Arsenic removal by iron based co-precipitation

Mechanisms in groundwater treatment

Arslan Ahmad

Arsenic removal by iron based co-precipitation: Mechanisms in groundwater treatment

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Propositions

1. A reduction of pH facilitates the removal of oxidized arsenic species from groundwater by iron based co-precipitation (this thesis).
2. Reduction of arsenic levels in a drinking water treatment plant is more effectively achieved by focussing on the effluent water of a rapid sand filter instead of the influent (this thesis).
3. Removal of arsenic from drinking water is possible to levels much lower than the WHO guideline (10 µg/L) and therefore global drinking water limits should be reassessed.
4. Availability of medical information on the internet is a health threat.
5. More nuclear power plants should be built in the Netherlands to rapidly reduce Dutch CO₂ emissions and effectively combat climate change.
6. A legal market in organs is required to increase the number of organ transplantations and therefore save lives.
7. Only in low-income countries with democratically chosen governments is international aid an effective method to reduce poverty.

Propositions belonging to the thesis, entitled

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Mechanisms in groundwater treatment

Arslan Ahmad
Wageningen, 5 June 2020

Arsenic removal by iron based co-precipitation

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Mechanisms in groundwater treatment

Arslan Ahmad

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*To my father and mother
And, to wife and daughter*

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Chapter 1

Introduction

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Ahmad, A., van der Wens, P., Baken, K., de Waal, L., Bhattacharya, P., & Stuyfzand, P. (2020). Arsenic reduction to $<1 \mu\text{g/L}$ in Dutch drinking water. *Environment International*, 134, 105253.

Ahmad, A., Richards, L. A., & Bhattacharya, P. (2017). Arsenic remediation of drinking water: an overview. In P. Bhattacharya, D. A. Polya, & D. Jovanovic (Eds.), *Best Practice Guide on the Control of Arsenic in Drinking Water* (pp. 79-98). IWA Publishing. London, UK.

1.1 ARSENIC IN GROUNDWATER

Arsenic (As) is a naturally occurring metalloid, widely found in groundwater. In reducing aqueous environments, trivalent arsenite As(III) is prevalent and in oxidizing environments pentavalent arsenate [As(V)] is prevalent. The distribution of aqueous As species as a function of pH and redox conditions is given in Fig 1.1. Arsenic is highly toxic for humans. Chronic intake of As can cause several types of cancer and other adverse effects on human health, as indicated in Fig 1.2 (Das and Sengupta 2008, Ferreccio et al. 2013, Gibb et al. 2011, IARC 2012, Islam et al. 2012, Jovanovic et al. 2013, Marshall et al. 2007, Parvez et al. 2011, Rahman et al. 2011, Sengupta et al. 2008, Smith et al. 1992).

Millions of people worldwide rely on As contaminated groundwater for potable use (Fig 1.3). Most of the affected populations live in South Asia, particularly in Bangladesh, India, Pakistan and Nepal (Ahmad and Bhattacharya 2018a, b, Ahmed et al. 2004, Bhattacharya et al. 2002b, Mukherjee et al. 2006, Mushtaq et al. 2018). Major reports of As contaminated groundwater have also emerged from several countries in the Eurasian region such as Turkey, Greece, Romania, Slovakia, Croatia, Serbia, Hungary, Spain (Baba and Sözbilir 2012, Bundschuh et al. 2013, García-Sánchez et al. 2005, Lindberg et al. 2006, Papić et al. 2012, Rowland et al. 2011, Varsányi and Kovács 2006) and several Latin American countries such as Argentina, Bolivia, Chile and Uruguay (Bundschuh et al. 2010, Kapaj et al., 2006, Litter et al. 2010, Ormachea Muñoz et al. 2013, 2016, Quino Lima et al., 2019, 2020, Ramos Ramos et al. 2012). The World Health Organization (WHO) guideline for As in drinking water is currently set at 10 µg/L. However, recent studies suggest that As can cause a considerable damage to human health even at concentrations lower than the WHO guideline (Ahmad and Bhattacharya 2019, Kozisek 2017, Saint-Jacques et al. 2018, Schmidt 2014). Consequently, several drinking water companies in the Netherlands are making efforts to reduce As concentrations in drinking water to very low concentrations, below 1 µg/L (Ahmad et al. 2020, Van der Wens et al. 2016).

Arsenic removal from water has been extensively investigated in recent years. Arsenic removal methods can be broadly grouped into four categories; (i) co-precipitation, (ii) adsorption, (iii) ion exchange and (iv) membrane separation. Salient features of different As removal methods are described in Table 1.1 (Ahmad et al. 2017, Hao et al. 2018, Hering et al. 2017, Litter et al. 2010, Luong et al. 2018, Mondal et al. 2013, Singh et al. 2015, Zouboulis and Katsoyiannis 2005).

Figure 1.1 Eh-pH diagram for aqueous As species in the system As–O₂–H₂O at 25 °C and 1 bar total pressure, produced with PhreePlot using the wateq4f.dat database.

Figure 1.2 Adverse health effects due to chronic As intake through drinking water.

Figure 1.3 Arsenic contamination of groundwater in various countries around the world.

1.2 ARSENIC AND DRINKING WATER IN THE NETHERLANDS

In the Netherlands, drinking water is produced at about 180 centralized water treatment plants. Most of the drinking water (65%) is obtained by treating natural or artificially infiltrated groundwater. In Public Supply Well Fields (PSWFs)¹ mean As concentrations range between <0.5–70 µg/L (Fig 1.4A). The As concentrations exceeding the WHO guideline (10 µg/L) are mainly observed in anoxic sand aquifers whereby As(III) is the predominant species (Ahmad et al. 2020, Flink 1985, Stuyfzand et al. 2008). Arsenic concentrations in the produced drinking water ranged between <0.5–6 µg/L, until recently (Fig 1.4B). Since 2017, several WTPs have received an upgrade to meet the 1 µg/L drinking water As guideline which has been voluntarily established by several water supply companies in the Netherlands since 2016 (Van der Wens et al. 2016).

Traditionally, As has been managed at the well-field level, e.g. by adjusting abstraction flows and well combinations. Some water treatment plants also exhibit natural As removal capacity up to some extent, attributed to co-precipitation of As with Fe(III) (oxyhydr)oxides that are formed due to oxidation of native Fe(II) in groundwater and subsequent hydrolysis (Gude et al. 2016). However, during groundwater treatment many interdependent physicochemical and biological processes (e.g. Fe(II), Mn(II) and NH_4^+ oxidation, taste and color removal etc.) take place whereby the fate of As is not yet fully elucidated. This knowledge is required to identify the water quality and operational parameters that can improve As removal at water treatment plants in order to produce drinking water with low As concentrations, below 1 µg/L.

1. A PSWF is typically a coherent set of pumping wells delivering natural groundwater, artificially recharged surface water or river bank filtrate to the public as drinking water, mostly with and rarely without treatment.

Table 1.1 Arsenic removal methods and their key advantages and disadvantages.

Method	Advantages	Disadvantages
Co-precipitation		
• Aeration-filtration of natural Fe(II) containing groundwater	• High As(V) removal efficiency over a wide pH range	• Pre-oxidation of As(III) by dosing a strong oxidant is required which increases cost of treatment
• Coagulation-filtration with Fe or Al coagulants	• Partial to complete As(III) oxidation during Fe(II) oxidation	• As removal efficiency is reduced due to competing ions
• Electrocoagulation with Fe or Al electrodes	• Partial to complete As(III) oxidation during rapid sand filtration	• As removal efficiency is lower at high pH (above PZC of solids)
• Natural corrosion of Fe(0) in the presence of oxygen	• Seasonal higher As concentrations can be managed by increasing coagulant dose	• As laced sludge is produced
Adsorption		
• Oxides and hydroxides of metals such as Fe, Al, zirconium and titanium	• Simple operation with low maintenance	• Production of As contaminated (exhausted) adsorption media which require regeneration or safe disposal
• Fe-Mn binary oxides	• Suitable for house hold filters	• As removal efficiency is low above PZC of solids and therefore pH adjustment may be required
• Low cost Geological materials	• Availability of wide range of adsorption media in market	• Pre-treatment for the removal of suspended solids is required to avoid bed clogging with suspended solids
• Nanoparticles		• Competing ions reduce As adsorption capacity
Ion exchange		
• Synthetic resins	• High As removal efficiency	• Not suitable for As(III) removal. Pre-oxidation of As(III) by dosing a strong oxidant is required
• Zeolites	• Commercial availability of resins	• Regeneration and brine disposal is costly • High capital cost for automated water production and media regeneration cycles
Membrane separation		
• Nanofiltration (NF)	• High As removal efficiency	• High capital and operation costs, especially due to replacement of the membranes due to scaling
• Reverse Osmosis (RO)	• Suitable for house hold level • Removal of multiple unwanted solutes together	• Production of As laced concentrate, that may also contain other solutes in high concentrations

Figure 1.4 Mean As concentrations in (A) raw water pumped by the 241 PSWFs in the Netherlands (Stuyfzand et al. 2008) and (B) produced drinking water (Ahmad et al. 2015). The PSWFs with As concentrations higher than 10 $\mu\text{g/L}$ are indicated. The abandoned PSWFs are marked with a graveyard icon. The water treatment plants with As concentrations higher than 1 $\mu\text{g/L}$ As are also indicated.

1.3 ARSENIC REMOVAL BY CO-PRECIPITATION WITH IRON

When Fe(III)(oxyhydr)oxides are produced in an As contaminated solution, As adsorbs to the surface of freshly formed Fe(III) precipitates by forming inner-sphere complexes (Fig. 1.5) (Hering et al. 1996a, Jain et al. 1999, Qiao et al. 2012, Van

Genuchten et al. 2012b, Waychunas et al. 1993). The As bearing Fe(III) precipitates are removed by filtration to produce As-safe water. Fe(III) precipitates can be generated by several methods, including oxidation of naturally occurring Fe(II) in groundwater by O_2 (Luong et al. 2018, Roberts et al. 2004, Vries et al. 2017, Xie et al. 2015), dosing an Fe(III) coagulant such as $FeCl_3$ in water (Hering et al. 1996b, Qiao et al. 2012), electrolytic dissolution of Fe(0) (Lakshmanan et al. 2009, Müller et al. 2019, Van Genuchten et al. 2012b, Wan et al. 2011) and by natural corrosion of Fe(0) filings under oxic conditions (Bang et al. 2005). The adsorption efficiency of As onto Fe(III) precipitates and the size of As bearing Fe(III) particles is governed by several interdependent factors such as oxidation state of As, solution pH and the concentration of As and co-occurring ions with respect to Fe in the initial solution (Jain and Ali 2000, Kanematsu et al. 2013b, Pierce and Moore 1982, Raven et al. 1998, Senn et al. 2017, Wilkie and Hering 1996).

Figure 1.5 Co-precipitation of groundwater ions with Fe(III)(oxyhydr)oxides. Inner-sphere adsorption of As and P, ternary complex formation between oxyanions and Ca, oxyanions and reduced Mn and structural incorporation of partially oxidized Mn is illustrated.

At pH relevant to most groundwaters (6.5–8.5), As(V) is negatively charged and exhibits a higher affinity for the surface of Fe(III) precipitates than As(III) which is uncharged (Fig 1.1) (Hering et al. 1996a, Lakshmanan et al. 2008, Smedley and Kinniburgh 2002). Therefore, in order to effectively remove As from groundwater, oxidizing As(III) to As(V) before co-precipitation with Fe(III)(oxyhydr)oxides has

been suggested (Guan et al. 2009a, Guan et al. 2009b, Sorlini and Gialdini 2010).

The most abundant oxyanions in natural waters which may reduce As co-precipitation are phosphate (i.e. H_2PO_4^- or HPO_4^{2-}) and silicate (i.e. H_4SiO_4), denoted further as Si and P respectively (Fig 1.5) (Meng et al. 2000, Van Genuchten et al. 2012b, Van Genuchten et al. 2014b). Moreover, natural organic matter (NOM), especially humic substances (HS), can adversely affect As removal (Davis and Edwards 2017, Sharma et al. 2010, Weng et al. 2009). Besides competing with As for adsorption sites, these inorganic and organic solutes can modify the structure, composition and identity of the Fe(III) precipitates, thereby affecting their size and As uptake behaviour (Sposito 2008, Van Genuchten et al. 2014b). A detailed understanding of the interdependencies between As co-precipitation with Fe(III) precipitates, precipitate structure and precipitation conditions is not yet fully obtained. Groundwaters usually also contain significant concentration of bivalent cations, such as calcium (Ca) and magnesium (Mg), which have been shown to counteract the negative effects of oxyanions on As removal by Fe based co-precipitation through mechanisms such as neutralization of the Fe(III) precipitate surface charge (Wilkie and Hering 1996), suppression of electrostatic repulsion (Masue et al. 2007) and the formation of ternary complexes (Kanematsu et al. 2013b, Van Genuchten et al. 2014a). Previous studies have mostly focused on the interactions between As and Fe(III) precipitates in simple, single and binary solute systems (Laky and Licskó 2011, Weng et al. 2008, Weng et al. 2009). Systematic studies providing understanding of the As–Fe(III) interactions in complex multi-solute solutions are limited which hampers accurate prediction and control of As removal by Fe based co-precipitation during water treatment.

1.4 OXIDATION OF AS(III) TO AS(V) WITH STRONG OXIDANTS

During groundwater treatment, dissolved Fe(II) in raw water oxidizes homogeneously, heterogeneously or biologically, or by a combination of these processes (Jessen et al. 2005, Van Beek et al. 2012, Vries et al. 2017). Oxidation of Mn(II) by O_2 alone in a treatment plant is generally negligible because of the slow oxidation kinetics (Diem and Stumm 1984, Lytle et al. 2005), nevertheless bacteria and surface catalysts on the filter media grains transform Mn(II) to insoluble MnO_x precipitates (Bruins et al. 2015, Katsoyiannis et al. 2008). The removal of NH_4^+ occurs in the filter bed, attributed to the biological oxidation (nitrification) executed by different bacterial species in the filter bed (De Moel et al. 2006, De Vet 2011).

Oxidation of As(III) by aeration introduced O_2 is thermodynamically possible, however the reaction proceeds very slowly (Frank and Clifford 1986, Kim and Nriagu

2000), rendering the traditional aeration techniques, e.g. spray or cascade aeration, inefficient in oxidizing As(III) (Jessen et al. 2005, Katsoyiannis et al. 2008, Lytle et al. 2007). To improve As removal capacity of water treatment plants, rapid oxidation of As(III) can be achieved by dosing a strong oxidant, such as KMnO_4 or NaOCl (Ghurye and Clifford 2001, Lihua et al. 2009, Sorlini and Gialdini 2010). Previous work has shown that strong oxidants can oxidize other groundwater constituents such as Fe(II) and Mn(II) (Allard et al. 2013, Hao et al. 1991, Knocke et al. 1991, Van Benschoten et al. 1992) and may also interfere with nitrification in rapid sand filters. Detailed understanding of the impact of oxidant dosing on the pre-established Fe(II), Mn(II) and NH_4^+ removal processes in rapid sand filters is not yet clear.

The structure, reactivity towards As and other ions, as well as the aggregation behaviour of Fe and Mn precipitates depend on Fe(II) and Mn(II) oxidation rates. For example, previous work has shown that poorly-ordered Fe(III) precipitates result from rapid Fe(II) oxidation by H_2O_2 and moderately crystalline Fe(III) precipitates form from slower Fe(II) oxidation by O_2 (Van Genuchten and Pena 2017a, Voegelin et al. 2010). Such differences in crystallinity are important because poorly-ordered Fe(III)(oxyhydr)oxides have a higher specific surface area than crystalline solids, which would increase adsorption of ions (e.g. As) per mass of added Fe. The differences in the structure and composition of Fe(III) precipitates also affect their availability as terminal electron acceptors in redox-sensitive environments (Hyacinthe et al. 2008, Voegelin et al. 2010). Little is known about how other strong oxidants such as KMnO_4 and NaOCl impact key properties e.g. structure, composition and precipitate aggregation behaviour of the Fe and Mn bearing precipitates generated by Fe(II) and Mn(II) co-oxidation.

1.5 IRON BASED CO-PRECIPITATION WITH LOW-PRESSURE MEMBRANE FILTRATION

At most groundwater treatment plants the As bearing Fe(III) precipitates are typically removed by rapid sand filtration (Gude et al. 2018a, Gude et al. 2016, 2018c, McNeill and Edwards 1995, Ruiping et al. 2009). These precipitates can also be removed by low-pressure membranes like microfiltration (MF) and ultrafiltration (UF), especially when effective removal of colloidal As bearing Fe(III) particles in a limited space is to be achieved (Brandhuber and Amy 1998, Choi and Dempsey 2004, Ghurye et al. 2004, Lee et al. 2004, Ruiping et al. 2009, Zouboulis and Katsoyiannis 2002). Depending on the size of Fe(III) particles and membrane pores, fouling in low-pressure membranes can be reversible or irreversible, involving mechanisms such as pore blocking, pore narrowing, entrapment (Zhang and Song

2000) and/or adsorption onto the membrane surface. Currently, one of the reasons for the restriction of wide-scale application of low-pressure membrane filtration for As removal is a lack of detailed knowledge about membrane fouling due to Fe(III) particles and operational consequences.

1.6 RESEARCH OBJECTIVES

The overall objective of this thesis is to discern mechanistic understanding of As removal by co-precipitation with Fe(III)(oxyhydr)oxides under differential redox, ion composition and filtration conditions and to investigate routes to reduce As in drinking water to very low levels, below 1 µg/L.

The specific research questions are:

- I. What are the most important mechanisms that determine the mobilization and attenuation of As during groundwater treatment?
- II. What is the impact of KMnO_4 dosing on the co-precipitation of As with Fe(III)(oxyhydr)oxides? And, how does dosing KMnO_4 affect As(III), Fe(II), Mn(II) and NH_4^+ removal mechanisms in rapid sand filters?
- III. What impact different oxidants (O_2 , KMnO_4 , NaOCl) have on the structure of formed Fe and Mn bearing precipitates? Also, how does the common groundwater ions such as Si, P and Ca affect the structure of the precipitates?
- IV. What are the opportunities to reduce As to very low levels in produced drinking at water treatment plants which use artificially infiltrated groundwater as source?
- V. How does Si, P and NOM influence As co-precipitation efficiency with Fe(III)(oxyhydr)oxides and the size of Fe(III) particles in waters with high Ca hardness?
- VI. How does in-line FeCl_3 dosing improve As removal in low-pressure membranes and what are the predominant membrane fouling mechanisms?

1.7 THESIS OUTLINE

Chapter 1 (this chapter) presents introduction and objectives of this thesis.

In Chapter 2 we provide details on pilot and full-scale investigations that were carried out at a groundwater treatment plant in the Netherlands. We discern mechanistic details of As removal during aeration and rapid sand filtration type anaerobic groundwater treatment systems (Research Question I). Moreover, we investigate the potential of As(III) oxidation with KMnO_4 and co-precipitation of resulting As(V) with Fe(III)(oxyhydr)oxides for As removal to below $1\text{ }\mu\text{g/L}$. In this chapter we also reveal the effects of adopting KMnO_4 and FeCl_3 dosing on the pre-existing Fe(II), Mn(II) and NH_4^+ removal mechanisms in rapid sand filters (Research Question II).

Chapter 3 is based on laboratory investigations whereby macroscopic measurements of precipitate aggregation and chemical composition are combined with X-ray absorption spectroscopy to investigate the solids formed by co-oxidation of Fe(II) and Mn(II) with O_2 , KMnO_4 and NaOCl in the presence and absence of groundwater ions such as Si, P and Ca (Research Question III).

In Chapter 4 we present insights into the mobility and redox transformation of As during treatment of artificially recharged groundwater which is typically much more extensive than the treatment of natural groundwater (Research Question I). In this chapter we also explore opportunities for reducing As in drinking water to very low levels, below $1\text{ }\mu\text{g/L}$ (Research Question IV).

Chapter 5 provides a detailed understanding of the independent and combined effects of Si, P and NOM on As removal by co-precipitation with Fe(III)(oxyhydr)oxides and the size of resulting Fe(III) precipitates in waters with high Ca hardness (Research Question V).

In Chapter 6 we present a laboratory study performed with different water types and low-pressure membranes to gain insights into the mechanisms of As removal and membrane fouling in Fe(III) based coprecipitation followed by low pressure membrane filtration systems (Research Question VI).

In Chapter 7 the results from this thesis are combined to address the main problem definition and research questions stated in Chapter 1.

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Chapter 2

Arsenite removal in groundwater treatment plants by permanganate and ferric treatment

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ABSTRACT

The Dutch drinking water sector is actively investigating methods to reduce arsenic (As) to $<1\text{ }\mu\text{g/L}$ in drinking water supply. We investigated (1) the effectiveness of sequential permanganate (MnO_4^-) – ferric (Fe(III)) dosing during aeration – rapid sand filtration to achieve $<1\text{ }\mu\text{g/L}$ As, (2) the influence of MnO_4^- – Fe(III) dosing on pre-established removal patterns of As(III) , Fe(II) , Mn(II) and NH_4^+ in rapid sand filters and (3) the influence of MnO_4^- – Fe(III) dosing on the settling and molecular-scale structural properties of the filter backwash solids. We report that MnO_4^- – Fe(III) dosing is an effective technique to improve arsenite [As(III)] removal at groundwater treatment plants. At a typical aeration – rapid sand filtration facility in the Netherlands effluent As concentrations of $<1\text{ }\mu\text{g/L}$ were achieved with 1.2 mg/L MnO_4^- and 1.8 mg/L Fe(III) . The optimized combination of MnO_4^- and Fe(III) doses did not affect the removal efficiency of Fe(II) , Mn(II) and NH_4^+ in rapid sand filters, however, the removal patterns of Fe(II) and Mn(II) in rapid sand filter were altered, as well as the settling behaviour of backwash solids. The characterization of backwash solids by Fe K-edge X-ray absorption spectroscopy (XAS) and X-ray diffraction (XRD) showed that the changed settling velocity of backwash solids with MnO_4^- – Fe(III) in place was not due to changes in the molecular-scale structure of Fe-precipitates that constitute the major portion of the backwash solids.

2.1 INTRODUCTION

Arsenic (As) in drinking water is one of the largest human health risks known at the present time, with well over 200 million people around the world being exposed to high As concentrations (McCarty et al. 2011, Murcott 2012, Naujokas et al. 2013). Arsenic can be released from the Earth's crust into drinking water sources by both natural (e.g. leaching from rocks and sediments, volcanism) and anthropogenic processes (e.g. mining, agrochemicals, wood preservatives) (Bhattacharya et al. 2002a, Borba et al. 2003, Bundschuh et al. 2017, Gunduz et al. 2010, MacDonald et al. 2016, Marszałek and Wąsik 2000, Nriagu et al. 2007, Woo and Choi 2001). In aqueous environments As may occur in organic and inorganic forms, whereby the latter is known to predominate in fresh water (Bhattacharya et al. 2007, Pontius et al. 1994, Smedley and Kinniburgh 2002). Inorganic As predominantly occurs in two oxidation states; +3 and +5, with varying level of protonation, depending on the pH (Ferguson and Gavis 1972, Pontius et al. 1994, Smedley and Kinniburgh 2002, Wang and Mulligan 2006).

Arsenic can cause a number of carcinogenic and non-carcinogenic adverse effects on human health (Schuhmacher-Wolz et al. 2009, Smith et al. 1992, Vahter 2008, Vahter et al. 2012), however, its mode of action and dose-response characteristics allowing for the identification of a safe exposure level are still not well-understood (Kozisek 2017, Pontius et al. 1994, Schmidt 2014, WHO 2011). This leads to considerable uncertainties about the actual risks of As exposure, especially at low concentrations (Kozisek 2017). Following a preventive approach, the Dutch drinking water sector is actively investigating treatment options to reduce trace levels of As from drinking water to <1 µg/L (Van der Wens et al. 2016). Groundwater is the main source of drinking water in the Netherlands and As concentration in raw groundwater ranges between <0.5-70 µg/L (Ahmad et al. 2015, Stuyfzand et al. 2008). In drinking water, produced at approximately 180 centralized Water Treatment Plants (WTPs), the concentration of As ranges between <0.5-6.2 µg/L (Ahmad et al. 2015, Stuyfzand et al. 2008) which shows that As is removed with varying efficiencies during treatment and the resulting concentrations in drinking water are well below the WHO guideline (10 µg/L).

Most groundwater treatment plants in the Netherlands typically apply aeration followed by rapid sand filtration to accomplish the removal of dissolved iron [Fe(II)], manganese [Mn(II)] and ammonium (NH₄⁺) from water through distinct removal pathways (De Moel et al. 2006). Iron(II) may oxidize homogeneously, heterogeneously and biologically, or by a combined mechanism involving these processes, leaving hydrous ferric oxide (HFO) precipitates (Fe(III)-precipitates) in the supernatant, in the pores and on the surface of the filter media (Jessen et al.

2005, Van Beek et al. 2012, Vries et al. 2017). Direct oxidation of Mn(II) by oxygen (O_2) is generally negligible (Diem and Stumm 1984, Lytle et al. 2005) and bacteria and surface catalysts on the filter media grains are known to transform Mn(II) to insoluble hydrous manganese oxide (MnO_2) (Bruins et al. 2015, Katsoyiannis et al. 2008). Ammonium is removed by nitrification which takes place in the filter bed, mediated by different bacterial species (De Moel et al. 2006, De Vet 2011). These treatment plants also remove As, attributed to adsorption to the precipitated HFO (Ahmad et al. 2015, Gude et al. 2016), as observed by McNeill and Edwards (1995) and Lytle et al. (2007) in several groundwater treatment plants in the United States, by Sorlini et al. (2014) in Italy and by Katsoyiannis et al. (2008) in Greece. The presence of anions in groundwater e.g. phosphate, sulfate, carbonate, silicate, as well as the natural organic matter may reduce the adsorption of As to Fe(III)-precipitates due to their competition for adsorption sites (Dixit and Hering 2003, Hering et al. 1996a, Qiao et al. 2012, Su and Puls 2001, Wilkie and Hering 1996, Younggran et al. 2007), sometimes rendering the amount of natural Fe in raw water insufficient to achieve the target effluent As concentration. The concentration of Fe nevertheless can be increased by dosing an Fe(III) or Fe(II) based coagulant such as ferric chloride ($FeCl_3$) or ferrous sulfate ($FeSO_4$). The As removal efficiency may differ when Fe(II) or Fe(III) is dosed, per equal concentration of precipitated Fe (Gude et al. 2017, Roberts et al. 2004). In the Netherlands, $FeCl_3$ is the most widely used coagulant in drinking water production and for this reason we chose it as the source of Fe in this study.

The adsorption of As to Fe(III)-precipitates is also sensitive to As species in water (Jain and Ali 2000, Pierce and Moore 1982, Raven et al. 1998, Wilkie and Hering 1996). The adsorption of As(V) to Fe(III)-precipitates at low As/Fe molar ratios and pH relevant for most groundwater (6.5-8.5) is more efficient compared to As(III) (Hering et al. 1996a, Hsu et al. 2008, Lakshmanan et al. 2008, Lytle et al. 2005, Qiao et al. 2012), mainly because of the anionic character of As(V). Therefore, at WTPs where As(III) is a dominant species in source water, (pre-)oxidation of As(III) to As(V) could increase As removal. Oxidation of As(III) by dissolved O_2 alone is thermodynamically possible, however the reaction proceeds very slowly (Frank and Clifford 1986, Kim and Nriagu 2000), rendering the traditional aeration techniques, e.g. spray or cascade aeration, inefficient in oxidizing As(III) (Jessen et al. 2005, Katsoyiannis et al. 2008, Lytle et al. 2007). Chemical oxidants, such as chlorine, ozone, hydrogen peroxide, permanganate (MnO_4^-) etc. have been shown to achieve rapid oxidation of As(III) (Bissen and Frimmel 2003). In this study MnO_4^- was used for As(III) oxidation because it has the ability to oxidize As(III) over a broad pH range and within time frame of seconds to one minute (Ghurye and Clifford 2001, Lihua et al. 2009, Sorlini and Gialdini 2010). Furthermore, MnO_4^- does not

form harmful by-products such as chlorination in the presence of humic substances (Smeets et al. 2009) and ozonation with bromide present (Von Gunten 2003) and is easy to dose and affordable (Borho and Wilderer 1996, Guan et al. 2009b).

Arsenic removal from water involving MnO_4^- and Fe(III) dosing has been previously investigated. Borho and Wilderer (1996) demonstrated at pilot scale that MnO_4^- dosing followed by Fe(III) dosing could lead to very low residual As concentration, provided the As containing Fe(III)-precipitates were sufficiently removed from water. Lihua et al. (2009) studied the MnO_4^- and Fe(III) dosing in water with the aim of developing a small system for rural populations in low income countries. They used tap water spiked with As(III) in their experiments and filtration was accomplished through a sand filter followed by ultrafiltration (UF). It was shown that when water was pre-treated with MnO_4^- for As(III) oxidation, lower and more stable effluent As concentrations were achieved and the sand filtration was mainly responsible for the removal of As-laced Fe(III)-precipitates. Bordoloi et al. (2013) studied As(III) removal from groundwater water by MnO_4^- and Fe(III) dosing at mild alkaline pH that was achieved through the addition of NaHCO_3 in water. Their study was also aimed at developing a process for rural application in low income countries. With laboratory and field experiments, Bordoloi et al. (2013) showed that As(III) could be efficiently removed to meet the WHO guideline for As in drinkingwater (10 $\mu\text{g/L}$).

All these studies show that MnO_4^- – Fe(III) dosing is a promising method to increase the As(III) removal efficiency at typical aeration – rapid sand filtration type groundwater treatment facilities where As(III) is present in the raw water, however As removal to <1 $\mu\text{g/L}$, as aimed in this study, has never been a goal of any of the previous studies. The effects of adopting MnO_4^- – Fe(III) dosing on the existing removal efficiencies of Fe(II), Mn(II) and NH_4^+ at typical aeration – rapid sand filtration type groundwater treatment facilities are also not well documented in literature. Moreover, the influence on settling characteristics of filter backwash water, which is an important parameter affecting the design and operation of backwash water treatment at WTPs, has not been studied before. Consequently, the aim of this study was (1) to achieve <1 $\mu\text{g/L}$ As by MnO_4^- – Fe(III) dosing at a typical aeration – rapid sand filtration facility (2) to study the influence of MnO_4^- – Fe(III) dosing on the removal of As, Fe, Mn and NH_4^+ in rapid sand filtration and (3) to study the influence of MnO_4^- – Fe(III) dosing on the settling and molecular scale structural properties of the filter backwash solids. The study, including batch, pilot and full-scale experiments, was carried out at a groundwater treatment facility (WTP Dorst) in the Netherlands with typical aeration–rapid sand filtration based treatment scheme.

2.2 MATERIALS AND METHODS

2.2.1 Treatment layout and water quality of WTP Dorst

WTP Dorst is a typical groundwater treatment facility (10 Mm³/year production) in the Netherlands which treats anaerobic groundwater in 10 parallel treatment trains, each comprising of a cascade aeration step followed by a submerged rapid sand filter (Fig 2.1). The surface area and bed height of the sand filters are 27 m² and 1.8 m respectively. They contain a single media filter material (silica sand D50=1.3 mm) and are operated at an average (superficial) filtration velocity of 4.6 m/h (filter loading Q=125 m³/h). Table 2.1 presents the raw and treated water quality at WTP Dorst.

Figure 2.1 Typical groundwater treatment layout in the Netherlands.

2.2.2 Optimizing MnO_4^- – Fe(III) doses to achieve <1 µg/L As

2.2.2.1 Preliminary batch experiments

To gain preliminary information on MnO_4^- – Fe(III) doses required to remove As to <1 µg/L, a series of batch tests was carried out using the raw water of WTP Dorst (Table 2.1). The experiments were performed with a jar test apparatus, which comprised a set of six transparent jars (2 L capacity each). Each jar was equipped with a dosing unit to add MnO_4^- and Fe(III), a paddle for mechanical stirring and a sampling point in the bottom. The timing of MnO_4^- and Fe(III) dosing and mixing speed in the jars could be automatically controlled. A 0.03 M KMnO_4 (3.6 g/L MnO_4^-) solution was used to dose MnO_4^- . It was prepared by dissolving 948 mg of

solid KMnO_4 (Cairox®, Carus Corporation) in 200 mL deionized (DI) water directly before the start of the batch experiments. A FeCl_3 solution (2.0 g Fe(III)/L) was used to dose Fe(III) in water. It was prepared by dissolving 1936 mg solid $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (J.T. Baker®) in 200 mL DI water directly before the start of the batch experiments.

The jar test procedure was designed to represent the process conditions at the full-scale facility, especially with respect to the residence time of water during aeration and rapid sand filtration. The jar test procedure included the following steps. Firstly, the 6 jars were filled with anaerobic raw groundwater of WTP Dorst (Table 2.1). Afterwards, a predetermined aliquot of MnO_4^- and/or Fe(III) was dosed in each jar while the solutions were mixed at 300 RPM. In the MnO_4^- – Fe(III) dosing experiments, the interval between MnO_4^- and Fe(III) doses was kept constant at 2 min. This interval was chosen to make sure that complete oxidation of As(III) to As(V) occurred before Fe(III) dosing, though Ghurye and Clifford (2001) and Sorlini and Gialdini (2010) found complete As(III) oxidation within 1 min of MnO_4^- dosing in their experiments with both synthetic and real groundwater samples. After 3 min of mixing at 300 RPM, the mixing speed was reduced to 50 RPM for the next 13.5 min to allow Fe(III) precipitates to grow into larger flocs. Finally, the process water was sampled from the jars by opening the bottom tap and filtering immediately using 0.45 μm filters (GE's GD/XP disposable syringe filters with nylon membrane). The filtered samples were analyzed for As and Fe. During the experiments the jars were kept open to the atmosphere, therefore the agitation caused by stirring at 300 RPM not only accomplished mixing of the chemicals, but also aeration of the raw water.

2.2.2.2 Pilot experiments

Pilot experiments were performed to optimize the dosing of MnO_4^- and Fe(III) . The pilot plant, installed at WTP Dorst, was fed with the raw water of WTP Dorst (Table 2.1). Fig 2 shows a schematic diagram of the pilot setup. The pilot setup consisted of an aeration cascade followed by a filtration column (0.3 m diameter, 2.5 m height) and peristaltic pumps for MnO_4^- and Fe(III) dosing. The column contained filtration media (1.8 m height) obtained from the full-scale filter of WTP Dorst (silica sand $\text{D}_{50}=1.3$ mm) in an attempt to achieve a similar rapid sand filtrate quality as the full-scale facility. Permanganate was dosed using 0.03 M KMnO_4 (3.6 g/L MnO_4^-) solution prepared onsite in 20 L jerry cans by dissolving solid KMnO_4 (Cairox®) in DI water 2-3 times per week. Ferric was dosed using 40 w/w % FeCl_3 solution (Ferralco Nederland BV). MnO_4^- was dosed at the top of the cascade for As(III) oxidation and Fe(III) was dosed for As(V) removal at the bottom, as shown in Fig 2.2. Two separate membrane pumps (GALA1602, ProMinent®) were used for dosing MnO_4^- and Fe(III) .

The pilot experiments were performed under three conditions, based on the outcomes of the preliminary batch experiments and further optimization of chemical dosing to achieve $<1 \mu\text{g/L}$ in pilot filtrate. In the first condition, the pilot plant was operated for 6 weeks without dosing of MnO_4^- and Fe(III) to replicate a filtrate quality similar to that of the full-scale facility. In the second condition, 0.8 mg/L MnO_4^- and 1.8 mg/L Fe(III) were dosed for 4 -weeks, and in the third condition, 1.2 mg/L MnO_4^- and 1.8 mg/L Fe(III) were dosed for 4 weeks in the pilot cascade. During all the experiments the pilot was operated at the filtration velocity of 4.6 m/h (filter loading $Q=1.3 \text{ m}^3/\text{h}$). Unfiltered and $0.45 \mu\text{m}$ filtered samples were collected from the pilot filtrate during 8-12 runs at each condition and analyzed for the determination of As, Fe, Mn and NH_4^+ concentrations.

Figure 2.2 Schematic diagram of the pilot set-up.

2.2.3 Influence of MnO_4^- – Fe(III) dosing on removal of As, Fe, Mn and NH_4^+

Soon after the completion of the pilot experiments, the full-scale facility received an upgrade with MnO_4^- – Fe(III) dosing. This enabled us to study the influence of MnO_4^- – Fe(III) dose on the removal of As, Fe, Mn and NH_4^+ on full-scale. Reference measurements were obtained before the upgrade, i.e. when the raw water (Table 2.1) was only treated with aeration – rapid sand filtration. The measurements with MnO_4^- – Fe(III) dosing were obtained one year after the upgrade, with 1.2 mg/L MnO_4^- and 1.8 mg/L Fe(III) dosed (dosing was based on the results of the pilot experiments) to achieve $<1 \mu\text{g/L}$ As in the produced drinking water. In both sampling campaigns, unfiltered and 0.45 μm filtered raw water, supernatant and filtrate samples were collected. Supernatant refers to the water storage on the top of the filter bed. Concentrations of As, Fe and Mn were determined in unfiltered and 0.45 μm filtered samples. Concentrations of NH_4^+ were determined in unfiltered samples only. Dissolved arsenic species were determined in 0.45 μm filtered samples.

2.2.4 Influence of MnO_4^- – Fe(III) dosage on filter backwash solids characteristics

The influence of MnO_4^- – Fe(III) dosing on the settling and molecular scale structural characteristics of the backwash solids was also studied at the full scale installation. Backwash water samples were collected under 3 conditions: (1) without dosing (no dose), i.e. prior to the upgrade (2) with only dosing 1.2 mg/L MnO_4^- and (3) with dosing 1.2 mg/L MnO_4^- and 1.8 mg/L Fe(III). Under each condition the backwash water sample were collected at the 60th hour of the filter run. To collect each sample during filter backwash, 5 L of backwash water was collected every minute during the first 4 minutes. The samples were subsequently mixed to form a secondary suspension, which was subsequently used for settling experiments and for solids characterization. Unfiltered and 0.45 μm filtered backwash water samples, collected at each setting, were analyzed for Fe and Mn concentration.

2.2.5 Settling characteristics of filter backwash solids

The settling characteristics of the filter backwash solids were studied using a method previously used by Van Genuchten et al. (2014b). 1.8 L transparent jars were filled with the backwash water samples, mixed with a magnetic stirrer for 1 min to achieve a homogeneous suspension of filter backwash solids and then allowed to settle under gravity for 1 h. During settling, an aliquot of sample was taken approximately 10 cm below the surface of the suspension, every 15 min between $t=0$ and 60 min, using a wide-mouthed syringe for turbidity measurements using a Hach 2100 N Turbidimeter. The settling behaviour was also recorded through photographs.

2.2.6 Solid phase characterization

Solids were collected on 0.45 μm filters from the backwash water samples under no dose and 1.2 mg/L MnO_4^- dose conditions. The samples were air dried for 24 hours at room temperature and then stored in closed containers at room temperature until analysis in 2 weeks. The solids were characterized by Fe K-edge X-ray absorption spectroscopy (XAS) and X-ray diffraction (XRD). Fe K-edge XAS data were collected at the DUBBLE beam line (BM-26) of the European Synchrotron Radiation Facility (ESRF). Spectra were recorded at room temperature in transmission mode out to k of 13 $\text{\AA}^{-1}$. X-Ray diffraction measurements (XRD) were performed at the X-Ray facility in Utrecht University, The Netherlands. The Samples for powder XRD measurements, were ground into a powder using an agate mortar and pestle. Powder diffraction patterns were collected with a Bruker D8 Advance diffractometer using Cu K-alpha radiation and a rotating sample stage. Measurements were performed from 5 to 75° 2 θ with 0.02° step sizes and total data collection time of approximately 4 h per sample.

2.2.7 Analysis of water samples

Determination of As, Fe and Mn concentrations was carried out by Inductively Coupled Plasma Mass Spectrometry (ICP—MS) (SXERIES 2, Thermo Fisher Scientific) at Aqualab Zuid laboratory in the Netherlands. The detection limits (DLs) for As, Fe, Mn were 0.5, 10 and 10 $\mu\text{g/L}$ respectively. Samples for As, Fe, Mn analysis were preserved immediately after sampling by adding 250 μL of 10% ultra-pure nitric acid (HNO_3). To obtain 0.45 μm filtered samples, GE's GD/XP disposable syringe filters were used. For the determination of Fe and Mn in the backwash water samples, samples were digested in acid and microwaved before ICP—MS. Arsenic speciation (As(III) versus As(V)) was determined using Amberlite® IRA-400 chloride form AIEX resin. The procedure included passing 100 mL of 0.45 μm filtered water through a 30 mL syringe filled with 20 mL of the resin. The As concentration that remained in the effluent after contact with the resin was considered to be uncharged As(III). As(V) was calculated by subtracting As(III) from the As concentration in the column influent (Clifford et al. 1983). NH_4^+ was analyzed by a discrete analyzer spectrophotometry (Aquakem 250, Thermo Scientific) at Aqualab Zuid laboratory (accredited NEN-EN-ISO/IEC 17025:2005). The method DL was 30 $\mu\text{g/L}$ NH_4^+ .

2.3 RESULTS AND DISCUSSION

2.3.1 Optimizing MnO_4^- – Fe(III) doses to achieve $<1 \mu\text{g/L}$ As

2.3.1.1 Preliminary batch experiments

To gain preliminary information on MnO_4^- and Fe(III) doses required to remove As to $<1 \mu\text{g/L}$, a series of batch tests was carried out. Fig 2.3a presents the residual As concentration in function of the Fe(III) dose. An As concentration of $<1 \mu\text{g/L}$ was not achieved even with a high dose of Fe(III) (10 mg/L). The residual concentration of As decreased with increasing Fe(III) dose which can be attributed to the increasing amount of Fe(III)-precipitates with each incremental Fe(III) dose (Cornell and Schwertmann 2003, Hering et al. 1996a, Wilkie and Hering 1996). The actual raw water of WTP Dorst used in these experiments (Table 2.1) contained As(III) as the predominant As species. As(III) adsorbs to the Fe(III)-precipitates produced by Fe(III) coagulants in solution (Hering et al. 1996a, Lakshmanan et al. 2008). Fig 2.3a shows that the residual As concentration in the absence of Fe(III) dosing was $8.7 \mu\text{g/L}$, thus significantly lower than the As concentration in the raw water ($11.9 \mu\text{g/L}$). This reduction can be attributed to coprecipitation of As with the natural Fe in raw groundwater of WTP Dorst (Edwards 1994, McNeill and Edwards 1995).

The residual As concentration as a function of MnO_4^- and MnO_4^- – Fe(III) dose is presented in Fig 2.3b. An As concentration of $<1 \mu\text{g/L}$ As was achieved when $\geq 1.2 \text{ mg/L}$ MnO_4^- was combined with an Fe(III) dose of 2.0 mg/L. Residual As concentrations decreased with increasing MnO_4^- dose for each Fe(III) dose and the curves appear to level-off beyond 1.2 mg/L of MnO_4^- dose indicating ineffectiveness of further increase in MnO_4^- dose for As removal. This result indicates that MnO_4^- dosages of $<1.2 \text{ mg/L}$ may not be sufficient to completely oxidize As(III) to As(V), thus limiting the As adsorption to Fe(III)-precipitates that were formed in water due to the oxidation and hydrolysis of the natural Fe(II) and dosed Fe (III) (Hering et al. 1996a, Hsu et al. 2008, Lakshmanan et al. 2008, Lytle et al. 2005, Qiao et al. 2012). It is worth mentioning that the residual Fe concentration in the entire series of batch experiments was $<10 \mu\text{g/L}$, indicating the Fe(III) precipitation was not limiting the As removal efficiency.

Comparing the residual As concentrations at 2.0 mg/L Fe(III) dose with and without MnO_4^- (Fig 2.3a and 2.3b respectively), it is evident that a significantly lower residual As was achieved when MnO_4^- and Fe(III) were dosed. The results of the batch experiments indicated that the dosing of around 1.0 mg/L MnO_4^- and 2.0 mg/L Fe(III) would be required to achieve As removal to $<1 \mu\text{g/L}$ at WTP Dorst. Using these concentrations as a starting point, the next topic is optimizing the MnO_4^- – Fe(III) dose in pilot experiments.

Figure 2.3 Residual concentration of As (A) as a function of Fe(III) dose and (B) as a function of MnO_4^- and MnO_4^- – Fe(III) dose. Results are based on batch experiments (single trials).

2.3.1.2 Pilot experiments

Arsenic and Fe concentrations in the pilot filtrate are presented in Fig 2.4a and 2.4b, respectively. In the absence of MnO_4^- – Fe(III) dosing, the average As concentration in the pilot filtrate was $6.3 \mu\text{g/L}$, which was comparable to the full-scale effluent quality (Table 2.1). However, the pilot filtrate contained a higher Fe concentration

($24.4 \pm 5.3 \mu\text{g/L}$) (Fig 2.4b) compared to the effluent of the full-scale facility where Fe was undetectable ($<10 \mu\text{g/L}$) (Table 2.1). When 0.8 mg/L MnO_4^- and 1.8 mg/L Fe(III) were dosed in the pilot cascade, the As concentration in the filtrate decreased to an average of $1.4 \mu\text{g/L}$ and the Fe concentration decreased to an average of $21.1 \mu\text{g/L}$. When the MnO_4^- dose was increased further to 1.2 mg/L with Fe(III) dose maintained at 1.8 mg/L , the As concentration in the filtrate decreased to an average of $0.9 \mu\text{g/L}$ and the Fe became undetectable ($<10 \mu\text{g/L}$).

The increased As removal with increment of MnO_4^- dose may be due to the oxidation of As(III) to As(V) (Bordoloi et al. 2013) and subsequent more efficient uptake of As(V) by Fe(III)-precipitates (Edwards 1994, Qiao et al. 2012, Wilkie and Hering 1996). The Fe speciation (Fe in unfiltered and $0.45 \mu\text{m}$ filtered samples) in the pilot filtrate showed that the dissolved Fe concentration in the pilot filtrate was consistently $<10 \mu\text{g/L}$ (DL) during the experiments with the three settings. This shows that the precipitation of Fe was not dependent on MnO_4^- . Thus the observed decrease in the Fe concentration in the pilot filtrate with the increase in MnO_4^- dose from 0 to 1.2 mg/L was apparently not related to the oxidizing capacity of MnO_4^- . It may, however, be due to improved aggregation (flocculation) and filterability of Fe(III)-precipitates triggered by MnO_x precipitates that form upon MnO_4^- reduction and oxidation of natural Mn(II) (Lihua et al. 2009).

Under all three experimental conditions, Mn and NH_4^+ concentrations in the pilot filtrate remained below the detection limit ($10 \mu\text{g/L}$ for Mn and $30 \mu\text{g/L}$ for NH_4^+). This result indicates that the dosing of MnO_4^- and Fe(III) did not decrease the overall removal efficiency of Mn(II) and NH_4^+ in the pilot filter.

It is worth mentioning that the run time of the pilot filter was reduced when MnO_4^- and Fe(III) were dosed. This can be attributed to the increased rate of filter clogging due to increased load of Fe(III)-precipitates and MnO_x precipitates to the filter compared to the condition when MnO_4^- and Fe(III) were not dosed.

2.3.2 Influence of MnO_4^- – Fe(III) dose on As, Fe, Mn and NH_4^+ removal profiles

Fig 2.5a, b, c and d presents As, Fe, Mn and NH_4^+ concentrations in the raw, supernatant and filtrate before the upgrade of the full-scale facility (no dose) and after the upgrade when 1.2 mg/L MnO_4^- and 1.8 mg/L Fe(III) were dosed (MnO_4^- – Fe(III)). Fig 2.5a shows that As was approximately $11.5 \mu\text{g/L}$ in the unfiltered and $0.45 \mu\text{m}$ filtered raw water samples, indicating the presence of As in dissolved form. In the supernatant, the As concentration in the unfiltered samples was similar to the raw water, indicating that As was not removed during aeration. However, approximately $1 \mu\text{g/L}$ As (8.7% of the total As) was removed by the $0.45 \mu\text{m}$ filter in the supernatant with no dose and $11.4 \mu\text{g/L}$ (99.2% of the total As) As became filterable in the supernatant with MnO_4^- – Fe(III) dose. Fig 2.5b shows that the raw

Figure 2.4 (A) Arsenic and (B) Fe concentrations in the pilot filtrate under three pilot experimental conditions.

water contained 1400 µg/L Fe, which entirely passed through the 0.45 µm filter. In the supernatant, 942.5 µg/L Fe (66.2% of total Fe) passed through the 0.45 µm filter in the absence of dosing. The As uptake in the supernatant is calculated to be $(1/0.942=)$ 1.1 µg/mg Fe in the absence of MnO₄⁻ – Fe(III) dosing. The Fe concentration in the supernatant with MnO₄⁻ – Fe(III) dose was much higher due to Fe(III) dosing in the feed, with 3682.3 µg/L Fe (97.6% of the total Fe) filterable through 0.45 µm filter. The As uptake in the supernatant is calculated to be $(11.4/3.37=)$ 3.3 µg/mg Fe with MnO₄⁻ – Fe(III) dosing. The 3-fold higher uptake of As in the supernatant with MnO₄⁻ – Fe(III) dose can be attributed to As(III) oxidation to As(V) by MnO₄⁻ (Borho and Wilderer 1996, Lihua et al. 2009). In the filtrate, a significant difference in As concentration was observed, with 6.1 µg/L at no dose and 0.54 µg/L with MnO₄⁻ – Fe(III) dose. In both the cases, As passed through the 0.45

μm filter, indicating its presence as dissolved As. Iron was below the detection limit ($10\text{ }\mu\text{g/L}$) in the filtrate in both the cases. Since most of the Fe was precipitated in the supernatant, homogeneous Fe(II) oxidation followed by flocculative removal can be regarded as the principle Fe removal mechanism both at no dose and with MnO_4^- – Fe(III) dosing. However, a significantly higher concentration of Fe was precipitated in the supernatant when MnO_4^- – Fe(III) was dosed.

Manganese did not pass through $0.45\text{ }\mu\text{m}$ filter in the raw water (Fig 2.5c), indicating its presence in dissolved form. It remained unfilterable in the supernatant at no dose. This showed that the cascade aeration was ineffective in oxidizing Mn(II) and confirmed the previous results (Diem and Stumm 1984, Lytle et al. 2005) that the transformation of Mn(II) to MnO_2 by dissolved O_2 alone is a slow process at pH below 9. At no dose, Mn was below the detection limit ($10\text{ }\mu\text{g/L}$) in the filtrate. This Mn removal can be attributed to the autocatalytic removal mechanism in which dissolved Mn(II) adsorbs to the filter media grains where it is oxidized to form MnO_2 coating (Bruins et al. 2015, Katsoyiannis et al. 2008). On the other hand, the Mn concentration in the supernatant with MnO_4^- – Fe(III) dose, though much higher due to MnO_4^- dosing, was entirely filterable through $0.45\text{ }\mu\text{m}$ filter. Thus, Mn entered the rapid sand filter mainly as particles (MnO_x) and its removal mechanism in the filter bed changed to flocculative.

At no dose, NH_4^+ removal took place entirely in the filter bed (Fig 2.5d), which is consistent with biological nitrification (De Vet 2011). With MnO_4^- – Fe(III) dose, the NH_4^+ concentration in the filtrate remained below the detection limit ($30\text{ }\mu\text{g/L}$), indicating that the nitrification was not affected in the filter bed.

Arsenic speciation was carried out in the raw, supernatant and filtrate samples to gain further mechanistic insight of the As removal process. Fig 2.6a presents As(III) and As(V) concentrations in $0.45\text{ }\mu\text{m}$ filtered samples. As(III) was the dominant form of As in the raw water (97.2%). In the supernatant, As(III) remained dominant (89.6%), indicating the inefficiency of the cascade aeration in oxidizing As(III) to a significant level, in agreement with Gude et al. (2016). In the filter effluent, the As concentration was lower than the supernatant due to co-removal with Fe in the filter bed although As(V) dominated (80%). The observed oxidation of As(III) in 9.3 min of rapid sand filtration was higher-than-expected because As(III) oxidation by dissolved oxygen alone proceeds slowly (Frank and Clifford 1986, Kim and Nriagu 2000). Similar rapid oxidation of As(III) during rapid sand filtration was reported by Gude et al. (2016) and Katsoyiannis et al. (2008) and may be attributed to the manganese oxides or microbial activity in the filter bed (Driehaus et al. 1995, Gude et al. 2017, Lytle et al. 2007). With MnO_4^- – Fe(III) dosing, the dissolved As in the supernatant and filtrate consisted entirely of As(V) (Fig 2.6b).

Figure 2.5 Concentrations of (A) As, (B) Fe, (C) Mn and (D) NH_4^+ in unfiltered and 0.45 μm filtered raw, supernatant and filtrate without and with $\text{MnO}_4^- - \text{Fe(III)}$ dosing. Supernatant refers the water storage on the top of the filter bed.

2.3.3 Influence of $\text{MnO}_4^- - \text{Fe(III)}$ dosing on filter backwash solids

2.3.3.1 Settling characteristics of filter backwash solids

Fig 2.7 presents the results of turbidity measurements in the top 10 cm of the backwash water samples as a function of time, as well as a visual comparison of the beginning ($t=0$) and the end ($t=60$ min) of settling tests among the backwash water samples that were collected under three conditions: without dosing (no dose), i.e. prior to the upgrade, with only dosing 1.2 mg/L MnO_4^- and with dosing 1.2 mg/L MnO_4^- and 1.8 mg/L Fe(III). The color of the backwash water with MnO_4^- and $\text{MnO}_4^- - \text{Fe(III)}$ dosing was darker, indicating the presence of solid phase MnO_x . The presence of Mn was also confirmed when backwash water samples were analyzed for Fe and Mn concentration by ICP—MS (see Table S2.1). The backwash water samples with MnO_4^- and $\text{MnO}_4^- - \text{Fe(III)}$ dose settled faster than the sample collected at no dose (Fig 2.7). Thus, the dosing of MnO_4^- and $\text{MnO}_4^- - \text{Fe(III)}$ improved the settling rate of the filter backwash solids.

Figure 2.6 Dissolved As species in raw, supernatant and filtrate (A) without and (B) with MnO_4^- – Fe(III) dosing. Supernatant refers the water storage on the top of the filter bed.

The dosing of MnO_4^- might have modified the floc characteristics by altering the molecular-scale structure of the Fe(III) -precipitates in backwash solids. The structure of Fe -oxides depends largely on the synthesis conditions (Cornell and Schwertmann 2003, Van Genuchten et al. 2014b) and since dosing of MnO_4^- oxidized Fe(II) faster than O_2 , the molecular-scale structure of the produced Fe(III) -precipitates might also be affected. Therefore, the backwash water solids produced under two conditions: without dosing (no dose), i.e. prior to the upgrade and with only dosing 1.2 mg/L MnO_4^- were characterized by Fe K-edge XAS (XANES and EXAFS) and XRD.

Figure 2.7 Decrease in backwash water turbidity as a function of time. Photos on top show backwash water samples at the beginning ($t=0$) and end ($t=60$ min) of the settling test.

2.3.3.2 Characterization of backwash water solids

Fig 2.8 shows the Fe-K edge XANES and EXAFS spectra of the backwash solids collected from the full scale filter. It can be observed that the position of the absorption edge in the XANES spectra (Fig 2.8a) of the sample with no dose and with MnO_4^- dose were similar and matched the absorption edge of the lepidocrocite and ferrihydrite XANES spectrum. This result shows that the Fe in both samples was primarily present as Fe(III). The oscillations in the post-edge region of the XANES spectra were similar for both the samples, but showed a slight shoulder (highlighted by the arrows in Fig 2.8a) near the absorption maximum. This oscillation was more pronounced than in the ferrihydrite and lepidocrocite XANES spectra.

The Fe K-edge EXAFS spectra (Fig 2.8b) of the samples showed a roughly symmetric first oscillation from 3.5 to $4.5 \text{ \AA}^{-1}$, a major fingerprint of poorly-crystalline Fe(III) precipitates. The first oscillation of the samples matches both the 2-line ferrihydrite reference spectrum and the silicate-rich hydrous ferric oxide (Si-HFO) reference spectrum. These two reference spectra represent poorly-ordered Fe(III)-precipitate phases that form via rapid oxidation of Fe(II) or polymerization of Fe(III) salts in the presence of strongly-sorbing oxyanions (e.g. silicate, phosphate) and have been characterized previously (Van Genuchten et al. 2014b). In addition, the small beat near $5.0 - 5.2 \text{ \AA}^{-1}$ in the ferrihydrite EXAFS spectrum, which is due to the corner-sharing Fe polyhedra, was weakened or absent in the spectra of both the backwash

Figure 2.8 (A) Fe K-edge XANES and (B) EXAFS spectra. Samples without dose (red) and with MnO_4^- (blue).

solids samples. The weakened feature indicative of corner-sharing Fe polyhedral in the backwash samples can be explained by the presence of silica in water during Fe(III) precipitation (Van Genuchten et al. 2014b). Finally, the peak near $6.2 \text{ \AA}^{-1}$ was reduced in the backwash solids and the oscillations at $k > 9 \text{ \AA}^{-1}$ in the MnO_4^- sample were broadened relative to lepidocrocite. Therefore, the XAS data showed that Fe in both the backwash solid samples was present as poorly-crystalline Fe(III) precipitates with structures that have slightly less polyhedral connectivity than ferrihydrite, regardless of the presence or absence of MnO_4^- .

The XRD data (Fig 2.9) of both the backwash solids samples were similar and showed only the broad peaks indicative of poorly crystalline hydrous ferric oxide. This result was consistent with the XAS data. Although Mn was present in the samples (much higher concentration in MnO_4^- dosed sample, Mn:Fe > 0.3 g:g, see Table S2.1), no evidence for any crystalline Mn oxides was observed in the XRD patterns. This result suggests that Mn in the solid phase was present as a nanocrystalline solid, such as poorly-ordered birnessite, or perhaps was incorporated into the structure of the nanocrystalline hydrous ferric oxide, which has been observed previously during the co-precipitation of Mn with Fe(III) precipitates (Ebinger and Schulze 1989, Van Genuchten and Pena 2017b). Although neither of these possible Mn coordination environments would produce strong Bragg diffraction peaks, which is consistent with our XRD data, we note that identifying the exact Mn speciation in the solid phase requires additional structural information. Because we observed

that MnO_4^- dosing alters substantially the settling characteristics of the backwash solids, and that MnO_4^- dosing did not impact solid phase Fe speciation, it is likely that Mn speciation plays a critical role in determining the macroscopic properties of the backwashed solids. Therefore, further investigation to elucidate the mechanism of Mn incorporation in the flocs, and the subsequent impact on floc size, density, filterability and settling is required.

Figure 2.9 X-ray diffraction patterns of the rapid sand filter backwash solids.

2.4 CONCLUSIONS

This study concludes that MnO_4^- – Fe(III) dosing is an effective technique to improve As(III) removal at groundwater treatment facilities that typically use aeration – rapid sand filtration for drinking water production. At WTP Dorst, a typical groundwater treatment facility in the Netherlands, drinking water As concentrations of $<1 \mu\text{g/L}$ were achieved with 1.2 mg/L MnO_4^- and 1.8 mg/L Fe(III) , based on the outcomes of systematic batch and pilot study. The optimized combination of MnO_4^- and Fe(III) doses did not decrease the removal efficiency of Fe(II), Mn(II) and NH_4^+ , although the removal patterns of Fe(II) and Mn(II) were altered. In the absence of MnO_4^- – Fe(III) dose, a significant part of Fe precipitation and the complete precipitation of Mn occurred in the filter bed whereby with MnO_4^- – Fe(III) dosing, both Fe and Mn were completely precipitated in the supernatant, before entering the filter bed, and resulted in a shortening of the filter run time. The dosing of MnO_4^- – Fe(III) improved the settling rate of backwash solids, which was not attributed to changes in molecular-scale structure of Fe-precipitates that form during treatment, but to the increased Mn concentration in the backwash solids.

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SUPPLEMENTARY INFORMATION

Table S2.1. Unfiltered and 0.45 µm filtered Fe and Mn concentration in the backwash water samples

Setting	Fe (unfiltered)	Fe (0.45 µm filtered)	Mn (unfiltered)	Mn (0.45 µm filtered)
	mg/L	mg/L	mg/L	mg/L
No dose	127.1	0.6	0.50	0.02
MnO ₄ ⁻	119.1	0.14	51.9	0.06
MnO ₄ ⁻ – Fe(III)	111.5	0.16	38.1	0.05

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Chapter 3

Characteristics of iron and manganese bearing precipitates generated by Fe(II) and Mn(II) co-oxidation with O_2 , MnO_4 and HOCl in the presence of groundwater ions

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ABSTRACT

In this work, we combined macroscopic measurements of precipitate aggregation and chemical composition (Mn/Fe solids ratio) with X-ray absorption spectroscopy to investigate the solids formed by co-oxidation of Fe(II) and Mn(II) with O_2 , MnO_4^- , and HOCl in the presence of groundwater ions. In the absence of the strongly sorbing oxyanions, phosphate (P) and silicate (Si), and calcium (Ca), O_2 and HOCl produced suspensions that aggregated rapidly, whereas co-oxidation of Fe(II) and Mn(II) by MnO_4^- generated colloidally stable suspensions. The aggregation of all suspensions decreased in P and Si solutions, but Ca counteracted these oxyanion effects. The speciation of oxidized Fe and Mn in the absence of P and Si also depended on the oxidant, with O_2 producing Mn(III)-incorporated lepidocrocite (Mn/Fe = 0.01 to 0.02 mol/mol), HOCl producing Mn(III)-incorporated hydrous ferric oxide (HFO) (Mn/Fe = 0.08 mol/mol), and MnO_4^- producing poorly-ordered MnO_2 and HFO (Mn/Fe > 0.5 mol/mol). In general, the presence of P and Si decreased the crystallinity of the Fe(III) phase and increased the Mn/Fe solids ratio, which was found by Mn K-edge XAS analysis to be due to an increase in surface-bound Mn(II). By contrast, Ca decreased the Mn/Fe solids ratio and decreased the fraction of Mn(II) associated with the solids, suggesting that Ca and Mn(II) compete for sorption sites. Based on these results, we discuss strategies to optimize the design (i.e. filter bed operation and chemical dosing) of water treatment plants that aim to remove Fe(II) and Mn(II) by co-oxidation.

3.1 INTRODUCTION

Groundwater is treated to remove dissolved iron (Fe(II)) and manganese (Mn(II)) to avoid sedimentation in distribution pipelines and discoloration of treated water (Vries et al. 2017). Typical schemes at groundwater treatment plants consist of aeration followed by rapid sand filtration (De Moel et al. 2006). Aeration saturates the groundwater with dissolved oxygen (O_2), which facilitates oxidation and precipitation of Fe and Mn solids. The Fe and Mn bearing precipitates accumulate in filters until backwashing is applied to dislodge the solids from the filtration media. While O_2 is often capable of oxidizing Fe(II) on the time scale of typical groundwater treatment, O_2 alone is ineffective at oxidizing Mn(II) to Mn(III,IV) and As(III) to As(V), the more easily removed arsenic species (Diem and Stumm 1984, Gude et al. 2016, Van Beek et al. 2012). To rapidly oxidize Mn(II) and As(III) at water treatment plants, stronger chemical oxidants, such as NaOCl or $KMnO_4$, can be used (Ahmad et al. 2018, Sorlini and Gialdini 2010). Strong oxidants are also used when high concentrations of Fe(II) are present in groundwater and rapid oxidation is desired (Allard et al. 2013, Knocke et al. 1991).

Although chemical oxidants (i.e. NaOCl and $KMnO_4$) can improve co-oxidative removal of Fe(II), Mn(II) and As(III), little is known about how different oxidants impact key properties of the solid end-products, including the structure and composition. Previous work has shown that the Fe(II) and Mn(II) oxidation rates alter the structure of the solid phase. For example, poorly-ordered Fe(III) precipitates result from rapid Fe(II) oxidation by H_2O_2 and moderately crystalline lepidocrocite forms from slower Fe(II) oxidation by O_2 (Van Genuchten and Pena 2017a, Voegelin et al. 2010). These differences in crystallinity are important because poorly-ordered Fe(III) (oxyhydr)oxides have a higher specific surface area than crystalline solids, which would increase sorption of ions (e.g. As) per mass of Fe added. Similarly, poorly-ordered Mn(IV) oxides are favoured when microorganisms oxidize Mn(II) rapidly, whereas Mn(III) oxides can form from slow, surface-catalyzed Mn(II) oxidation by O_2 (Lan et al. 2017, Tebo et al. 2005). However, the co-occurrence of Fe(II) and Mn(II), which is common in groundwater (McArthur et al. 2012), can alter the pathways of co-oxidation since strong Fenton-type oxidants generated from Fe(II) oxidation can react rapidly with reduced species, including Mn(II) (Hug and Leupin 2003, Van Genuchten and Pena 2017a). In addition to the type of chemical oxidant, the structure of Fe and Mn bearing solids can also be altered by the presence of common groundwater ions, such as silicate (Si), phosphate (P), As, and calcium (Ca). By binding strongly to precipitate surfaces, P and Si oxyanions can inhibit crystal growth, leading to poorly-ordered solids (Kaegi et al. 2010, Senn et al. 2017). Moreover, Si and P oxyanions can decrease the particle surface charge, which

strongly influences particle aggregation and sedimentation efficiency (Sposito 2008), whereas Ca can counteract the effects of P and Si. Since the sorption reactivity and colloidal stability of Fe and Mn precipitates depend strongly on their structure and composition, it is critical to investigate how structural properties of the precipitates are altered by oxidant type and solution composition.

In this work, we combine macroscopic measurements of aggregation and sedimentation (i.e. turbidity and filterability) with Fe and Mn K-edge X-ray absorption spectroscopy to investigate the solids formed by Fe(II) and Mn(II) co-oxidation with O_2 , MnO_4^- , and HOCl. We perform batch Fe(II) and Mn(II) co-oxidation experiments in solutions with systematically varied concentrations of As, P, Si, and Ca. We focus primarily on characterizing the speciation of Fe and Mn in this work, but note that the redox and sorption behavior of As in identical experiments will be reported in a follow-up study. The knowledge generated in our investigation is critical to select the most effective oxidant in groundwater treatment, considering the co-removal of Fe(II), Mn(II) and As(III) and the aggregation properties of the end-products.

3.2 MATERIALS AND METHODS

3.2.1 Chemicals

All chemicals were reagent grade. The stock solutions for Fe(II), Mn(II) and HOCl were prepared by dissolving 24.9 g/L $FeSO_4 \cdot 7H_2O$ (Boom BV[®]), 1.8 g/L $MnCl_2$ (Merck[®]) and 4.66 g/L NaOCl (Acors Organics[®]) in 100 mL oxygen-free ultrapure water (18.2 M Ω cm, Purelab[®] Chorus: Veolia Water). The stock solutions for Si, HCO_3^- , NaCl and MnO_4^- were prepared by dissolving 75.7 g/L $Na_2SiO_3 \cdot 5H_2O$ (Aldrich[®]), 0.87 g/L $NaHCO_3$ (J.T. Baker[®]), 0.26 g/L NaCl (J.T. Baker[®]) and 6.3 g/L $KMnO_4$ (J.T. Baker[®]) in ultrapure water. The stock solutions for P and Ca were obtained by dissolving 1.11 g/L $NaH_2PO_4 \cdot H_2O$ (J.T. Baker[®]) and 138.5 g/L $CaCl_2$ (J.T. Baker[®]) in 0.1 M HCl. For As(III) addition, a certified solution (1000 mg As(III)/L, Inorganic ventures[®]) set in HCl matrix was used without any dilution. The concentration of the As(III) stock was 1000 mg/L. For pH control during the experiments, 0.1 M NaOH and 0.1 M HCl solutions were used.

3.2.2 Oxidation and precipitation experiments

Experiments were performed with a 5 L glass reactor connected to a controller (ez-Control, Applikon[®] Biotechnology) for adjusting, maintaining and logging (BioXpertV2 software) reaction parameters, including the pH, temperature, oxidant supply and stirring speed (Fig 3.1). The experiments were carried out at pH 7.5

and 20°C, with stirring set to 100 rpm. Fe(II) and Mn(II) oxidation was initiated by dosing O_2 , $KMnO_4$ or NaOCl to anaerobic solutions that initially contained Fe(II), Mn(II), As(III), Si, P and Ca in different concentrations (Table 3.1). The range of ionic compositions studied in this work was derived from an analysis of groundwater quality in the Netherlands (Ahmad et al. 2015). For each oxidant, the initial solutions in the reference experiments (herein referred to as Ref) contained 90 μM Fe(II) (5.0 mg/L), 9.0 μM Mn(II) (0.5 mg/L) and 0.7 μM As(III) (0.05 mg/L) without Si, P and Ca. In Mn18 experiments, the initial solution contained 18 μM Mn instead of 9 μM Mn. The rest of the experiments are identified by the ions added in μM to the Ref solution (i.e. Si150 consists of 150 μM Si, 90 μM Fe(II), 9.0 μM Mn(II) and 0.7 μM As(III)). All solutions also contained 2.5 mM $NaHCO_3$ and 0.6 mM NaCl to provide alkalinity and ionic strength.

Figure 3.1 A schematic overview of the assembly used in precipitation and settling experiments. a. data logger (pH, temperature, dissolved oxygen); b. acid pump; c. alkali pump; d. nitrogen and air supply; e. on/off; f. stirrer; g. chemical injection port; h. sampling port; i. controller display; j. power supply.

For the O_2 experiments, the initial solutions were bubbled with air to reach saturation (≈ 9 mg O_2 /L). For MnO_4^- and HOCl systems, the doses of the $KMnO_4$ and NaOCl stocks were based on the combined stoichiometric demand of Fe(II), Mn(II) and As(III) oxidation to produce Fe(III), Mn(IV) and As(V), respectively

(chemical reactions are provided in the supplementary data) (Ghurye and Clifford 2001).

The experimental procedure included: (i) preparation of the initial solutions in the reaction vessel under anaerobic conditions, (ii) dosing the oxidant (O_2 , MnO_4^- or $HOCl$) and allowing for oxidation and precipitation while stirring at 100 rpm and (iii) collection of suspension samples 30 min after oxidant addition, which were filtered over $0.45\ \mu m$ filters and stored for subsequent analysis. A 30 min reaction interval was selected based on PHREEQC simulations showing complete Fe(II) oxidation in the O_2 system in 30 min (Fig S3.1). Samples for aqueous and total Fe and Mn were collected in 100 mL plastic bottles that contained 0.5 mL of 65% HNO_3 and were stored at $4\ ^\circ C$ until analysis by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) (Thermo Scientific XSERIES 2 ICP-MS, Thermo Fisher Scientific, Breda, The Netherlands) at Aqualab Zuid B.V. in The Netherlands. The removal of Mn and Fe and the Mn/Fe solid ratios (mol/mol) were determined from the difference between the Fe and Mn concentrations of the initial and final filtered solutions. Solids generated in each experiment were also collected and reserved for XAS analysis.

3.2.3 Settling experiments

The aggregation and settling characteristics of the particles were studied by measuring the turbidity of the suspensions as a function of time using a 2100Q Portable Turbidimeter, Hach* USA. Following the addition of oxidant and 30 min of mixing, the turbidity of the suspension was measured by removing an aliquot 5 cm below the water surface during mixing. After the initial turbidity measurement, the stirring was stopped and the suspension was allowed to settle by gravity. A second turbidity measurement was made after 1 h of settling by removing another aliquot 5 cm below the water surface. The turbidity measurement vessel was rinsed twice with ultrapure water and oxalic acid (pH 1-3) between measurements.

3.2.4 X-ray absorption spectroscopy

3.2.4.1 Data collection

X-ray absorption spectra at the Fe and Mn K-edges were collected at room temperature at beamline 4-1 of the Stanford Synchrotron Radiation Lightsource (SSRL) and the DUBBLE beamline (BM-26a) of the European Synchrotron Radiation Facility (ESRF). The design of the DUBBLE beamline is described by Borsboom et al., (1998) and Nikitenko et al., (2008). Fe K-edge XAS data were recorded in transmission mode out to k of $13\ \text{\AA}^{-1}$. Mn K-edge XAS data were collected in transmission and fluorescence modes out to k of $12\ \text{\AA}^{-1}$, with spectra of superior data quality selected for subsequent analysis. Fe(0) or Mn(0) foils were used to calibrate the beam at

Table 3.1 Nomenclature, initial composition, Fe and Mn removed by 0.45 μm filtration and solids ratio in O_2 , MnO_4^- and HOCl experiments.

Experiment code	Initial solution composition											Fe and Mn removed by 0.45 µm filter							Solids ratio				
	Fe	Mn	As	Si	P	Ca	Mn/Fe	As/Fe	Si/Fe	P/Fe	Ca/Fe	O ₂			MnO ₄			HOCl		O ₂	Mn/Fe	MnO ₄	HOCl
												Fe	Mn	Fe	Mn	Fe	Mn	Fe	Mn				
												(%)			(%)			(%)		(molar ratio)			
Ref	90	9	0.7	—	—	—	0.1	0.008	—	—	—	99.9	18.6	54.5	44.8	99.1	79.6	0.01	0.50	0.08			
Mn18	90	18	0.7	—	—	—	0.2	0.008	—	—	—	99.9	8.2	6.1	55.6	98.3	83.2	0.02	x	0.18			
Si150	90	9	0.7	150	—	—	0.1	0.008	1.7	—	—	67.4	16.0	27.0	23.0	80.7	57.4	0.03	0.53	0.08			
Si350	90	9	0.7	350	—	—	0.1	0.008	3.9	—	—	2.2	5.8	*	*	35.4	28.6	x	*	0.08			
Si750	90	9	0.7	750	—	—	0.1	0.008	8.3	—	—	0.0	1.9	4.8	16.6	12.0	12.0	x	x	x			
Si350 + Ca500	90	9	0.7	350	—	500	0.1	0.008	3.9	—	6	96.8	26.0	99.8	93.2	97.7	47.2	0.03	0.53	0.05			
Si750 + Ca1000	90	9	0.7	750	—	1000	0.1	0.008	8.3	—	11	95.7	16.8	99.8	92.4	95.8	45.9	0.02	0.56	0.05			
Si750 + Ca2500	90	9	0.7	750	—	2500	0.1	0.008	8.3	—	28	92.1	13.0	99.9	93.0	97.7	50.5	0.01	0.56	0.06			
P4	90	9	0.7	—	4	—	0.1	0.008	—	0.04	—	98.9	30.0	34.7	24.1	98.4	75.1	0.03	0.52	0.08			
P10	90	9	0.7	—	10	—	0.1	0.008	—	0.11	—	96.8	36.7	9.3	9.8	96.5	68.0	0.04	x	0.08			
P16	90	9	0.7	—	16	—	0.1	0.008	—	0.18	—	89.0	39.0	0.0	4.4	75.1	51.4	0.05	x	0.08			
P16 + Ca1000	90	9	0.7	—	16	1000	0.1	0.008	—	0.18	11	99.9	14.8	99.9	87.2	99.9	50.0	0.02	0.54	0.05			

* Data not available

x Not determined because of low precipitate retention

The (range of) concentration of Fe, Mn, As, Si, P and Ca in the initial solution in mg/L was 5.0, 0.5, 0.05, 0.5—1.0, 5.0—20, 0.1—0.5 and 20—100, respectively.

7112 eV or 6539 eV, respectively. Spectra were aligned, averaged and background-subtracted using SixPack software (Webb 2005) following standard methods described previously (Van Genuchten et al. 2012a). The k^3 -weighted EXAFS spectra ($\chi(k)k^3$) were Fourier-transformed using a Kaiser-Bessel window with Δk of 3 $\text{\AA}^{-1}$ typically over the k -range 2 – 12 $\text{\AA}^{-1}$ for the Fe spectra and 2 – 10.5 $\text{\AA}^{-1}$ for the Mn spectra. Further details of the data collection are given in the Supplementary Data.

3.2.4.2 Data Analysis

The Fe K-edge EXAFS spectra were analyzed by principal component analysis (PCA) and linear combination fits (LCFs). For the PCA, the ITFA program suite (Rossberg et al. 2003, Scheinost et al. 2006) was used to determine the number of independent components that reproduced the major variance of the data set based on minimizing the indicator (IND) function. The LCFs were performed with the SixPack software (Webb 2005) using the EXAFS spectra of Fe(III)-bearing standard minerals. Details on the synthesis of these standards (e.g. lepidocrocite, 2-line ferrihydrite, oxyanion-rich hydrous ferric oxide) are reported elsewhere (Van Genuchten et al. 2018a, Van Genuchten et al. 2014b). The fit-derived fractions of the standards in each sample were normalized to one.

The Mn K-edge XANES spectra were analyzed by LCFs to determine the fraction of solid-associated Mn(II), Mn(III), and Mn(IV). SixPack software was used to perform the LCFs on the normalized XANES spectra, with a fit range of 6530 to 6590 eV. The Mn K-edge EXAFS spectra of representative samples were analyzed by shell-by-shell fits. Since the presence of multiple Mn oxidation states in a single sample complicates the interpretation of shell-by-shell fits, we applied this approach on samples that were determined by XANES LCFs to consist of primarily a single oxidation state (i.e. Mn(II), Mn(III), or Mn(IV)). Theoretical curve fits were performed in $R+\Delta R$ -space ($\text{\AA}$) using the SixPack software with algorithms based on the IFEFFIT library (Newville 2001). Single scattering paths (Mn-O, Mn-Mn) were derived from the structure of birnessite (MnO_2) (Lanson et al. 2002), with theoretical phase and amplitude functions calculated using FEFF6 (Rehr et al. 1992). Because Mn and Fe have similar atomic numbers, these backscattering atoms cannot be distinguished in shell-by-shell fits. Consequently, the second shell fitting results for the Mn data are reported as $\text{CN}_{\text{Mn-Mn/Fe}}$ and $R_{\text{Mn-Mn/Fe}}$. The goodness-of-fit was assessed based on the R-factor, which is the mean square difference between the fit and the data on a point-by-point basis: $R = \sum_i (\text{data}_i - \text{fit}_i)^2 / \sum_i (\text{data}_i)^2$. A reasonable fit is considered to yield an R-factor less than 0.05 (Kelly et al. 2008). A similar shell-by-shell fitting approach was followed for select Fe spectra. Further details regarding the XANES and EXAFS analyses are reporting in the Supplementary Data.

3.3 RESULTS

3.3.1 Macroscopic precipitate properties

3.3.1.1 Settling and filterability

In the O₂ system, the Ref and Mn18 experiments had an initial turbidity of ≈ 8 NTU (Fig 3.2) and a similarly low final turbidity of <3 NTU ($\approx 70\%$ turbidity decrease), which indicates rapid flocculation and sedimentation. These particles were highly filterable ($>99\%$) by 0.45 μm filters (pore size used to approximate filterable particles in rapid sand filters). The addition of 150 to 750 μM Si decreased the initial turbidity from 6 to 2 NTU, resulting in translucent light yellow suspensions that were colloidally stable (i.e. no difference in initial and final turbidity, Fig 3.2A, and low filterability, Table 3.1). The addition of Ca to the 350 and 750 μM Si solutions increased the initial turbidity to match the Ref O₂ sample, but the final turbidity was higher than the Ref O₂ sample. In the P series, 4 and 10 μM P did not alter significantly the initial or final turbidity relative to the Ref O₂ sample and the precipitates settled effectively ($\approx 65\%$ turbidity decrease). However, the 16 μM P experiment resulted in a colloidally stable suspension. When 1000 μM Ca was added to the 16 μM P solution, the suspension had the highest initial turbidity in the O₂ experiments (14 NTU), with effective turbidity reduction (70%) and good filterability ($>99\%$ Fe removed, Table 3.1).

The settling behavior and filterability of the precipitates formed in the MnO₄ system (Fig 3.2B, Table 3.1) differed considerably from those in the O₂ system. The darker Ref and Mn18 suspensions formed in the MnO₄ system were colloidally stable, having initial and final turbidity >5.5 NTU, which contrasts the rapid settling of the Ref O₂ sample. The 150 to 750 μM Si samples in the MnO₄ system were also colloidally stable, but the initial turbidity was slightly lower than the Ref MnO₄ sample. The addition of Ca to the Si solutions produced cloudy suspensions that settled more effectively ($\approx 60\%$ turbidity decrease) than the Ca+Si samples in the O₂ system. The 4, 10 and 16 μM P samples in the MnO₄ system were all colloidally stable (turbidity = 3 to 5 NTU) with low filterability (Table 3.1). Similar to the O₂ system, P16+Ca1000 sample in the MnO₄ system had an higher initial turbidity (≈ 8 NTU) and improved particle settling (70% turbidity reduction) and filterability ($>99\%$ Fe removed).

In the HOCl system (Fig 3.2C), the initial turbidity of all suspensions (<4 NTU) was systematically lower than the O₂ or MnO₄ systems. The Ref and Mn18 HOCl suspensions were light yellow with visible flocs that settled quickly and were effectively filtered ($\approx 90\%$), despite their low initial turbidity. The 150 to 750 μM Si samples were colloidally stable, similar to the O₂ and MnO₄ systems. When Ca was added to the Si solutions, turbidity removal improved (20%), but was lower than the

Ref HOCl sample. The HOCl experiments in P solutions resembled the O_2 system more than the MnO_4 system, with 46% and 41% decreases in turbidity for P4 and P10 samples, but only 8% for the P16 sample. The impact of Ca in P solutions was similar in all HOCl, O_2 and MnO_4 systems, with the P16+Ca1000 sample displaying increased aggregation and sedimentation (40% turbidity decrease).

Figure 3.2 Initial and final turbidity as function of the oxidant used and solution composition. A. O_2 system, B. MnO_4 system, C. HOCl system.

3.3.2 Mn/Fe solid ratios

In the O_2 system, the precipitate Mn/Fe ratio content was low (≤ 0.05) and varied with solution composition. The Mn/Fe ratio of the Ref experiment was 0.01 mol/mol, which doubled to 0.02 mol/mol in the Mn18 experiment, matching the doubled initial Mn concentration. The presence of Si and P increased the precipitate Mn content, with the Si150 and P16 samples having solids ratios of 0.03 mol/mol and 0.05 mol/mol, respectively. By contrast, Ca addition decreased the Mn/Fe ratio. The precipitate Mn content was only 0.02 mol/mol in the P16+Ca1000 sample.

In MnO_4 system the Mn/Fe ratio ranged from 0.5 to 0.55, with no significant trends in the presence of Si, P and Ca. The higher Mn/Fe ratio relative to the O_2 and HOCl systems is attributed to the dosing of MnO_4^- , which increased the total Mn concentration.

In the HOCl system, the precipitate Mn/Fe ratio was higher than in the O_2 system, indicating more effective Mn uptake. The Mn/Fe ratio of the Ref and Mn18 experiments was 0.08 and 0.18 mol/mol, which was near the total Mn/Fe ratio dosed into solution. The presence of Si and P did not impact significantly the Mn/Fe ratio in the HOCl system (Table 3.1), with Mn/Fe ratios of ≈ 0.08 mol/mol for the Si350 and P16 samples. However, Ca addition decreased Mn uptake, leading to an Mn/Fe solids ratio of 0.05 mol/mol for the Si350+Ca500 and P16+Ca1000 samples.

Figure 3.3 Precipitate Mn/Fe ratio (mol/mol). Samples without data were colloiddally stable and could not to be separated with 0.45 μm filters. The Mn/Fe ratio was between 0.5 and 0.55 for all the samples in MnO_4 system and is thus not given. Note the break in the y-axis from 0.10 to 0.17 mol/mol.

3.3.3 Fe K-edge EXAFS spectroscopy

Principal component analysis (PCA) of the Fe K-edge EXAFS spectra of the entire data set (O_2 , MnO_4 , and HOCl systems) revealed a significant decrease in the indicator function (Fig S3.2) with three independent components and a gradual plateau in the indicator function with increasing components. Based on the PCA results and the experimental conditions, we used three Fe(III) (oxyhydr)oxide standards in the linear combination fits (LCFs) of the experimental spectra: lepidocrocite ($\gamma\text{-FeOOH}$), 2-line ferrihydrite (2LFh), and an oxyanion-rich hydrous ferric oxide (oxy-HFO) that was produced by Fe(II) oxidation in the presence of P and that contains no Fe-Fe corner-sharing bonds (Van Genuchten et al. 2014b). The LCF output is overlain to the data in Fig 3.4 and results of the LCFs of the experimental spectra using lepidocrocite, 2LFh, and oxy-HFO are given Fig 3.5.

The Ref and Mn18 experiments in the O_2 system consisted of dominantly lepidocrocite (>85%). The minor fraction (<15%) of oxy-HFO determined in the LCFs of these samples likely arises from subtle differences in the structure of the lepidocrocite standard and the type of lepidocrocite formed in the experiments (Van Genuchten et al. 2014b, Voegelin et al. 2010). Lepidocrocite formation was largely inhibited in the presence of Si, with the LCFs of all Si series samples returning fractions of 15 to 26% oxy-HFO and 72 to 82% 2LFh without clear trends in the fractions oxy-HFO and 2LFh with increasing Si or presence of Ca. In the P experiments, the LCFs indicated the formation of lepidocrocite, but its fraction depended on the P concentration (i.e. P/Fe ratio). Increasing P from 4 to 16 μM decreased the lepidocrocite fraction from 64 to 27%, which was balanced by an increase in oxy-HFO from 16 to 37% (the 2LFh fraction was stable at $\approx 30\%$). The addition of Ca to the P16 solution increased the lepidocrocite fraction from 27 to 55% at the expense of oxy-HFO and 2LFh. This impact of Ca on the Fe(II) oxidation products in the P solutions is consistent with the sequential formation of Ca- and P-rich Fe(III) polymers (Voegelin et al. 2010) which remove P from solution with P/Fe ratios near 1, followed by lepidocrocite formation with excess Fe(II) after P is removed from solution.

In contrast to the O_2 experiments, no sample in the MnO_4 system consisted of lepidocrocite, regardless of solution composition. The LCFs indicated poorly-ordered Fe(III) precipitates formed in MnO_4 experiments, which had average structures consistent with mixtures of 2LFh and oxy-HFO (30 to 73% oxy-HFO, 25 to 69% 2LFh). Increasing the Si concentration from 150 to 750 μM increased the fraction of oxy-HFO from 32 to 60%, with 2LFh making up the remainder. The Fe(III) precipitates formed from Fe(II) oxidation by MnO_4 in P solutions were similar to those in Si solutions, with the LCFs yielding mixtures of 2LFh and oxy-HFO without clear trends in the presence of Ca.

In the HOCl system, lepidocrocite was not detected in any sample. The LCFs of the Ref sample yielded 53% oxy-HFO and 40% 2LFh, whereas the Mn18 sample consisted of 40% oxy-HFO and 54% 2LFh. Although P and Si increased the fraction of poorly-ordered Fe(III) precipitates in the O_2 system, the analogous trend was not observed in the HOCl system. No trends in the fractions of 2LFh and oxy-rich HFO with increasing Si or P were observed in the HOCl samples. Comparing the LCFs across all oxidants (i.e. O_2 , MnO_4 , and HOCl) reveals that Si and P impacted Fe(III) speciation in the O_2 experiments more than in MnO_4 and HOCl experiments.

Figure 3.4 Fe K-edge EXAFS spectra of precipitate samples (dotted lines) and output of linear combination fits (solid lines) using lepidocrocite, 2-line ferrihydrite, and oxyanion-rich hydrous ferric oxide.

3.3.4 Mn K-edge XANES spectroscopy

The Mn K-edge XANES LCFs of the Ref O_2 sample (Fig 3.6, Table 3.2) indicated that Mn(III) was the dominant species ($96\pm3\%$) in the solids, consistent with the absorption maximum near 6556 eV. However, the Si150 sample displayed an absorption maximum at lower X-ray energy (6552 eV) and the LCFs indicated Mn(II) was the dominant species (Mn(II) = $75\pm2\%$, Mn(III) = $26\pm4\%$). The trend in increased Mn(II) in the presence of oxyanions was also observed in the P16 experiment, which consisted of $85\pm3\%$ Mn(II), with Mn(III) making up

the remainder. When Ca was added to the P16 electrolyte, the LCFs indicated a significant decrease in solid-associated Mn(II) ($52\pm3\%$) and an increase in Mn(III) ($45\pm5\%$). The presence of Mn(IV) was not supported by the LCFs of any O₂ samples.

The XANES spectra of the MnO₄ samples were largely independent of solution chemistry, with $>98\%$ Mn(IV) detected by the LCFs in all samples (absorption maximum near 6558 eV). While the LCFs returned a small fraction of Mn(III) in some samples ($<20\%$), the standard deviation was nearly as high as the fit-derived value (Table 3.2). No clear trends in the Mn oxidation state with Si, P, or Ca were detected in the LCFs of the MnO₄ samples. The presence of residual, unreacted Mn(VII), which has a prominent pre-edge peak near 6541 eV, was not supported by the XANES spectra.

Co-oxidation of Fe(II) and Mn(II) by HOCl produced primarily Mn(III) in the Ref and Mn18 samples, with a slight increase in the Mn(IV) fraction from $15\pm10\%$ in the Ref sample to $23\pm11\%$ in the Mn18 sample. The LCFs of the Si150 sample indicated that Mn(III) remained the dominant solid-phase Mn species ($>85\%$). At P concentrations of 4 and 16 μM , the solid-phase Mn(II) fraction increased from 9 ± 5 to $41\pm4\%$. When Ca was added to the P16 solution, the solid-phase Mn(II) fraction decreased from 41 ± 4 to $14\pm5\%$. A similar decrease in Mn(II) fraction in favor of Mn(III) was observed in the O₂ experiments when Ca was added to the P16 solution.

3.3.5 Mn K-edge EXAFS spectroscopy

3.3.5.1 O₂ experiments

In Fig 3.7, the Mn K-edge EXAFS spectra of samples produced in the O₂, MnO₄, and HOCl experiments are shown alongside the spectra of Mn standards. The Ref O₂ sample, which was found by the LCFs to be dominantly Mn(III), differed relative to the other spectra in Fig 3.7, including the aqueous Mn(II), bixbyite ($\alpha\text{-Mn}_2\text{O}_3$) and $\delta\text{-MnO}_2$ standards. In particular, the first oscillation from 3 to 5.5 $\text{\AA}^{-1}$ became a doublet, which is not present in other Mn(III)-bearing material (e.g. groutite, manganite, feitnechtite) (Manceau et al. 2012b). Furthermore, the next major peaks at 6.2 and 7.5 $\text{\AA}^{-1}$ in the Ref O₂ sample are out of phase with the standards, which suggests a unique Mn coordination environment. In the presence of P and Si, the EXAFS oscillations for the O₂ samples match more closely those of aqueous Mn(II), which is consistent with the XANES-derived predominance of Mn(II) in these samples.

Shell-by-shell fits of the Fourier-transformed Mn K-edge EXAFS spectrum of the Ref O₂ sample (Fig 3.8, Table 3.3) returned an Mn-O interatomic distance ($R_{\text{Mn-O}}$) of 1.93 ± 0.02 $\text{\AA}$ and an Mn-O coordination number ($\text{CN}_{\text{Mn-O}}$) of 1.9 ± 0.5 , which is lower than the theoretical CN of 6 for octahedrally coordinated Mn(III). These

Figure 3.6 Mn K-edge XANES spectra for precipitate samples formed in the O_2 (left panel), MnO_4^- (middle panel) and $HOCl$ (right panel) experiments. The experimental data is plotted below Mn(II), Mn(III), and Mn(IV) standards.

Table 3.2 Summary of XANES LCF Results.

Oxidant	Experiment Code	% Mn ²⁺	% Mn ³⁺	% Mn ⁴⁺
O ₂ System	Ref	<1	96 ± 3	<1
	Si150	75 ± 2	26 ± 4	<1
	Si750 + Ca1000	65 ± 3	35 ± 5	<1
	P16	85 ± 3	20 ± 4	<1
	P16 + Ca1000	52 ± 3	45 ± 5	<1
MnO ₄ System	Ref	<1	8 ± 8	106 ± 15
	Mn18	<1	6 ± 7	109 ± 15
	Si150	<1	7 ± 8	105 ± 14
	Si350 + Ca500	<1	8 ± 9	108 ± 14
	Si750 + Ca1000	<1	16 ± 6	99 ± 16
	Si750 + Ca2500	<1	17 ± 8	102 ± 14
	P4	<1	10 ± 7	104 ± 15
	P16 + Ca1000	<1	13 ± 6	98 ± 15
HOCl System	Ref	5 ± 4	84 ± 16	15 ± 10
	Mn18	<1	79 ± 15	23 ± 11
	Si150	11 ± 5	85 ± 18	10 ± 11
	Si750 + Ca1000	33 ± 8	85 ± 12	<1
	Si750 + Ca2500	27 ± 6	95 ± 11	<1
	P4	9 ± 5	87 ± 18	11 ± 12
	P16	41 ± 4	63 ± 11	3 ± 4
	P16 + Ca1000	14 ± 5	88 ± 18	10 ± 11

fit-derived $R_{\text{Mn-O}}$ and $\text{CN}_{\text{Mn-O}}$ values matched the first shell fits of bixbyite ($R_{\text{Mn-O}} = 1.92 \pm 0.02$ Å, $\text{CN}_{\text{Mn-O}} = 2.4 \pm 0.5$) and are consistent Jahn-Teller distorted Mn(III) octahedra. Fits of the second shell of the Ref O₂ sample resulted in a $\text{CN}_{\text{Mn-Mn/Fe}} = 2.8 \pm 1.1$ and $R_{\text{Mn-Mn/Fe}} = 3.04 \pm 0.02$ Å. This $R_{\text{Mn-Mn/Fe}}$ is significantly shorter than the edge-sharing Mn-Mn bond in bixbyite (Table 3.3) and longer than the edge-sharing Mn-Mn bond in groutite (Wyckoff 1963). However, the fit-derived $R_{\text{Mn-Mn/Fe}}$ value for this sample is in good agreement with the edge-sharing Fe-Fe bond length in the Fe(III) precipitates that formed in this sample (i.e. lepidocrocite, $R_{\text{Fe-Fe}} = 3.07 \pm 0.01$ Å, Table S3.1).

3.3.5.2 MnO₄ experiments

The Mn K-edge EXAFS spectra of MnO₄ samples were similar regardless solution composition, with all samples resembling the EXAFS spectrum of the δ -MnO₂ standard. All experimental EXAFS spectra contained the characteristic staircase feature from 4 to 6 Å⁻¹ indicative of MnO₂ minerals (Manceau et al. 2012b), which implies that Mn(II) and Fe(II) co-oxidation by MnO₄ in a variety of solutions leads to solid-phase Mn in a MnO₂-like bonding environment.

Shell-by-shell fits of the Ref MnO₄ sample, which contained <10% Mn(III) (Table 3.2), indicated a Mn-O coordination shell of CN_{Mn-O} = 5.2±0.9 and R_{Mn-O} = 1.91±0.01 Å. These fit-derived values are in excellent agreement with the first shell fits of the δ -MnO₂ standard (Table 3.3) and are representative of Mn(IV) in octahedral coordination. The second shell fit of the Ref MnO₄ sample returned values of CN_{Mn-Mn/Fe} = 3.2±0.4 and R_{Mn-Mn/Fe} = 2.89±0.01 Å, which also matches the fits δ -MnO₂ standard (Table 3.3) and is consistent with edge-sharing MnO₆ octahedra. Furthermore, this fit-derived R_{Mn-Mn/Fe} value is considerably shorter than the fit-derived R_{Mn-Mn-Fe} of the Ref O₂ sample and is also shorter than the edge-sharing Fe-Fe bond in Fe(III) (oxyhydr)oxide minerals (Manceau and Combes 1988). Interestingly, the shell-by-shell fits of the Ref MnO₄ sample and the MnO₄ sample generated in the highest oxyanion solution (i.e. Si750+Ca2500) were identical within fit-derived standard errors (Table 3.3). This result suggests that oxyanions do not modify the structure of MnO₂ solids as much as Fe(III) precipitates, which is attributed to the lower affinity of oxyanions for MnO₂ surfaces than Fe(III) (oxyhydr)oxides (Van Genuchten and Peña 2016a).

3.3.5.3 HOCl experiments

The EXAFS spectra of the Ref and Mn18 samples in the HOCl system, which consisted of primarily Mn(III) (Table 3.3), were nearly identical. Both Ref and Mn18 spectra displayed a split oscillation from 3 to 5 Å⁻¹, which is similar to that of the Ref O₂ sample, but the split in this oscillation was less prominent in the HOCl samples. The Ref and Mn18 HOCl samples also exhibited an asymmetric oscillation near 6.5 Å⁻¹ that was less pronounced or absent from the EXAFS spectra of other samples and standards (Fig 3.7). In the presence of P and Si, some features in the EXAFS spectra changed, including the disappearance of the asymmetric oscillation near 6.5 Å, but the first oscillation from 3 to 5 Å⁻¹ was still split. The similarity of key EXAFS features across all HOCl samples regardless of the presence (e.g. Si150, P4) or absence (Ref, Mn18) of oxyanions is consistent with the XANES LCFs, which identified Mn(III) as the predominant Mn oxidation state in all HOCl samples (Table 3.2).

Shell-by-shell fits of the Fourier-transformed EXAFS spectrum of the Ref HOCl sample (Table 3.3) revealed a first shell Mn-O coordination environment similar

to the Ref O_2 sample, with $CN_{Mn-O} = 2.4 \pm 0.4$ and $R_{Mn-O} = 1.91 \pm 0.01 \text{ \AA}$, which is consistent with Jahn-Teller distorted Mn(III) octahedra. Fits of the second shell of the Ref HOCl sample returned values of 1.7 ± 0.4 for $CN_{Mn-Mn/Fe}$ and $3.01 \pm 0.02 \text{ \AA}$ for $R_{Mn-Mn/Fe}$. Similar to the O_2 system, the second shell fits of the Ref HOCl sample produced a $R_{Mn-Mn/Fe}$ value that is shorter than the edge-sharing Mn-Mn bond in Mn(III)-bearing minerals. However, the $R_{Mn-Mn/Fe}$ for the HOCl sample is in good agreement with the Fe-Fe bond length for edge-sharing FeO_6 octahedra in Fe(III) precipitates that formed in this sample (i.e. hydrous ferric oxide, $R_{Fe-Fe} = 3.05 \pm 0.01 \text{ \AA}$, Table S3.1).

Figure 3.7 Mn K-edge EXAFS spectra for precipitate samples formed in the O_2 (left panel), MnO_4 (middle panel) and HOCl (right panel) experiments. The experimental data is plotted below Mn(II), Mn(III), and Mn(IV) standards.

Figure 3.8 Fourier-transformed Mn K-edge EXAFS spectra of precipitate samples (dotted lines) overlain to the output of shell-by-shell fits.

3.4 DISCUSSION

3.4.1 Effect of oxidant and solution chemistry on Fe(III) speciation and particle aggregation

3.4.1.1 Fe(II) oxidation in O₂, MnO₄⁻, and HOCl Ref experiments

Comparison of the Ref experiments across all oxidants shows that Fe(II) and Mn(II) co-oxidation by O₂ and HOCl produced suspensions that aggregated rapidly and that can be separated by gravitational settling or filtering easily, whereas the MnO₄⁻ Ref experiment generated a colloiddally stable suspension. However, Fe(III) speciation differed between Ref O₂ and Ref HOCl experiments, with O₂ producing lepidocrocite and both HOCl and MnO₄⁻ producing poorly-crystalline Fe(III) precipitates. These differences in aggregation and Fe(III) speciation with oxidant can be explained by the different Fe(II) reaction rates with O₂, HOCl, and MnO₄⁻ and the different end-products of each reaction. The Fe(II) oxidation rate by O₂ depends strongly on pH (Van Beek et al. 2016, Van Beek et al. 2012, Vries et al. 2017), but at circumneutral pH is orders of magnitude lower than HOCl and MnO₄⁻ (Ghurye and Clifford 2001, Knocke et al. 1991, Stumm and Morgan 1996). Although our experiments were designed to allow for complete Fe(II) oxidation in the O₂ experiments, Fe(II) reactions with O₂ are not instantaneous, which ensures that freshly-oxidized

Table 3.3 Summary of Shell Fits of Mn-bearing Standards and Precipitate Samples.

Experiment Code	Atomic Pairs	CN	R (Å)	σ^2 (Å ²)	ΔE_0 (eV)	R-Factor
Aqueous Mn(II)	Mn-O	7.0 (0.6)	2.18 (0.01)	0.010 (0.001)	-11.0 (1.0)	0.015
α -Mn ₂ O ₃	Mn-O	2.4 (0.7)	1.92 (0.02)	0.004 (0.002)	-16.7 (1.8)	0.041
	Mn-Mn1	4.8 (2.3)	3.10 (0.03)	0.009 (0.004)		
	Mn-Mn2	3.4 (1.7)	3.53 (0.04)	σ^2 (Mn-Mn1)		
δ -MnO ₂	Mn-O	4.4 (1.0)	1.90 (0.01)	0.001 (0.001)	-17.6 (2.7)	0.047
	Mn-Mn	4.3 (0.6)	2.88 (0.02)	0.007		
Ref O ₂	Mn-O	1.9 (0.5)	1.93 (0.02)	0.004 (0.003)	-11.4 (3.0)	0.067
	Mn-Mn/Fe	2.8 (1.1)	3.04 (0.02)	0.009 (0.003)		
Ref HOCl	Mn-O	2.4 (0.4)	1.91 (0.01)	0.002 (0.001)	-10.0 (2.1)	0.032
	Mn-Mn/Fe	1.7 (0.4)	3.01 (0.02)	0.01		
Ref MnO ₄	Mn-O	5.2 (0.9)	1.91 (0.01)	0.005 (0.002)	-16.7 (2.1)	0.031
	Mn-Mn/Fe	3.2 (0.4)	2.89 (0.01)	0.007		
MnO ₄	Mn-O	4.9 (0.7)	1.90 (0.01)	0.004 (0.001)	-17.3 (1.7)	0.020
Si750 + Ca1000	Mn-Mn/Fe	3.3 (0.3)	2.87 (0.01)	0.007		

CN represents the coordination number. R the interatomic distance. σ^2 the mean squared atomic displacement and ΔE_0 represents the change in threshold energy. The passive electron reduction factor. $S0^2$ was fixed at 0.7. Fitting parameters allowed to float are accompanied by fit-determined standard errors in parenthesis, while constrained parameters appear without a parenthesis. All fits were carried out from 1 to 3.5 Å in R+ ΔR -space. The number of independent point (N_{IDP}) in the fits was 13.4 and the number of variables (N_{var}) was 4 to 9.

Fe(III) precursors form in the presence of Fe(II). Aqueous Fe(II) catalyzes the rapid transformation of poorly-ordered Fe(III) precipitates into lepidocrocite, which was the dominant Fe(III) phase of the Ref O₂ experiment (Pedersen et al. 2005). By contrast, the reaction rate of HOCl and MnO₄ with Fe(II) is high enough that aqueous Fe(II) is too unstable to catalyze the transformation of freshly-formed Fe(III) to lepidocrocite, leading to the persistence of poorly-ordered Fe(III) precipitates. Although Fe(III) speciation was similar in the Ref HOCl and MnO₄ experiments, the Ref MnO₄ solids contained a major fraction of MnO₂ that did not form in the O₂ and HOCl experiments. The presence of MnO₂ likely enhances the colloidal stability of the MnO₄ samples because of the much lower point of zero charge of MnO₂ ($\approx 2\text{--}3$) compared to lepidocrocite and poorly-ordered Fe(III) precipitates ($\approx 7\text{--}8$) (Sposito 2008). At circumneutral pH, suspensions containing MnO₂ will have a strong negative charge, preventing aggregation, whereas suspensions of Fe(III) precipitates will be near the optimum pH to induce aggregation (Sposito 2008).

3.4.1.2 Impact of ionic composition

Solution chemistry was found to alter both the suspension stability and Fe(III) speciation, with different impacts depending on the Fe(II) oxidant and ionic composition. The Fe(III) speciation in the O₂ samples was impacted the most by solution composition, but similar trends were observed in the MnO₄ and HOCl experiments. The presence of oxyanions in the O₂ samples decreased particle aggregation and resulted in a transition from lepidocrocite to poorly-ordered Fe(III) precipitates. Oxyanions, such as Si and P, bind strongly to Fe(III) precipitate surfaces during Fe(III) polymerization, which modifies two key properties of the suspension. First, by binding strongly to crystal growth sites on the Fe(III) precipitate surface, oxyanions inhibit the formation of crystalline Fe(III) minerals (i.e. lepidocrocite), leading to the persistence of poorly-ordered Fe(III) precipitates with a large specific surface area (Van Genuchten et al. 2014b, Voegelin et al. 2010). Second, sorption of oxyanions leads to negatively charged Fe(III) precipitate surfaces, even in the case of Si, which is uncharged in solution circumneutral pH (Delaire et al. 2016, Kanematsu et al. 2013a). Therefore, oxyanion sorption generates particles with highly negative surface charge that are less likely to aggregate. Both consequences of co-occurring oxyanions during Fe(III) precipitation (i.e. changes in suspension aggregation and Fe(III) speciation) were observed in the O₂ experiments. These effects were less pronounced in the MnO₄ experiments since the Ref MnO₄ suspension was already colloidally stable and consisted of poorly-ordered Fe(III) precipitates even in the absence of Si and P.

The presence of Ca can counteract some of the oxyanion effects, particularly with respect to particle surface charge. Ca addition enhanced aggregation (i.e. settling and

filterability) in nearly every O_2 , HOCl and MnO_4 experiment, with stronger impact in P solutions than Si. The pronounced impact of Ca in P solutions is attributed to the formation of Ca-O-P linkages during Fe(III) polymerization that enhance particle aggregation by neutralizing more effectively the negative surface charge of P-rich Fe(III) precipitates (Senn et al. 2015, Van Genuchten et al. 2014a, Voegelin et al. 2010). The presence of Ca was also important to enhancing the aggregation of MnO_4 suspensions, which is explained by positively charged Ca neutralizing the negatively charged MnO_2 produced in the MnO_4 experiments.

3.4.2 Behavior of Mn(II) during co-oxidation with Fe(II)

3.4.2.1 Mn(II) removal in O_2 , MnO_4 , and HOCl Ref experiments

A visual representation of the structure and composition of the solids formed in the Ref experiments is given in Fig 3.9. The Ref O_2 , MnO_4 and HOCl experiments were performed in solutions with the least ionic complexity and form the baseline for comparing Mn(II) removal in the simulated groundwater solutions. In the Ref O_2 experiment, the Mn/Fe solids ratio was ≈ 0.01 mol/mol (i.e. $\approx 10\%$ Mn(II) removal) and the XANES LCFs indicated solid-phase Mn was dominantly Mn(III). Shell-by-shell fits of the Ref O_2 sample were consistent with a first shell Mn(III)-O coordination environment and a second shell that consisted of Mn-Mn/Fe atomic pairs at $R = 3.04 \pm 0.02$ Å. This R-value matches that of edge-sharing FeO_6 octahedra in the Fe(III) precipitates formed in this sample (Table S3.1). Therefore, Mn(II) removal in the Ref O_2 experiment likely occurs via Mn(II) oxidation to Mn(III) by the reactive Fenton-type oxidants produced during Fe(II) oxidation by O_2 ($^{\bullet}O_2^-$, Fe(IV)) and subsequent (partial) incorporation into the resulting Fe(III) precipitate. This Mn(II) removal mechanism has been observed in experiments that dosed Fe(II) slowly by Fe(0) electrolysis into air-saturated solutions of Mn(II), allowing Fe(II) and Mn(II) co-oxidize by O_2 (Van Genuchten and Pena 2017a).

The Ref MnO_4 experiment had a high Mn/Fe solids ratio of >0.5 mol/mol, which matches the total Mn/Fe ratio dosed into the initial solution. The XANES LCFs of the Ref MnO_4 sample indicated Mn was present as Mn(IV). The line shape and position of the Mn K-edge EXAFS spectrum and the shell-by-shell fitting output of the Ref MnO_4 sample indicated an Mn coordination environment similar to the δ - MnO_2 standard. The formation of nanoscale MnO_2 by reaction of Mn(II) and MnO_4 has been well documented in many studies (Knocke et al. 1991, Lee et al. 2011) and our results suggest that the presence of Fe(II) and other background ions in the Ref MnO_4 experiment did not alter this reaction pathway.

Effective removal of approximately 80% of the initial Mn(II) was observed in the Ref HOCl, leading to an Mn/Fe solids ratio of ≈ 0.08 mol/mol, which was significantly higher than the Ref O_2 sample. The XANES LCFs of the Ref HOCl

sample indicated that solid-phase Mn was dominantly Mn(III). Similar to the O₂ system, the shell-by-shell fits of the Ref HOCl sample were consistent with a first shell Mn(III)-O coordination environment and second shell that consisted of Mn-Mn/Fe atomic pairs at an R-value (3.01 ± 0.02 Å) that is not found in Mn(III) (oxyhydr)oxide minerals. However, this R-value is similar to that of the edge-sharing Fe octahedra in the Fe(III) precipitates that formed in this sample (3.05 ± 0.01 Å, Table S3.1). Therefore, we propose that Mn(II) removal in the Ref HOCl experiment proceeds by a single electron transfer from Mn(II) to Mn(III), with Mn(III) stabilized by co-precipitating Fe(III) (oxyhydr)oxides. While a similar Mn(II) removal pathway has been documented for Mn(II) and Fe(II) co-oxidation by H₂O₂, this pathway is inconsistent with previous research investigating Mn(II) removal by chlorination, which report the formation of Mn(IV) species (Allard et al. 2013, Hao et al. 1991). In our experiments, the precipitation of Fe(III) during Mn(II) oxidation likely stabilizes the initial Mn(III) product by incorporation into the solid phase, which prevents subsequent Mn(III) oxidation to Mn(IV).

3.4.3 Impact of ionic composition

A visual representation of the impact of oxyanions and bivalent cations on the structure and composition of the precipitates formed by Fe(II) and Mn(II) co-oxidation is given in Fig 3.9. Solution composition modified the uptake and removal mechanism of Mn(II) in many experiments, with the most pronounced impacts in the O₂ and HOCl systems. Based on the XANES LCFs and Mn K-edge EXAFS spectra, Mn(II) was removed by reaction with MnO₄ to form nanoscale MnO₂ in every experiment in the MnO₄ system, regardless of solution composition. However, in the O₂ and HOCl experiments, Si and P increased the fraction of solid-phase Mn(II). For example, whereas <5% Mn(II) was present in the Ref O₂ and HOCl samples, the P16 samples in the O₂ and HOCl systems consisted of 85 ± 3 and $41 \pm 4\%$ Mn(II), respectively. The impact of Si was weaker than P, but still increased the Mn(II) fraction in the Si150 sample in the O₂ system to $75 \pm 2\%$. Furthermore, the increased fraction of sorbed Mn(II) in the O₂ experiments coincided with an increase in Mn/Fe solids ratio, particularly in the P experiment ($\text{Mn/Fe}_{\text{Ref}} = 0.01$ mol/mol, $\text{Mn/Fe}_{\text{P16}} = 0.05$ mol/mol). These results indicate that P, and Si to a lesser extent, can enhance Mn(II) sorption when Mn(II) oxidation is incomplete. The enhanced Mn(II) removal in the presence of oxyanions can be explained by the interaction between positively charged Mn(II) and negatively charged surfaces of oxyanion-rich Fe(III) precipitates. The more pronounced impact of P relative to Si could arise from direct Mn(II)-O-P bonding on the Fe(III) precipitate surface (i.e. ternary complexes), analogous to Ca-O-P linkages.

In contrast to the effect of oxyanions, the presence of Ca in Si and P solutions systematically decreased the fraction of solid-phase Mn(II) in both O₂ and HOCl

Figure 3.9. Visual representations and Mn/Fe ratios of the experimental solids derived from the wet chemical measurements and XAS analyses. We expect that sorbed Mn(II) increased in the oxanion experiments due to Mn(II) interactions with P and Si bound to the Fe(III) precipitate. We did not include P or Si oxanions bound to the Fe(III) precipitates in the MnO₄ panels since Mn(II) was not detected in these samples.

experiments. The impact of Ca was most pronounced in the P16 solutions, with decreases in the Mn(II) fraction from 85 ± 3 to $20 \pm 4\%$ in the O₂ system and from 41 ± 4 and $14 \pm 5\%$ in the HOCl system. The Ca-induced decrease in sorbed Mn(II) was coupled to a decrease in the Mn/Fe solids ratio (Fig 3.3), which suggests that Ca can compete effectively with Mn(II) for sorption sites, especially in the case of P-rich Fe(III) precipitates. This conclusion is consistent with the similar ionic potential (charge/ionic radius) of Mn(II) ($IP_{Mn(II)} \approx 24$) and Ca ($IP_{Ca} \approx 20$) ions, which suggests similar sorption reactivity between Mn(II) and Ca.

3.5 CONCLUSIONS AND IMPLICATIONS FOR WATER TREATMENT

We found that the composition of water and the identity of the oxidant strongly determines the macroscopic and molecular-scale characteristics of Fe and Mn bearing precipitates generated by Fe(II) and Mn(II) co-oxidation. The higher Mn/

Fe ratio of the precipitates produced with MnO_4 or HOCl indicates that the Mn removal mechanism will differ between the typical aeration—rapid sand filtration type groundwater treatment systems that rely on bacteria and surface catalysts for Mn(II) removal (Bruins et al. 2015) and the ones that use strong oxidants such as KMnO_4 and NaOCl . In the prior case, Mn removal will take place deeper in the filter bed, whereas Mn is expected to precipitate in the supernatant storage with KMnO_4 and NaOCl , resulting in accumulation of Mn bearing solids in the top sand filter layer.

Our study shows that the addition of Ca counteracts the negative effect of oxyanions and enhances the settling and filterability of Fe and Mn bearing precipitates. Thus, water treatment utilities that plan to implement softening at Fe/Mn removal plants should consider placing softening reactors after Fe/Mn removal to avoid colloiddally stable suspensions arising from solutions low in bivalent cations. If colloiddally stable suspensions are unavoidable, low pressure membrane systems (microfiltration/ultrafiltration) may replace rapid sand filters for effective removal of colloiddal precipitates, but the fouling of membranes will be a critical issue. Precipitates can foul the membranes in different ways, depending on particle size. Particle sizes larger than the membrane pores will deposit on membrane surfaces, resulting in cake layer formation, which is often easily reversible (Floris et al. 2016). However, smaller particles can deposit in the membrane internal structure, resulting in undesirable pore entrapment and pore narrowing, which severely decreases the flux over time (irreversible fouling).

With respect to contaminant removal during treatment, the formation of MnO_2 by MnO_4 addition should not be overlooked. The characterization data in the MnO_4 experiments indicated that the Mn solids were structurally similar to $\delta\text{-MnO}_2$, a nanoscale MnO_2 mineral. These types of Mn(IV) oxides have remarkable reactivity with respect to sorption of a wide variety of toxic heavy metals (e.g. Cd(II), Pb(II), Cu(II), Ni(II)) (Peña et al. 2015, Pena et al. 2010, Villalobos 2015). For example, the Pb/Mn solids ratio for $\delta\text{-MnO}_2$ can reach 0.4 mol/mol (Villalobos et al. 2005), which is partly due to highly reactive Mn(IV) vacancies in MnO_2 sheets (Lanson et al. 2002). In our study, MnO_4 was investigated primarily because it improves the kinetics of Fe(II), Mn(II) and As(III) oxidation. However, our results suggest that Fe(II) oxidation by MnO_4 and the production of mixtures of Fe(III) and MnO_2 would be ideal for concurrent treatment of As(III) and heavy metals. This result is particularly important for the co-removal of As(III) and Cd(II), which can often occur simultaneously in polluted environments (Perera et al. 2016), since Cd(II) removal by Fe(III) precipitates is much less effective than MnO_2 (Van Genuchten and Peña 2016b).

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SUPPLEMENTARY INFORMATION

1. Oxidation reactions of Fe(II), Mn(II) and As(III) with O₂, MnO₄ and HOCl (Ghurye and Clifford 2001)

Fe(II) oxidation with O₂, MnO₄ and HOCl

Mn(II) oxidation with O₂, MnO₄ and HOCl

As(III) oxidation with O₂, MnO₄ and HOCl

2. X-ray absorption spectroscopy sample preparation and data collection

Solids for X-ray absorption spectroscopy (XAS) analysis were collected from the precipitation experiments on 0.45 μm filters and encapsulated in Kapton tape while the filter was wet. The amount of solid material trapped on the filter was selected to optimize Fe K-edge XAS measurements in transmission mode i.e. the total absorption from the entire sample was less than 2.5 absorption lengths, while the absorption of Fe was 1.0 absorption length. Fe and Mn K-edge XAS data were collected at room temperature at beamline 4-1 of the Stanford Synchrotron Radiation Lightsource (SSRL) and the DUBBLE beamline (BM-26a) of the European Synchrotron Radiation Facility (ESRF). Transmission measurements were made using ion chambers for measurements of I_0 (40% N_2 , 60% He) and I_t (20% Ar, 80% He), whereas a 9-element solid state Ge detector was used for fluorescence measurements. The vertical and horizontal dimensions of the X-ray beam during the measurement were 0.5 to 1 mm and 3 mm, respectively. Harmonic rejection mirrors were used to remove second-order harmonics or the X-ray beam was detuned 40%. The XANES region was measured with 0.35 eV steps, whereas step sizes of 0.05 $\text{\AA}^{-1}$ were used for the EXAFS region. Two to 8 scans were collected for each sample and beam damage was not observed in replicate scans for any sample.

3. Fe K-edge EXAFS analysis

The Fe K-edge EXAFS spectra of select samples and reference material was analyzed by shell-by-shell fits. Theoretical curve fits were performed in $R+\Delta R$ -space ($\text{\AA}$) using SixPack software, which is built on algorithms derived from the IFEFFIT library (Newville 2001). Scattering paths used in the fits were derived from the structure of goethite (Gualtieri and Venturelli 1999). Fits were typically performed by varying the coordination number (CN), change in threshold energy (ΔE_0), interatomic distance (R) and the mean squared displacement parameter (σ^2) for each path in the fit. For several of the samples, the σ^2 for the first and second shell Fe-Fe paths were constrained to 0.01 to reduce the high fit-derived standard error on CN and σ^2 produced in preliminary fits. The passive electron reduction factor (S_0^2) was set to 0.8. The goodness of fit was determined using the R-factor.

4. Mn K-edge XANES analysis

The Mn K-edge XANES spectra of experimental samples were analyzed by LCFs to determine the fraction of solid-associated Mn(II), Mn(III), and Mn(IV). SixPack software was used to perform the LCFs on the normalized XANES spectra, with a fit range of 6530 to 6590 eV. Following previous approaches (Manceau et al. 2012a), negative fit-derived fractions were not permitted in the fit. Since the selection of particular Mn(II), Mn(III), and Mn(IV) standards used in the LCFs

can impact the fit-derived Mn(II), Mn(III), and Mn(IV) fractions (Manceau et al. 2012a), we adopted a previous approach where several LCFs were performed for each experimental sample using different combinations of 5 different Mn-bearing standards (Van Genuchten and Pena 2017a). The standard XANES spectra used in the LCFs were aqueous Mn(II), bixbyite (α -Mn₂O₃), manganite (γ -MnOOH), δ -MnO₂, and ramsdellite (β -MnO₂), which were collected as part of previous studies or were obtained from X-ray absorption spectra databases (Manceau et al. 2012a, Van Genuchten and Pena 2017a). Four LCFs were performed and the fraction of Mn(II), Mn(III), and Mn(IV) for each experimental sample was calculated by taking the average and standard deviation of the four LCFs.

5. Mn K-edge EXAFS analysis

The Mn K-edge EXAFS spectra of select samples and standards were analyzed by shell-by-shell fits. Theoretical curve fits were performed in $R+\Delta R$ -space ($\text{\AA}$) using the SixPack software with algorithms based on the IFEFFIT library (Newville 2001). Single scattering paths (Mn-O, Mn-Mn/Fe) were derived from the structure of birnessite (MnO₂) (Lanson et al. 2002), with theoretical phase and amplitude functions calculated using FEFF6 (Rehr et al. 1992). Fits were performed by varying CN , ΔE_0 , R , and σ^2 . The passive electron reduction factor was set to 0.7. In preliminary fits, the fit-derived uncertainties on CN and σ^2 were large due to their high correlation. Therefore, we constrained the σ^2 value in the fits of some experimental samples and standards, which is a common shell-by-shell fitting approach for nanoscale metal oxides (Mikutta et al. 2010).

SUPPLEMENTARY INFORMATION

Iron oxidation for different oxidation

Figure S3.1 PHREEQC simulations of Fe(II) oxidation by O_2 as a function of the ionic composition of initial solutions studied in Fe(II) and Mn(II) co-oxidation experiments.

Figure S3.2. Results of the principal component analysis of the Fe K-edge EXAFS spectra. The indicator function (IND) decreases with increasing number of principal components. The arrow highlights the number of principal components used in the LCFs.

Figure S3.3 Fe K-edge EXAFS spectra and Fourier transforms of Fe-bearing standards and precipitate samples formed in the O_2 and HOCl experiments. The output of shell-by-shell fits (solid lines) is overlain to the data (dotted lines).

Table S3.1. Summary of Fe Shell Fits of Fe-bearing References and Precipitate Samples.

Sample	Atomic Pairs	CN	R (Å)	σ^2 (Å ²)	ΔE_0 (eV)	R-Factor
γ -FeOOH	Fe-O	6.2 (0.8)	2.01 (0.01)	0.007 (0.001)	-3.0 (1.0)	0.021
	Fe-Fe	6.5 (0.9)	3.07 (0.01)	0.007 (0.001)		
2LFh	Fe-O	4.1 (0.7)	1.97 (0.01)	0.008 (0.002)	-2.6 (2.0)	0.044
	Fe-Fe1	1.7 (0.5)	3.04 (0.02)	0.01		
	Fe-Fe2	1.8 (0.7)	3.46 (0.03)	0.01		
Oxy-rich HFO	Fe-O	4.4 (0.5)	2.00 (0.01)	0.005 (0.001)	-2.1 (1.3)	0.035
	Fe-Fe	1.6 (0.4)	3.06 (0.02)	0.01		
Ref O ₂	Fe-O	6.3 (0.7)	2.01 (0.01)	0.008 (0.001)	-3.1 (0.9)	0.017
	Fe-Fe	5.7 (0.8)	3.07 (0.01)	0.007 (0.001)		
Ref HOCl	Fe-O	6.2 (0.7)	1.98 (0.01)	0.011 (0.001)	-3.9 (1.3)	0.031
	Fe-Fe	2.0 (0.3)	3.05 (0.01)	0.01		

CN represents the coordination number. R the interatomic distance. σ^2 the mean squared atomic displacement and ΔE_0 represents the change in threshold energy. The passive electron reduction factor. S_0^2 , was fixed at 0.8. Fitting parameters allowed to float are accompanied by fit-determined standard errors in parenthesis, whereas constrained parameters appear without a parenthesis.

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Chapter 4

Mobility and redox transformation of arsenic during treatment of artificially recharged groundwater for drinking water production

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ABSTRACT

In this study we investigate opportunities for reducing arsenic (As) to very low levels, below 1 $\mu\text{g/L}$ in produced drinking water from artificially infiltrated groundwater. We observe that rapid sand filtration is the most important treatment step for the oxidation and removal of As at water treatment plants which use artificially recharged groundwater as source. Removal of As is mainly due to As co-precipitation with Fe(III)(oxyhydr)oxides, which shows higher efficiency in rapid sand filter beds compared to aeration and supernatant storage. This is due to an accelerated oxidation of As(III) to As(V) in the filter bed which may be caused by the manganese oxides and/or As(III) oxidizing bacteria, as both are found in the coating of rapid sand filter media grains by chemical analysis and taxonomic profiling of the bacterial communities. Arsenic removal does not take place in treatment steps such as granular activated carbon filtration, ultrafiltration or slow sand filtration, due to a lack of hydrolyzing iron in their influent and a lack of adsorption affinity between As and the filtration surfaces. Further, we found that As reduction to below 1 $\mu\text{g/L}$ can be effectively achieved at water treatment plants either by treating the influent of rapid sand filters by dosing potassium permanganate in combination with ferric chloride or by treating the effluent of rapid sand filters with ferric chloride dosing only. Finally, we observe that reducing the pH is an effective measure for increasing As co-precipitation with Fe(III)(oxyhydr)oxides, but only when the oxidized arsenic, As(V), is the predominant species in water.

4.1 INTRODUCTION

Artificial recharge of groundwater with surface water is a widely used approach for drinking water production. Infiltration of the surface water into underground aquifers often leads to an improved chemical and/or microbiological quality (De Moel et al. 2006). After retention in the underground aquifers, the infiltrated water is recovered and further purified at water treatment plants (WTPs) to meet drinking water quality criteria before supply to consumer houses. Arsenic (As) concentrations in surface water are generally low (Smedley and Kinniburgh 2002), however, high concentrations of As can be introduced into the recharged water from aquifer matrix (Dillon et al. 2019, Fakhreddine et al. 2015). In the Netherlands, trace-level release of As into the recharged water in coastal dunes has been observed which results in elevated As levels in the recovered water (Ahmad et al. 2015, Stuyfzand et al. 2008). Although the As levels in the recovered water are well below the WHO guideline of 10 µg/L, recent studies indicate that human health might be affected by As concentrations below the WHO guideline of 10 µg/L (Ahmad and Bhattacharya 2019, Kozisek 2017, Saint-Jacques et al. 2018, Schmidt 2014). Therefore, as a precautionary measure, Dutch drinking water sector aims to supply drinking water with <1 µg/L As (Ahmad et al. 2020, Van der Wens et al. 2016).

The removal of As from natural anaerobic groundwater, in addition to Fe(II), Mn(II) and NH_4^+ removal, has been extensively investigated in previous studies (Ahmad et al. 2018, Gude et al. 2016, Jessen et al. 2005, Lytle et al. 2007, Lytle et al. 2005). The treatment of natural groundwater is generally simple, consisting of aeration followed by rapid sand filtration whereby As is mainly removed by co-precipitation with Fe(III)(oxyhydr)oxides which are formed due to oxidation of native Fe(II) and subsequent hydrolysis (Gude et al. 2016, McNeill and Edwards 1995). The treatment of artificially recharged water, on the other hand, often requires more treatment steps than that of natural groundwater. For example, granular activated carbon (GAC) filtration is often used to remove color, improve the taste of the water and additional disinfection steps may be required to achieve microbiological stability of water (e.g. by ultrafiltration (UF) or ultraviolet (UV) treatment). A complete understanding of the fate of As at low levels during the treatment of artificially recharged dune-water is not yet fully obtained. Nevertheless, this knowledge is required to identify the water quality and operational parameters that can improve As removal at dune-water treatment plants in order to achieve very low As concentration (<1 µg/L) in drinking water. In this study, we develop a detailed understanding of As removal during dune-water treatment and investigate opportunities to reduce As levels in the recharged water to even lower levels below 1 µg/L in produced drinking water.

4.2 MATERIALS AND METHODS

4.2.1 Water treatment plants

Two water treatment plants (WTPs) in the Netherlands, Ouddorp (WTP 1) and Katwijk (WTP 2), which rely on artificially recharged dune-water for drinking water production were chosen for this study. For both WTPs, the treatment schemes are shown in Fig 4.1, the influent and effluent quality in Table 4.1 and design and operational details in Table 4.2.

Figure 4.1 Process schemes of (A) general pre-treatment of surface water before dune infiltration applicable to both WTPs. (B) Dune-water treatment at WTP 1. (C) Dune-water treatment at WTP 2. Markings 1b–5b and 1c–4c indicate sampling points at WTP 1 and WTP 2 respectively.

Table 4.1 Raw dune-water and treatment plant effluent (drinking water) quality at WTP 1 and WTP 2. Data is based on the regular water quality monitoring programs of the drinking water companies in the period 2016–2019. For comparison the drinking water quality standards in the Netherlands are also given.

Parameter	Unit	WTP 1		WTP 2		Drinking water quality standard in the Netherlands*
		Raw dune-water	Treatment plant effluent (drinking water)	Raw dune-water	Treatment plant effluent (drinking water)	
Temperature	°C	11.5–12.2	11.7–15.0	7.7–12.4	13.7–16.8	<25
pH	–	7.45–7.85	7.74–7.91	7.62–7.71	8.17–8.42 ¹	7.0–9.5
Dissolved Oxygen	mg/L O ₂	<0.1–2.0	9.2–10.1	1.7–3.5	9.7	>2
Electrical Conductivity	mS/m	64.5–67.5	n.m.	47–56	48.5–52.6	<125
Bicarbonate	mg/L HCO ₃	230–250	n.m.	200–210	167–184	>60
Turbidity	NTU	n.m.	<0.03	0.3–3.5	<0.03	<1
Iron	mg/L Fe	0.7–1.9	<0.01	<0.01–1.5	<0.01	<0.2
Manganese	mg/L Mn	0.08–0.11	<0.01	0.03–0.2	<0.01	<0.05
Calcium	mg/L Ca	83–88	82–87	66–72	40–46	n.r.
Magnesium	mg/L Mg	10	10	7.4–8.3	7.7–8.3	n.r.
Ammonium	mg/L NH ₄	0.25–0.33	<0.02	0.03–0.2	<0.02	<0.2
Nitrite	mg/L NO ₂	0.013–0.02	<0.007	0.05–0.10	<0.007	<0.1
Nitrate	mg/L NO ₃	<0.2–0.3	2.6–3.7	2.0–6.2	1.7–2.2	<50
Arsenic	µg/L As	6.9–12.1	2.4–3.6	3.5–4.2	3.2–3.4	<10
Ortho-phosphate	mg/L P	0.03–0.25	0.007–0.03	0.07–0.2	0.02–0.05	n.r.
Silicate	mg/L Si	3.0–4.6	3.1–4.5	n.m.	n.m.	n.r.
Total organic carbon	mg/L C	3.3–3.9	1.6–3.0	2.6–2.9	2.1	n.r.
Sulphate	mg/L SO ₄	27–50	30–52	40–46	45–51	<150
Sodium	mg/L Na	34–55	34–55	30–36	57–60	<150
Chloride	mg/L Cl	67–110	66–108	45–54	54–56	<150

n.m., not measured, n.r. not regulated, ¹ pH higher than the raw water because of NaOH dosing during softening, * based on national guideline “Drinkwaterbesluit” in act since July 2018 which is available online at <https://wetten.overheid.nl/BWBR0030111/2018-07-01#BijlageA>

Table 4.2 Process details of WTP 1 and WTP 2. Abbreviations are as follows. RSF: Rapid Sand Filter HRT: Hydraulic Residence Time. GAC: Granular Activated Carbon filter, PAC: Powdered Activated Carbon, UF: Ultrafiltration, SSF: Slow Sand Filter.

	WTP 1	WTP 2
Pre-treatment		
Surface water source	Rhine-Meuse estuary	River Meuse
Treatment before dune infiltration	Coagulation-Flocculation-Rapid sand filtration	Coagulation-Flocculation-Rapid sand filtration
Dune storage	30 days	60 days
Post-treatment		
Dune-water abstraction	4.8 Mm ³ /year	24.8 Mm ³ /year
Aeration	Spray	Cascade
Rapid sand filtration	<ul style="list-style-type: none"> • Single media RSF with silica sand (h=1.4 m; d= 2.0–3.8 mm) • Supernatant level: 0.35 m • HRT of supernatant: 11 min • Filtration velocity: 2 m/h • HRT in filter bed: 17 min • Filter run time: 3–4 days 	<ul style="list-style-type: none"> • Double media RSF; top layer anthracite (h₁=0.5 m; d₁=1.7–2.8 mm) + bottom silica sand (h₂=1.0 m; d₂=0.8–1.3 mm) • Supernatant level: 1.0 m • HRT of supernatant: 21 min • Filtration velocity: 4 m/h • HRT in filter bed: 10 min • Filter run time: 7 days
Activated carbon treatment	<ul style="list-style-type: none"> • GAC filter with media. Filtrasorb F300 Chemviron Carbon in Belgium (h=2.0 m; d=1.5–1.7 mm) • Supernatant level: 0.30 m • Filtration velocity: 2.5 m/h • Filter run time Run time: 10 days 	<ul style="list-style-type: none"> • PAC dosing (2 mg/L) in the feed of rapid sand filters. NORIT® SA SUPER (Cabot Norit Netherlands B.V.)
Polishing filter	<ul style="list-style-type: none"> • UF (pore size 20 nm). Norit X-flow S-225 • Flux 55 L/m².h; Recovery>98% • Operational transmembrane pressure (TMP)=0.2 bar • Hydraulic backwash after 180 min 	<ul style="list-style-type: none"> • SSF with silica sand (h=1.0 m; d= 0.3–1.2 mm). • Supernatant level: 1 m • Filtration velocity: 0.3 m/h • Filter surface is scrapped 10 cm and replenished after every 2 years

4.2.2 Sampling campaigns

4.2.2.1 Water samples

To understand the removal of As, sampling campaigns were carried out at both WTPs which included collection of water samples before and after each treatment step and

analysis of the samples for a range of water quality parameters (Table 4.3 and Fig 4.1). Approximately 24 h before sampling, rotation of the dune-water abstraction wells was stopped and the filters were backwashed to ensure a stable water quality during the sampling campaign. For sampling, each sampling point was flushed for at least 5 min and subsequently 2 L of water was collected in an acid-washed glass beaker. From that primary 2 L sample volume, 200 mL of water was directly preserved for analysis and another 200 mL was filtered through 0.45 μm filters before preservation (see section 4.2.7 for conservation and analysis details). The residual sample volume (1.6 L) was used for the measurements of pH, temperature and dissolved oxygen. For the sampling of dune-water, care was taken to avoid aeration of the samples during collection. The pore water over the height of the rapid sand filters (RSFs) was sampled using the available sampling points (at least 10 cm apart) in the full-scale filters at an approximate flow rate of 50 mL/min.

4.2.2.2 Sampling of rapid sand filter material

To determine the chemical composition of the coating on the RSF media, microbial community analysis and to perform batch experiments aimed to gain insights into As adsorption, filter material from the full-scale RSFs of both WTPs were analyzed. For these purposes, approximately 5 kg of the filter material from the upper 10 cm of each filter bed was collected with a stainless steel spade directly after backwash and stored in a closed bucket.

4.2.3 Batch experiments

A number of batch experiments with influent, supernatant and effluent water of the RSFs were performed to elucidate the effect of different water quality and operational parameters on As removal. Approximately 10 min before each batch experiment, 20 L of water was collected from the relevant sample point in the full-scale WTP using a jerry can (Fig 4.1). Further details about the experiments are provided in the following sections.

4.2.3.1 Supernatant water experiments

Arsenic removal as a function of residence time in RSF supernatant was studied with supernatant water samples from both WTPs using a standard jar test apparatus which has been described previously (Ahmad et al. 2018). The supernatant water sample was poured in 4 jars (2 L each jar) of the jar test apparatus. This was considered $t=0$, i.e. start of the experiment. Unfiltered and 0.45 μm filtered samples of the initial solution were collected and preserved for analysis. These jars were then stirred at 100 RPM for 60 min. Unfiltered and 0.45 μm filtered samples were collected at $t=15$, 30, 45 and 60 min using a sterile syringe while the jars were continuously mixed. Collection of the 60 min samples marked the end of the jar test.

4.2.3.2 Experiments with influent and effluent of rapid sand filters

To investigate options to achieve a reduction in As concentration to $<1 \mu\text{g/L}$, batch experiments were performed with the influent and effluent of RSFs. In the experiments with the RSF influent, the impact of different Fe(III) doses (achieved by FeCl_3 dosing) alone or after potassium permanganate (KMnO_4) pre-treatment (0.5 mg/L MnO_4^- , determined by preliminary experiments to achieve complete As(III) oxidation in all cases) was studied. For the RSF effluent, we investigated only the effect of different Fe(III) doses because of the absence of As(III) in RSF effluent. To investigate the effect of pH on As removal, experiments were performed at natural pH (pH 7.8 for WTP 1 and pH 8.2 for WTP 2) and at an experimentally lowered pH of 7.0 (achieved by HCl dosing).

First of all, the jars were filled with the influent or the effluent of the RSFs from both WTPs. Subsequently, a predetermined aliquot of KMnO_4 and/or FeCl_3 was dosed in each jar while the solutions were mixed at 100 RPM. In the KMnO_4 - FeCl_3 dosing experiments, the interval between KMnO_4 and FeCl_3 doses was kept constant at 2 min. This interval was chosen to ensure that complete oxidation of As(III) to As(V) had occurred before the Fe(III) dosing (Ahmad et al. 2018). For the pH adjustment, 0.1 M HCl or 0.1 M NaOH was used before the addition of KMnO_4 and/or FeCl_3 . Finally, unfiltered and $0.45 \mu\text{m}$ filtered water samples were collected from the jars at $t=30 \text{ min}$ using a sterile syringe while the jars were continuously mixed. The samples were analyzed for As and Fe concentrations.

4.2.3.3 Experiments with rapid sand filter material

Adsorption and desorption of As by RSF media was studied as a function of pH (7.0–9.0), As concentration and As speciation. The RSF effluent of each WTP was used as the initial solution in the experiments with RSF media of that WTP. Before experiments, the filter media samples were washed at least 5 times with ultrapure water to remove loose precipitates and afterwards air dried for 24 h at room temperature. The solid-solution ratio used in the batch experiments was 250 g/L . All the suspensions were agitated by back-and-forth strokes at a rate of 120 min^{-1} . Sample aliquots of 100 mL were collected using a sterile syringe with a 30 cm Teflon tube on the tip were taken at $t=0$, i.e. directly after solid addition and intermittently until $t=24 \text{ h}$.

4.2.4 Chemical characterization of rapid sand filter material

The RSF media grains from both WTPs were characterized for the chemical composition of the coating to investigate As(III) oxidation in RSFs. For each sample, the coating of 4.0 g of the filter material was dissolved in 50 mL ultrapure water and 6.3 mL concentrated HNO_3 (65%) followed by heating the suspension at 105°C for

24 h. After cooling down the solution was filtered through Whatman 589/1 paper filter and analyzed for the elemental composition.

4.2.5 Microbial community analysis on rapid sand filter material

To further investigate As(III) oxidation in RSFs, insights into the microbial community in RSFs were obtained by DNA extraction and 16S rRNA taxonomic profiling using next generation sequencing (NGS). To perform the analysis, 40 mL of ultrapure water (Invitrogen, ThermoFisher scientific) was added to 7.0 g of freshly collected filter material from each WTP. High energy sonication was used to release the biomass from the filter material as described previously (Magic-Knezev and van der Kooij 2004). The suspended biomass was subsequently concentrated on polycarbonate track-etched membrane filters having a pore size of 0.2 μm (Sartorius). The PowerBiofilm Kit (Qiagen) was used for DNA extraction using the protocol described by the manufacturer. The V4 variable region of the 16S rRNA genes was amplified using the 515F-806R primer pair. Amplicons were barcoded and the size and concentration was checked on an Agilent Bioanalyser. DNA concentrations were determined using the Qubit fluorescent measurement (Fisher Scientific). Equimolar amplicon concentrations were pooled and sequenced using the Miseq v2 (2x 250 bp) reagents (Illumina) on an Illumina MiSeq platform. Subsequent processing of sequence data was performed using the MOTHUR pipeline (Schloss et al. 2009). In short, raw paired end sequence reads were assembled, aligned against the Silva alignment db (version 132; (Quast et al. 2013)) and potential chimeric sequences were removed. Finally, Operational Taxonomic Units (OTUs) with 97% sequence identity were predicted and taxonomic identification of the OTUs until genus-level depth was performed against the Silva taxonomic database, only prokaryote OTUs were retained.

4.2.6 Chemicals and other apparatus

All chemicals were reagent grade. KMnO_4 was dosed using a 0.03 M KMnO_4 (3.6 g/L MnO_4) stock solution. It was prepared by dissolving 948 mg of solid KMnO_4 (Cairox®, Carus Corporation) in 200 mL ultrapure water directly before the start of batch experiments. A FeCl_3 solution (2.0 g Fe(III)/L) was used to dose Fe(III) in water. It was prepared by dissolving 1936 mg solid $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (J.T. Baker®) in 200 mL ultrapure water directly before the start of the batch experiments. For As(III) and As(V) spike, certified solutions (1000 mg As(III) and As(V)/L, Inorganic ventures®) set in HCl and H_2O matrices respectively were used without any dilution. For pH control during the experiments, 0.1 M NaOH and 0.1 M HCl solutions were used. The PP/PE 50 mL sterile syringes (Sigma-Aldrich) were used for the filtration of water samples. To obtain 0.45 μm filtered samples, GE's GD/XP disposable syringe filters were used.

4.2.7 Conservation and analysis of water samples

The determination of arsenic (As), iron (Fe), manganese (Mn), phosphate (P), calcium (Ca), magnesium (Mg) and silicate (Si) concentrations was carried out by Inductively Coupled Plasma Mass Spectrometry (ICP–MS) (XSERIES 2, Thermo Fisher Scientific). These samples were preserved immediately after sampling by adding 250 μL of 10% ultra-pure nitric acid (HNO_3). The total organic carbon (TOC) samples were measured by high temperature combustion and infrared detection. After collection the TOC samples were conserved with 0.18 mL of 9.1 M H_2SO_4 (59% w/w) added in 100 mL sample. The samples for As speciation were conserved with 2 mL of 125 mM EDTA added to 100 mL of the water sample. The As speciation was determined by IC–ICP–MS. The NH_4^+ was analysed by a discrete analyser spectrophotometry (Aquakem 250, Thermo Scientific). All samples were stored at 4°C before analysis.

4.3 RESULTS AND DISCUSSION

4.3.1 Arsenic removal during dune-water treatment

Table 4.3 presents results of the sampling campaigns that were carried out at WTP 1 and WTP 2 to gain insights into As removal during dune-water treatment. A fraction of As and Fe concentrations in raw dune-water was removed by $0.45\ \mu\text{m}$ filtration at both WTPs which shows that some portion of As and Fe is already co-precipitated in the raw dune-water at both WTPs. During treatment of dune-water, As removal is strongly correlated with Fe removal at both WTPs, attributed to further co-precipitation of As with Fe(III) (oxyhydr)oxides that are formed due to the (oxidative) hydrolysis of natural and dosed Fe in water (latter only at WTP 1). At WTP 1, the effluent of RSF is treated by GAC filtration and UF (Fig 4.1B) and at WTP 2 the effluent of RSF is treated by SSF to produce drinking water (Fig 4.1C). We observe that the As concentrations in RSF effluent were not reduced further by any of these treatment steps (Table 4.3). This can be attributed to the absence of As adsorbing Fe(III)(oxyhydr)oxides in the RSF effluent at both WTPs and low adsorption affinity between As(V) (the predominant As species in RSF effluent) and the negatively charged surfaces of activated carbon media (Newcombe et al. 1993), UF membranes (Floris et al. 2016, Li et al. 2011) and SSF media (Śmiech et al. 2018).

Complete Mn removal is observed in the RSF bed at both WTPs (Table 4.3). The direct oxidation of Mn(II) to form solid MnO_x with oxygen in the relevant pH range is a kinetically slow process and can explain the occurrence of dissolved Mn in the supernatant storage at both WTPs (Diem and Stumm 1984, Knocke et al. 1991, Sogaard and Madsen 2013, Van Benschoten et al. 1992). The Mn removal in RSFs

is attributed to bacteria and surface catalysts on the filter media grains which are known to mediate the Mn(II) transformation to insoluble MnO_x (Bruins et al. 2015, Katsoyiannis et al. 2008). The removal of NH_4^+ at both WTPs also occurs in the filter bed, attributed to the biological oxidation (nitrification) executed by different bacterial species in the filter bed (De Moel et al. 2006, De Vet 2011).

Arsenic in the raw dune-water at both WTPs occurs as a combination of As(III) and As(V) (Table 4.1). No significant differences are observed between the concentrations of aqueous As(III) in the raw dune-water and RSF supernatant at both WTPs. This shows that aeration is not effective in As(III) oxidation to As(V). Similar slow oxidation kinetics of As(III) in oxygen systems has been observed in previous studies (Frank and Clifford 1986, Ghurye and Clifford 2001).

Irrespective of As speciation in the RSF influent, As(V) is the predominant species of residual As in the effluent of RSFs at both WTPs which can be attributed to oxidation of aqueous As(III) in RSFs. At WTP 1, the difference between aqueous As and Fe concentrations in the supernatant and the RSF effluent indicates an uptake of $9.7 \mu\text{g As per mg}$ of the precipitated Fe during rapid sand filtration. This is much higher than the As uptake by Fe(III) precipitates during aeration and supernatant storage ($1.3 \mu\text{g As per mg Fe}$). The higher As uptake by Fe(III) precipitates in the filter bed can be explained by the oxidation of aqueous As(III) due to either MnO_x and/or As-oxidizing bacteria which have been observed both on RSF media grains (see section 3.2, 3.3 and 3.4 for further discussion). At WTP 2, As concentration in the effluent of RSF is similar to the aqueous As in the supernatant. This can be explained by the fact that in the supernatant of WTP 2 Fe is already precipitated and therefore further Fe(III)(oxyhydr)oxide precipitation and corresponding As co-precipitation is not possible in RSF bed at WTP 2. Thus, it can be concluded that a higher As co-precipitation efficiency is achieved when a higher proportion of Fe is precipitated in RSF bed where at the same time As(III) is oxidized into As(V).

In summary, the sampling campaigns reveal that during dune-water treatment rapid sand filtration is the most important treatment step for the oxidation and removal of As. The efficiency of As co-precipitation with Fe(III)(oxyhydr)oxides is higher in RSF bed compared to aeration and supernatant storage, because of the rapid oxidation of As(III) to As(V) in the RSF bed. Therefore As removal can be increased by ensuring that more of the Fe is precipitated in the RSF bed. After the RSF no further As removal is observed due to the low affinity between As(V) and the negatively charged filtration surfaces of subsequent treatment steps.

4.3.2 Oxidation and removal of arsenic over filter bed height

The oxidation and removal of As during rapid sand filtration was further studied by collecting pore water samples over the RSF beds at both WTPs. The results show

Table 4.3 Concentrations of As and other elements at various points along the treatment trains of WTP 1 and WTP 2. UNF and 0.45 µm FIL refer to unfiltered and 0.45 µm filtered samples, used to distinguish between total and dissolved elemental concentrations. The increase in supernatant Fe concentration in WTP 1 compared to raw dune-water is due to FeCl₃ dosing in the influent of RSF at WTP 1. In the supernatant of WTP 2, UNF As and Fe concentrations were slightly lower compared to the raw dune-water ($\approx 5\%$) due to removal during softening.

Water sample code	As µg/l	As(III) µg/l	As(V) µg/l	Fe mg/l	Mn mg/l	NH ₄ ⁺ mg/l	P mg/l	Si mg/l	OC mg/l	Ca mg/l	Mg mg/l	pH
WTP 1												
Raw dune-water_UNF	10.3	—	—	1.20	0.11	0.30	—	—	—	80	10.1	7.5
Raw dune-water_0.45 µm FIL	9.5	8.5	0.8	0.92	0.11	—	0.20	3.5	3.1	—	—	—
Supernatant RSF_UNF	9.8	—	—	1.50	0.12	0.30	—	—	—	80	10.0	7.5
Supernatant RSF_0.45 µm FIL	8.5	7.2	0.7	0.62	0.11	—	0.10	3.4	2.9	—	—	—
Effluent RSF_UNF	2.5	—	—	<0.005	<0.005	<0.02	—	—	—	81	10.4	7.7
Effluent RSF_0.45 µm FIL	2.5	<0.5	2.4	<0.005	<0.005	—	0.02	3.5	2.6	—	—	—
Effluent ACF_UNF	2.5	—	—	<0.005	<0.005	<0.02	—	—	—	82	10.3	—
Effluent ACF_0.45 µm FIL	2.5	<0.5	2.5	<0.005	<0.005	—	—	—	2.4	—	—	—
Effluent UF_UNF	2.5	—	—	<0.005	<0.005	<0.02	—	—	—	81	9.9	7.8
Effluent UF_0.45 µm FIL	2.5	<0.5	2.5	<0.005	<0.005	—	0.02	3.5	—	—	—	—
WTP 2												
Raw dune-water_UNF	4.1	—	—	0.21	0.04	0.13	—	—	—	70	8.5	7.7
Raw dune-water_0.45 µm FIL	3.6	1.3	2.3	0.08	0.04	—	0.10	3.7	2.9	70	8.7	—
Supernatant RSF_UNF	3.8	—	—	0.19	0.04	0.13	—	—	—	48	8.5	8.3
Supernatant RSF_0.45 µm FIL	3.2	1.3	1.9	<0.005	0.03	—	0.05	3.7	2.7	48	8.7	—
Effluent RSF_UNF	3.2	—	—	<0.005	<0.005	<0.02	—	—	—	47	8.5	8.3
Effluent RSF_0.45 µm FIL	3.2	<0.5	3.1	<0.005	<0.005	—	0.05	3.6	2.6	47	8.6	—
Effluent SSF_UNF	3.2	—	—	<0.005	<0.005	<0.02	—	—	—	48	8.4	8.2
Effluent SSF_0.45 µm FIL	3.2	<0.5	3.2	<0.005	<0.005	—	0.05	3.6	2.6	47	8.5	—

that removal of As, Fe, Mn and NH_4^+ predominantly occurs in the upper region (0.5 m and 0.7 m for WTP 1 and WTP 2 respectively) of the filter bed at both WTPs (Fig 4.2A and Fig 4.2D). Simultaneously, the oxidation of dissolved As(III) into As(V) also occurs in the upper (~ 0.7 m) region of RSFs (Fig 4.2C and Fig 4.2F). Nevertheless, clear differences are observed between WTP 1 and WTP 2 for As and Fe co-precipitation profiles. At WTP 1, As and Fe co-precipitation increases with filter depth until 0.5 m below the filter bed surface, due to the fact that no further Fe(III)(oxyhydr)oxides were formed below 0.5 m onto which As could adsorb (Fig 4.2B). On the other hand, at WTP 2 no further As co-precipitation in the filter bed occurs (Fig 4.2E) because all Fe is already oxidized and precipitated in the supernatant. Thus, though removal and oxidation of As is concentrated in the upper part of the RSFs at both WTPs, As(III) oxidation appears to be independent of Fe oxidation and precipitation.

Figure 4.2 Removal of total As, Fe, Mn and NH_4^+ over rapid sand filter bed height at (A) WTP 1 and (D) WTP 2. Dissolved As(III) and As(V) over rapid sand filter bed height at (C) WTP 1 and (F) WTP 2. To calculate % of co-precipitated As (or Fe), we first subtracted the dissolved As (or Fe) concentration at each sampling point from the total As (or Fe) concentration in the RSF influent and then we divided this quantity by the total As (or Fe) concentration in the RSF influent.

4.3.3 Rapid sand filter media surface coating

The RSF media at both WTPs have been used for over a decade. To further understand the mechanism of As(III) oxidation in RSFs, the brown-black filter media coating was analyzed to determine the chemical composition (Fig 4.3 and Table 4.4). Besides other elements such as Ca, Mg, Si, P and As, significant concentrations of Fe and Mn are found in the coating of both filter media (Table 4.4, Fig S4.1), indicating the presence of Fe and Mn oxides in the filter material coating (Bruins et al. 2015, Gude et al. 2016, 2017, Jessen et al. 2005, Sharma 2001). While the oxidation of As(III) by Fe(III) oxides is known to be slow (Oscarson et al. 1981), the MnO_x on the filter media grains can rapidly oxidize As(III) into As(V) (Driehaus et al. 1995, Gude et al. 2017, Lafferty et al. 2010, Moore et al. 1990, Oscarson et al. 1983) and therefore the MnO_x may be responsible for the observed rapid oxidation of As(III) in the RSFs. However, several recent studies argue that As(III) oxidation in RSFs is microbiologically mediated (Crognale et al. 2019, Gude et al. 2018b, c). Therefore, microbial communities in RSFs of both WTPs were analyzed to investigate the presence of As-oxidizing bacteria.

Figure 4.3 Images of rapid sand filter media grains obtained from (A) WTP 1 and (B) WTP 2. Both filter media have been used for over a decade.

4.3.4 Taxonomic community profiling of 16S rRNA sequences

Taxonomic profiling of the bacterial communities was performed on the filter media grains obtained from both WTPs. The overview of the relative proportions of the different bacterial taxa at family and genus level in the microbial communities (Fig 4.4) shows only minor differences between the duplicate samples from the WTPs,

Table 4.4 Elemental composition of rapid sand filter media coating in g/kg ds (ds: dry solid). The numbers in brackets represent the relative abundance in %.

Element	Filter media grains WTP 1	Filter media grains WTP 2
	g/kg ds (%)	g/kg ds (%)
Arsenic (As)	0.2 (<1)	0.004 (<1)
Calcium (Ca)	29.7 (12)	105 (84)
Iron (Fe)	109 (44)	8.0 (6)
Magnesium (Mg)	5.8 (2)	1.6 (1)
Manganese (Mn)	85.8 (34)	6.9 (6)
Silica (Si)	8.4 (3)	2.8 (2)
Phosphorous (P)	8.4 (3)	0.7 (<1)

Figure 4.4 Relative abundance of the 25 most abundant bacterial taxa in the microbial communities of duplicate samples from the WTP 1 and WTP 2 rapid sand filters. The names of the taxa are shown at family and genus level (from left to right separated with semi-colons).

demonstrating limited experimental variation and indicating that representative samples were analyzed. Family level taxonomic profiling indicates that, though much less abundant than the other genera like *Nitrospira* or *Methyloglobulus*, bacterial

sequences related to *Xanthobacteraceae* and *Burkholderiaceae* are present on both the filter media. Some strains in these bacterial families carry *aioA* genes encoding for As(III) oxidase and are thus able to rapidly oxidize As(III) (Heinrich-Salmeron et al. 2011). Therefore, we hypothesize that As(III) oxidation in rapid sand filters during dune-water treatment is biologically mediated by As(III) oxidizing bacteria.

4.3.5 Arsenic adsorption onto rapid sand filter material

The chemical characterization of filter media coating (Table 4.4) shows that Fe(III) (oxyhydr)oxides are present on filter media grains which may contribute to As removal in RSFs. To investigate this we performed batch experiments with RSF media and RSF effluent samples of both WTPs under different conditions of pH, initial As concentration and As speciation. The adsorption-desorption distribution coefficient (K_d) under different conditions is presented in Fig 4.5 and Fig 4.6. We observe that at natural pH and As concentrations, K_d value after a long equilibration time of 1440 min (24 h) is very low ($K_d \approx 0$) for both WTPs (Fig 4.5A and Fig 4.5B), indicating absence of any adsorption of As onto RSF media coating even after a prolonged contact of 24 h (the contact time in RSFs is 17 min and 10 min for WTP 1 and WTP 2 respectively, Table 4.2). These results show that the adsorption sites on the Fe(III)(oxyhydr)oxides present in filter media coating are already in equilibrium with the As concentration in water and therefore no further As adsorption takes place. Moreover, this result confirms that co-precipitation of As with freshly formed Fe(III) (oxyhydr)oxides is the main As removal mechanism at both WTPs and filter media coating does not contribute to As removal. At a pH of 7.0, a positive K_d is observed for both WTPs, indicating adsorption of As onto the RSF media coating. On the other hand, when pH is increased to 9.0, a negative K_d is observed for both WTPs,

Figure 4.5 Distribution coefficient (K_d) at $t=1440$ min (24 h) for As adsorption/desorption from RSF effluent to rapid sand filter material of (A) WTP 1 and (B) WTP 2 as a function of pH. natural pH of RSF effluent for WTP 1 and WTP 2 is 7.8 and 8.2 respectively.

indicating desorption of As from the RSF media coating. The observed adsorption/desorption of As as a function of pH can be explained by the fact that the number of adsorption sites for As(V) (which is a deprotonated oxyanion) on Fe(III) (oxyhydr)oxides increases with a decrease in pH (Dixit and Hering 2003, Kanematsu et al. 2013b, L. Pierce and Moore 1982, Manning et al. 1998, Meng et al. 2000, Qiao et al. 2012, Raven 1998). Thus, from these results it can be concluded that filter media coating does not contribute to As removal and that a reduction in pH is required to adsorb more As onto the Fe(III)(oxyhydr)oxides.

At natural pH, the adsorption of As onto filter media occurs only in the experiments with higher As concentration (100 µg/L As(III) or As(V) spike, Fig 4.6A and 4.6B), which can be explained by the fact that the equilibrium loading of an adsorbent increases with an increase in adsorbate/adsorbent ratio until adsorption capacity of the adsorbent is reached (Raven et al. 1998, Wilkie and Hering 1996). We also observe that the adsorption of As is similar when As(III) or As(V) is the initial As species (Fig 4.6A and Fig 4.6B). This can be attributed to the oxidation of aqueous As(III) to As(V) before adsorption (Fig S4.2), thus again confirming the accelerating effect of filter media grains on As(III) oxidation.

Figure 4.6 Distribution coefficient (K_d) in function of time for As adsorption/desorption from RSF effluent to rapid sand filter material of (A) WTP 1 and (B) WTP 2 at initial As(III) or As(V) concentration of 100 µg/L. The natural pH of the RSF effluent from WTP 1 and WTP 2 is 7.8 and 8.2 respectively.

4.3.6 Impact of extended residence time in supernatant

Jar tests were performed with the supernatant water samples from the RSFs of both WTPs to investigate whether increasing residence time of water in the supernatant storage could increase As removal. For WTP 1, As and Fe removal is $\approx 30\%$ and $\approx 70\%$ respectively at $t=0$ (Fig 4.7A, $t=0$ refers to the occasion of supernatant sample collection which corresponds to the residence time in the supernatant (Table 4.2). Arsenic and Fe removal increases to 35% and 85% respectively at $t=15$ min and 40% and 100% at $t=30$ min (Fig 4.7A). No further increase in As removal occurs after 30 min because of the absence of freshly formed additional Fe(III) precipitates. The achieved As removal efficiency in this case is much lower compared to As removal at WTP 1 (40% compared to 75%), which can be due to the fact that As(III) was not oxidized in the absence of RSF media (Fig 4.7C). Thus, it can be concluded that the extended residence time in the supernatant storage is ineffective for increasing As removal during dune-water treatment. In contrast to WTP 1, no considerable increase in As removal is observed with extended residence time in jar tests with supernatant water of WTP 2 (Fig 4.7B), which can be attributed to the absence of fresh formation of Fe(III) precipitates.

Figure 4.7 Removal of As, Fe, P and Si from the supernatant water by $0.45\ \mu\text{m}$ filtration in batch experiments as function of time. (A) WTP 1. (B) WTP 2. (C) the aqueous As speciation in the supernatant water of WTP 1 during the batch experiment.

We also monitored removal of P and Si as a function of extended residence time in the supernatant. The results show that P is better removed than As, e.g. for WTP 1 removal of P is $\approx 60\%$ at $t=0$ which increases to 75 % and 85% at $t=15$ min and 30 min respectively (Fig 4.7A). The relatively lower removal of As compared to P can be attributed to the lower As concentration in the initial solution and the presence of a major proportion (80–85%) of aqueous As in the form of As(III) (Fig 4.7C) which is generally outcompeted by P for the adsorption sites on Fe(III) precipitates due to lower affinity of As(III) than P (Dixit and Hering 2003, Jain and Loeppert 2000, Stachowicz et al. 2008). The removal of Si remains low ($<5\%$) in all the cases which can be attributed to the uncharged nature of Si species at the given pH (Kanematsu et al. 2013b, Roberts et al. 2004, Swedlund and Webster 1999).

4.3.7 Arsenic reduction below 1 $\mu\text{g/L}$ at dune-water treatment plants

4.3.7.1 KMnO_4 — FeCl_3 dosing in RSF influent

The sampling campaigns show that As removal during dune-water treatment depends on As speciation, pH and amount of freshly precipitated Fe(III)(oxyhydr)oxides in water. To explore opportunities for As reduction to very low levels ($<1 \mu\text{g/L}$), we studied As co-precipitation efficiency in RSF influent as a function of Fe(III) dosing and pH, with and without pre-treatment with KMnO_4 – which is known to rapidly oxidize As(III). At natural pH of RSF influent, the As co-precipitation efficiency increases with Fe(III) dosing for both WTPs (Fig 4.8A and Fig 4.8C), attributed to the availability of a higher amount of Fe(III) precipitates in water that adsorb more As (Dixit and Hering 2003, Hering et al. 1996a, Qiao et al. 2012, Su and Puls 2001, Wilkie and Hering 1996, Youngran et al. 2007). We further observe that As co-precipitation efficiency corresponding to a residual As concentration of significantly $<1 \mu\text{g/L}$ is achieved only in case of WTP 2 (at 3 mg/L Fe(III)) and the increase in As co-precipitation is steeper for WTP 2 than WTP 1. This can be explained by the fact that in the RSF influent of WTP 2 the proportion of As(V) is higher than WTP 1 (Table 4.3). Interestingly, in case of WTP 1 when the pH is lowered to 7.0, the As removal efficiency remains similar to pH 7.8 (Fig 4.8A). Although the amount of precipitated Fe is slightly lower at pH 7.0 compared to results obtained at pH 7.8 (due to the slower oxidation of natural Fe(II) at pH 7.0 (Vries et al. 2017)), we attribute the insignificant impact of pH on As co-precipitation to the presence of a large proportion of As in the form of As(III) at WTP 1 (Fig S4.3) whose adsorption onto Fe(III)(oxyhydr)oxides is known to remain unaffected over a pH range of 4–9 (Dixit and Hering 2003, Kanematsu et al. 2013b, Raven 1998, Stachowicz et al. 2006, Stachowicz et al. 2008).

When the co-precipitation of As in RSF influent is studied with KMnO_4 pre-treatment which facilitates the oxidation of As(III) to As(V), the As removal efficiency

drastically improves for both WTPs (Fig 4.8B and Fig 4.8D). For WTP 1 (Fig 4.8B), the residual As concentration of $\approx 1 \mu\text{g/L}$ ($\approx 90\%$) is achieved with Fe(III) dose of only 1.5 mg/L. Similarly for WTP 2, the residual As concentration of $0.9 \mu\text{g/L}$ As ($\approx 80\%$ removal) is achieved with only 0.7 mg/L Fe(III) dose (Fig 4.8D). Thus, As reduction to $<1 \mu\text{g/L}$ can be achieved at a much lower Fe(III) dose if KMnO_4 pre-treatment is applied. Oxidizing As(III) to As(V) by dosing a strong oxidant such as KMnO_4 has also been previously shown to increase As co-precipitation with Fe(III) (oxyhydr)oxides (Ahmad et al. 2018, Bissen and Frimmel 2003, Sorlini and Gialdini 2010) because As(V) adsorbs to Fe(III) precipitates more readily compared to As(III) (Hering et al. 1996a, Hsu et al. 2008, Lakshmanan et al. 2008, Lytle et al. 2005, Qiao et al. 2012). For WTP 1, at the reduced pH 7.0 a residual As concentration of $0.8 \mu\text{g/L}$ (93% removal) with Fe(III) dose of only 0.9 mg/L is achieved which can be explained by the availability of higher number of adsorption sites for As(V) of Fe(III) precipitates at lower pH.

Figure 4.8 Arsenic and Fe removal in batch experiments performed with the influent rapid sand filters at WTP 1 (A and B) and at WTP 2 (C and D). The rapid sand filter influent of WTP 1 and WTP 2 contained 10.8 and $4.1 \mu\text{g/L}$ As respectively. The dashed line on each figure indicates As removal corresponding to $1 \mu\text{g/L}$ residual As.

From these results it can be concluded that the presence of As(III) restricts the efficiency of As co-precipitation with Fe(III)(oxyhydr)oxides, even with pH adjustment to lower values. When As(III) is oxidized to As(V) by a strong oxidant (KMnO_4), not only the As uptake by Fe(III) precipitates increases but also As co-precipitation efficiency can be further increased by lowering the pH. Thus, KMnO_4 – FeCl_3 dosing in the influent of RSFs is an effective approach for As reduction to <1 $\mu\text{g/L}$.

4.3.7.2 FeCl_3 dosing in RSF effluent

The sampling campaigns have revealed that As(III) oxidizes completely into As(V) during rapid sand filtration. We investigated if As reduction to <1 $\mu\text{g/L}$ can be achieved by FeCl_3 dosing in RSF effluent of WTP 1. The results show that As removal of $\approx 70\%$ is achieved (reduction from 2.3 $\mu\text{g/L}$ to 0.7 $\mu\text{g/L}$) at an Fe(III) dose of 0.75 mg/L for WTP 1 (Fig 4.9). Compared to the RSF influent of WTP 1, in which As reduction to <1 $\mu\text{g/L}$ was not achieved even at an Fe(III) dose of 5 mg/L (Fig 4.8A), the As co-precipitation efficiency with Fe(III)(oxyhydr)oxides in RSF effluent is much higher due to the fact that in RSF effluent As is predominantly present in the form of As(V) which has a higher affinity for Fe(III) precipitates than As(III). From this, we conclude that the use of KMnO_4 in dune-water treatment can be avoided by treating the RSF effluent by FeCl_3 for As(V) removal instead of treating the RSF influent for As(III) removal by KMnO_4 – FeCl_3 dosing.

Figure 4.9 Arsenic in batch experiments performed with the effluent of rapid sand filters at WTP 1. The rapid sand filter effluent of WTP 1 contained 2.3 $\mu\text{g/L}$ As respectively. The dashed line indicates % As removal corresponding to 1 $\mu\text{g/L}$ residual As.

4.4 CONCLUSIONS AND IMPLICATIONS FOR WATER TREATMENT

From this study we conclude that rapid sand filtration is the most important treatment step for oxidation and removal of As during treatment of artificially recharged groundwater. Removal of As is mainly due to As co-precipitation with Fe(III)(oxyhydr)oxides and the efficiency of As co-precipitation with Fe(III)(oxyhydr)oxides is much higher in rapid sand filter beds compared to the preceding aeration and supernatant storage steps. This is due to an accelerated oxidation of As(III) to As(V) in the filter beds which may be caused by the manganese oxides and/or As(III) oxidizing bacteria, as both exist in the coating of rapid sand filter media grains. While more research is needed to unravel the actual As(III) oxidation mechanism, we conclude that a higher As co-precipitation efficiency can be achieved during rapid sand filtration by allowing precipitation of Fe(III)(oxyhydr)oxides to take place inside rapid sand filter bed. Arsenic removal does not take place in treatment steps such as granular activated carbon filtration, ultrafiltration or slow sand filtration, due to a lack of hydrolyzing Fe in their influent and a lack of adsorption affinity between As and the filtration surfaces.

In this study we also investigated opportunities to reduce As levels in produced drinking water. We conclude that As reduction to very low levels ($<1 \mu\text{g/L}$) at dune-water treatment plants can be achieved either by treating the influent or the effluent of rapid sand filters. Oxidizing As(III) in the rapid sand filter influent by a strong oxidant, KMnO_4 , results in a significant increase in the amount of As co-precipitated with Fe and therefore leads to a reduction in the amount of Fe(III) coagulant required to reduce As to $<1 \mu\text{g/L}$. On the other hand, the occurrence of As in the form of As(V) in the RSF effluent can eliminate the need to dose KMnO_4 and As reduction to $<1 \mu\text{g/L}$ can be achieved by low FeCl_3 dosing alone. Based on these results, treating the RSF effluent for As removal is expected to be more cost-effective than treating the RSF influent.

We also found in this study that a slight pH reduction is an effective approach to improve As(V) co-precipitation with Fe(III)(oxyhydr)oxides, but it is relatively ineffective for As(III) co-precipitation. Therefore, we suggest pH reduction only when As(V) is the predominant As species, e.g. in rapid sand filter influent which has been pre-treated with KMnO_4 or in rapid sand filter effluent.

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SUPPLEMENTARY INFORMATION

Figure S4.1 SEM-EDX analysis of the surface of RSF media grain. Fe and Mn are clearly detected by EDX in the coating of media from both WTPs. A high degree of surface roughness is observed for both the materials when analyzed with SEM, as well as cracks in the surface coating. Similar physical characteristics of the surface of the RSF media collected from full-scale WTPs were also observed by Jessen et al. (2005) and Sharma (2001). The surface morphologies nevertheless are quite distinct, with the surface relatively smooth and less porous for WTP 1 than WTP 2. Moreover, the surface coating on both the materials consists of agglomerated spherical phases.

Figure S4.2 Aqueous As species in function of time during batch experiments with WTP 1 filter media and rapid sand filter effluent with (A) 100 µg/L As(V) spike and (B) 100 µg/L As(III) spike.

Figure S4.3 Arsenic speciation in the influent of rapid sand filters at WTP 1, without or with treatment with KMnO_4 .

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Chapter 5

Impact of phosphate, silicate and natural organic matter on the size of Fe(III) precipitates and arsenate co-precipitation efficiency in calcium containing water

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ABSTRACT

Removal of arsenic (As) from water by co-precipitation with Fe(III) (oxyhydr)oxides is a widely used technique in water treatment. Nevertheless, As removal efficiency appears to be sensitive to the composition of the water matrix. The aim of this study was to gain a deeper understanding of the independent and combined effects of silicate (Si), phosphate (P), natural organic matter (NOM) and calcium (Ca) on arsenate [As(V)] co-precipitation efficiency and the size of Fe(III) precipitates. We found that, in complex solutions containing multiple solutes and high levels of Ca, (variations in) Si and P concentrations reduce As(V) removal to some extent, mainly due to a decreased adsorption of As(V) onto Fe(III) precipitates. On the other hand, NOM concentrations reduced As(V) removal to a much greater extent, due to possible formation of mobile Fe(III)–NOM complexes that were difficult to remove by filtration. These findings have a great significance for predicting As(V) removal as a function of seasonal and process-related water quality changes at water treatment plants.

5.1 INTRODUCTION

The co-precipitation of arsenic (As) with *in situ* produced Fe(III)(oxyhydr)oxides is a widely used As removal technique in water treatment (Fuller et al. 1993, Roberts et al. 2004, Van Genuchten et al. 2012b). Typically, an Fe(III) coagulant such as ferric chloride (FeCl_3) is dosed which, in contact with water, undergoes hydrolysis to form Fe(III)(oxyhydr)oxide precipitates. Arsenic adsorbs onto the surface of the Fe(III) precipitates, at an early stage of the precipitate growth (Hering et al. 1996a, Jain et al. 1999, Qiao et al. 2012, Van Genuchten et al. 2012b, Waychunas et al. 1993). The As bearing Fe(III) precipitates (i.e. co-precipitated As and Fe(III)) can be removed from water in a downstream granular media filter or e.g. with low-pressure membranes (Choi and Dempsey 2004, Jessen et al. 2005). At pH relevant to most natural waters (6.5–8.5), As(V) is negatively charged and therefore exhibits a higher affinity for the surface of Fe(III) precipitates than As(III) which is uncharged (Hering et al. 1996a, Lakshmanan et al. 2008, Smedley and Kinniburgh 2002). Therefore, in order to effectively remove As from ground water, oxidizing As(III) to As(V) e.g. by adding potassium permanganate (KMnO_4) before co-precipitation with Fe(III)(oxyhydr)oxides has previously been suggested (Ahmad et al. 2018, Guan et al. 2009a, Guan et al. 2009b, Sorlini and Gialdini 2010). Recent studies have shown that As(III) also oxidizes rapidly to As(V) during rapid sand filtration (RSF), a treatment step commonly used at water treatment plants (Ahmad et al. 2018, Gude et al. 2018a, Gude et al. 2016). Thus, the use of KMnO_4 in water treatment can be avoided by treating the RSF effluent for As(V) removal instead of treating the raw groundwater for As(III) removal.

The removal efficiency of As(V) with Fe(III) based co-precipitation is sensitive to the ionic composition of water (Davis and Edwards 2017, Dong et al. 2011, Guan et al. 2009a, Guan et al. 2009b, Kanematsu et al. 2010, 2013b, Qiao et al. 2012). The most abundant oxyanions that may impact As(V) removal are silicate (i.e. H_4SiO_4) and phosphate (i.e. H_2PO_4^- or HPO_4^{2-}), denoted further as Si and P respectively (Meng et al. 2000, Van Genuchten et al. 2012b, Van Genuchten et al. 2014b). Moreover, natural organic matter (NOM), especially humic substances (HS), can adversely affect As(V) removal (Davis and Edwards 2017, Sharma et al. 2010, Weng et al. 2009). These inorganic and organic solutes can modify the structure, composition and identity of the Fe(III) precipitates, thereby affecting their size and As(V) uptake behaviour (Sposito 2008, Van Genuchten et al. 2014b). Moreover, these solutes compete with As(V) for adsorption sites on Fe(III) precipitates (Chen et al. 2014, Dixit and Hering 2003, Hering et al. 1996a, Meng et al. 2000, Su and Puls 2001, Weng et al. 2009, Wilkie and Hering 1996, Younggran et al. 2007). On the other hand, natural waters often contain calcium ions (Ca) which can increase As(V)

removal during Fe(III) based co-precipitation. It has been shown that Ca increases the size of Fe(III) precipitates (Ahmad et al. 2019b) and also results in an increased uptake of As(V) by Fe(III) precipitates. Several mechanisms have been proposed to explain these observations, such as neutralization of the Fe(III) precipitate surface charge by Ca (Wilkie and Hering 1996), suppression of electrostatic repulsion (Masue et al. 2007) and the formation of ternary complexes between Fe(III), As(V) and Ca (Kanematsu et al. 2013b, Van Genuchten et al. 2014a).

So far, most of the available studies have focused on the interactions between As(V) and Fe(III) precipitates in simple solutions (Laky and Licskó 2011, Weng et al. 2008, Weng et al. 2009), whereas systematic studies providing understanding of the As(V)–Fe(III) interactions in complex multi-solute solutions are lacking. In this study, we aim to provide more insights into the independent and combined effects of Si, P, NOM and Ca on As(V) co-precipitation efficiency and the size of formed Fe(III) precipitates.

5.2 MATERIALS AND METHODS

5.2.1 Chemicals and stock solutions

All chemicals were reagent grade and used without any purification. The stock solutions of 1.4 g/L FeCl_3 , 92.9 g/L NaHCO_3 , 15 g/L NaCl , and 30.2 g/L Na_2SiO_3 were prepared by dissolving the required amounts of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (CAS: 10025-77-1, 97% purity, J.T Baker The Netherlands), NaHCO_3 (CAS: 144-55-8, >99% purity, J.T Baker The Netherlands), NaCl (CAS: 7647-14-5, 99% purity, J. T Baker The Netherlands) and $\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$ (CAS: 10213-79-3, 99% purity, Sigma-Aldrich) respectively in ultrapure water (Mill-Q, produced by purifying distilled water with a Purelab Chorus provided by Veolia). The stock solutions of 73.8 g/L CaCl_2 , 39.2 g/L MgCl_2 and 0.45 g/L NaH_2PO_4 were prepared by dissolving CaCl_2 anhydrous (CAS: 10043-52-4, 96% purity, J. T Baker), $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ (CAS: 7791-18-6, 99% purity, Boom B.V.) and $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ (CAS: 10049-21-5, >98% purity, J.T Baker) respectively in 0.1 M HCl. The NOM stock solution of 2.4 g DOC/L was prepared by diluting a primary stock (HumVi, Vitens, The Netherlands, 117.4 g DOC/L) that contained ca. 75% HS (LC-OCD results given in Table S5.1). Arsenate was dosed using a stock solution of 1.0 g/l As_2O_5 (CAS: 12044-50-7, 99% purity, Inorganic Ventures). pH was adjusted with 0.1 M HCl or 0.1 M NaOH.

5.2.2 Composition of initial solutions

The experiments were performed with synthetic solutions and real RSF effluent collected from WTP Ouddorp (Table 5.1). The ionic composition of the synthetic

initial solutions in the experiments (Table 5.1) was based on the yearly variation recorded in the quality of RSF effluent at the WTP (Table S5.2). The synthetic initial solution in the reference experiment contained 0.07 μM As(V) and 2000 μM Ca, without Si, P and NOM. The rest of the experiments are identified by the ions added in μM to the reference solution (i.e. 70Si consists of 70 μM Si, 0.07 μM As(III) and 2000 μM Ca). All the synthetic initial solutions also contained 4.1 mM NaHCO_3 and 0.6 mM NaCl to provide alkalinity and ionic strength.

The experiments with the RSF effluent were performed with and without pre-treatment with anion exchange (AEX) or cation exchange (CEX). The objective of the AEX or CEX pre-treatment was to remove the naturally present anions or cations from the RSF effluent before use as initial solution in the experiments, to determine the impact of natural anions or cations on Fe(III) precipitation and As(V) removal. The AEX was performed with Amberlite® IRA-400 chloride form resin (CAS: 60177-39-1) and the CEX was carried out with Amberlite® IR120 N⁺ form (CAS: 68441-33-8), both were obtained from Sigma Aldrich, Zwijndrecht, The Netherlands. Each IEX treatment was performed in a glass column with a contact time of 1 min and bed volumes of 78 cm³. The RSF effluent based initial solutions were spiked with As(V) to achieve As concentration of 0.07 $\mu\text{mol/L}$ (i.e. similar As concentration as synthetic initial solutions). The AEX effluent samples were dosed with NaHCO_3 to compensate for the loss of HCO_3^- during AEX.

5.2.3 Co-precipitation experiments

The experiments were performed with a 5 L glass reactor connected to a controller (ez-Control, Applikon® Biotechnology) for adjusting, maintaining and logging (BioXpertV2 software) reaction parameters, including the pH, temperature, oxidant supply and stirring speed (Fig 5.1). The reactor was connected to a Mastersizer 2000 (Malvern Instruments, UK). The experiments were carried out at pH 7.5 and 20°C, with stirring set to 100 rpm. The experimental procedure included: (i) preparation of the initial solutions in the reaction vessel and collection of solution samples for control, (ii) dosing the FeCl_3 stock to result in Fe(III) concentration of 5 $\mu\text{mol/L}$ and allowing the hydrolysis and precipitation of Fe(III) to take place while the suspension was stirred at 100 rpm and (iii) collection of suspension samples after 1 and 60 min of FeCl_3 addition, which were filtered over 0.45 μm filters to determine the removal of Fe(III) precipitates. The samples were preserved for subsequent analysis. The unfiltered samples without conservation were collected for zeta-potential measurements.

For the filtration of samples Spartan™ 30/0.45 RC 0.45 μm syringe filters (GE Healthcare, Buckinghamshire, UK) were used. Samples for Fe, As, Si, Ca and P were conserved by addition of 50 μL 60% HNO_3 solution to 50 mL of sample and stored

at 4 °C. The removal of As and Fe were determined from the difference between the measured values of the initial solution and final filtered solution. Samples for DOC analysis were conserved by adding 200 µL 40% HCl solution to 100 ml of sample which was closed off airtight and stored at 4 °C.

Table 5.1 Nomenclature and composition of the initial solutions used in the co-precipitation experiments. In all the initial solutions the concentration of Fe(III) was 5 µmol/L, As(V) was 0.07 µmol/L (As/Fe=0.014) and HCO₃ was 4100 µmol/L. The concentration of Ca was 2000 µmol/L in all the synthetic initial solutions (Ca/Fe=400). In RSF effluent the concentration of Ca was 2200 µmol/L (Ca/Fe=440), which was reduced to <1 µmol/L after CIEX treatment.

Experiment code	Si	P	DOC	Si/Fe	P/Fe	DOC/Fe
	µmol/L			mol/mol		
Reference (Ref)	–	–	–	–	–	–
Si70	70	–	–	14	–	–
Si140	140	–	–	28	–	–
Si280	280	–	–	56	–	–
P1.3	–	1.3	–	–	0.26	–
P2.5	–	2.5	–	–	0.5	–
P3.3	–	3.3	–	–	0.66	–
DOC165	–	–	165	–	–	33
DOC330	–	–	330	–	–	66
DOC500	–	–	500	–	–	100
Si0 + P1.3+ DOC165	–	1.3	165	–	0.26	33
Si140 + P1.3 + DOC165	140	1.3	165	28	0.26	33
Si280 + P1.3 + DOC165	280	1.3	165	56	0.26	33
Si140 + P2.5 + DOC165	140	2.5	165	28	0.5	33
Si140 + P3.3 + DOC165	140	3.3	165	28	0.66	33
Si140 + P1.3 + DOC330	140	1.3	330	28	0.26	66
Si140 + P1.3 + DOC500	140	1.3	500	28	0.26	100
Effluent RSF ⁺	153	1.5	172	31	0.3	34
Effluent RSF after CIEX ⁺	159	1.5	175	32	0.3	35
Effluent RSF after AIEX ⁺	160	BDL	59	32	–	12

*HCO₃ was compensated after the AIEX treatment. ⁺ As(V) was spiked using a stock solution. BDL: below detection limit (<0.2 µmol/L)

Figure 5.1 A schematic overview of the laboratory setup.

5.2.4 Wet analysis

Arsenic, Fe, Ca, Si, P were measured in water samples by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) (XSERIES 2, Thermo Fisher Scientific, The Netherlands). The analysis of DOC in water samples was carried out with a Shimadzu TOC-V_{CPH} total organic carbon analyzer (Shimadzu Benelux, 's-Hertogenbosch, The Netherlands). Bicarbonate was analyzed by titration (HI-3811, Hanna Instruments).

5.2.5 Particle characterization

The size distribution of the Fe(III) precipitates was determined by Multiple Light Scattering (MLS) using the Mastersizer 2000 (Malvern Instruments, UK). The Mastersizer was connected to the co-precipitation reactor and the suspension was fed to the Mastersizer at a constant flow of 216 mL/min through a masterflex easy-load II peristaltic pump combination (Metrohm Nederland B.V. The Netherlands). Malvern instruments mastersizer 2000 software v5.61 recorded the particle size distribution every 20 seconds for 5 min. The Zetasizer Nano-ZS (Malvern Instruments) was used for the determination of electrophoretic mobility and the calculated zeta-potential of the particles in a sub-set of samples collected after 60 min of FeCl₃ dosing. Each sample was equilibrated at 20 °C for 300 seconds prior to measurement which were obtained in duplicate. The measurement cell (cuvette) was rinsed with ethanol and demineralized water and dried between the measurements.

5.3 RESULTS AND DISCUSSION

5.3.1 Size distribution and filterability of Fe(III) precipitates

5.3.1.1 Impact of independent Si, P and NOM addition

The particle size distribution and the removal efficiency of Fe(III) precipitates by 0.45 μm filters as a function of the composition of initial solution are given in Fig 5.2 and Fig 5.3 respectively. For the reference experiment, (initial solution free of Si, P and NOM), the particles were in the range of 5–180 μm with the mode of the distribution (d_m , the most commonly occurring particle diameter) at 70 μm . The precipitates in both 1 min and 60 min samples were completely removed ($\approx 100\%$ removal) by 0.45 μm filtration, indicating a rapid growth of Fe(III) precipitates within the first minute. When different concentrations of Si or P were added, the size distribution of the precipitates was not significantly affected, although a slightly lower d_m ($\approx 50 \mu\text{m}$) was noted for the highest Si and P additions (i.e. 280 μM Si and 3.3 μM P) compared to the reference ($d_m \approx 70 \mu\text{m}$). Nevertheless, the precipitates were completely removed by 0.45 μm filtration in all the samples, indicating yet effective and rapid Fe(III) precipitate growth. Silicate and P oxyanions bind to the surface of Fe(III) precipitates and result in colloidally stable suspensions (Doelsch et al. 2000, Rose et al. 1996). On the other hand, it has been shown that in the presence of Ca the electrostatic repulsion between the particles is reduced, which can result in coagulation/destabilization of colloidal Fe(III) precipitates. For example, Mayer and Jarrell (1996) reported an improved flocculation, settling and filtration of Fe(III) precipitates in a solution where the molar Si/Fe and Ca/Fe ratio was 4.5 and 20 (Ca/Si = 0.2). In our study, however, the molar Ca/Si ratio was much higher (Ca/Si = 7–28) than in the study of Mayer and Jarrell (1996). Similarly, Van Genuchten et al. (2014b), in their co-precipitation experiments, noticed a stabilization of Fe(III) suspensions at molar P/Fe ratio of 0.3 and destabilization of the colloids was observed when Ca was present at Ca/Fe = 2.0 (Ca/P = 6.7). In our study the molar Ca/P was 570–1300, thus much higher than Van Genuchten et al. (2014b). From this we conclude that in our study the large size and highly efficient removal of the Fe(III) precipitates by 0.45 μm filtration with the independent additions of Si and P was due to the presence of high Ca concentration in water (Table 5.1).

Unlike the Si and P additions, the independent NOM addition altered the particle size distribution significantly (Fig 5.2). The particle size distribution was bimodal for 330 and 500 μM DOC additions, consisting of a larger contribution from particles in the non-colloidal size range (i.e. $\geq 1 \mu\text{m}$) and a relatively small contribution in the colloidal range ($< 1 \mu\text{m}$) for each case (please note that the precipitate size distribution was not measured for 165 μM DOC addition). Moreover, Fe(III) removal by 0.45 μm filtration was significantly reduced (e.g. with the additions of 165, 330 and 500

μM DOC, Fe(III) removal after 60 min was ≈ 40 , 30 and 20% respectively, Fig 5.3). These observations are in agreement with several previous studies which also report a similar reduction in the removal of Fe(III) in the presence NOM. The suppression of Fe(III) removal by filtration has been attributed to formation of soluble Fe(III)–NOM complexes, as well as formation of Fe(III)–NOM and Fe(III)(oxyhydr)oxide–NOM colloids (Davis and Edwards 2017, Kim et al. 2015, Sharma et al. 2010). These different Fe(III)–NOM complexes, which can be soluble and/or colloidal, are not removed from water by $0.45\ \mu\text{m}$ filtration due to their small size. Although the exact mechanism for the decreased Fe(III) removal in the presence of NOM in our study is not clarified, it is proposed that the mobility of Fe(III) was attributed to the formation of soluble and colloidal Fe(III)–NOM complexes.

To study further the precipitate aggregation, we characterized the particles from a subset of experiments by zeta-potential measurements. The zeta-potential of the reference sample was low ($-2.6\ \text{mV}$, Table 5.2) and no considerable decrease was observed with the addition of $3.3\ \mu\text{M}$ P ($-2.8\ \text{mV}$). This is in agreement with the yet effective aggregation of Fe(III) precipitates with the independent P addition, similar to the reference. In the presence of $165\ \mu\text{M}$ DOC the zeta-potential decreased somewhat ($-11.1\ \text{mV}$), which is in agreement with the restricted growth of the precipitates in the presence of $165\ \mu\text{M}$ DOC, due to electrostatic repulsion between the Fe(III) particles.

5.3.1.2 Impact of combined Si, P and NOM addition

In experiments where P and NOM were present with and without Si, the Fe(III) particles were smaller than in the reference (Fig 5.2). Moreover, the removal of Fe(III) precipitates by $0.45\ \mu\text{m}$ filtration was lower than the reference ($\leq 80\%$ compared to 100%) (Fig 5.3). Minor changes in the precipitate size were observed with the variation in solution composition. For example, in the absence of Si when $1.3\ \mu\text{M}$ P was present with $165\ \mu\text{M}$ DOC, particles in the range of $1.4\text{--}70\ \mu\text{m}$ were observed with d_m of $\approx 20\ \mu\text{m}$. The addition of 140 to $280\ \mu\text{M}$ Si in this solution resulted in a very slight decrease in the removal of Fe(III) precipitates by $0.45\ \mu\text{m}$ filtration ($\approx 10\%$). Moreover, the precipitate size range was similar to the solution that did not contain Si (i.e. $1.3\ \mu\text{M}$ P and $165\ \mu\text{M}$ DOC). Similarly, the precipitate size distribution and the removal efficiency of Fe(III) was not significantly affected in the experiments where the concentration of P was increased from 1.3 to $3.3\ \mu\text{M}$, keeping Si and DOC fixed at 140 and $165\ \mu\text{M}$ respectively. Thus, the studied variations in Si and P concentrations with fixed concentrations of NOM and Ca in water, did not severely impact the size of Fe(III) precipitates.

Compared to when only NOM ($165\ \mu\text{M}$ DOC) was present, the Fe(III) removal by $0.45\ \mu\text{m}$ filtration was higher when NOM was present with P and Si (Fig 5.3).

Figure 5.2 Independent and combined effects of silicate, phosphate and natural organic matter on Fe(III) precipitate size. X-axis: particle size (μm). Y-axis: abundance (%). *Ref* refers to the reference experiment performed in the absence of Si, P and NOM. In (Figure 5.2f & 5.2g) complete Y-axis is not shown. In Figure 5.2f the abundance peak of *Si140+P1.3+DOC 500* is at 35.4%. In Figure 5.2g the abundance peak of *Effluent RSF after CEX* is at 25.5%.

Also, the zeta-potential with the independent NOM addition was -11.1 mV, which was lower relative to the experiments in which NOM was present with Si and P (Table 5.2). The higher zeta-potential obviously is in agreement with the large size and higher removal of Fe(III) precipitates in the complex NOM bearing solutions (Fig 5.2 and Fig 5.3). However, the exact mechanism responsible for the higher zeta-potential when NOM co-occurred with Si and P is not clarified. Nevertheless, we note that the interactions between NOM and Fe(III) in the absence and presence of P and Si appear to follow different mechanisms.

When the concentration of NOM was increased (from 165 to 330 μM DOC), keeping Si and P (140 and 1.3 μM respectively) fixed, the Fe(III) removal by 0.45 μm filtration was reduced significantly. A further increase in NOM concentration (to 500 μM DOC) resulted in no Fe(III) removal (Fig 5.3). This increasing mobility of Fe(III) may be attributed to the formation of soluble and colloidal Fe(III) – NOM complexes that were not removed with the 0.45 μm membrane filters. The presence of colloidal particles is also confirmed with the particle size distribution measurements (Fig 5.2). However, the identity of the particles (Fe(III)–NOM or Fe(III)(oxyhydr)oxide–NOM colloids) was not investigated. Moreover, the properties of the soluble fraction of Fe(III)–NOM complexes remain unclear. Nevertheless, our results indicate that the variations in NOM concentrations, in solution with fixed concentrations of Si, P and Ca exhibit a strong impact on the size of Fe(III) precipitates and their removal.

5.3.1.3 Impact of removing anions and cations from RSF effluent

In the RSF effluent, the Fe(III) precipitate size ranged from 2–80 μm with the d_m at 25 μm (Fig 5.2). The Fe(III) precipitates were effectively removed ($\approx 95\%$ removal) by 0.45 μm filtration in both 1 min and 60 min samples (Fig 5.3). The removal of Fe(III) precipitates in the RSF effluent was slightly higher than the synthetic solutions that contained Si, P and NOM in comparable concentrations. This can be explained by a higher charge neutralization due to the higher Ca concentration and an additional presence of ≈ 10 mg/L magnesium (Mg) in the RSF effluent compared to the synthetic solutions (Table S5.2). When the RSF effluent was pre-treated with AEX, P and a major portion of the NOM (negatively charged) was removed from water (Table 5.1). The AEX did not remove Si (H_4SiO_4) because it is not disassociated at the given pH of 7.5 (de Ridder et al. 2018). Interestingly, the precipitate size distribution was quite similar to the reference (i.e. in the absence of Si, P, NOM) and in solutions where we added Si. The removal efficiency of Fe(III) in the AEX treated RSF effluent was clearly higher than the untreated RSF effluent (Fig 5.3) which can be attributed to a lower charge repulsion between the particles in the absence of surface sorbed (negatively charged) P and NOM ions.

When the CEX treated RSF effluent, which lacked Ca and Mg ions (Table 5.1), was used as the initial solution in the co-precipitation experiments, the particle size decreased and the removal of Fe(III) precipitates by 0.45 μm filtration strongly depleted (Fe(III) removal <10%). It has been shown previously that the presence of cations in solutions result in neutralization of Fe(III) precipitate surface charge and a lower electrostatic repulsion which promotes growth of Fe(III) precipitates (Ahmad et al. 2019b, Van Genuchten et al. 2014a, Van Genuchten et al. 2014b). In this study, when Ca and Mg were removed from water by CEX, the sorption of Si, P and NOM on Fe(III) precipitate surface resulted in a negatively charged precipitate surface with high electrostatic repulsion which hindered the precipitate growth (de Ridder et al. 2018).

Figure 5.3 Percentage Fe(III) removed by 0.45 μm filtration as a function of the composition of the initial solution and time. *Ref* refers to the reference experiment performed in the absence of Si, P and NOM.

5.3.2 Arsenic removal

5.3.2.1 Impact of independent Si, P and NOM additions

Arsenate removal was the highest in the reference experiment (i.e. in the absence of Si, P and NOM), with As(V) removal efficiency of 65% and $\approx 90\%$ after 1 min and 60 min respectively (Fig 5.4A). This represents a $\approx 75\%$ of the total As(V) removed in the first minute, indicating a rapid adsorption of As(V) to Fe(III) precipitate

surfaces. Since Fe(III) precipitates were completely removed by 0.45 μm filtration after both 1 min and 60 min (Fig 5.3), the $\approx 25\%$ increase in As(V) removal in reference experiment was attributed to the diffusion-controlled mass transfer of As to adsorption sites located in the internal porosity of Fe(III) precipitates (Fig 5.4). The similar time-dependent As(V) adsorption kinetics observed in the presence of Si, P and NOM can also be explained by the slow transfer of As towards the internal adsorption sites (Fig 5.4B). The independent additions of Si, P and NOM resulted in a lower As(V) removal efficiency compared to the reference (Fig 5.4A). The addition of 70 μM Si resulted in As(V) removal efficiency of 45% and 75% after 1 min and 60 min, which decreased to $\approx 40\%$ and 60% respectively, with the independent addition of the highest concentration of (280 μM Si). The addition of 1.3 μM P resulted in an As(V) removal efficiency of 25% and 44% after 1 min and 60 min, which decreased to $\approx 20\%$ and 30% respectively, with the independent addition of the highest concentration of P (3.3 μM P). As the removal of Fe(III) precipitates by 0.45 μm filtration was (nearly) complete (Fig 5.3), we conclude that the reduced As(V) removal was due to a reduced adsorption of As(V) onto the surface of Fe(III) precipitates, similar to the reference (Dixit and Hering 2003, Meng et al. 2000).

Fig 5.4B shows that the independent P additions, though much smaller compared to Si (Table 5.1), results in a lower As(V) adsorption efficiency than with Si additions. These results can be explained by the pH dependent affinity of As(V), P and Si for the adsorption sites on Fe(III) precipitates (Ahmad et al. 2019b, Van Genuchten et al. 2014b, Voegelin et al. 2010) and the concentration differences between Si and P relative to As(V). The adsorption of As(V), Si and P onto the surface of Fe(III) precipitates is competitive. However, at pH 7.5 (this study), As(V) and P exhibit a similarly high affinity for adsorption sites on Fe(III) precipitates due to their negative charge and similar chemical properties. Silicate, on the other hand, is uncharged at pH 7.5 and the adsorption onto Fe(III) precipitates is much lower than As(V) and P. Thus, the greater reduction in As(V) adsorption due to lower P concentrations than Si is rationalized.

The As(V) removal efficiency was the lowest with the independent NOM additions. For example, the addition of 165 μM DOC resulted in As(V) removal efficiency of $\approx 20\%$ and 35% after 1 min and 60 min, which decreased to 10% and 15% respectively with the independent addition of 500 μM DOC. The lower As(V) removal efficiency (Fig 5.4A) compared to the reference was due to i) the lower adsorption of As(V) onto the surface of Fe(III) precipitates, as reflected in the lower As/Fe solids ratio for NOM additions (Fig 5.4B), and ii) a higher mobility of Fe(III) due to the formation of Fe(III)–NOM complexes that were not removed by 0.45 μm filtration (Fig 5.3). With NOM additions, the As/Fe solid ratio was higher than the As/Fe solid ratio with P additions. This indicates a stronger competition with As(V)

for adsorption sites by P than NOM (Fig 5.4B). Compared to the Si additions, the As/Fe solid ratio was slightly lower in case of NOM additions. This indicates a stronger competition with As(V) for adsorption sites by NOM than Si (Fig 5.4B). Thus, in the given conditions, P competed with As(V) for adsorption sites on Fe(III) precipitates most strongly and reduced the As(V) adsorption followed by NOM, whereby Si showed had the least negative impact on As(V) adsorption.

From these results it can be concluded that the removal of As(V) in the presence of Si and P was affected mainly because of the reduced adsorption of As(V), whereas in the presence of NOM a reduced adsorption and a reduced Fe(III) removal both were responsible. Phosphate reduced As(V) adsorption the most, mainly because of its similar affinity for adsorption sites and higher concentration than As(V). But, the overall As(V) removal efficiency was reduced the most with the variations in NOM concentrations, mainly because NOM rendered a large portion of Fe(III) mobile in the solution.

5.3.2.2 Impact of combined Si, P and NOM additions

In the experiments where 165 μM DOC was fixed and P and Si concentrations were varied, the As(V) removal efficiency was lower than the reference experiment and the experiments with the corresponding independent Si, P and NOM additions (Fig 5.4A). For example, with 165 μM DOC fixed, the addition of 1.3 μM P resulted in As(V) removal efficiency of 17 and 32% after 1 min and 60 min. This was lower than the As(V) removal efficiencies observed for the independent 1.3 μM P (25% and 44% after 1 min and 60 min) and 165 μM DOC (22% and 37% after 1 min and 60 min) additions. The lower As removal can be attributed to i) a greater competition for the adsorption of As(V) onto Fe(III) precipitates due to the presence of multiple inorganic and organic ions, as also confirmed by the lower As/Fe solid ratios, and ii) a NOM-induced higher mobility of Fe(III) (Fig 5.3), as discussed previously.

At fixed P and NOM concentrations (1.3 μM P and 165 μM DOC), the addition of Si up to 280 μM resulted in only a slight reduction in As(V) removal efficiency compared to the absence of Si. Similarly, the removal efficiency of As(V) was reduced only slightly when P concentrations were increased up to 3.3 μM in the presence of 140 and 165 μM Si and DOC respectively. The subtle decrease in As(V) removal was attributed to a stronger competition for As(V) adsorption onto Fe(III) precipitates which resulted in a lower As/Fe solid ratio (Fig 5.4B). Arsenate removal efficiency was majorly reduced with an increase in NOM concentration, with Si and P also present in water at fixed concentrations. For example, when 500 μM DOC was added along with 140 μM Si and 1.3 μM P, As(V) removal was reduced to zero. The absence of As(V) removal (Fig 5.4A) was due to formation of Fe–NOM complexes that could not be filtered, as discussed previously.

Figure 5.4 (a) Percentage As(V) removed by 0.45 μm filtration and (b) As(V) uptake by Fe(III) precipitates as a function of the composition of the initial solution and time. *Ref* refers to the reference experiment performed in the absence of Si, P and NOM.

Overall, it can be concluded that in complex solutions, containing Si, P, NOM and Ca, As(V) removal appears to be most sensitive to variations in NOM concentration, with NOM- Fe(III) complexation a key determinant.

5.3.2.3 Impact of removing anions and cations from RSF effluent

In the RSF effluent, the As(V) removal was lower than the reference experiment, i.e. As(V) removal was 46% in the RSF effluent compared to $\approx 90\%$ for the reference solution after 60 min (Fig 5.4A). The lower As(V) removal in RSF effluent compared to the reference was largely due to competition for As(V) adsorption from the anions

such as Si, P and NOM. This was also confirmed by pre-treating the RSF effluent by AEX which showed that As(V) removal significantly increased with the removal of P and NOM (Table 5.1). The removal of Si with AEX treatment was not effective and therefore Si competed with As(V) for the adsorption sites, resulting in As/Fe solid ratio that matched the experiments where independent Si additions were investigated (Fig 5.4B).

Arsenate removal was absent when the CEX-pre-treated RSF effluent was used as initial solution. The fact that no removal was observed in the absence of Ca and Mg is mainly due to the high mobility of Fe(III), which can be attributed to the highly negative surface of Fe(III) precipitates that hinders the growth of Fe(III) precipitates to become larger particles. The mechanistic understanding of how cations like Ca interact with Fe(III) precipitates in multi-anionic solutions has been presented in previous studies. It has been reported that when Ca is present during co-precipitation of Fe(III) and (oxy)anions such as Si, P, As(V) and NOM, it is incorporated in the structure of the growing Fe(III) precipitates due to chemical bonding with the surface-sorbed oxyanions (Van Genuchten et al. 2014a). Moreover, Ca interacts electrostatically with the surface of Fe(III) precipitates. Magnesium ions have also been shown to enhance aggregation of Fe(III) precipitates, but the effect is less pronounced than Ca (Senn et al. 2015, Van Genuchten et al. 2014b).

Table 5.2. The zeta-potential of Fe(III) precipitates in a sub-set of experiments.

Experiment code	Zeta-potential [mV]
Reference	-2.6 ± 0.9
P3.3	-2.8 ± 0.6
DOC165	-11.1 ± 1.5
P1.3 + DOC165	-5.5 ± 1.9
Si140 + P1.3 + DOC165	-5.7 ± 0.9
Si280 + P1.3 + DOC165	-7.6 ± 0.2
Si140 + P2.5 + DOC165	-7.1 ± 0.6
Si140 + P1.3 + DOC330	-13.1 ± 0.3
RSF effluent	-7.0 ± 1.2

5.4 CONCLUSIONS AND IMPLICATIONS FOR WATER TREATMENT

This study shows that As(V) removal in Fe(III) based co-precipitation is sensitive to the composition of water matrix. In complex solutions containing multiple solutes and high levels of Ca, (variations in) Si and P concentrations reduce As(V) removal to some extent, mainly due to a decreased adsorption of As(V) onto Fe(III) precipitates. On the other hand, NOM concentrations reduce As(V) removal quite drastically, which we attribute largely to the formation of soluble and colloidal Fe(III)–NOM complexes.

The findings presented in this study have a great significance for predicting As removal at water treatment plants where water quality changes may take place, e.g. due to seasonal effects. Surface complexation modeling (Dzombak and Morel 1990, Hiemstra and Van Riemsdijk 1999, Kanematsu et al. 2010, 2013b, Stachowicz et al. 2008) is useful in gaining further insights in the As uptake by Fe(III) precipitates, but its application to real water treatment systems is limited. In water treatment plants, the effectiveness of As removal also depends on the separation of Fe(III) precipitates from water. Calcium effectively counteracts the negative effect of oxyanions and promotes the growth of Fe(III) precipitates, which can be easily separated from water by gravitation settling and rapid sand filtration. Thus, hardness of water should be carefully considered in designing As removal processes that rely on the co-precipitation of As and Fe. Obviously, effective separation of the colloidal particles can also be achieved by employing low-pressure membrane filtration (MF/UF) instead of the conventional rapid sand filtration for effective separation of the colloidal particles. Nevertheless, also in this case, the charge and size distribution of Fe(III) precipitates will remain crucial in determining the membrane fouling mechanisms.

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SUPPLEMENTARY INFORMATION

Table S5.1 NOM characterization of a solution of ultrapure water spiked with NF concentrate to achieve ca. 3 mg/L DOC, obtained by LC–OCD analysis.

DOC - Dissolved	µg/l C	3140
DOC - HOC, hydrophobic	µg/l C	451
DOC - CDOC, hydrophilic	µg/l C	2689
CDOC - Bio-polymers	µg/l C	6
CDOC - Bio-polymers - DON	µg/l N	3
CDOC - Bio-polymers - N/C	µg/µg	0.51
CDOC - Bio-polymers - Proteins	%	unknown
CDOC - Humic substances (HS)	µg/l C	2370
CDOC - Humic substances - DON	µg/l N	30
CDOC - Humic substances - N/C	µg/µg	0,01
CDOC - Humic substances - Aromaticity	L/(mg*m)	3,82
CDOC - Humic substances - Mol-Weight	g/mol	749
CDOC - Building Blocks	µg/l C	183
CDOC - LMW acids	µg/l C	<1
CDOC - LMW Neutrals	µg/l C	130
Inorganic Colloidal (SAC)	m-1	<0.01
SUVA (SAC/DOC)	L/(mg*m)	3.18

Table S5.2 Quality of rapid sand filter effluent collected from WTP Ouddorp in The Netherlands, based on the 2016-18 (n=25) data provided by the in charge water company.

Parameter	Unit	RSF effluent Ouddorp
Temp	°C	9.4-16.2
pH		7.75-7.87
Dissolved Oxygen	mg/L O ₂	6.5-8.0
Electrical Conductivity	mS/m	55-68
Bicarbonate	mg/L HCO ₃	235-260
Turbidity	NTU	0.01-0.03
Arsenic	µg/L As	1.9-3.2
Iron	mg/L Fe	<0.01-0.08
Manganese	mg/L Mn	<0.01
Orthophosphate	µg/L P	6.0-120
Silicate	mg/L Si	3.0-4.0
Total organic carbon	mg/L C	1.5-3.9
Ammonium	mg/L NH ₄	<0.02
Nitrite	mg/L NO ₂	<0.007
Nitrate	mg/L NO ₃	1.4-2.5
Calcium	mg/L Ca	77-83
Magnesium	mg/L Mg	9.7-10
Sulphate	mg/L SO ₄	30-39
Sodium	mg/L Na	34-50
Chloride	mg/L Cl	67-94

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Chapter 6

Mechanisms of arsenate removal and membrane fouling in ferric based co-precipitation and low pressure membrane filtration systems

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ABSTRACT

Ferric based coprecipitation–low pressure membrane filtration is a promising arsenic (As) removal method, however, membrane fouling mechanisms are not fully understood. In this study we investigated the effect of feed water composition and membrane pore size on As removal and membrane fouling. We observed that As removal efficiency was independent of the membrane pore size because the size of the Fe(III) particles was larger than the pore size of the membranes, attributed to a high calcium concentration in the feed water. Arsenic coprecipitation with Fe(III) (oxyhydr)oxides rapidly reached equilibrium before membrane filtration, within 1 min. Therefore, As removal efficiency was not improved by increasing residence times before membrane filtration. The removal of As(V) was strongly dependent on feed water composition and a higher Fe(III) dose was required to reduce As to sub- $\mu\text{g/L}$ levels for feed water having a higher concentration of oxyanions and a lower concentration of cations. Cake-layer formation was observed to be the predominant membrane fouling mechanism.

6.1 INTRODUCTION

Arsenic (As) is a well-known human carcinogen, classified in Group 1 by International Agency for Research on Cancer - IARC (Ferrecchio et al. 2000, Kapaj et al. 2006, Steinmaus et al. 2010). The WHO guideline for As in drinking water is 10 µg/L, however concerns are growing that chronic ingestion of low As concentrations can also adversely affect human health (Ahmad and Bhattacharya 2019, Saint-Jacques et al. 2018). Therefore, certain water treatment companies aim to produce drinking water with As concentrations below 1 µg/L (Ahmad and Bhattacharya 2019, Ahmad et al. 2019c, Van der Wens et al. 2016).

Coprecipitation of arsenate [As(V)] with Fe(III)(oxyhydr)oxides is a widely used As removal method (Dixit and Hering 2003, Fuller et al. 1993, Hering et al. 1996a, Qiao et al. 2012, Shi et al. 2018). For arsenite [As(III)], coprecipitation with Fe(III)(oxyhydr)oxides is less effective in the pH range of most groundwaters because As(III) is uncharged and have a significantly lower affinity for adsorption to Fe(III)(oxyhydr)oxide surfaces. Typically, a Fe(III) coagulant is dosed in water to produce Fe(III)(oxyhydr)oxides which adsorb As(V) from water (Hering et al. 1996a, Qiao et al. 2012). The As(V) bearing Fe(III) precipitates are subsequently removed in a granular media filter (Gude et al. 2018a, Gude et al. 2016, 2018c, McNeill and Edwards 1995, Ruiping et al. 2009). These precipitates can also be removed by low-pressure membranes like microfiltration (MF) and ultrafiltration (UF), especially when removal of colloidal As bearing Fe(III) particles is to be achieved (Brandhuber and Amy 1998, Choi and Dempsey 2004, Ghurye et al. 2004, Lee et al. 2004, Ruiping et al. 2009, Zouboulis and Katsoyiannis 2002). However, wide-scale application of low-pressure membrane filtration for As removal is restricted, because of a lack of detailed knowledge about membrane fouling due to Fe(III) particles and operational consequences.

Arsenate coprecipitation efficiency with Fe(III)(oxyhydr)oxides and the size of resulting Fe(III) particles is dependent on the ionic composition of water (Senn et al. 2018, Voegelin et al. 2010). An overview of possible fouling mechanisms for low pressure membranes is presented in Fig 6.1. It is expected that the Fe(III) particles which are larger than the membrane pores will be deposited on the membrane surface, i.e. form a cake-layer (Fig 6.1A) whereas Fe(III) particles smaller or comparable to the membrane pores will penetrate deeper into membrane structure and cause internal particle deposition (Fig 6.1B). Also, fouling can occur due to adhesion of Fe(III) particles to the membrane material (Fig 6.1C). To what extent these different Fe(III) deposits are removed by backwashing is not yet fully understood. This understanding is required to develop advanced membrane cleaning strategies for sustainable membrane operation.

We have previously shown that As levels much lower than 1 µg/L can be achieved by oxidizing As(III), the predominant As species in anoxic groundwater, by potassium permanganate (KMnO_4) before co-precipitation with Fe(III)(oxyhydr)oxides (Ahmad et al. 2018). The use of KMnO_4 , however, can be avoided by treating the effluents of rapid sand filters (RSFs) which predominantly contain As(V) due to complete As(III) oxidation to As(V) in rapid sand filters (Fig S6.1) (Ahmad et al. 2018, Gude et al. 2018a, Gude et al. 2016). Consequently, the aim of this study is to investigate As(V) removal efficiency and membrane fouling mechanisms during Fe(III) based coprecipitation in combination with low-pressure membrane filtration with the objective to achieve an As reduction to below 1 µg/L in RSF effluents.

Figure 6.1 Different removal mechanisms for As bearing Fe(III) particles expected for low-pressure membrane filtration. (A) Pore size smaller than Fe(III) particles results in cake layer formation and pore blocking (B) Pore size larger or comparable to Fe(III) particles results in internal deposition. (C) Pore size larger than Fe(III) particles and adsorption affinity resulting in internal membrane fouling. (D) Pore size larger than Fe(III) particles without adsorption affinity resulting in transport of particles through the membrane.

6.2 MATERIALS AND METHODS

6.2.1 Feed water

Ionic composition of water affects both As(V) adsorption and size of Fe(III) particles (Ahmad et al. 2019a). Also the size of Fe(III) particles is expected to impact membrane fouling (Fig 6.1). Therefore, we used rapid sand filter effluent samples from two different water treatment plants in the Netherlands (Fig S6.2) which are significantly different in ionic composition (Table 6.1 and Table S6.1).

Table 6.1 Composition rapid sand filter effluent samples, designated as feed 1 and feed 2, obtained from two water treatment plants in the Netherlands.

Parameter	Unit	Feed 1	Feed 2
pH	–	7.8	8.2
Arsenic	µg/L As	2.3	3.3
Iron	µg/L Fe	<10	<10
Manganese	µg/L Mn	<10	<10
Ortho-phosphate	µg/L P	8	62
Silicate	µg/L Si	3640	4585
Dissolved organic carbon	mg/L C	1.9	2.1
Calcium	mg/L Ca	90	48
Magnesium	mg/L Mg	11	8.5

6.2.2 Membrane and module characteristics

To investigate the effect of membrane pore size on As removal and membrane fouling, two commercially available hollow fiber membranes (Pentair X-Flow, The Netherlands) were used which had different average pore sizes (MF: 200 nm and UF: 20 nm, Table 6.2). Both types of membranes were made of a similar polymeric polyethersulfone and polyvinylpyrrolidone (PES/PVP) material. Also, both membranes were operated inside-out. Fig 6.2 presents the scanning electron microscope (SEM) images of the inner-surface and the cross-section of the membranes.

Experiments were performed with laboratory scale membrane modules that were made by potting (with an epoxy resin) multiple hollow fibre membranes in a transparent polyvinyl chloride (PVC) tube, as previously described by Floris et al. (2016). The total filtration area for both membranes was 20 cm², which was realized by installing 2 and 4 hollow fibre membranes for MF and UF respectively.

6.2.3 Membrane filtration apparatus and filtration procedure

An automated laboratory scale set-up was used for the experiments (Fig 6.3). The setup consisted of a pulsation-free neMYSIS syringe pump (Cetoni GmbH, Germany) that supplied feed solution to the membrane module at a constant flow of 8.3 mL/min (corresponding to the flux of 250 L/m².h). A membrane pump (ProMinent GmbH, Heidelberg, Germany) was used for in-line dosing of the FeCl₃ stock solution in the feed at a constant flow of 0.3 mL/min. The concentration of the FeCl₃ stock solution was adjusted to change Fe(III) dose in different experiments. The hydraulic residence time (HRT) between the point of Fe(III) dose and membrane filtration was 1 min in all the experiments except for the study of coprecipitation kinetics where a HRT

of 5 min was applied. The increased HRT before membrane filtration was achieved by increasing the length of the feed tube. The trans-membrane pressure (TMP) was measured by a sensor (Wika Transmitter 891.13.500) every second and logged using SquirrelView Data Logger (Grant Instruments, Cambridge, UK).

Table 6.2 Membrane and module characteristics. Membranes were supplied by Pentair X-Flow, the Netherlands. Modules were constructed at KWR Water Cycle Research Institute, the Netherlands.

	UF membrane	MF membrane
Commercial identification	UFC M5	MF02 M2
Membrane process	Ultrafiltration	Microfiltration
Membrane material	PES/PVP	PES/PVP
Pore size [nm]	20	200
Filtration area [cm ²]	20	20
No. of fibers per module [-]	4	2
Inner fiber diameter [mm]	0.8	1.5
Volume/Area ratio [mm]	0.2	0.4

Each experiment consisted of 6 consecutive filtration (1 hour each) and backwash cycles (33.3 mL/min, 20 sec each cycle). Ultrapure water was used for backwashing and the backwash flow was provided by a pressurised vessel (3 bars) combined with an adjustable flow control. Samples of the feed water, including Fe(III) dosing, were collected directly by opening the valve (point 2 in Fig 6.3). Permeate was sampled from a beaker that collected the entire permeate volume produced during a filtration cycle (point 1 in Fig 6.3), except in the experiments where the effect of successive filtration cycles on As(V) removal was studied. Backwash samples were collected from a beaker that collected the entire backwash water volume produced during a backwash cycle (point 3 in Fig 6.3).

6.2.4 Reagents and chemicals

Ferric chloride was dosed using a stock solution that was prepared by dissolving $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (CAS: 10025-77-1, 97% purity, J.T Baker, Deventer, the Netherlands) in 0.5 L ultrapure water. A stock solution of 1.0 g/L As_2O_5 (CAS: 12044-50-7, 99% purity) obtained from inorganic ventures (Nieuwegein, the Netherlands) was used to spike the water with As(V). The ultrapure water was obtained by treating distilled water with a Purelab Chorus (Veolia, the Netherlands).

Figure 6.2 The SEM micrographs of the UF and MF membranes. The membranes were pre-conditioned with ultrapure water. (A) and (C) show the inner-surface of the UF and MF respectively and (B) and (D) show the cross-section of the UF and MF respectively.

6.2.5 Analysis methods for water samples

Arsenic, Fe, Ca, Mg, Si, P were measured by inductively coupled plasma mass spectrometry (ICP-MS) using the Thermo Scientific iCAP TQ (Thermo Fisher Scientific, Breda, the Netherlands). Total organic carbon analysis was carried out with a Shimadzu TOC-V_{CPH} total organic carbon analyser (Shimadzu Benelux, 's-Hertogenbosch, the Netherlands).

6.2.6 SEM-EDX analysis

Samples of the fouled UF membranes (membrane after 6 filtration and 5 backwash cycles) and backwashed membranes (6 filtration and 6 backwash cycles) were analyzed by SEM to gain further insights into fouling mechanisms. The analysis was carried out at the Wageningen Electron Microscopy Centre at Wageningen University (WUR), using a SEM device (FEI Magellan 400) that was equipped with an Oxford Instruments X-MAX X-ray detector for energy dispersive X-ray (EDX) analysis. The virgin MF and UF membranes were conditioned by ultrapure water

passage before the SEM analysis. For analysis of each sample, two fragments of the bore side (longitudinal cut) and two fragments of the cross-section (transversal cut) were fixed on a sample holder and coated with tungsten using a Leica SCD 500 sputtercoater.

Figure 6.3 Schematic diagram of the experimental setup. Points marked as 1, 2 and 3 indicate permeate, feed and backwash water sampling points, respectively.

6.2.7 Calculations

6.2.7.1 Rejection efficiency

The rejection efficiency of a solute (e.g. As and Fe) during filtration is given by

$$R_i = \left(1 - \frac{C_p}{C_f}\right)_i \times 100 \quad [\%] \quad (1)$$

where R_i is the rejection efficiency of a solute i , C_p is the permeate concentration and C_f is the feed concentration (mg/L).

6.2.7.2 Membrane permeability recovery

To assess the retention mechanism of Fe(III) particles, the evolution of membrane permeability under different conditions was analyzed. The membrane permeability was calculated according to

$$k = \frac{J}{TMP} \quad [L/m^2.h.bar] \quad (2)$$

where k is the membrane permeability, J is the flux ($L/m^2.h$) and TMP is the trans-membrane pressure (bar). The permeability recovery for each backwash cycle was

$$k_R = \frac{k_{after\ backwash}}{k_{clean\ membrane}} \times 100 \quad [\%] \quad (3)$$

where k_R is the permeability recovery, $k_{after\ backwash}$ is the membrane permeability after backwash and $k_{clean\ membrane}$ is the permeability of the virgin membrane.

6.2.7.3 Fouling analysis with resistance-in-series model

To assess the predominant membrane fouling mechanisms, we developed a resistance in series model (Bella and Trapani 2019, Floris et al. 2016, Mulder 2012).

For the flux in porous media we use Darcy's Law (Busch et al. 2007, Ng and Kim 2007) which is given by

$$J = TMP / (v \cdot R_T) \quad [L/m^2.h.bar] \quad (4)$$

where v is the dynamic viscosity of the solution (Pa.s) and R_T is the total resistance to filtration ($1/m$) which is the sum of clean membrane resistance (R_M), resistance due to the external cake-layer deposition (R_E) and the resistance due to the internal deposition (R_I).

$$R_T = R_M + R_E + R_I \quad [1/m] \quad (5)$$

We obtain R_M by filtration of ultrapure water through a virgin membrane according to eq. 4 and is given by

$$R_M = \left(\frac{TMP}{v \cdot J} \right)_{\text{virgin, ultra pure water}}$$

The filtration of feed water, which includes Fe(III) particles, through a virgin membrane is expected to cause membrane fouling due to particle deposition and therefore R_T can be obtained as follows.

$$R_T = \left(\frac{TMP}{v \cdot J} \right)_{\text{fouled}}$$

The internal and external fouling resistance ($R_E + R_I$) is equal to $R_T - R_M$.

We further assume that the hydraulic backwash will remove all the external fouling (we checked this assumption by SEM–EDX, see section 6.3.2.2). We therefore obtain R_f as follows

$$R_f = \left(\frac{TMP}{v \cdot J} \right)_{backwashed}$$

We finally determine R_e by subtracting the membrane resistance (R_M) and internal resistance (R_f) from the total resistance (R_T).

6.3 RESULTS AND DISCUSSION

6.3.1 Arsenic removal efficiency

6.3.1.1 Impact of membrane pore size

The effect of membrane pore size on As(V) removal efficiency was studied using Feed 1 which had been spiked to achieve 5 µg/L As(V) concentration. The experiments included dosing of different Fe(III) concentrations (0–4 mg/L) into the feed solution and filtration-backwash cycles. We observed that in the absence of Fe(III) dose, no As(V) was removed for both MF and UF membranes (Fig 6.4A and 6.4B) due to the small size of As(V) oxyanion (Ahmad et al. 2017, Luong et al. 2018). Also, adsorption of As(V) to the membranes did not occur because of lack of affinity between As(V) oxyanion (Fig S6.3) and the membranes which have been shown to have a negative surface charge in previous studies (Floris et al. 2016, Li et al. 2011, Trzaskus et al. 2016). With Fe(III) dosing, As(V) removal was significant, due to coprecipitation of As(V) with formed Fe(III)(oxyhydr)oxides (Ghurye et al. 2004). Arsenic removal efficiency increased with increasing Fe(III) dosage for both MF and UF membranes. Also, the removal of Fe close to 100% was observed in all cases (Fig 6.4A and 6.4B). These results indicate that As removal efficiency was independent of membrane pore sizes because the size of Fe(III) particles was larger than, or at least comparable to, the membrane pore sizes. This conclusion is also supported by (Ahmad et al. 2019a) where we observed Fe(III) particle sizes in the range of 2–80 µm (25 µm most abundant). The growth of Fe(III) precipitates to such large sizes can be attributed to the natural presence of high Ca concentrations in given feed water (Ahmad et al. 2019a).

6.3.1.2 Impact of feed water composition and hydraulic residence time

Arsenic coprecipitation with Fe(III)(oxyhydr)oxides is known to be sensitive to ionic composition of water (Ahmad et al. 2019a, Qiao et al. 2012, Van Genuchten et al. 2014b). To gain further insights into the effect of water composition on As

Figure 6.4 Removal efficiency of As and Fe in function of Fe(III) dose in experiments with (A) UF and (B) MF. The experiments were performed with Feed 1 after spiking with As(V) to achieve initial As=As(V)=5 µg/L. The removal of 80% corresponds to 1 µg/L residual As in water. (C) Residual As in function of Fe(III) dose, feed water quality and hydraulic residence time between point of Fe(III) dosing and UF. Feed 1 and Feed 2 were not spiked with additional As(V).

removal, experiments were carried out with the two feed solutions with different ionic composition using UF membranes. Arsenic concentrations below 1 µg/L were obtained by dosing 1 mg/L Fe(III) dose for Feed 1 and 3 mg/L Fe(III) dose for Feed 2 (Fig 6.4C). The lower As(V) removal efficiency for Feed 1 compared to Feed 2 can be explained by taking into account the effect of feed water composition on the coprecipitation of As(V) and Fe(III)(oxyhydr)oxides. For example, the concentration of phosphate and silicate oxyanions, which compete with As(V) for adsorption sites on Fe(III)(oxyhydr)oxides, is much higher in Feed 2 than Feed 1 (Table 6.1). In addition, Feed 2 has a lower concentration of bivalent cations than Feed 1 (90 mg/L compared to 48 mg/L Ca). It is known that the presence of bivalent cations can enhance the efficiency of As(V) coprecipitation with Fe(III)(oxyhydr)oxides involving mechanisms such as neutralization of the Fe(III) precipitate surface charge by Ca and

formation of ternary complexes between Fe(III), As(V) and Ca (Van Genuchten et al. 2014a, Van Genuchten et al. 2014b, Voegelin et al. 2010). Finally, Feed 1 has a lower pH compared to Feed 2 which can also contribute to the higher As adsorption to Fe(III) precipitates due to the fact that Fe(III) (oxyhydr)oxides at lower pH will have more positive charge on the surface and hence a higher number of adsorption sites for oxyanions (Kanematsu et al. 2013b, Raven et al. 1998).

To gain insights into the kinetics of As(V) and Fe(III) (oxyhydr)oxide coprecipitation, a set of experiments was carried out at an increased HRT of 5 min before removal of the formed Fe(III)(oxyhydr)oxides by the membranes. Results show that As(V) concentrations in the permeate at 5 min HRT is comparable to As(V) concentrations found in experiments having 1 min HRT (applied in all experiments) (Fig 6.4C), indicating that As(V) coprecipitation with Fe(III)(oxyhydr)oxides rapidly reached equilibrium within 1 min. Such rapid coprecipitation of As has also been reported in previous studies (Fuller et al. 1993, Gude et al. 2017, Raven et al. 1998).

We also studied As(V) removal as a function of the successive number of filtration cycles (filtration cycles 1, 3 and 6). No differences were observed for As(V) removal between the filtration cycles (Fig 6.5), confirming that As(V) uptake by Fe(III) precipitates reached equilibrium before the suspension entered the membrane, i.e. in 1 min.

Figure 6.5 Arsenic removal in function of the number of filtration cycles. Only UF membranes were used for this experiment. Fe(III) dose for Feed 1 and Feed 2 was 1 mg/L and 3 mg/L, respectively. Bulk permeate refers to total permeate volume produced by the 6 filtration cycles.

6.3.2 Membrane fouling

6.3.2.1 Clean water flux measurements

Prior to dosing Fe(III), the membranes were conditioned using ultrapure water at a flux of 250 L/m².h until a stable TMP was achieved (normally 1 hour). The calculated permeability (k) and the membrane resistance (R_M) (Table 6.3) were used for the permeability recovery calculations (following sections) and to verify the integrity of the membrane modules before each experiment. The TMP for MF was lower than the measurement limit of the sensor in the experimental setup (0.0008 bar) and therefore the exact permeability could not be calculated for MF. In the following sections we discuss Fe(III) particle retention and fouling of UF membranes.

Table 6.3 Clean water permeability and corresponding resistance calculated from the ultrapure water flux.

	UF	MF*
Permeability (L/m ² .hour.bar)	$(1.25 \pm 0.08) \times 10^3$	$>3.13 \times 10^5$
Membrane resistance (1/m)	$(2.88 \pm 0.24) \times 10^{11}$	$<1.15 \times 10^9$

*TMP was lower than the lower measurement limit of the sensor (0.0008 bar)

6.3.2.2 Fouling of UF membranes

Fig 6.6 presents the effect of Fe(III) particle deposition on TMP during 6 filtration–backwash cycles for Feed 1 and Feed 2 with 1 and 3 mg/L Fe(III) dosing respectively which resulted in As below 1 µg/L in the permeate. The initial TMP (clean membrane) was similar for both feeds, but the difference in Fe(III) dose produced clear differences in TMP increase during the filtration cycles. For example, the average TMP increase per cycle for Feed 1 and Feed 2 was 0.012 and 0.072 bar/h respectively which shows the higher susceptibility of membrane fouling at a higher Fe(III) dose. Nevertheless, in both cases the initial TMP was effectively restored after the backwash procedure (Fig 6.6 and Fig S6.4), indicating a predominance of reversible fouling at 1 and 3 mg/L Fe(III) dosing.

Figure 6.6 Evolution of TMP during UF experiments. During the experiments, flux was constant at 250 L/m².h. For MF the TMP was consistently lower than the lower measurement limit (0.0008 bar) therefore not shown in the graph.

To further elucidate fouling mechanisms, membranes were analyzed visually and with SEM–EDX (Fig 6.7 – 6.9). The visual effect of the deposition of Fe(III) precipitates on UF membrane before backwash (i.e. after 6 filtration and 5 backwash cycles) compared to after backwash (i.e. 6 filtration and 6 backwash cycles) in an experiment with Feed 2 dosed with 3 mg/L Fe(III) (As below 1 µg/L) is presented in Fig 6.7. The surface of the UF before backwash is visually very different from both the virgin UF membrane and the backwashed UF membrane. It shows an irregular layer of reddish-brown deposit (As bearing Fe(III) precipitates). No such deposits are observed in the virgin and backwashed UF membranes which implies that the hydraulic backwash effectively removed the Fe(III) deposits.

SEM micrographs and EDX scans of the cross section of the fouled UF membrane (i.e. the membrane specimen shown in Fig 6.7B), show Fe-signal restricted only to an approximate depth of 7 µm on the membrane surface (Fig 6.8). This confirms that Fe(III) particles were deposited as a cake-layer on membrane surface. Thus, based on membrane permeability recovery and complimentary visual and SEM–EDX analysis we conclude that the removal of As bearing Fe(III) particles occurred largely on the surface of UF membrane i.e. by cake-layer formation. Membrane permeability was reduced during a filtration cycle probably due to a growing cake on the membrane surface and a hydraulic backwash effectively removed the surface deposits and restored membrane permeability (Fig 6.6 and Fig S6.4).

Figure 6.7 The visuals of the UF membranes after experiments with Feed 2 dosed with 3 mg/L Fe(III). (A) Virgin membrane after conditioning with ultrapure water, (B) UF before backwash (membrane after 6 filtration and 5 backwash cycles) and (C) UF after backwash (6 filtration and 6 backwash cycles).

6.3.2.3 Fouling analysis by resistance-in-series model

The resistance model (see section 6.2.7.3) was used to further understand the fouling and contribution of different resistances during filtration. For both Feed 1 and Feed 2, dosed with different Fe(III) concentrations, the total resistance was dominated by membrane resistance (R_M) followed by external resistance (R_E) (Fig 6.10A). The internal resistance (R_I), on the other hand, was very small and may be due to some internal deposition of Fe(III) particles which might have penetrated somewhat deeper into the membrane pores (Shi et al. 2014). Particles deposited within the membrane pore structure are likely to be subjected to lower hydraulic shear forces and are therefore not effectively removed by hydraulic backwashing (Fane et al. 2006). The contribution of R_E for Feed 2 was higher than Feed 1 which can be explained easily by the higher Fe(III) dose applied for Feed 2.

The resistance analysis was also carried out with different Fe(III) doses in Feed 1 (Fig 6.10B). The total resistance systematically increased with the increments in Fe(III) dose. Again, R_M dominated the total resistance followed by R_E and the R_I was the smallest. The systematic increase in the R_E as a function of Fe(III) dose is consistent with the trend observed (cake-layer build-up) in the experiments with Feed 1 and Feed 2 at their specific optimum Fe(III) doses required for As removal to below 1 $\mu\text{g/L}$ (Fig 6.10A). Thus, cake-layer formation was found to be the major proportion of fouling resistance.

Figure 6.8 SEM micrograph (A and C) and EDX scans (B and D) of the cross section of the UF membrane specimen shown in Fig 6.7B. (A) Cross section of UF membrane before backwash. (B) EDX spectrum of Fig 6.8A, showing signal from Fe-atoms, indicating the presence of a Fe-based cake layer on the membrane surface. (C) enlarged section of Fig 6.8A, indicating the line at which EDX data is acquired. (D) EDX data of the line in Fig 6.8C, highlighting Fe (yellow), O (green) and S (blue) signals along the line as function of detector-counts per second (cps). The dot on the line in Fig 6.8C equals 0 μm on the y-axis of Fig 6.8D. At distance $>8 \mu\text{m}$, increasing sulfur signal indicates the presence of the supporting layer. At distance 8–2 μm , low sulfur signal and higher iron and oxygen signal indicates the presence (and thickness) of the deposited Fe(III)(oxyhydr)oxide cake-layer.

6.4 CONCLUSIONS AND IMPLICATIONS FOR THE PRACTICE

The removal of As(V) and membrane fouling mechanisms during Fe(III) based coprecipitation–low pressure membrane filtration were studied for achieving As reduction to very low levels below 1 $\mu\text{g/L}$ in rapid sand filter effluents. We found that As(V) removal efficiency was independent of the membrane pore size because the size of the Fe(III) particles was larger than the pore size of UF and MF membranes. Also, As(V) coprecipitation with Fe(III)(oxyhydr)oxides rapidly reached equilibrium before membrane filtration, within 1 min. This resulted in a stable As removal efficiency even at an increased residence time of 5 min before membrane filtration. The removal efficiency of As(V) was nevertheless dependent on feed water composition, in such a way that a higher Fe(III) dose was required to reduce As to below 1 $\mu\text{g/L}$ for the feed water which had higher phosphate and silicate concentrations and lower calcium and magnesium concentrations.

Figure 6.9 SEM–EDX of the solid depositions found on the bored side of the UF membrane. (A) 50 000 x magnified image (B) 150 000 x magnified image. (C) spectrum shows the elemental composition at the bored side of the UF before backwash. Na and Cl are present due to the drying and crystallization of NaCl. The small calcium peak can be explained by coprecipitation of calcium with Fe(III)(oxyhydr) oxides. The high carbon, oxygen and sulfur peaks are from the membrane material (PES, $(C_{12}H_8O_3S)_n$). Tungsten was used to coat the sample. The observed fractures in the cake layer in Fig 6.9A is an artefact and caused by drying during preparation or storage. The deposits in Fig 6.9B appear to consist of primary spherical particles with an average size 65 nm.

In all the UF experiments, Fe(III) particles formed a cake-layer on the membrane surface which reduced membrane permeability during filtration. The cake on the UF membranes was effectively removed with a hydraulic backwash, resulting in near-complete restoration of membrane permeability. The fouling mechanisms for MF, on the other hand, could not be studied in detail and therefore it is difficult to draw clear conclusions about MF fouling. However, we postulate for future work that more open low-pressure membranes may be more susceptible to irreversible fouling due to a large pore size which can allow some Fe(III) particles to penetrate deeper into the membrane structure and get immobilized there.

It is noteworthy that direct translation of our results for long-term application may be limited by the fact that we studied the membrane fouling only for 6 filtration and backwash cycles. At water treatment plants, long term membrane operation

can result in a significant permeability reduction due to slow build-up of internal membrane fouling which was negligibly small in our UF experiments.

Figure 6.10 Resistance model analysis for the UF experiments for (A) Feed 1 which was dosed with 1 mg/L Fe(III) and Feed 2 which was dosed with 3 mg/L Fe(III) and (B) Feed 1 which was dosed with different Fe(III) doses (0.2–2 mg/L).

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SUPPLEMENTARY INFORMATION

Figure S6.1. The mechanisms controlling the fate and removal of As(III) and Fe(II) during conventional groundwater treatment. Modified from (Ahmad et al. 2018). Note that As(III) oxidizes to As(V) in rapid sand filters and the effluent contains only As(V).

Figure S6.2 Process schemes of water treatment plants (A) Ouddorp and (B) Katwijk. The coprecipitation–low pressure membrane filtration experiments were performed using the effluent samples of the rapid sand filters from both treatment plants (sample points marked by red arrows).

Figure S6.3 E_h -pH diagram for aqueous As species in the system As–O₂–H₂O at 25 °C and 1 bar total pressure. This Fig. is created with Phreeqplot using the wateq4f.dat database. All As-species shown are aqueous species except for native As.

Figure S6.4 Cumulative permeability recovery with respect to the number of backwash cycles in UF experiments with Feed 1 which was dosed in-line with 1 mg/L Fe(III) and Feed 2 which was dosed in-line with 3 mg/L Fe(III). The dotted line represents 100% recovery of the permeability.

Table S6.1 Quality of rapid sand filter effluent at WTP Ouddorp and WTP Katwijk in the Netherlands, based on the historical data (2016-2019) provided by the operating water companies.

Parameter	Unit	RSF effluent Ouddorp (Feed 1)	RSF effluent Katwijk (Feed 2)
Temp	°C	9.4-16.2	13.7-16.8
pH		7.75-7.87	8.37-8.62
Dissolved Oxygen	mg/L O ₂	6.5-8.0	9.7
Electrical Conductivity	mS/m	55-68	48.5-52.6
Bicarbonate	mg/L HCO ₃	235-260	167-184
Turbidity	NTU	0.01-0.03	<0.03
Arsenic	µg/L As	1.9-3.2	3.2-3.4
Iron	mg/L Fe	<0.01-0.08	<0.01
Manganese	mg/L Mn	<0.01	<0.01
Orthophosphate	µg/L P	6.0-120	50-150
Silicate	mg/L Si	3.0-4.0	3.5-5.0
Total organic carbon	mg/L C	1.5-3.9	2.1
Ammonium	mg/L NH ₄	<0.02	<0.02
Nitrite	mg/L NO ₂	<0.007	<0.007
Nitrate	mg/L NO ₃	1.4-2.5	1.7-2.2
Calcium	mg/L Ca	77-83	40-46
Magnesium	mg/L Mg	9.7-10	7.7-8.3
Sulphate	mg/L SO ₄	30-39	45-51
Sodium	mg/L Na	34-50	57-60
Chloride	mg/L Cl	67-94	54-56

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Chapter 7

General discussion and outlook

7.1 MAIN FINDINGS AND PERSPECTIVES

The objective of this thesis was to provide detailed understanding of arsenic (As) removal during groundwater treatment by co-precipitation with Fe(III)(oxyhydr)oxides under different redox, ion composition and filtration conditions. Moreover, we investigated routes to reduce As in drinking water to below 1 µg/L. In the following sections we highlight our main contributions and their significance.

7.1.1 Rapid sand filters are the arsenic removal hotspots

From this study we conclude that rapid sand filtration is the most important treatment step for the oxidation and removal of As during groundwater treatment. The removal of As is tightly coupled to Fe removal in rapid sand filters and mainly attributed to co-precipitation of As with Fe(III)(oxyhydr)oxides, which are generated by oxidation and subsequent hydrolysis of Fe(II). No As removal takes place in additional treatment such as granular activated carbon filtration, ultrafiltration or slow sand filtration, due to a lack of hydrolyzing iron in their influent and a lack of adsorption affinity between As and the media surfaces.

The As co-precipitation efficiency with Fe(III)(oxyhydr)oxides is much higher in rapid sand filter beds compared to aeration and supernatant storage. This is ascribed to oxidation of As(III) to As(V) in the rapid sand filter beds, potentially executed by manganese oxides and/or As(III) oxidizing bacteria, as both are observed in the coating of rapid sand filter media grains. This study shows that during groundwater treatment Fe(II) oxidation begins as soon as the raw groundwater is aerated and Fe(III)(oxyhydr)oxide precipitation proceeds in the supernatant and rapid sand filter bed. On the other hand, the natural As(III) oxidation only occurs in rapid sand filter bed. This prevents effective As-uptake by the formed Fe(III)(oxyhydr)oxides during groundwater treatment. We propose that this problem can be solved by managing the sequence of As(III) and Fe(II) oxidation so that Fe(II) oxidation is delayed during rapid sand filtration, e.g. by lowering the influent pH which can decrease the rate of Fe(II) oxidation (Van Beek et al. 2016, Van Beek et al. 2012, Vries et al. 2017). The pH reduction is also expected to increase adsorption of As(V) to the freshly formed Fe(III) precipitates in rapid sand filters because Fe(III)(oxyhydr)oxides have a higher number of adsorption sites for As at lower pH.

7.1.2 Dosing strong oxidant improves arsenic removal but impacts iron and manganese oxidation mechanisms in rapid sand filters

This study shows that typical aeration techniques (e.g. cascades) are inefficient in oxidizing As(III) to As(V) before rapid sand filters at water treatment plants, resulting in inefficient As co-precipitation with Fe(III)(oxyhydr)oxides. Potassium

permanganate is a strong oxidant which rapidly accomplishes As(III) oxidation to As(V) and drastically improves As co-precipitation efficiency with Fe(III)(oxyhydr)oxides, resulting in As reduction to very low levels, below 1 µg/L.

While no negative effect on the removal efficiency of Fe(II), Mn(II) and NH_4^+ in rapid sand filters is observed due to KMnO_4 dosing, the pre-established Fe(II) and Mn(II) removal mechanisms in rapid sand filters are affected due to KMnO_4 dosing. Typically, without KMnO_4 dosing, a significant part of Fe(II) oxidation and complete Mn(II) oxidation occurs in the rapid sand filter bed, due to surface catalytic and biological processes. However when KMnO_4 is dosed in the influent of rapid sand filters for As(III) oxidation, both Fe(II) and Mn(II) are completely oxidized (and precipitated) before entering the rapid sand filter bed. In this case, the Fe and Mn precipitates are removed primarily by cake-filtration and shorten filter run time. This conclusion underlines the great potential of strong oxidants such as KMnO_4 for improving As(III) removal at groundwater treatment plants, but also points out an important practical implication for water treatment which can be solved by adjustments in the design of rapid sand filters, e.g. by replacing the existing filter media with a coarser grain size.

7.1.3 Oxidant identity impacts the composition and structure of iron and manganese oxidation products

This study reveals that dosing of strong oxidants in groundwater impacts the composition and structure of the formed Fe and Mn bearing precipitates. In co-oxidation of Fe(II) and Mn(II) with different oxidants, the Mn content in the oxidation products increases in the order $\text{O}_2 < \text{NaOCl} < \text{KMnO}_4$, whereby a significant fraction of Mn in KMnO_4 driven oxidation products is MnO_2 originating from KMnO_4 reduction. The oxidant identity also impacts the speciation of oxidized Fe and Mn in the precipitates. For example, we show that in the absence of competing ions, O_2 produces Mn(III)-incorporated moderately crystalline lepidocrocite, NaOCl produces Mn(III)-incorporated poorly-ordered hydrous ferric oxide, and KMnO_4 produces poorly-ordered MnO_2 and poorly-ordered hydrous ferric oxide phases. In general, ion uptake capacity of a poorly-crystalline phase is higher than the crystalline solid phase. Therefore, the diversity of precipitates must be considered when enhancing As(III) oxidation and removal in water treatment processes by the use of strong oxidants.

The formation of MnO_2 by KMnO_4 addition is fascinating. These types of Mn(IV) oxides have remarkable reactivity with respect to adsorption of a wide variety of toxic heavy metals (e.g. Cd(II), Pb(II), Cu(II), Ni(II)) (Peña et al. 2015, Pena et al. 2010, Villalobos 2015). Our results suggest that Fe(II) oxidation by KMnO_4 and the production of mixtures of Fe(III) and MnO_2 would be ideal for concurrent

treatment of As(III) and heavy metals. This result is particularly important for the co-removal of As(III) and Cd(II), which can often occur simultaneously in polluted environments (Perera et al. 2016), since Cd(II) removal by Fe(III) precipitates is much less effective than MnO_2 (Van Genuchten and Peña 2016b).

7.1.4 Ionic composition of water affects arsenic removal by iron based co-precipitation

Arsenic is oxidized during rapid sand filtration. Thus, the use of KMnO_4 is avoided and As levels below 1 $\mu\text{g/L}$ are achieved by treating the effluent of rapid sand filter for As(V) removal by dosing a small amount of Fe(III) coagulant such as FeCl_3 . Nevertheless, the ionic composition of water strongly controls As(V) removal, by affecting the adsorption efficiency of As(V) with Fe(III)(oxyhydr)oxides and the size of As bearing Fe(III) particles. We show that Si and P reduce As(V) removal by Fe(III) based co-precipitation, mainly due to competition with As(V) adsorption to Fe(III) precipitates. Though Si and P oxyanions are known to strongly reduce Fe(III) precipitate growth, we show that presence of high Ca concentrations in groundwater (common in the Netherlands and several other parts of the world) counteracts the negative effects of both Si and P and promote coagulation of Fe(III) precipitates to form large particles which are easily separated from water by gravitation settling and rapid sand filtration.

Despite presence of high Ca concentrations, NOM reduces As(V) removal quite drastically, attributed largely to the formation of soluble and colloidal Fe(III)–NOM complexes which are not easily separated by conventional filtration. These findings indicate that elevated NOM concentrations, e.g. due to seasonal effects or climate change, can pose an increasing challenge for water utilities for As removal because NOM can seriously inhibit co-precipitation of As with Fe(III)(oxyhydr)oxides and increase the mobility of As during water treatment.

7.1.5 Ferric based co-precipitation of arsenic in combination with ultrafiltration is a highly viable arsenic removal technology post rapid sand filtration

At water treatment plants ultrafiltration is frequently used as a final treatment step for disinfection. Arsenic is oxidized in prior rapid sand filters, resulting in As(V) being the predominant As species in UF feed. In-line dosing of a small amount of FeCl_3 before UF is shown to be effective for As reduction to $<1 \mu\text{g/L}$ in such situations. In this process, As(V) co-precipitation with Fe(III)(oxyhydr)oxides rapidly reaches equilibrium, thus little contact time before the membranes is required. Moreover, when As bearing Fe(III) precipitates grow to sizes larger than the pore size of UF membranes (expected for most Ca bearing groundwaters) the Fe(III) particles foul the membranes mainly by forming a cake-layer on the surface which is effectively removed with a hydraulic backwash. Thus, sustainable long term operation of UF

membranes with in-line FeCl_3 dosing for As removal is highly viable. More open low-pressure membranes may be more susceptible to irreversible fouling than UF due to a large pore size which can allow some Fe(III) particles to penetrate deeper into the membrane structure and get immobilized there, however further research is needed to gain insights into fouling mechanisms in MF membranes.

7.2 Implementation of results and further considerations

Triggered by the potential of As toxicity in extremely low concentrations, in this thesis reduction of already low As concentrations in Dutch groundwater to even lower As concentrations, below $1\text{ }\mu\text{g/L}$ was the objective. Nevertheless, the findings in this thesis are also of highly relevance for water utilities which struggle to comply with the current WHO guideline of $10\text{ }\mu\text{g/L}$ As in drinking water, e.g. in several South East Asian, East European and Latin American countries. Building on this work, three groundwater treatment plants in the Netherlands have received an upgrade with KMnO_4 dosing, sometimes in combination with FeCl_3 dosing for reducing As reduction to below $1\text{ }\mu\text{g/L}$. One treatment plant which makes use of artificially recharged groundwater will receive an upgrade with FeCl_3 dosing before the polishing UF step. Several projects are under discussion in Bangladesh, India and Pakistan where As(III) is the predominant species of As in groundwater, for co-removal of As(III) , Fe(II) and Mn(II) by dosing KMnO_4 in groundwater. The Fe(III) based co-precipitation in combination with UF method is proposed for As removal in Argentina and Mexico where As(V) is the predominant As species in groundwater, mobilized predominantly from young volcanic rocks and their weathering products (Bundschuh et al. 2012). Especially, the capability of UF for bacteria and virus removal makes Fe(III) based co-precipitation–UF an interesting technology for combined As removal and disinfection of groundwater.

Use of KMnO_4 may not be appealing to some utilities because of its relatively high cost or extra safety precautions needed for safe storage at water treatment plants. In that case, cleverly exploiting the natural As(III) oxidation capacity of rapid sand filters is required. However, current knowledge of the intricate physicochemical and biological processes in rapid sand filters is limited and clear guidelines for controlling the sequence of Fe(II) and As(III) oxidation in rapid sand filters have not been discerned. Research is ongoing to gain a better understanding of As(III) and Fe(II) oxidation in rapid sand filters.

We underline that As(III) can also be oxidized by oxidative hydrolysis of Fe(II) , attributed to the oxidizing radical species (Fe(IV) and H_2O_2 at near-neutral pH) that form during oxidation of Fe(II) by dissolved O_2 (Hug and Leupin 2003, Roberts et al. 2004). The effective exploitation of Fe -catalyzed As(III) oxidation requires a more controlled dosing and oxidation of Fe(II) , rather than a single step dose

of an Fe(II) bearing solution (e.g. FeSO_4) (Roberts et al. 2004, Van Genuchten et al. 2018b). In this context Electrocoagulation is a highly promising alternative to chemical coagulation. In Electrocoagulation, in-situ Fe hydroxide species (Fe precipitates) are formed due to electro-dissolution of sacrificial anodes. Fe(0) oxidizes to dissolved Fe(II) which is subsequently oxidized to generate Fe precipitates in water. In Electrocoagulation the dissolution rate of Fe electrodes can be conveniently controlled by varying the current. Also, due to its potential low carbon-foot print and high coagulation efficiency.

Management of As-laced treatment residuals is an important consideration in water treatment. In this thesis we observed that in the backwash water, the Fe and As were almost entirely removed by 0.45 μm filtration, indicating that As was strongly bound to the Fe(III) precipitates and easy separation of these As bearing-Fe(III) precipitates from the backwash water should not be problematic. However, it is noteworthy that some As(V) may be mobilized from the solid phase over years of storage, particularly if the solid phase crystallizes over time (Fuller et al. 1993, Senn et al. 2018) or is exposed to reducing conditions that transform As(V) and Fe(III) (oxyhydr)oxides (Meng et al. 2001). The differences in the structure and composition of Fe(III) precipitates can result in differences in their availability as terminal electron acceptors in redox-sensitive environments (Hyacinthe et al. 2008, Voegelin et al. 2010). More research is required in this area.

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SUMMARY

Arsenic (As) is a well-known human carcinogen, classified in Group 1 by the International Agency for Research on Cancer (IARC). Contamination of groundwater with As is a wide-scale problem affecting health of millions of people around the world. The World Health Organization (WHO) guideline for As in drinking water is currently set at 10 µg/L, however recent studies suggest that As can cause a considerable damage to human health even at concentrations lower than the WHO guideline. As a result, several drinking water companies are making efforts to reduce As concentrations in drinking water to very low concentrations, below 1 µg/L.

Co-precipitation of As with iron(III)(oxyhydr)oxides [Fe(III)(oxyhydr)oxides] is a widely used As removal method in groundwater treatment. Fe(III)(oxyhydr)oxides are produced in an As contaminated water, typically by oxidation of naturally occurring ferrous iron [Fe(II)] in groundwater using oxygen (O₂) and/or dosing a ferric iron [Fe(III)] coagulant such as Ferric Chloride (FeCl₃). Arsenic strongly adsorbs to the surface of freshly formed Fe(III) precipitates and subsequently the As bearing Fe(III) precipitates are removed by filtration to produce As-safe water. The adsorption efficiency of As onto Fe(III) precipitates and the size of As bearing Fe(III) particles is governed by several interdependent factors such as the conditions of Fe(III)(oxyhydr)oxide generation in water, oxidation state of As, solution pH and the concentration of As and co-occurring ions with respect to Fe in the initial solution. The overall objective of this thesis is to discern mechanistic understanding of As removal by co-precipitation with Fe(III)(oxyhydr)oxides under different redox, ion composition and filtration conditions and to investigate routes to reduce As in drinking water to very low levels, below 1 µg/L.

We carried out sampling campaigns at full-scale water treatment plants in the Netherlands to develop detailed understanding of the pertinent As removal mechanisms during groundwater treatment. It was found that rapid sand filtration is the most important treatment step for the oxidation and removal of As during groundwater treatment. The removal of As is tightly coupled to Fe removal in rapid sand filters and mainly attributed to co-precipitation of As with Fe(III)(oxyhydr)oxides, which are generated by oxidation and subsequent hydrolysis of Fe(II). The As co-precipitation efficiency with Fe(III)(oxyhydr)oxides is much higher in rapid sand filter beds compared to aeration and supernatant storage. This is ascribed to oxidation of arsenite [As(III)] to arsenate [As(V)] in the rapid sand filter beds, potentially executed by manganese oxides (MnO₂) and/or As(III) oxidizing bacteria, as both are observed in the coating of rapid sand filter media grains. In the pH range of most groundwaters, As(V) adsorbs to Fe(III)(oxyhydr)oxides much more effectively than As(III).

Typical aeration techniques such as cascades are inefficient in oxidizing As(III) to As(V) before rapid sand filters at water treatment plants, resulting in inefficient As co-precipitation with Fe(III)(oxyhydr)oxides. Nevertheless, dosing a strong oxidant such as potassium permanganate (KMnO_4) rapidly accomplishes As(III) oxidation to As(V) and drastically improves As co-precipitation efficiency with Fe(III)(oxyhydr)oxides, resulting in As reduction to very low levels, below 1 $\mu\text{g/L}$. While no negative effect on the removal efficiency of Fe(II), Mn(II) and ammonium (NH_4^+) in rapid sand filters is observed due to KMnO_4 dosing, the pre-established Fe(II) and Mn(II) removal mechanisms in rapid sand filters are altered due to KMnO_4 dosing, generating a need for rapid sand filter media replacement. We also found that dosing of strong oxidants during groundwater treatment impacts the composition and structure of the formed Fe and Mn bearing precipitates. For example, in the absence of competing ions, O_2 produces Mn(III)-incorporated moderately crystalline lepidocrocite, sodium hypochlorite (NaOCl) produces Mn(III)-incorporated poorly-ordered hydrous ferric oxide, and KMnO_4 produces poorly-ordered MnO_2 and poorly-ordered hydrous ferric oxide phases. This diversity of formed precipitates under different redox conditions should be considered in As removal during groundwater treatment.

In this thesis we show that As levels below 1 $\mu\text{g/L}$ can alternatively be achieved by dosing a small amount of FeCl_3 in the effluent of rapid sand filter at groundwater treatment plants. The effluent of rapid sand filter predominantly contains arsenate [As(V)] which is much more effectively adsorbed to Fe(III)(oxyhydr)oxides than As(III). In this way use of KMnO_4 or other strong oxidants can be avoided at groundwater treatment plants. Nevertheless, the ionic composition of water strongly controls As(V) removal by iron based co-precipitation, by affecting the adsorption efficiency of As(V) with Fe(III)(oxyhydr)oxides and the size of As bearing Fe(III) particles. We show that silicate (SiO_4^{-4}) and phosphate (PO_4^{-3}) reduce As(V) removal, mainly due to competition with As(V) adsorption to Fe(III) precipitates. Though SiO_4^{-4} en PO_4^{-3} oxyanions are known to strongly reduce Fe(III) precipitate growth, we show that presence of high calcium (Ca) concentrations in groundwater (common in the Netherlands and several other parts of the world) counteracts the negative effects of both SiO_4^{-4} en PO_4^{-3} and promote coagulation of Fe(III) precipitates to form large particles which are easily separated from water by gravitation settling and rapid sand filtration. Despite presence of high Ca concentrations, Natural Organic Matter (NOM) reduces As(V) removal quite drastically, attributed largely to the formation of soluble and colloidal Fe(III)–NOM complexes which are not easily separated by conventional filtration.

In-line dosing of a small amount of FeCl_3 in the feed water of ultrafiltration (UF) step (typically used for final polishing and disinfection) is shown to be effective for

As reduction to $<1 \mu\text{g/L}$ at water treatment plants which use artificially recharged water as source. In this process, As(V) co-precipitation with Fe(III)(oxyhydr)oxides rapidly reaches equilibrium, thus little contact time before the membranes is required. Moreover, when As bearing Fe(III) precipitates grow to sizes larger than the pore size of UF membranes (expected for most Ca bearing groundwaters) the Fe(III) particles foul the membranes mainly by forming a cake-layer on the surface which is effectively removed with a hydraulic backwash. Thus, we conclude that sustainable long term operation of UF membranes with in-line FeCl_3 dosing for As removal is highly viable.

Based on the present work, three groundwater treatment plants in the Netherlands have received an upgrade with KMnO_4 dosing for reducing As to below $1 \mu\text{g/L}$. Another treatment plant, which makes use of artificially recharged groundwater, will receive an upgrade with FeCl_3 dosing before the polishing UF step.

SAMENVATTING

Arseen (As) staat bekend als zeer carcinogeen voor mensen, en het wordt dan ook door het International Agency for Research on Cancer (IARC) in Groep 1 geclassificeerd. Verontreiniging van grondwater met As is een probleem dat wereldwijd voorkomt, en de gezondheid van miljoenen mensen over de hele wereld bedreigt. De World Health Organization (WHO) heeft het maximaal toelaatbare gehalte van drinkwater op 10 µg/L vastgesteld, maar recente studies suggereren dat As zelfs bij concentraties lager dan deze limiet ernstige schade aan de menselijke gezondheid kan toebrengen. Daarom proberen verschillende drinkwaterbedrijven de As concentraties in drinkwater te verlagen tot heel lage concentraties, lager zelfs dan 1 µg/L.

Co-precipitatie van As met ijzer(III)(oxyhydr)oxides [Fe(III)(oxyhydr)oxides] wordt op grote schaal toegepast als een verwijderingsmethode voor As in grondwater-zuivering. Fe(III)(oxyhydr)oxides worden gevormd in met As vervuild water, door de oxidatie via beluchting (O_2) van van nature voorkomend ferro-ijzer [Fe(II)] in grondwater, en/of door het doseren van ferri ijzer [Fe(III)] als een vlokmiddel (bijvoorbeeld ferrichloride, $FeCl_3$). Arseen adsorbeert sterk op het oppervlak van vers gevormd Fe(III)-neerslag, en vervolgens kan het met As beladen neerslag worden verwijderd via filtratie, om veilig As-vrij water te produceren. De effectiviteit van de adsorptie van As op Fe(III)-neerslag en de grootte van de met As beladen Fe(III)-deeltjes wordt bepaald door verscheidene onderling afhankelijke factoren, zoals de omstandigheden waaronder Fe(III)(oxyhydr)oxide wordt gevormd in water, de oxidatietoestand van As, de pH van de oplossing en de concentraties van As en andere ionen ten opzichte van ijzer in de oorspronkelijke oplossing. Het doel van deze dissertatie is begrip te krijgen van het mechanisme van As-verwijdering via co-precipitatie met Fe(III)(oxyhydr)oxides onder verschillende redox-omstandigheden, als gevolg van de samenstelling van de aanwezige ionen, en van de filtratie-omstandigheden. Op deze manier zijn verschillende wegen onderzocht om het As-gehalte van drinkwater te kunnen verlagen tot een laag niveau, bij voorkeur lager dan 1 µg/L.

We hebben verschillende monstername-campagnes uitgevoerd bij full-scale drinkwaterprocessen in Nederland, om een gedetailleerd begrip te krijgen van relevante As-verwijderingsmechanismen tijdens de behandeling van grondwater. Het bleek dat snelfiltratie de belangrijkste stap is voor de oxidatie en verwijdering van As hierbij. De verwijdering van As is hierbij sterk gerelateerd aan de verwijdering van ijzer in snelfilters, en wordt vooral toegeschreven aan de co-precipitatie van As met Fe(III)(oxyhydr)oxides, die worden gevormd door de oxidatie en daaropvolgende hydrolyse van Fe(II). De effectiviteit van de As co-precipitatie met deze oxides is veel hoger in snelfilters dan tijdens beluchting en opslag van het supernatant. Dit

wordt toegeschreven aan de oxidatie van arseniet [As(III)] naar arsenaat [As(V)] in snelfilterbedden, mogelijk veroorzaakt door mangaanoxides (MnO_2) en/of As(III) oxiderende bacteriën, die beiden blijken voor te komen in de coating van de zandkorrels van het filterbed. In het pH-bereik van de meeste grondwateren zal As(V) veel effectiever op Fe(III)(oxyhydr)oxides worden geadsorbeerd dan As(III).

Veel voorkomende beluchtingstechnieken bij drinkwaterbedrijven, zoals cascades, zijn niet effectief voor de oxidatie van As(III) naar As(V) vóór snelfilters, wat leidt tot een inefficiënte co-precipitatie van As met Fe(III)(oxyhydr)oxides. Door echter een sterke oxidator als kalium permanganaat (KMnO_4) toe te voegen, zal de oxidatie van As(III) naar As(V) snel worden voltooid, en verbetert de co-precipitatie met Fe(III)(oxyhydr)oxides significant, waardoor zeer lage concentraties, onder $1 \mu\text{g/L}$, worden bereikt. Dit gaat niet gepaard met een verlaging van de verwijderingsefficiëntie van de snelfilters voor Fe(II), Mn(II) en ammonium (NH_4^+), maar de bekende verwijderingsmechanismen voor Fe(II) en Mn(II) worden door de toevoeging van KMnO_4 wel veranderd. Hierdoor moet het zand in de snelfilters eerder verwijderd worden. Verder hebben we vastgesteld dat het doseren van een sterke oxidator tijdens grondwaterbehandeling de samenstelling en structuur van de gevormde Fe en Mn bevattende neerslagen verandert. Zo vormt zuurstof bijvoorbeeld in afwezigheid van concurrerende ionen Mn(III)-houdend matig kristallijn lepidocrociet, terwijl natrium hypochloriet (NaOCl) Mn(III)-houdend slecht geordend waterhoudend ijzer(III) oxide vormt, en KMnO_4 leidt tot slecht geordende MnO_2 - en waterhoudende ijzer oxide-fasen. Tijdens de behandeling van grondwater moet met deze verschillen in de gevormde neerslagen als gevolg van andere redoxomstandigheden rekening worden gehouden.

In deze dissertatie laten we zien dat As-concentraties onder $1 \mu\text{g/L}$ ook kunnen worden bereikt door een kleine hoeveelheid FeCl_3 in het effluent van een snelfilters bij grondwaterbehandeling toe te voegen.

Het effluent van een snelfilter bevat vooral arsenaat [As(V)], wat veel effectiever op Fe(III)(oxyhydr)oxides geadsorbeerd kan worden dan As(III). Op deze manier kan het gebruik van KMnO_4 of andere sterke oxidatoren voorkomen worden bij drinkwaterbedrijven die grondwater gebruiken. Toch bepaalt de samenstelling van de ionen in het water in hoge mate de verwijdering van As(V) via co-precipitatie gebaseerd op ijzer, door de efficiëntie van de adsorptie van As(V) op Fe(III)(oxyhydr)oxides en de grootte van de met As beladen Fe(III) deeltjes te beïnvloeden. We laten zien dat de aanwezigheid van silicaat (SiO_4^{-4}) en fosfaat (PO_4^{-3}) de As(V)-verwijdering verminderen, vooral door concurrentie met As(V) over adsorptieplekken op Fe(III) neerslag. Hoewel SiO_4^{-4} en PO_4^{-3} oxyanionen erom bekend staan dat ze de groei van Fe(III) neerslag verminderen, laten we zien dat de aanwezigheid van hoge calcium (Ca) concentraties in grondwater (wat in Nederland en veel andere delen van de

wereld vaak voorkomt) de negatieve effecten van zowel SiO_4^{-4} en PO_4^{-3} teniet doet, en de coagulatie van Fe(III) neerslag in grote deeltjes, die gemakkelijk uit water verwijderd kunnen worden via bezinking onder invloed van de zwaartekracht en snelfiltratie, bevordert. Ondanks de aanwezigheid van hoge Ca concentraties, vermindert de aanwezigheid van Natuurlijk Organisch Materiaal (NOM) de As(V)-verwijdering significant, wat voornamelijk wordt toegeschreven aan de vorming van oplosbare en colloïdale Fe(III)-NOM complexen, die niet gemakkelijk te verwijderen zijn via conventionele filtratie.

Het in-line doseren van een kleine hoeveelheid FeCl_3 in het voedingswater van een ultrafiltratiestap (UF), wat veel wordt toegepast voor een laatste behandelingsstap en desinfectie, blijkt effectief te zijn om de As-concentratie te verlagen tot $<1 \mu\text{g/L}$ bij drinkwaterbedrijven die duin-filtraat als bron gebruiken. In dit proces bereikt As(V) co-precipitatie met Fe(III)(oxyhydr)oxides snel een evenwicht, en dus is slechts een korte contacttijd voor de membranen nodig. Bovendien blijkt dat als As-beladen Fe(III) neerslag grotere deeltjes vormt dan de poriegrootte van UF-membranen (zoals verwacht voor het meeste Ca-houdende grondwater), de Fe(III)-deeltjes de membranen vooral vervuilen door een koeklaag op het oppervlak te vormen, die effectief kan worden verwijderd via hydraulisch terugspoelen. Daarom concluderen we dat een duurzame langdurige toepassing van UF-membranen met in-line FeCl_3 -dosering erg rendabel is voor As-verwijdering.

Op basis van de huidige studie hebben in Nederland drie drinkwaterbedrijven die grondwater gebruiken een upgrade gekregen met een KMnO_4 -dosering om de As-concentratie tot onder $1 \mu\text{g/L}$ te verlagen. Een ander proces, dat gebruik maakt van bodemfiltraat, zal een upgrade krijgen met FeCl_3 -dosering voor de laatste UF-stap.

LIST OF PUBLICATIONS IN THIS THESIS

- Ahmad, A., Richards, L. A., Bhattacharya, P. (2017). Arsenic remediation of drinking water: an overview. In P. Bhattacharya, D. A. Polya, & D. Jovanovic (Eds.), *Best Practice Guide on the Control of Arsenic in Drinking Water* (pp. 79-98). IWA Publishing. London, UK
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