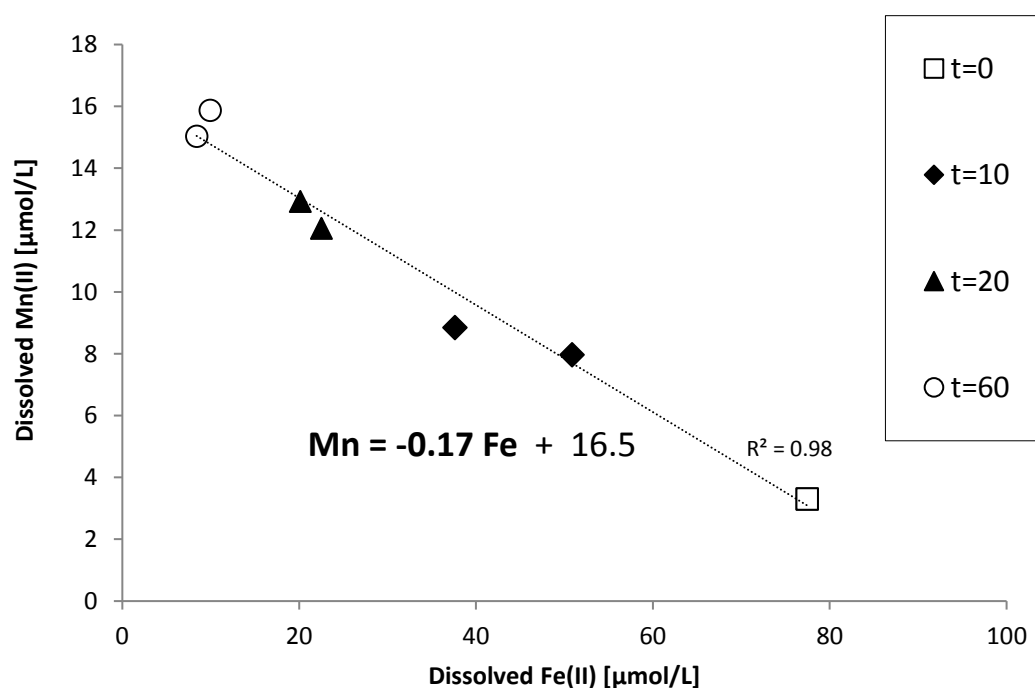


Figure 4 Concentrations of Fe(II) and Mn(II) in µmol/L in the same time interval as a result of adding 0.28 g/L MnO₂ powder to aerating groundwater at pH 7.4.

From the mobilisation of Mn(II) and the decreased concentration of Fe(II), it is concluded that the Fe oxidation is enhanced by the added MnO₂ powder. The total oxidised Fe(II) concentration was 68 µM, and this mobilised 12.5 µM Mn, which corresponds to a molar ratio of 0.17 Mn/Fe. According to

Equation 3, Fe(II) reacts to mobilise Mn(II) at a ratio of 0.5 Mn/Fe. The difference between the theoretical and actual Mn/Fe ratio indicates that Fe(II) had also oxidation pathways other than MnO₂, e.g. through homogenous oxidation with O₂ in the aerated water (Stumm and Lee, 1961). An additional explanation is that soluble Mn and/or Fe concentrations were affected by co-occurring adsorption processes during the experiment, i.e. Fe and/or Mn adsorption and oxidation onto HFO or MnO₂ (Lafferty et al., 2010; Postma, 1985). Either way, a considerable proportion of Fe(II) was oxidised by MnO₂ and may have been responsible for inhibiting As(III) oxidation. Apparently the HFO precipitated in the presence of MnO₂ removed less PO₄ than the HFO in absence of MnO₂, even though more HFO was formed (Table 2). It is therefore suggested that the HFO formation on MnO₂ reduced formation of Fe-PO₄ precipitates as described by Voegelin et al. (2010).

3. Inhibition by Mn(II) and Fe(II)

In order to differentiate between the effect of Mn(II) and Fe(II) on As(III) oxidation by MnO₂, jar tests were executed, adding these constituents to demineralised water. Figure 5 depicts As speciation during the 60 min experiments in the presence of either 2 mg/L Mn(II) (left) or 2 mg/L Fe(II) (right).

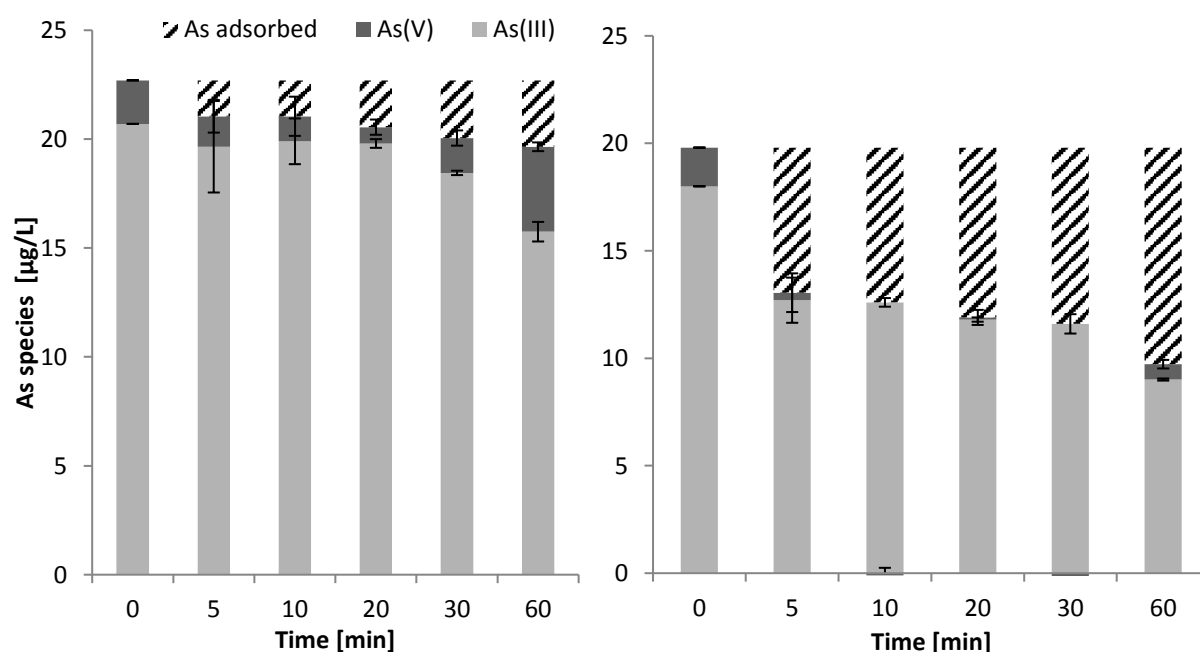


Figure 5 Effect of 2 mg/L Mn(II) (left) and 2 mg/L Fe(II) (right) on As(III) oxidation by 0.1 g/L MnO₂ powder at pH 7.

After Mn(II) addition to the As(III)-MnO₂ system, mobile As(V) remained <2 µg/L throughout the first 30 min and increased to 4 µg/L (17%) in the second half of the experiment, leaving 16 µg/L As(III) mobile. This in contrast with the As(III)-MnO₂ system without Mn(II) dosing (Figure 3), where only 2 µg/L As(III) remained mobile after 60 min and the mobile As(V) concentration increased to 13 µg/L. Therefore, the resulting conclusion is that the added Mn(II) inhibited the As(III) oxidation by MnO₂. In addition, less As was adsorbed to the MnO₂ in the presence of Mn(II): MnO₂ adsorbed 5 µg/L As without addition of Mn(II) (either directly, or after oxidation), and by addition of Mn(II) only to 3 µg/L As was adsorbed to the MnO₂ powder.

In the experiment where Fe(II) was dosed to the demineralised water containing As(III) and MnO₂ (Figure 5 right), the mobile As(III) concentration decreased to 9 µg/L while the concentration of mobile As(V) remained negligible and <1 µg/L. The added Fe(II) reacted to form HFO, which subsequently has a strong affinity for As adsorption (Dixit and Hering, 2003). This can be observed by the higher total As removal when adding Fe(II) to MnO₂ (50% As removal) compared to the Mn(II) addition to MnO₂ (13% As removal). In the HFO-MnO₂ system, As may be directly adsorbed as As(III) or indirectly after oxidation to As(V). Still, the As(III) concentration decreased less than in the As(III)-MnO₂ system alone (Figure 3). Indicating that both Mn(II) and Fe(II) inhibited As(III) oxidation. In order to assess whether Mn(II) and Fe(II) reacted with the MnO₂ surface, the mobilisation of Mn(II) during the experiments is depicted in Figure 6. As a reference, Fe(III) addition to the As(III)-MnO₂ is included as well.

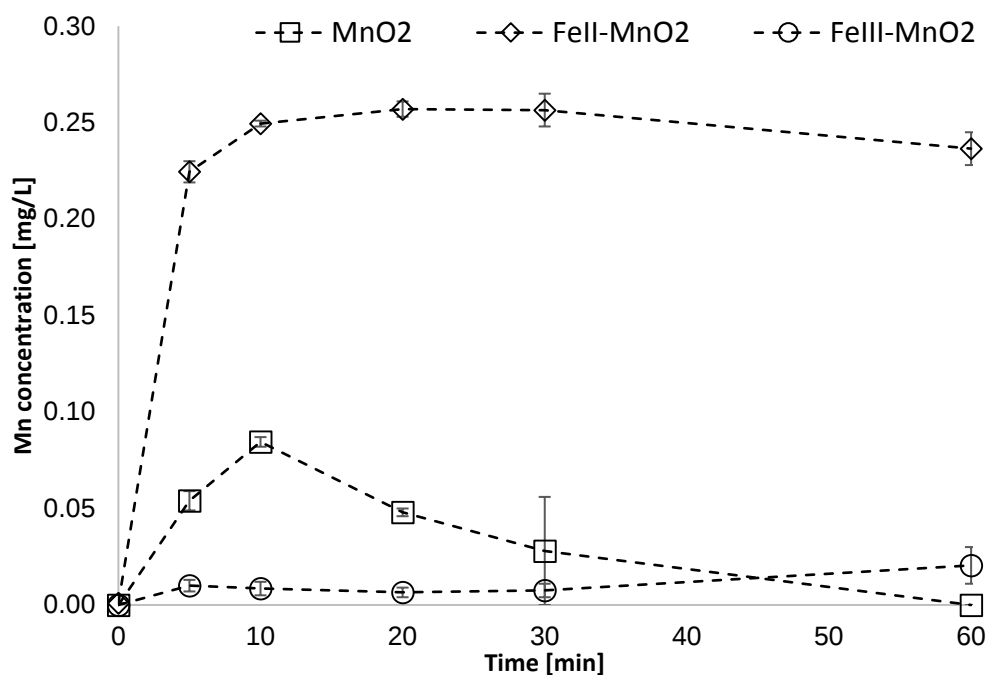


Figure 6 Mobilisation of Mn(II) from 100 mg/L MnO₂ powder; without Fe dosage (As(III)-MnO₂), with 2 mg/L Fe(II) dosage (As(III)-FeII-MnO₂) and with 2 mg/L Fe(III) dosage (As(III)-FeIII-MnO₂).

MnO₂ powder added to a 20 µg/L As(III) solution increased mobile Mn(II) concentrations to approximately 0.09 mg/L. However, based on Equations 1 and 2, As(III) oxidation by MnO₂ should only release 0.03 mg/L. It is therefore suggested that during the experiment, also some Mn(II) leached from the mineral surface. However, when adding Fe(II) to the jar, mobile Mn(II) concentrations increased up to 0.26 mg/L, which subsequently cannot be explained by leaching alone. From Equation 3 it can be concluded that at least 0.3 mg/L Fe(II) must have been oxidised by MnO₂ to account for the Mn(II) release, whereas the remaining Fe(II) may have been oxidised at the mineral surface, but did not result in mobile Mn(II) or was homogeneously oxidised by dissolved O₂ in the water (Stumm and Lee, 1961). Altogether, the results show that Fe(II) was active on the MnO₂ surface and therefore inhibited As(III) oxidation. The reference graph with Fe(III) addition to MnO₂ powder does not show such reactivity, as Mn(II) was hardly mobilised. This indicates that either Fe(III) prevented the MnO₂ surface from mobilising Mn(II) or that the mobilised Mn(II) was adsorbed to HFO originating from Fe(III).

4. As adsorption onto HFO

The previous experiments illustrate that Fe and Mn played a vital role in both the oxidation and removal of As(III) from natural groundwater in the presence of MnO₂. In order to differentiate between the added effect of MnO₂ on As(III) adsorption on HFO, experiments were executed in the presence of Fe but in absence of MnO₂. Table 3 depicts the removal of either As(III) or As(V) in contact with 2 mg/L Fe(III). The comparison of As(III) and As(V) at low concentrations (+/- 20 µg/L) and the resulting adsorption to HFO originating from Fe(III) show that the 23 µg/L As(V) is already lowered to <1 µg/L at the first measuring interval (2 min). Under identical settings, 23 µg/L As(III) was lowered to 16.9 µg/L (only 26% removal) in 2 min and was further lowered to 10.2 µg/L (55% removal) after 60 min contact time.

Table 3 Adsorption of As(III) and As(V) onto HFO originating from addition of Fe(III) at pH 7.

Experiments are averaged from duplicates.

Time [min]	As(III) [µg/L]	As(V) [µg/L]
0	23.0	23.5
2	16.9	0.9
5	15.4	<0.5
10	13.9	<0.5
30	11.9	-
60	10.2	-

This illustrates that for rapid As(III) removal with Fe(III), it is crucial to oxidise to As(V) first. To confirm this observation, the experiment was repeated for higher As(V) concentrations in the presence of HFO originating from different sources: (a) Fe(III), (b) Fe(II), hypochlorite (Cl₂) and O₂ and (c) Fe(II) and O₂. Table 4 provides an overview of the As(V) and filterable Fe (0.45µm) during these 60 min experiments.

328

329 **Table 4 Adsorption of As(III) and As(V) onto HFO originating from Fe(III), Fe(II)+O₂+Cl₂ and Fe(II)+O₂**
 330 **at pH 7. Experiments were executed in duplicate and averaged.**

	Fe(III)	Fe(II)+O ₂ +Cl ₂	Fe(II)+O ₂
Time	As(V) Fe	As(V) Fe	As(V) Fe
[min]	[µg/L] [mg/L]	[µg/L] [mg/L]	[µg/L] [mg/L]
0	84.4 1.9	85.6 2.0	86.0 1.9
2	1.2 0.01	1.4 <0.01	58.1 1.5
5	1.0 <0.01	1.1 <0.01	31.5 1.0
10	1.0 <0.01	1.0 <0.01	18.2 0.8
30	0.8 <0.01	0.7 <0.01	6.7 0.3
60	0.6 <0.01	0.6 <0.01	4.9 0.1

331

332 Even with four times higher As(V) concentrations than the former experiment, As concentrations
 333 dropped to <1.0 µg/L within 5 min contact time when adding Fe(III). Both Fe(III) and Fe(II)+O₂+Cl₂
 334 removed As(V) identically; within 2 min, the bulk of the As was removed, and simultaneously the
 335 soluble Fe dropped to <10 µg/L. For HFO originating from homogeneous Fe(II) oxidation by O₂, the
 336 As(V) removal was less efficient. After 60 min contact time, most Fe(II) was oxidised, however the
 337 As(V) concentration remained 4.9 µg/L. This finding, in combination with the similarity in As(V)
 338 removal between Fe(III) and Fe(II)+Cl₂+O₂, leads to the conclusion that the mode of oxidation-
 339 precipitation, and not the source of Fe (as Fe(II) or Fe(III)), determined As(V) removal. Figure 7
 340 depicts the HFO colour at the end of the three experiments, which illustrates that instantly oxidised
 341 Fe(II) by Cl₂ is similar in colour to Fe(III) than to Fe(II) oxidised by O₂. Different colours of HFO
 342 could hint to a different HFO structure. Jeon et al. (2003) reported a brown HFO suspension to make a
 343 colour shift to yellow by addition of Fe(II). Dixit and Hering (2003) showed different Fe minerals,
 344 such as Ferrihydrite, Goethite and Magnetite, have different site densities. Therefore, it is
 345 hypothesised that the precipitated HFO in the homogeneous Fe(II) oxidation process, adsorbed Fe(II)

as described by Silvester et al. (2005) which resulted in a denser Fe framework and a lower sorption site density than HFO originating from Fe(III).

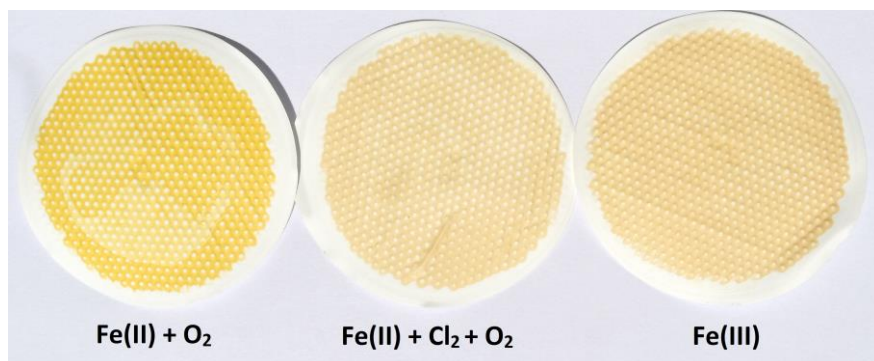


Figure 7 The colour of HFO originating from Fe(II)+O₂, Fe(II)+Cl₂ and Fe(III).

In the presence of O₂, As(V) removal by Fe(II) lagged behind compared to As(V) removal by Fe(III), therefore a series of experiments were performed to also investigate this for As(III). Results of As(III) removal after 60 and 120 min for 1, 2 and 4 mg/L Fe(II) or Fe(III) are depicted in Figure 8.

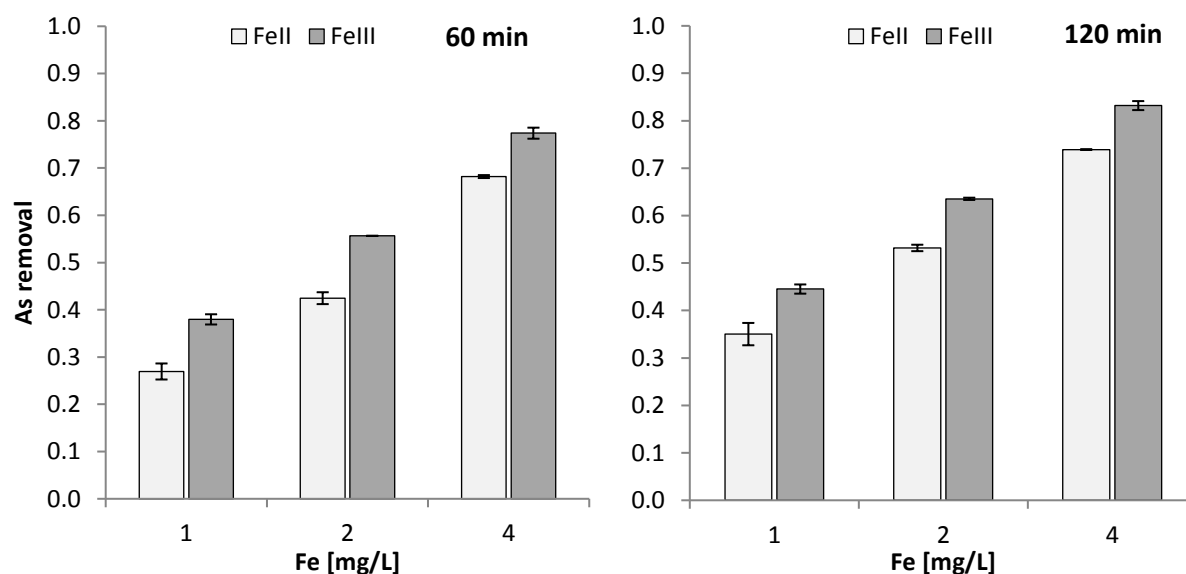


Figure 8. As(III) removal by Fe(II) and Fe(III) after 60 min (left) and 120 min (right) contact time. Fe concentration range 1, 2 and 4 mg/L and 20 µg/L As(III) at pH 7.

HFO, either originating from Fe(II) or Fe(III), partly adsorbed the As(III) in all cases. For both Fe(II) and Fe(III), As(III) removal was increased at a higher Fe/As ratio. This is consistent with findings of Qiao et al. (2012), since higher Fe concentrations increase the amount of adsorption sites available for

As(III) adsorption. Figure 8 also shows that after 60 and 120 min contact time, the HFO, originating from Fe(III), consistently removed more As(III) than Fe(II). Even after 120 min, Fe(II) removed less As(III) than Fe(III) after 60 min. The removal efficiencies were: 35%, 53%, 74% for Fe(II) at 120 min versus 38%, 56% and 77% for Fe(III) at 60 min for 1, 2 and 4 mg/L, respectively. The higher As(III) removal by Fe(III) is inconsistent with the general finding of Roberts et al. (2004), who found that addition of Fe(II), even though Fe(III) resulted in more sorption sites, resulted in increased As(III) removal due to the co-oxidative effect of Fe(II) oxidation described by Hug and Du (2003). However, for their experiments 4 h reaction time was chosen and As, Fe and high concentrations of co-occurring ions were used. So either the co-oxidation effect did not occur, or it was of less importance than other processes, like the co-occurring ions or the mode of oxidation-precipitation of the HFO. For this reason the pH effect on possible As(III) co-oxidation by Fe(II) and adsorption onto HFO originating from Fe(II) or Fe(III) was investigated in a 2 h kinetics experiment, the results of which are depicted in Figure 9.

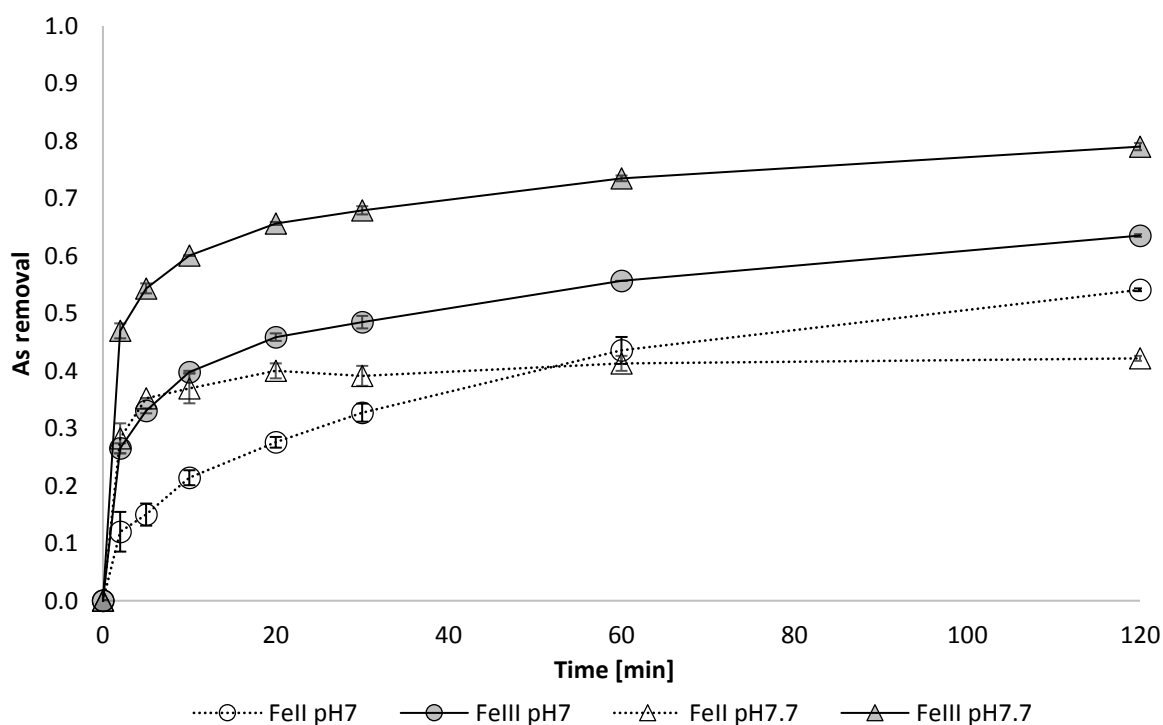


Figure 9 As(III) removal by HFO originating from Fe(II) and Fe(III) over time. 2 mg/L Fe and 20 µg/L As(III) at pH 7 and 7.7.

HFO originating from Fe(III) at pH 7.7 achieved a higher As(III) removal than at pH 7, 64% versus 79%, after 120 min. The majority of the removal difference was achieved by the first sample interval at 2 min contact time. The concentration of HFO during the Fe(III) was considered to be constant and no beneficial effects may be expected for As(III) adsorption to HFO at pH 7.7 compared to pH 7, because the adsorption efficiency difference of As(III) to HFO is very limited at these pH values and becomes even less pronounced at low As/Fe ratios (Dixit and Hering, 2003; Goldberg and Johnston, 2001). Therefore, the 30% higher As(III) removal efficiency by the HFO originating from Fe(III) at pH 7.7 is ascribed to a beneficial precipitation-flocculation process since the point of zero charge of HFO in demineralised water ≈ 0 at pH 7.7 (Du et al., 2014).

For Fe(II), pH plays an important role in a kinetics experiment since it largely affected the Fe oxidation rate (Morgan and Lahav, 2007). In Figure 9, at pH 7.7, within 2 min, 99% of the Fe(II) was oxidised into HFO compared to only 87% after 30 min at pH 7. The amount of HFO greatly affected the As(III) adsorption efficiency as seen in Figure 8. Therefore, the increased As(III) adsorption until 60 min at pH 7.7 can be mainly ascribed to the higher HFO concentration. However, the slower oxidation of Fe(II) at pH 7 resulted in an overall higher As(III) removal during the 120 min experiment. The general conclusion of the experiment is that Fe(III) and Fe(II) showed different effects with pH alteration on As(III) removal. For Fe(III), As(III) adsorption was mainly affected at the start of the experiment and was suggested to be ascribed to the initial flocculation speed. Fe(II) on the other hand was largely affected by oxidation speed at different pH; at pH 7 a slower Fe(II) precipitation rate and therefore a prolonged new HFO formation over time may have led to the increased overall As(III) removal. This is in line with experiments of Roberts et al. (2004) where multiple additions of Fe(II) led to an increased As(III) removal compared to the same Fe(II) concentration in a single addition. These experiments suggest that HFO formation plays a key role in As(III) adsorption for both HFO originating from Fe(III) and Fe(II).

5. Influence of Fe(II) versus Fe(III) on As(III)-MnO₂ system

In the previous sections, we determined that both Mn(II) and Fe(II) were active on the MnO₂ surface, thereby inhibiting As(III) oxidation and subsequently lowering As(III) removal efficiency. Additionally it was shown that HFO originating from either Fe(II) and Fe(III) was of a different structure. Therefore, the combined effect of As(III) oxidation and removal in the presence of MnO₂, Fe(III), Fe(II) and/or Mn(II) was investigated, and the results are depicted in Figure 10. The setups of the experiments presented in Figure 10 were identical except for the oxidation state of the added Fe. The left graph depicts the results of Fe(II) and the right graph of Fe(III) addition.

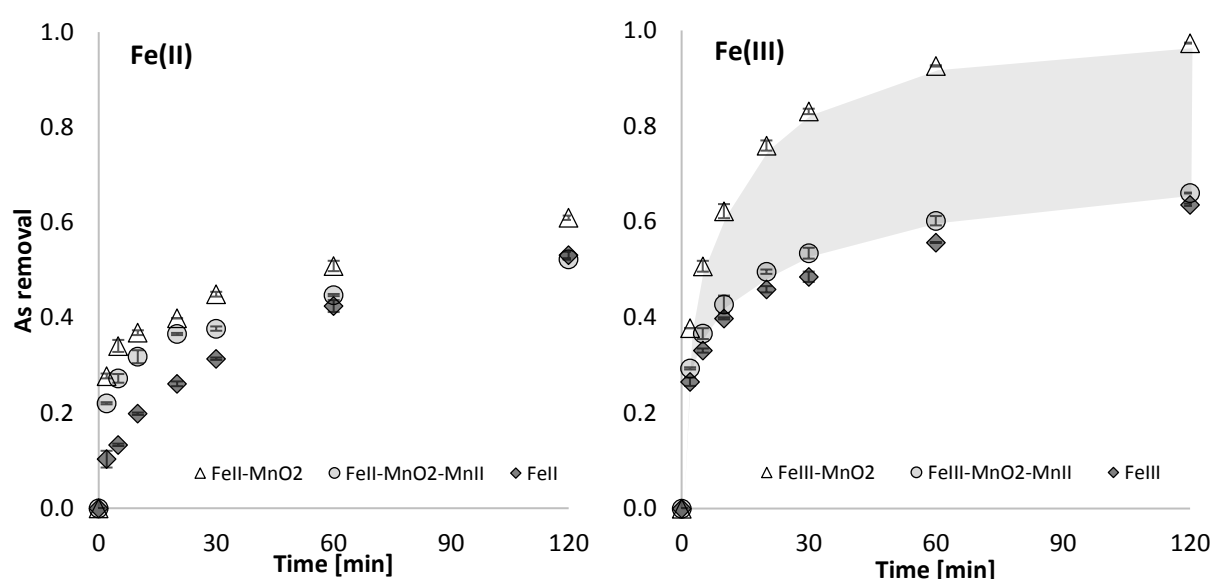


Figure 10 As(III) removal by Fe(II) and Fe(III) in presence and absence of MnO₂ and Mn(II) at pH 7 over 120 min. Concentrations were 20 µg/L As(III), 2 mg/L Fe, 2 mg/L Mn and 100 mg/L MnO₂ powder. Left Figure is As(III) removal by Fe(II) and right Figure Fe(III).

The data for HFO originating from Fe(III) and Fe(II) are the same as in Figure 9 and set a reference for As(III) adsorption to HFO (diamonds) without MnO₂ addition. The triangles in Figure 10 show the added effect of MnO₂ powder to As(III) adsorption on HFO originating from Fe(II) and Fe(III). MnO₂ addition to the As(III)-Fe(II) system resulted in a limited (16%) increased As removal, whereas the addition of MnO₂ to As(III)-Fe(III) caused a 52% improved removal; the combination Fe(III) and MnO₂ resulted in a As(III) concentration decrease from 20 µg/L As(III) to < 1 µg/L. In order to identify why Fe(III) and MnO₂ were better capable of removing As(III) than Fe(II) and MnO₂, a set of

experiments were conducted with an extra addition of Mn(II) to both systems, results are depicted by the circles in Figure 10. As concluded earlier, Mn(II) inhibits As(III) oxidation by MnO₂. Therefore, this experiment was considered an indicator for As(III) removal in the presence of MnO₂ *without* its oxidising capabilities. In the case of Fe(III), it was concluded that 66% of As(III) was adsorbed onto the HFO or MnO₂ surface (circles; right) thereby removing only 2% more As(III) than HFO alone. For Fe(II), it was concluded that the addition of Mn(II) did not inhibit the oxidation of Fe(II) by MnO₂ and subsequently did not influence As removal much, since Fe(II) already inhibited As(III) oxidation. This is illustrated by the limited decreased As removal in the Fe(II)-MnO₂-Mn(II) system (circles; left) compared to Fe(II) and MnO₂ alone (triangles; left), but increased removal in the beginning over Fe(II) alone (diamonds; left).

As a result of dosing of Fe(III) and MnO₂ together, As(III) was oxidised to As(V), and subsequently adsorbed onto the precipitating HFO resulting in a near complete As(III) removal (triangles; right/grey area). However, in the case of Fe(II), the oxidation process of As(III) by MnO₂ was inhibited by Fe(II), as shown in Figure 4, therefore limiting As(V) production (triangles; left). This explains the removal difference between Fe(II) and Fe(III) in Figure 10, since the oxidation of As(III) to As(V), which is required for efficient removal by HFO, was only achieved in the presence of Fe(III).

Soluble Fe and Mn concentrations during these experiments are plotted in Figure 11 in order to confirm that Fe(II) and Mn(II) reacted with the MnO₂ surface. It shows that Fe(II) concentrations decreased faster in the presence of MnO₂, either in the presence or absence of Mn(II). This confirms that Fe(II) oxidation took place on the MnO₂ surface and was not subject to interference by the presence of Mn(II). In Figure 11 (right), the Mn(II) concentrations illustrate that the added 2 mg/L Mn(II) was partially removed over time by the Fe(III)-MnO₂ system or by MnO₂ alone. Fe(III), without MnO₂, did not considerably remove Mn(II), so this suggests that Mn(II) was only adsorbed onto MnO₂. The presence of Fe(II) resulted in an increased Mn(II) concentration of 0.10 mg/L. The mobilisation of Mn(II) from the MnO₂, even in the presence of 2 mg/L Mn(II), is a clear indication that Fe(II), independent of Mn(II) concentrations, was active on the MnO₂ surface and was the preferred ion by the MnO₂ mineral surface.

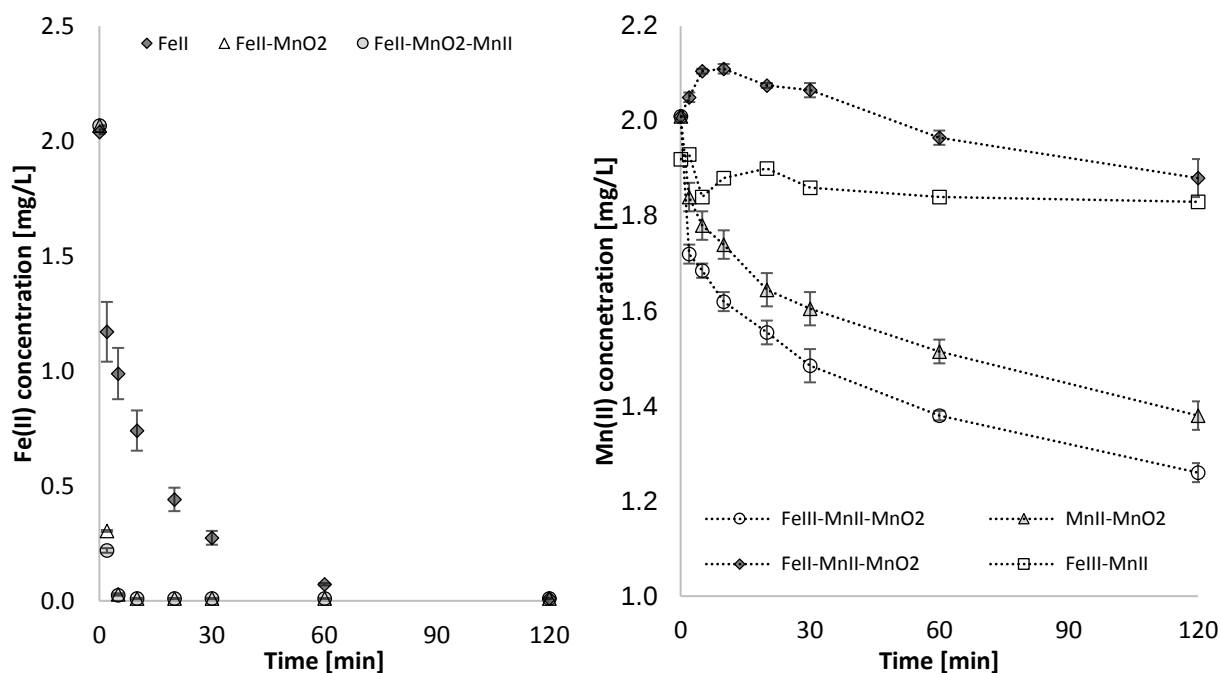


Figure 11 Fe(II) concentrations (left) and Mn(II) concentrations (right) at pH 7 over time. 2 mg/L Fe, 2 mg/L Mn(II) and 0.1 g/L MnO₂ powder.

The Fe and Mn concentrations in Figure 11 confirm that Fe(III) did not pacify the MnO₂ surface and thereby did not inhibit the As(III) oxidation on MnO₂. On the other hand, Fe(II) reacted on MnO₂ and thereby inhibited As(III) oxidation. For Mn(II) addition to the MnO₂, a similar explanation as for Fe(II) is justified since Mn(II) does not oxidise homogenously in aerated water at pH 7 (Diem and Stumm, 1984) and the observed loss in dissolved Mn(II) was 30%. Therefore, the Mn(II) must have been retained on the MnO₂ surface, which could have led to similar surface passivation of the MnO₂ as Fe(II). Leading to the overall conclusion that, in the presence of Fe(II) and Mn(II), MnO₂ cannot durably contribute to efficient As(III) removal by HFO.

Conclusions

In this study, it was investigated whether MnO₂ could be responsible for the observed As(III) oxidation in the top layer of rapid sand filters treating aerated groundwater. Although it is known that MnO₂ is capable of oxidising As(III), it is unknown whether naturally grown MnO₂ on filter sand grains are oxidising As(III) in competition with other reduced constituents (Fe(II), Mn(II)). In a series

of jar test experiments it was found that both commercial and 22-year old filter grain MnO_2 were capable of rapidly oxidising As(III) by reduction to Mn(II). However, this process was inhibited in the presence of Fe(II) and Mn(II), as Fe(II) and Mn(II) adsorption and oxidation were preferred over As(III) on the MnO_2 surface (at pH 7). Under these conditions, the unavailability of the MnO_2 surface for As(III) oxidation limited subsequent removal of As(V) by the precipitating HFO. Therefore it is concluded that just because MnO_2 is present in a filter bed, it does not necessarily mean that MnO_2 will be available to oxidise As(III). However, unlike Fe(II), the addition of Fe(III) did not hinder As(III) oxidation on the MnO_2 surface; resulting in subsequent effective As(V) removal by the flocculating HFO.

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