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As(III) oxidation by MnO$_2$ during groundwater treatment

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Graphical abstract

Highlights

- MnO$_2$ rapidly oxidises As(III) in demineralised water;
- MnO$_2$, in absence of bacteria, did not enhance As(III) removal in natural groundwater;
- Fe(II) and Mn(II) prevented As(III) oxidation by MnO$_2$;
- Fe(III) did not hinder As(III) oxidation on MnO$_2$; 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 (MnO$_2$), 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 MnO$_2$ identified as Birnessite (Bruins et al., 2014). NH$_4^+$ is removed in the rapid sand filter bed by biotic oxidation in a two-step oxidation process from NO$_2^-$ to NO$_3^-$ (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 MnO$_2$ 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 MnO$_2$ (Spiro et al., 2010) present on the filter grains.

In this reaction, MnO$_2$ is the electron acceptor for As(III) oxidation, resulting in the reduction of MnO$_2$ to Mn(II). The reduction of MnO$_2$ by As(III) entails a two-step reaction where both the initial MnO$_2$ and the intermediate product, MnOOH, can oxidise As(III) (Manning et al., 2002; Nesbitt et al., 1998):

$$2\text{MnO}_2 + H_3\text{AsO}_3 + H_2O = 2\text{MnOOH}^+ + H_3\text{AsO}_4$$  \hspace{1cm} \text{Equation 1}

$$2\text{MnOOH}^+ + H_3\text{AsO}_3 + 4H^+ = 2\text{Mn}^{2+} + H_3\text{AsO}_4 + 3H_2O$$  \hspace{1cm} \text{Equation 2}

During this oxidation process, depending on pH, As can either adsorb onto MnO$_2$ surface (Manning et al., 2002) or remain in solution. Apart from As(III), Fe(II) can also react on the MnO$_2$ mineral surface, resulting in formation of HFO and mobilization of Mn(II) (Postma, 1985; Postma and Appelo, 2000).

$$2\text{Fe}^{2+} + \text{MnO}_2 + 2H_2O \rightarrow 2\text{FeOOH} + \text{Mn}^{2+} + 2H^+$$  \hspace{1cm} \text{Equation 3}

Wu et al. (2015) studied the redox and sorption interactions between MnO$_2$, 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 MnO$_2$ 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 MnO$_2$ 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 MnO₂ mineral as a results of Mn(II) sorption. The interactions of As(III), Fe(II) and Mn(II) individually on MnO₂ are schematically depicted in Figure 1.

Figure 1 Schematics of As(III), Fe(II) and Mn(II) interaction with MnO₂ 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 $O_2$ and brought to pH 7 or to 7.7 by addition of HNO$_3$. 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 MnO$_2$ 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: NaHCO$_3$, As(III)/As(V), Cl$_2$ (only used in combination with As(V)), Mn(II), Fe(II,III) and MnO$_2$ as the final additive. For the natural groundwater tests 0.28 g/L MnO$_2$ powder was used because more Fe(II) and competing ions were present. Before addition to the natural groundwater and the demineralised water, the MnO$_2$ powder was brought into suspension using 20 mL demi water; 1.8 mL NaOH 10 mM was added to the MnO$_2$ suspension when used with Fe(II) and Fe(III) to compensate for the pH drop. For all experiments, fresh, dry MnO$_2$ 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 HNO₃ to prevent further Fe(II) oxidation during As speciation.

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 HNO₃ to prevent further Fe(II) oxidation during As speciation.

F50 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 MnO₂ 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 HNO₃ intermittently.

**Chemicals and preparation**

As(III), NaAsO₂, 0.05M, Company (Fluka Analytical) and As(V) HAsNa₂O₄·7H₂O, ≥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 NaHCO₃ (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 Cl₂Fe·4H₂O (99.99%, Sigma-Aldrich), Cl₃Fe·8H₂O (≥98%, Sigma-Aldrich) and Cl₂Mn·4H₂O (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 Cl₂ used for instantaneous oxidation of Fe(II) was diluted from a stock solution of 15% Cl (Brenntag) sodium hypochlorite to 20 mg/L Cl₂ in the test water. At the start of an experiment, the stock solutions were dosed to the ambient air saturated (> 9 mg/L O₂) demineralised water (21-23°C) with a calibrated ThermoFisher Finnpipette 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; HCO\(_3\) 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, NH\(_4^+\) 0.29 mg/L-N, phosphate (PO\(_4\)) 0.19 μg /L-P, total organic carbon 2.56 mg/L and sulphate 7.72 mg/L.

MnO\(_2\) grains

Two types of MnO\(_2\) powders were used. The first was the commercially available Mangalox-K-45 (Sibelco; d\(_{10}\) 2.2 μm, d\(_{50}\) 9.4 μm, d\(_{90}\) 36.1 μm), hereafter ‘MnO\(_2\)’. 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 MnO\(_2\)’. 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 MnO\(_2\) 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(H\(_2\)SO\(_4\))=96% and 0.36 g H\(_2\)C\(_2\)O\(_4\) in powder were added to sample containers with 100 mL demineralised water. 0.1g of the two MnO\(_2\) 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 MnO\(_2\) powder were measured with a Malvern Mastersizer 2000. The relevant properties of both MnO\(_2\) powders are summarised in Table 1.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>MnO(_2)</th>
<th>WTP MnO(_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn</td>
<td>mg/g</td>
<td>548</td>
<td>301</td>
</tr>
<tr>
<td>Fe</td>
<td>mg/g</td>
<td>20</td>
<td>126</td>
</tr>
<tr>
<td>Ca</td>
<td>mg/g</td>
<td>2</td>
<td>38</td>
</tr>
<tr>
<td>XRD&lt;sup&gt;1&lt;/sup&gt;</td>
<td>compound</td>
<td>Vernadite (Mn(OH)&lt;sub&gt;4&lt;/sub&gt;)</td>
<td>Ramsdellite (MnO&lt;sub&gt;2&lt;/sub&gt;)</td>
</tr>
<tr>
<td>----------------</td>
<td>----------</td>
<td>------------------------------</td>
<td>------------------------------</td>
</tr>
<tr>
<td>XRF</td>
<td>compound</td>
<td>MnO&lt;sub&gt;2&lt;/sub&gt; (82%)</td>
<td>Al&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt; (6%)</td>
</tr>
</tbody>
</table>

<sup>1</sup>Not all peaks were identified

**Analyses**

pH, EC, ORP, O<sub>2</sub> 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 HNO<sub>3</sub> 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).
indicating that (1) no measurable As(III) oxidation occurred within the 2 h experiment and (2) some unwanted As(III) removal by the resin cannot be excluded with this method. An additional check was performed by exposing 100 µg/L As(III) to aerated drinking water for 24 h. It was found that only 6% of the As(III) was oxidised, thereby excluding homogeneous As(III) oxidation by O₂ as an oxidation pathway within the timeframe of our experiments (max. 120 min).
Results and discussion

1. As(III) oxidation by MnO$_2$ containing powder

As(III) was put into contact with MnO$_2$ powder and WTP MnO$_2$ powder in demineralised water at pH 7. The oxidation of As(III) and formation of As(V) over time on both MnO$_2$ powders in oxygenated, buffered, demineralised water is depicted in Figure 3.

![Figure 3: Oxidation of As(III) in 60 min by MnO$_2$ (left) and WTP MnO$_2$ (right); oxygenated, buffered demineralised water with 20 µg/L As(III) and 0.1 g/L MnO$_2$ containing powder at pH 7.](image)

Addition of both MnO$_2$ 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 MnO$_2$ 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 MnO$_2$ powder resulted in 5 µg/L As(III), 7 µg/L As(V) and adsorbing 9 µg/L of the initial As(III). The MnO$_2$ powder, containing mainly MnO$_2$, decreased the concentration of mobile As(III) more effectively, whereas the WTP MnO$_2$ 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 MnO$_2$ present in the powder, and the HFO, mainly present in the WTP MnO$_2$, resulted in adsorbing As. This is in line with Oscarson et al. (1981) who found MnO$_2$ 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.

<table>
<thead>
<tr>
<th></th>
<th>Time</th>
<th>As</th>
<th>Fe</th>
<th>Mn</th>
<th>PO₄</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>[min]</td>
<td>µg/L</td>
<td>Removal</td>
<td>mg/L</td>
<td>Removal</td>
</tr>
<tr>
<td>Groundwater</td>
<td>t=0</td>
<td>26.1</td>
<td>4.3</td>
<td>0.18</td>
<td>0.18</td>
</tr>
<tr>
<td>Aeration</td>
<td>t=60</td>
<td>17.3</td>
<td>34%</td>
<td>1.2</td>
<td>72%</td>
</tr>
<tr>
<td>Aeration + MnO₂</td>
<td>t=60</td>
<td>17.3</td>
<td>34%</td>
<td>0.5</td>
<td>88%</td>
</tr>
</tbody>
</table>

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 MnO$_2$ 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 MnO$_2$ 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 MnO$_2$ surface, thereby reducing the MnO$_2$ (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.

![Graph](image.png)

**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 MnO$_2$ 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 MnO$_2$ 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

\[
R^2 = 0.98
\]

\[
\text{Mn} = -0.17 \text{Fe} + 16.5
\]
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 MnO$_2$ powder at pH 7.

After Mn(II) addition to the As(III)-MnO$_2$ 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)-MnO$_2$ 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 MnO$_2$. In addition, less As was adsorbed to the MnO$_2$ in the presence of Mn(II): MnO$_2$ 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 MnO$_2$ powder.

In the experiment where Fe(II) was dosed to the demineralised water containing As(III) and MnO$_2$ (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 MnO$_2$ (50% As removal) compared to the Mn(II) addition to MnO$_2$ (13% As removal). In the HFO-MnO$_2$ 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)-MnO$_2$ 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 MnO$_2$ surface, the mobilisation of Mn(II) during the experiments is depicted in Figure 6. As a reference, Fe(III) addition to the As(III)-MnO$_2$ is included as well.
Figure 6 Mobilisation of Mn(II) from 100 mg/L MnO$_2$ powder; without Fe dosage (As(III)-MnO$_2$), with 2 mg/L Fe(II) dosage (As(III)-FeII-MnO$_2$) and with 2 mg/L Fe(III) dosage (As(III)-FeIII-MnO$_2$).

MnO$_2$ 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 MnO$_2$ 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 MnO$_2$ 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 O$_2$ in the water (Stumm and Lee, 1961). Altogether, the results show that Fe(II) was active on the MnO$_2$ surface and therefore inhibited As(III) oxidation. The reference graph with Fe(III) addition to MnO$_2$ powder does not show such reactivity, as Mn(II) was hardly mobilised. This indicates that either Fe(III) prevented the MnO$_2$ 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 MnO$_2$. In order to differentiate between the added effect of MnO$_2$ on As(III) adsorption on HFO, experiments were executed in the presence of Fe but in absence of MnO$_2$. 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.

<table>
<thead>
<tr>
<th>Time [min]</th>
<th>As(III) [µg/L]</th>
<th>As(V) [µg/L]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>23.0</td>
<td>23.5</td>
</tr>
<tr>
<td>2</td>
<td>16.9</td>
<td>0.9</td>
</tr>
<tr>
<td>5</td>
<td>15.4</td>
<td>&lt;0.5</td>
</tr>
<tr>
<td>10</td>
<td>13.9</td>
<td>&lt;0.5</td>
</tr>
<tr>
<td>30</td>
<td>11.9</td>
<td>-</td>
</tr>
<tr>
<td>60</td>
<td>10.2</td>
<td>-</td>
</tr>
</tbody>
</table>

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 (Cl$_2$) and O$_2$ and (c) Fe(II) and O$_2$. Table 4 provides an overview of the As(V) and filterable Fe (0.45µm) during these 60 min experiments.
Adsorption of As(III) and As(V) on HFO originating from Fe(III), Fe(II)+O₂+Cl₂ and Fe(II)+O₂ at pH 7. Experiments were executed in duplicate and averaged.

<table>
<thead>
<tr>
<th>Time [min]</th>
<th>Fe(III) As(V) [µg/L]</th>
<th>Fe(III) Fe [mg/L]</th>
<th>Fe(II)+O₂+Cl₂ As(V) [µg/L]</th>
<th>Fe(II)+O₂+Cl₂ Fe [mg/L]</th>
<th>Fe(II)+O₂ As(V) [µg/L]</th>
<th>Fe(II)+O₂ Fe [mg/L]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>84.4 1.9</td>
<td></td>
<td>85.6 2.0</td>
<td></td>
<td>86.0 1.9</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>1.2 0.01</td>
<td></td>
<td>1.4 &lt;0.01</td>
<td></td>
<td>58.1 1.5</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>1.0 &lt;0.01</td>
<td></td>
<td>1.1 &lt;0.01</td>
<td></td>
<td>31.5 1.0</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>1.0 &lt;0.01</td>
<td></td>
<td>1.0 &lt;0.01</td>
<td></td>
<td>18.2 0.8</td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>0.8 &lt;0.01</td>
<td></td>
<td>0.7 &lt;0.01</td>
<td></td>
<td>6.7 0.3</td>
<td></td>
</tr>
<tr>
<td>60</td>
<td>0.6 &lt;0.01</td>
<td></td>
<td>0.6 &lt;0.01</td>
<td></td>
<td>4.9 0.1</td>
<td></td>
</tr>
</tbody>
</table>

Even with four times higher As(V) concentrations than the former experiment, As concentrations dropped to <1.0 µg/L within 5 min contact time when adding Fe(III). Both Fe(III) and Fe(II)+O₂+Cl₂ removed As(V) identically; within 2 min, the bulk of the As was removed, and simultaneously the soluble Fe dropped to <10 µg/L. For HFO originating from homogeneous Fe(II) oxidation by O₂, the As(V) removal was less efficient. After 60 min contact time, most Fe(II) was oxidised, however the As(V) concentration remained 4.9 µg/L. This finding, in combination with the similarity in As(V) removal between Fe(III) and Fe(II)+Cl₂+O₂, leads to the conclusion that the mode of oxidation-precipitation, and not the source of Fe (as Fe(II) or Fe(III)), determined As(V) removal. Figure 7 depicts the HFO colour at the end of the three experiments, which illustrates that instantly oxidised Fe(II) by Cl₂ is similar in colour to Fe(III) than to Fe(II) oxidised by O₂. Different colours of HFO could hint to a different HFO structure. Jeon et al. (2003) reported a brown HFO suspension to make a colour shift to yellow by addition of Fe(II). Dixit and Hering (2003) showed different Fe minerals, such as Ferrihydrite, Goethite and Magnetite, have different site densities. Therefore, it is 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 \( \approx 0 \) 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)-MnO\(_2\) system
In the previous sections, we determined that both Mn(II) and Fe(II) were active on the MnO$_2$ 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 MnO$_2$, 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 MnO$_2$ 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 MnO$_2$ 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 MnO$_2$ addition. The triangles in Figure 10 show the added effect of MnO$_2$ powder to As(III) adsorption on HFO originating from Fe(II) and Fe(III). MnO$_2$ addition to the As(III)-Fe(II) system resulted in a limited (16%) increased As removal, whereas the addition of MnO$_2$ to As(III)-Fe(III) caused a 52% improved removal; the combination Fe(III) and MnO$_2$ 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 MnO$_2$ were better capable of removing As(III) than Fe(II) and MnO$_2$, 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 MnO$_2$. Therefore,
this experiment was considered an indicator for As(III) removal in the presence of MnO$_2$ without its
oxidising capabilities. In the case of Fe(III), it was concluded that 66% of As(III) was adsorbed onto
the HFO or MnO$_2$ 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 MnO$_2$ 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)-MnO$_2$-Mn(II) system (circles; left)
compared to Fe(II) and MnO$_2$ alone (triangles; left), but increased removal in the beginning over
Fe(II) alone (diamonds; left).

As a result of dosing of Fe(III) and MnO$_2$ 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 MnO$_2$ 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 MnO$_2$ surface. It shows that Fe(II) concentrations
decreased faster in the presence of MnO$_2$, either in the presence or absence of Mn(II). This confirms
that Fe(II) oxidation took place on the MnO$_2$ 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)-MnO$_2$ system or by MnO$_2$ alone. Fe(III),
without MnO$_2$, did not considerably remove Mn(II), so this suggests that Mn(II) was only adsorbed
onto MnO$_2$. The presence of Fe(II) resulted in an increased Mn(II) concentration of 0.10 mg/L. The
mobilisation of Mn(II) from the MnO$_2$, 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 MnO$_2$ surface and was the
preferred ion by the MnO$_2$ 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 MnO₂ 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 MnO₂ surface (at pH 7). Under these conditions, the unavailability of the MnO₂ surface for As(III) oxidation limited subsequent removal of As(V) by the precipitating HFO. 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 HFO.

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