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DOI
10.4233/uuid:46d78438-a10b-4df4-a022-6c818a65d1f7

Publication date
2022

Document Version
Final published version

Citation (APA)
Annaduzzaman, M. (2022). *Enhancing Arsenic Removal from Bangladesh Groundwater by Controlled Iron Oxidation in Filters*. [Dissertation (TU Delft), Delft University of Technology].
https://doi.org/10.4233/uuid:46d78438-a10b-4df4-a022-6c818a65d1f7

ENHANCING ARSENIC REMOVAL FROM BANGLADESH GROUNDWATER BY CONTROLLED IRON OXIDATION IN FILTERS

MD ANNADUZZAMAN

Enhancing Arsenic Removal from Bangladesh Groundwater by Controlled Iron Oxidation in Filters

Dessertation

For the purpose of obtaining the degree of doctor
at Delft University of Technology
by the authority of the Rector Magnificus, Prof.dr.ir. T.H.J.J. van der Hagen
chair of the Board for Doctorates
to be defended publicly on
Tuesday 12 July 2022 at 12:30 o'clock
by

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This research study was supported by NWO-WOTRO funded DELTAP project.
ISBN : 978-94-93270-75-6
Printed by: Proefshrift All In One (AIO) - the Netherlands
Cover design: Proefshrift All In One (AIO) - the Netherlands

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To the people who suffer from arsenic-contaminated drinking water...............

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Chapter 1

Introduction

1.1 Arsenic in natural groundwater

Arsenic (As) in natural groundwater is a geogenic, carcinogenic constituent that causes severe drinking water quality problems in various countries worldwide (Bhattacharya et al., 2004; Mukherjee et al., 2008; Smith et al., 2000). Regular consumption of arsenic-contaminated water beyond the standards may lead to chronic diseases such as skin lesions, skin, bladder and kidney cancer, peripheral vascular disease, neurological effects, hypertension, and cardiovascular disease (Huaming et al., 2013; Li et al., 2012; Luzi et al., 2004). The World Health Organization (WHO) recommends that As concentrations in drinking water should not be more than 10 µg/L (WHO, 2011). However, in many areas, the concentration of As in groundwater, used for drinking purposes, could contain >1000 µg/L, such as in Argentina, Bangladesh, Bolivia, Canada, China, Finland, Germany, Ghana, Hungary, India, Myanmar, Nepal, Netherlands, Nicaragua, Pakistan, Romania, Sweden, The United States of America (USA), and Vietnam (Bhattacharya et al., 2007; Smedley and Kinniburgh, 2002). The WHO has reported that about 200 million people depend on As contaminated water that exceeds the recommended value of 10 µg/L (Guglielmi, 2017; Podgorski and Berg, 2020).

In reducing groundwater with near-neutral pH, As exists in the thermodynamically stable form as arsenite, or As(III) (Cullen and Reimer, 1989; Smedley and Kinniburgh, 2002), while, in oxidizing conditions, arsenate, or As(V), is the predominant species (Jones et al., 2012; Lafferty et al., 2010; Villalobos et al., 2014). The speciation of As is pH-dependent. Under reducing conditions and pH below 9.2, the dominant As(III) species is the neutral $H_3AsO_3^0$. However, in oxidizing conditions and at low pH (<6.9), As(V) mainly exists as monovalent $H_2AsO_4^-$ species, and at high pH (>6.9), the dominant species is $HAsO_4^{2-}$ (Welch and Stollenwerk, 2003). The distribution and concentration of As in groundwater is the consequence of geochemical and geo-microbial processes, resulting in its dissolution from solid sources into the groundwater (Ravenscroft et al., 2009; Smedley and Kinniburgh, 2002). The possible four mobilization mechanisms include sulfide oxidation, alkali desorption, geothermal As mobilization, and reductive dissolution (Nordstrom, 2002; Ravenscroft et al., 2009). Sulfide oxidation is commonly reported in mining areas (e.g., Ghana and Thailand), where sulfide minerals (FeS_2 and FeAsS) are exposed to oxygenation, and the subsequent desorption of these minerals result in high concentrations of As(V) in groundwater (Ravenscroft et al., 2009; Smedley and Kinniburgh, 2002). The alkali desorption of As in groundwater (e.g., in Argentina) is often mentioned in aerobic and oxidizing aquifers, which is also known for its low iron and manganese content, and high As(V) and HCO_3^- concentrations (Bhattacharya et al., 1997; Ravenscroft et al., 2009; Smedley and Kinniburgh, 2002). Arsenic dissolution by geothermal activities is related to high temperature and a high chloride (Cl^-) concentration in water. Once the As(III) enriched geothermal fluids mix with oxygenated water from shallow aquifers (<70 m), As(III) oxidizes and enriches these source waters with As(V) (Smedley and

Kinniburgh, 2002; Welch and Stollenwerk, 2003; Wilkie and Hering, 1998). The geothermal dissolution of As in drinking water sources is mainly found in the American continent, such as in Nicaragua (Bayardo, 2019), the USA (Plummer, 2003), and Argentina (Bhattacharya et al., 2006). Reductive dissolution is mainly found in anoxic and strongly reducing aquifers, where As-bearing minerals (e.g., iron oxides) are dissolved in groundwater, leading to the presence of As(III) (Bhattacharya et al., 1997; Nickson et al., 2000). The reductive dissolution mobilization is generally the dominant mechanism in Asian regions like in the Bengal Delta Plain (Bangladesh, West Bengal, India) (Bhattacharya et al., 2004; Nickson et al., 2000) and the Mekong Delta Plain (Vietnam and Cambodia) (Berg et al., 2007).

1.2 Drinking water practices in Bangladesh

Like many developing countries, Bangladesh, part of the vast Ganges-Brahmaputra-Meghna (GBM) Delta plan, suffers from huge drinking water quality problems (Bhattacharya et al., 2007; Smedley and Kinniburgh, 2002). In Bangladesh, people relied on surface water bodies (e.g., canals, rivers, ponds, lakes, and ring wells) before installing shallow (<70 m) tubewells in the early 1970 (Ahmad et al., 2018). Until discovering As contamination in 1993, it was assumed that groundwater sources were safe for drinking water supply (Smith et al., 2000). Nowadays, about 90% of the people in Bangladesh depend on groundwater for their drinking purposes, while As concentrations frequently exceed the Bangladesh Drinking Water Standards (BDWS) of 50 µg/L, five times higher than the WHO guideline (10 µg/L), sometimes even upto 1500 µgAs/L (Nordstrom, 2002; Zecchin et al., 2019). In arsenic-contaminated regions, two potential mitigation options or solutions are considered to be appropriate. Firstly, identification of the arsenic-safe alternative sources, such as safe shallow wells (<70 m) or deep wells (>70 m), combined with a piped water supply system. Secondly, As removal (treatment) technology-based (piped) water supply.

1.3 Groundwater treatment

The treatment technologies used in arsenic-affected rural areas are commonly based on complicated and sophisticated technologies such as adsorption, chemical precipitation, ion exchange, membrane filtration, nanofiltration (NF), and reverse osmosis (RO) (Alka et al., 2021). Although effective in removing As from water during the initial period of operation, these technologies are not sustainable on the long run, resulting in high failure rates (Hossain et al., 2016; Unicef, 2020). These systems are complicated to operate and maintain, requiring regular parts replacement and aftermarket services, and demanding skilled personnel, and high costs. The sustainability of any treatment technology mainly depends on low implementation cost, efficiency, minimal installation complexity, and low operation and maintenance requirements.

A conventional sand filter can be a safe and sustainable alternative that uses locally available skills, materials, and crafts. However, a sand filter is not as effective in removing high As concentrations, since they mainly designed to remove iron (Fe), manganese (Mn), and ammonium (NH_4^+) from the groundwater. A key reason for poor As removal is that the uncharged As(III), in reduced groundwater, does not effectively adsorb to the hydrous ferric oxides (HFO) flocs that are naturally formed during aeration-filtration (Bissen and Frimmel, 2003). As such, pre-oxidation of As(III) to As(V) is typically needed for effective As removal (Cui et al., 2018; Ghurye and Clifford, 2004; Lee et al., 2003). However, As(III) oxidation with dissolved oxygen (DO) is a slow process (half-life of days) and, therefore, chemical oxidants (e.g., chlorine, permanganate, and ozone) are frequently applied to accelerate As(III) oxidation before removal. However, these chemical oxidants can produce residual and harmful chemical by-products, demanding further removal and management (Katsoyiannis and Zouboulis, 2006; Mondal et al., 2013), and are costly and complicated to handle, making them less sustainable for rural Bangladesh. As an alternative, the conventional groundwater treatment consisting of aeration and rapid sand filtration (RSF) could be optimised for As(III) removal. In earlier studies it has been found that rapid As(III) oxidation to As(V) occurs in the top layer of RSF (Gude et al., 2016; 2017). However, subsequent removal of As with the formed HFO flocs is ineffective, because of the rapid and (almost) complete iron oxidation and removal in the same toplayer, leaving insufficient HFO for effective adsorption of the formed As(V) (van Beek et al., 2015; de Vet et al., 2011). Moreover, the rise in pH during aeration increases the negative surface charge on HFO flocs, also decreasing the As removal potential (Dixit and Hering, 2003; Han et al., 2016). Finally, phosphate and As(V) can compete for HFO flocs adsorption sites (Liu et al., 2001; Sahai et al., 2007), leading to reduced As uptake by HFO flocs when phosphate (and silicate) are present at higher concentrations (Kanematsu et al., 2013; Li et al., 2012).

1.4 Knowledge gap, research questions and approach

Currently, conventional aeration-filtration is thus used for the removal of iron, ammonium, and manganese (Bruins et al., 2014; Katsoyiannis et al., 2008b, 2008a; Vries et al., 2017). However, this treatment method is not considered a robust barrier for As removal, as its efficiencies typically vary between 15% and 95% (Gude et al., 2016; Lowry and Lowry, 2002; Sorlini and Gialdini, 2010), depending on the water chemistry (Sorlini and Gialdini, 2014). Co-removal of As with groundwater native-iron is reported to be only possible if As concentrations are low (<50 µg/L) (Gude et al., 2018; Katsoyiannis et al., 2015), despite having sufficient iron to As ratio in the source water (Annaduzzaman et al., 2018; Biswas et al., 2012; Sharma et al., 2016). Furthermore, studies by Holm and Wilson (2006) showed that although groundwater having native-Fe^{2+}iron of >1.5 mg/L, only 20–25% (8–10 µg/L) of As could be removed. This was also the case in Lowry and Lowry's (2002) study that showed that aeration and storage of iron containing groundwater facilitated only partial As removal with HFO flocs. Roberts et al. (2004) also revealed that 50–55 mg/L of iron was required to achieve <50 µg/L As in the treated solution from 500 µg/L of As in a system with iron oxidation (single-step) prior to As(III) oxidation. However, Robert et al. (2004) also explained that if the iron oxidation was performed in sequence (step-wise), only 20–25 mg/L of iron could be sufficient to achieve over 90% As removal efficiency.

Therefore, in the present thesis is was hypothesized that anoxic storage of groundwater, before aeration-sand filtration, could allow step-wise/delayed iron oxidation, enhancing As removal under minimum iron to As ratios. However, the oxidation mechanisms and effects of temporal changes in various water quality parameters in such storage containers are not fully understood. Therefore, the interactions between iron, As, phosphate and manganese after aeration and in sand filtration need to be studied to understand the effect of the various water quality parameters on As removal with HFO flocs.

In order to achieve this main objective, the following research questions are answered:

- How is As removal affected by delaying the groundwater native-iron oxidation using anoxic storage?
- How does anoxic storage followed by aeration and rapid sand filtration improve overall As removal compared to conventional oxic storage?
- Does the step-wise/sequential iron oxidation reduce the inhibitory effects of phosphate and silicate on arsenic removal?
- What are the differences when operating this novel, passive treatment process with varying groundwater composition in Bangladesh?

By answering these research questions, it should be possible to treat As-contaminated groundwater and supply safe drinking water without using any chemicals or complex methods but only locally available materials and crafts. The research was conducted on a pilot scale using different natural groundwaters (in Bangladesh). In addition, additional experimental research was performed at the Waterlab at the Water Management Department of Delft University of Technology, the Netherlands.

1.5 Outline of the thesis

In **Chapter 2**, anoxic storage of natural groundwater was monitored to understand the oxidation processes of native-iron and As(III). The influence on As removal efficiency by delayed/step-wise groundwater native-Fe^{2+} oxidation in anoxic storage followed by aeration and dual-media sand filtration is discussed in **Chapter 3**. **Chapter 4** scrutinizes the impact of individual and combined presence of phosphate and silicate on As removal under step-wise/sequential Fe^{2+} oxidation conditions with an initial pH of 7.0, representing targeted groundwater conditions in Bangladesh. Based on the findings from previous chapters, in **Chapter 5** the entire treatment concept is validated at pilot-scales using various natural groundwaters at different locations to maximize As adsorption to HFO flocs in rapid sand filters in As contaminated rural villages in Rajshahi district of Bangladesh. Finally, conclusions and recommendations for future research are discussed in **Chapter 6**.

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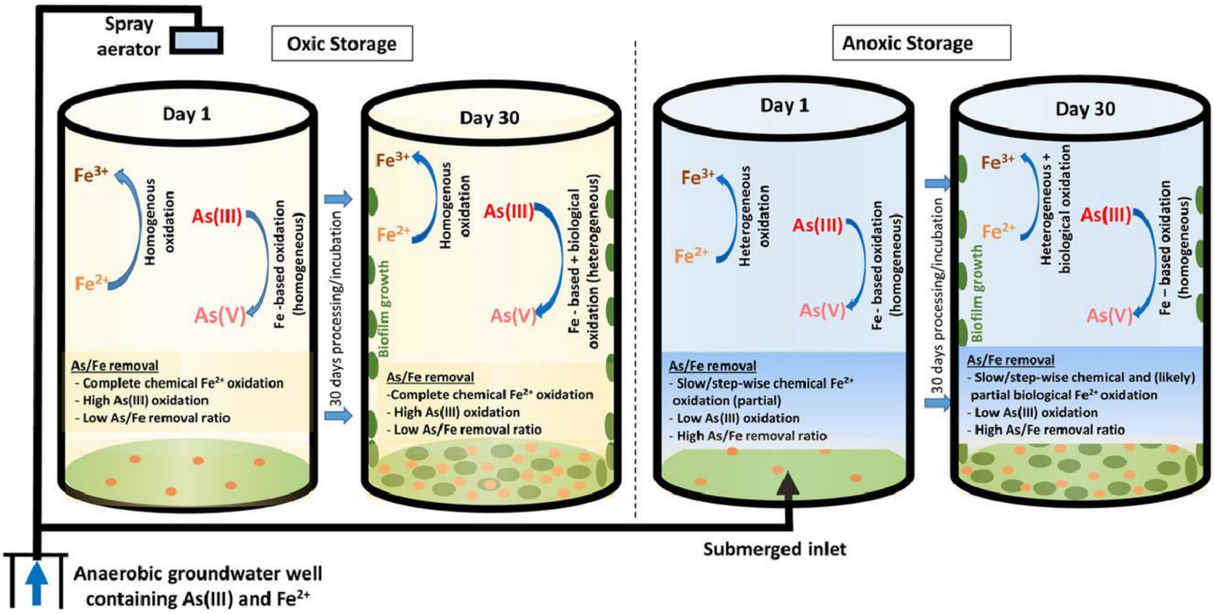
Chapter 2

Anoxic storage to promote arsenic removal with groundwater-native iron



This chapter is based on:

Md Annaduzzaman, Luuk C. Rietveld, Devanita Ghosh, Bilqis A. Hoque, Doris van Halem (2021). Anoxic storage to promote arsenic removal with groundwater-native iron, Water Research, Volume 202, 2021, 117404, https://doi.org/10.1016/j.watres.2021.117404

Abstract

Storage containers are usually used to provide a constant water head in decentralized, community groundwater treatment systems for the removal of iron (Fe) and arsenic (As). However, the commonly practiced aeration prior to storage assists in rapid and complete Fe^{2+} oxidation, resulting in poor As removal, despite sufficient native-Fe^{2+} in the source water. In the this study, it was found that application of anoxic storage enhanced As removal from groundwater, containing ≥300 µg/L of As(III) and 2.33 mg/L of Fe^{2+} in an As affected village of Rajshahi district in Bangladesh. Although the oxidation of Fe^{2+} and As(III) during oxic storage was considerably faster, the As/Fe removal ratio was higher during anoxic storage (61- 80±5 µgAs/mgFe) compared to the oxic storage (45±5 µgAs/mgFe). This higher As removal efficacy in anoxic storage containers could not be attributed to the speciation of As, since As(V) concentrations were higher during oxic storage due to more favorable abiotic (As(III) oxidation by O_2 and Fenton-like intermediates) and biotic (As(III) oxidizing bacteria, e.g., *Sideroxydans, Gallionella, Hydrogenophaga)* conditions. The continuous, in-situ hydrous ferric oxide floc formation *during flow-through operation*, and the favorable lower pH aiding higher sorption capacities for the gradually formed As likely contributed to the improved performance in the anoxic storage containers.

Keywords: Groundwater; Treatment; Anoxic; Storage container; Arsenic; Iron

2.1 Introduction

The geogenic groundwater contamination of arsenic (As) negatively affects the quality of drinking water, leading to health risks in many countries including Bangladesh and India (Chakraborty et al., 2015; Smedley and Kinniburgh, 2002). Long-term consumption of As contaminated water may cause skin lesions, melanosis, hyperkeratosis, skin cancer and internal organs damage (Farmer and Johnson, 1990; Guo et al., 2013; Li et al., 2012; Luzi et al., 2004). According to the World Health Organization (WHO), the recommended values for As in drinking water should not exceed 10 µg/L (WHO, 2011), whereas 50 µg/L is the maximum allowable limit in Bangladesh. However, As can be found in groundwater-based drinking water supplies in Bangladesh up to several mg/L (Nordstrom, 2002). In oxidizing conditions and circumneutral pH, such as in surface waters, arsenate [As(V)] is the predominant species, which is usually present in the immobile state, forming oxyanions ($H_2AsO_4^-$, $HAsO_4^{2-}$) (Katsoyiannis and Zouboulis, 2004; Lafferty et al., 2010). However, under circumneutral pH and reducing conditions like in groundwater aquifers, arsenite [As(III)] specie is the more toxic, mobile, and thermodynamically stable in the non-ionic form (H_3AsO_3) (Villalobos et al., 2014). Therefore, pre-oxidation from As(III) to As(V) is an essential step for As contaminated water treatment processes such as precipitation, co-precipitation, coagulation-filtration, and adsorption on iron (Fe)-oxides, activated alumina or bone char (Bai et al., 2016; Begum et al., 2016; Niazi et al., 2018; Pio et al., 2015; Zhang et al., 2010). However, oxidation of As(III) through dissolved oxygen (DO) is thermodynamically feasible but is slow (Gude et al., 2018b; Sorlini and Gialdini, 2010).

Aeration is commonly used for oxidizing Fe^{2+} and removing carbon dioxide, methane, hydrogen sulfide, and volatile organic compounds from water (Bruins et al., 2014; Katsoyiannis et al., 2008; Vries et al., 2017). Moreover, if the water source also contains As, the oxidation of Fe^{2+} can also enhance As(III) oxidation by reactive oxidation species (ROS) and/or Fenton-like chemical reactions (Hug et al., 2001; Hug and Leupin, 2003; Roberts et al., 2004). The freshly formed hydrous ferric oxide (HFO) flocs from Fe^{2+} oxidation can bind and co-precipitate with As (Katsoyiannis et al., 2015; Roberts et al., 2004; Senn et al., 2018), where the binding-affinity for As(V) is stronger than for As(III) (Bissen and Frimmel, 2003; Cui et al., 2018). However, the removal of As with oxidized HFO flocs has been found to be inefficient due to rapid and almost complete Fe^{2+} oxidation during storage or filtration before complete As(III) oxidation (Annaduzzaman et al., 2021; Gude et al., 2016; Roberts et al., 2004). Moreover, as formerly observed, the rise in pH during aeration increases the negative surface charge on HFO flocs and hence decreases As removal potential (Dixit and Hering, 2003; Han et al., 2016).

Storage containers are usually used to provide a constant water head in decentralized, community treatment systems for the removal of iron (Fe) and arsenic (As) (Chakraborty et al., 2016). However, the commonly practiced aeration prior to storage results in rapid and complete Fe^{2+} oxidation, resulting in poor As removal despite sufficient native-Fe^{2+} in the source water. As a result, the conventional oxic storage and filtration processes require additional chemical oxidants/adsorbents for As removal. In a recent study (Annaduzzaman et al., 2021), it was found that delayed aeration before sand filtration enhanced overall As removal. It is hypothesized that the observed partial Fe^{2+} oxidation during anoxic storage promoted As removal in the following aeration-filtration steps. However, the oxidation mechanisms and effects of temporal changes in various water quality parameters in such storage containers are not yet fully understood. Therefore, this study aims to address the following knowledge gaps: (i) the mode of Fe^{2+} and As(III) oxidation, being either homogeneous, heterogeneous (surface-related process), biological, or in various combinations (van Beek et al., 2015; Vries et al., 2017), (ii) the role of various biological processes by subsurface-derived indigenous microorganisms (Crognale et al., 2019; Gude et al., 2018a), and (iii) the effect of a larger surface area to adhere biofilms by application of bio-carriers in the storage container.

Thus, this novel concept of anoxic storage was monitored to understand the oxidation processes of groundwater native-Fe^{2+} and As(III), and their effect on As removal, compared to the conventional oxic storage in the presence and absence of bio-carriers. The oxic and anoxic storage container experiments were conducted over 30 days with natural (ground)water, in the presence of native-Fe^{2+} (2.33 mg/L), As (>300 µg/L), and other ions like PO_4^{3-} (2.15 mg/L)and NH_4^+ (0.96 mg/L). Furthermore, this research also studied the role of bio-carriers and consequent changes in bacterial growth in the storage containers.

2.2 Materials and methods

2.2.1 Groundwater sample quality

The experiments were performed in polypropylene storage containers (GAZI, Bangladesh) with a capacity of 75L, using As contaminated groundwater in the affected Uttar Kazirpara village in Paba, Rajshahi district, Bangladesh. The relevant water composition of the used groundwater is shown in Table 1. The anoxic groundwater was extracted from a borehole of 50±1 m depth using a submersible pump (GAZI, Bangladesh).

Table 1. The relevant groundwater compositions used in the study.

Water Quality Parameters	Unit	Raw Groundwater
pH	[-]	6.94
Dissolved Oxygen (DO)	mg/L	0.07*
Oxygen Reduction Potential (ORP)	mV	-110±10
Electrical Conductivity (EC)	µS/cm	675
Temperature	°C	26.7
As(total)	µg/L	329±3%
As(V)	µg/L	39±5%
As(III)	µg/L	290±5%
Fe^{2+}	mg/L	2.33±3%
Manganese (Mn)	µg/L	600±5%
Ammonium (NH_4^+)	mg/L	0.96±0.02(SD)
Nitrate (NO_3^-)	mg/L	0.39±0.02(SD)
Phosphate (PO_4^{3-})	mg/L	2.15±0.03 (SD)

*The observed DO value is the lower limit of the measuring device.

2.2.2 Experimental set-up of storage containers

The experimental set-up consisted of eight 75L polypropylene containers (GAZI, Bangladesh) to study four storage conditions in duplicate, namely, oxic (with/without bio-carriers) and anoxic (with/without bio-carriers) (Fig. 1). The containers with bio-carriers were half-filled with AnoxKaldnes K3 shaped bio-carriers, purchased from a local shop in Dhaka (OSMOSIA Water) Bangladesh (Fig. 1). To ensure an abiotic environment at the start of the experiments, the containers were thoroughly sterilized with 35% (w/w) hydrogen peroxide (H_2O_2) (Sigma-Aldrich). Every 24 hours, the stored water was replaced with freshly extracted groundwater without removing the precipitated Fe-oxide sludge. This refill process was chosen to replicate the conventional storage practices, where the precipitated Fe-oxide sludge generally accumulates in the storage container for several weeks. The groundwater was aerated by passing it through a showerhead, placed 35 cm above the top of the containers with oxic storage.

In the containers with anoxic storage, the inlet of the extracted groundwater was filled without aeration from the bottom of the containers. The anoxic containers were overflown for an additional five minutes to avoid any incidental aeration of water. The water sampling was performed every 60 minutes for the first eight hours on days 1, 5, 10, 20, and 30 of the experimental period. The experimental time of eight hours was selected to prevent full emptying of the storage container (max ±90%) and consequent discontinuation of the column feed.

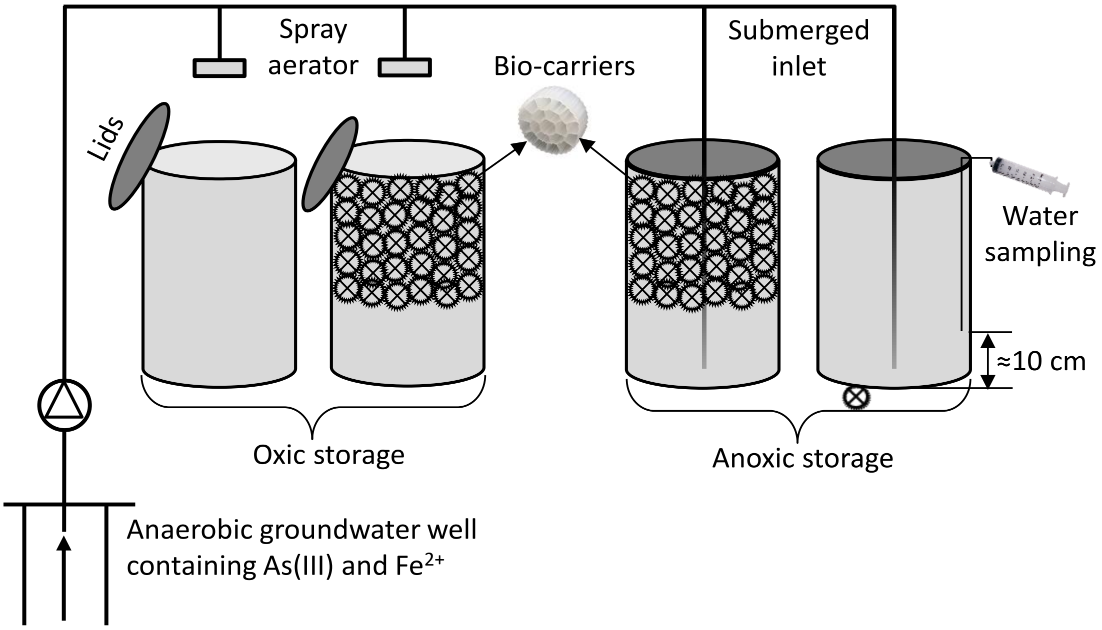


Fig. 1. Schematic overview of the experimental storage container set-up with oxic (left) and anoxic (right) storage conditions. Half of the containers were filled with bio-carriers and all container settings were constructed in duplicate.

During each sampling event, the pH, dissolved oxygen (DO), oxygen reduction potential (ORP), and temperature (T) were directly measured on-site. In the course of each sampling time, 15 mL water samples (both 45 µm (VWR) filtered and unfiltered) were collected in polypropylene transparent 15 mL centrifuge tube (Sigma Aldrich) and acidified with ultrapure HNO_3 acid (ACS reagent, 70%; Formula weight 60.01 g/mol; Sigma Aldrich) to make up for 1.5% acidification of the solutions to preserve for elemental quantification (such as Fe, As, etc.). The water sample was collected using a 60 mL syringe and pre-fixed sampling tube (IV injection tube, SQUARE, Bangladesh) at approximately 10 cm above the bottom of the container (Fig. 1). This arrangement was used to avoid opening of the container's lids, risk of aeration during water sampling and to maintain consistency of sample quality. Additionally, three times a day (0, 4, and 8 hours), 250 mL filtered water samples (without acidification) were collected in the 250 mL polypropylene laboratory-grade water vials for ammonium (NH_4^+), nitrate (NO_3^-

), and phosphate (PO_4^{3-}) analyses. The used chemicals, instruments and reagents during this pilot-scale study are detailed in supplementary data (Table S1), where Fig. S1 represents the experimental approach with relevant parameters in the respective steps. All sample collections and parameter measurements were performed in duplicate from each container.

2.2.3 Chemical analyses

The pH, DO, ORP, and T were directly measured in the field using WTW electrodes (SenTix 940, FDO®925, SenTix ORP 900, and TerraCon 925, respectively) and calibrated using standard method before use. The measurement consistency was maintained by placing the WTW electrodes at ±10 cm above the bottom of the container. All sample collections and parameter measurements were performed in duplicate from each container. Elemental analysis was carried out by Inductively Coupled Plasma Mass Spectrometry, ICP-MS (Alanlytik Jena model PlasmaQuant MS) at Delft University of Technology, the Netherlands. Other ions such as NH_4^+, NO_3^-, and PO_4^{3-} were quantified at Rajshahi Regional Laboratory, Department of Public Health Engineering (DPHE), Bangladesh.

2.2.4 Arsenic speciation

For the As speciation, the ion-exchange resin Amberlite® IRA-400 chlorite was used. This speciation was performed by a 60 mL syringe with 30 mL ion-exchange resin. After 0.45 µm filtration, 100 mL sample were passed through 30 mL ion-exchange resin column. The remaining As concentration in the resin filtrate was considered as reduced As(III) species (Gude et al., 2016; Karori et al., 2006). Finally, the obtained As(III) specie level from the resin filtrate was subtracted from 0.45 µm filtrate (total) As concentration to determine dissolved As(V).

2.2.5 Microbial sampling and analyses

For the microbial community profiling, the biomass from the container wall (inside) and bio-carriers were collected and stored at -80˚C. From these samples, around 0.25 g was used for DNA extraction using the DNeasy UltraClean microbial kit (Qiagen) at Department of Biochemistry and Molecular Biology, Rajshahi University, Bangladesh. Afterward, the DNA samples were used for metagenomics analysis at Novogene Hongkong, China. The cetyl-trimethylammonium bromide/sodium dodecyl sulfate (CTAB/SDS) method was used to extract total environmental DNA from the samples. The purity and concentration of the DNA were examined on 1% agarose gel horizontal electrophoresis. The environmental DNA samples were used for metagenomics analysis with further dilution to 1 ng/µL and amplification of the V3 region of 16S rRNA genes were performed using the universal primers 341F (5'-

CCT ACG CGA GGC AGC AG -3′) and 517r (5′- ATT ACC GCG GCT GCT GG -3′) (Muyzer et al., 1993) at Novogene Hongkong, China. Polymerase chain reactions (PCR) were performed with Phusion® High-Fidelity PCR Master Mix (New England Biolabs). The same volume of 1X loading buffer was mixed (containing SYBR green) with PCR products and electrophoresis on 2% agarose gel electrophoresis was performed for detection. Samples with a bright prominent band strip between size 400-450 bp were chosen for further experiments. The PCR products were mixed in equal ratios and purified with the Qiagen Gel Extraction Kit (Qiagen, Germany). The Illumina HiSeq paired-end raw reads were generated with NEBNext® UltraTM DNA Library Prep Kit and quantified via Qubit and qPCR.

The Illumina HiSeq paired-end raw reads were checked for quality (Base quality, base composition, GC content) using the FastQC tool (Andrews et al., 2010). The QIIME (Version: 1.9.1) pipeline (Caporaso et al., 2010) was used for the selection of 16S RNA, clustering, and OTU picking followed by taxonomic classification based on the SILVA database and statistical analysis. The chimeric sequences were removed from the libraries using the de-novo chimera removal method UCHIME implemented in the tool VSEARCH. Pre-processed reads from all samples were pooled and clustered into Operational Taxonomic Units (OTUs), based on their sequence similarity using the Uclust program (similarity cutoff = 0.97). A representative sequence was identified for each OTU and aligned against the SILVA core set of sequences using the PyNAST program (Caporaso et al., 2010). The representative sequences of the OTUs were also used to predict KEGG orthodoxy (KO) abundances using PICRUSt2 (Langille et al., 2013) and microbial pathways were inferred. The six metagenomic library datasets from the containers under oxic (S1, S2, S3) and anoxic (S1, S2, S3) conditions were clustered, based on the arithmetic mean of weighted Unifrac distance using Unweighted Pair Group Method (UPGMA). An unrooted Neighbor-Joining (NJ) tree of the 35 predominant and common bacterial 16S rRNA sequences was build using the software MEGA X version 10.1. The raw sequencing data have been submitted to the NCBI Sequence Read Archive; accession number PRJNA673456 (https://www.ncbi.nlm.nih.gov/sra/ PRJNA673456).

2.3 Results and Discussion

2.3.1 Immediate changes in pH, DO, ORP and Fe^{2+}

The pH, ORP, DO, and Fe^{2+} concentration during oxic and anoxic storage without the presence of bio-carriers, measured at the start of the experiment (day 1), are shown in Fig. 2. While the natural groundwater pH, DO, and ORP were 6.94, 0.07 mg/L, and -110 mV, respectively, after aeration the average pH, DO, and ORP increased to 7.5(±0.03), 6.75(±0.05) mg/L, and 130(±10) mV, respectively. This was due to atmospheric gaseous exchange resulting in the release of CO_2 and uptake of O_2. The results for the containers with bio-carriers are shown in Supplementary Fig. S2. During the 8 hours of observation, the pH and ORP remained stable during oxic storage (Fig. 2a,c, and S1a,c), and DO remained above 6.26 mg/L (Fig. 2b, S2b). The dissolved Fe concentration (considered as Fe^{2+}) dropped to an average of 0.30 mg/L from its initial (groundwater) concentration of 2.33 mg/L, which was due to rapid Fe^{2+} oxidation at the high DO and pH ($t_{1/2}$: roughly 2-3 minutes; Fig. 2d) (Morgan and Lahav, 2007; Stumm and Lee, 1961).

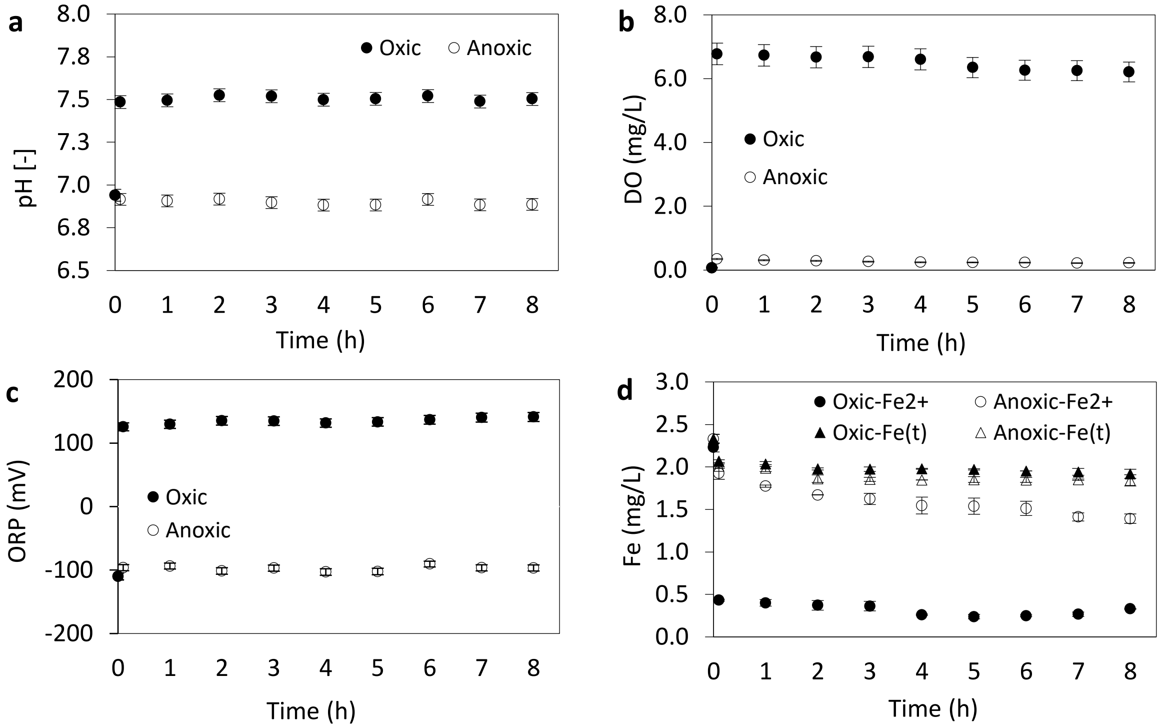


Fig. 2. Physicochemical parameters during the first 24 hours of the experiment during oxic and anoxic storage containers without bio-carriers (a) pH, (b) DO, (c) ORP changes, and (d) physicochemical parameters as a function of Fe^{2+} concentration. The error bars represent the standard deviations.

During anoxic storage Fe^{2+} oxidation was slow in comparison with the oxidation rate during oxic storage, due to the lower levels of pH (6.9), DO (0.35 mg/L), and ORP (± - 100 mV) (Fig. 2a,b,c), as evidenced during earlier studies (Vollrath et al., 2012; Wang et al., 2013). The ORP remained stable, similar to its initial value (± - 110 mV) over 8 hours (Fig. 2c), while DO dropped from 0.35 mg/L to 0.23 mg/L. After the experimental 8 hours, 1.39(±0.05) mg/L of Fe^{2+} remained dissolved in the water (Fig. 2d, S2d). The observed 0.94 mg/L of Fe^{2+} oxidation during anoxic storage corresponded to the average consumed 0.13 mg/L of DO, which was equal to the DO drop over 8 hours. Part of the Fe^{2+} (0.40 mg/L) oxidized immediately during the filling of the containers, as minor DO intrusion could not be avoided upon filling the container. In the first 24 hours of the experiments, no or negligible biological growth and metabolic processes could be expected, thus abiotic Fe^{2+} oxidation must have been predominated, where DO acted as an electron-acceptor in both storage conditions.

2.3.2 Immediate changes in As(III) oxidation and removal

Under both oxic and anoxic conditions, As(III) oxidation started immediately upon filling of the containers (t = 0) and continued over the observed experimental period of 8 hours, as shown in Fig. 3. At the start of the experiment, 100 µg/L and 55 µg/L of As(III) was oxidized during oxic and anoxic storage, respectively. Over the next 8 hours, an additional 48% As(III) oxidation (from 188 µg/L to 97 µg/L) was detected in the oxic storage (Fig. 3a), whereas in the anoxic storage only 22% (from 236 µg/L to 183 µg/L) additional As(III) oxidation (Fig. 3b) was observed. As a result, the dissolved As(V) concentration increased in both storage conditions.

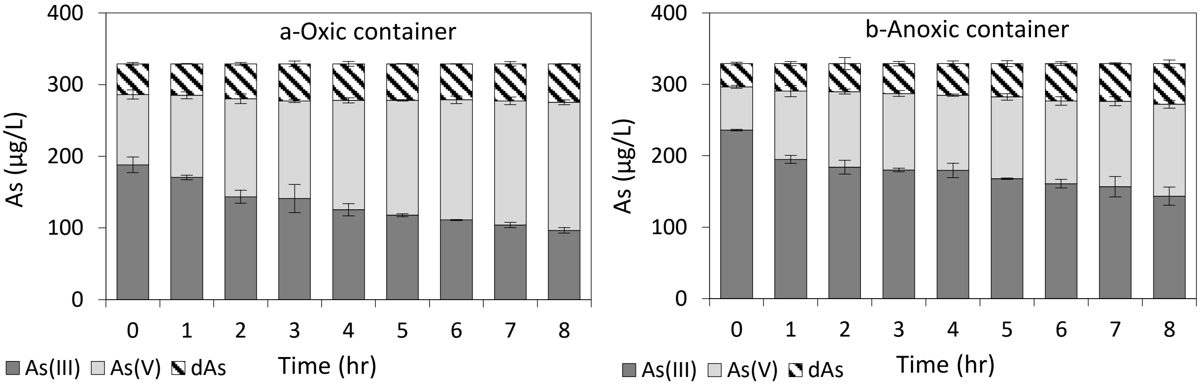


Fig. 3. Arsenic speciation during (a) oxic and (b) anoxic storage contaners without bio-carriers over a period of 8 hours on the first experimental day. The error bars represent the standard deviations.

During oxic storage, As(III) oxidation was faster than in the anoxic storage, probably due to the oxidation of 2.03 mg/L Fe^{2+}, which is known to result in reactive intermediate species (Ciardelli et al., 2008; Cui et al., 2018; Leupin and Hug, 2005; Tian et al., 2017). After almost complete oxidation of Fe^{2+} (2.03 mg/L) in oxic storage (after 5 minutes), the oxidation of As(III) slowed down to a rate of 11 µg/L/h, probably due to homogeneous oxidation with O_2 (DO >6.3 mg/L) (Lowry and Lowry, 2002; Shafiquzzaman et al., 2011), which was in the same order of magnitude as the homogeneous As(III) oxidation observed by Shumlas et al. (2016). The oxidation of As(III) under anoxic conditions was slow (6.5 µg/L/h). The limited concentrations of DO in the anoxic containers resulted in partial/slow Fe^{2+} oxidation and, consequently, the coexistence of Fe^{2+} and oxidized Fe (HFO flocs) stimulated heterogeneous As(III) oxidation (Amstaetter et al., 2010; Tian et al., 2017; Wang and Giammar, 2015). Although the overall removal of As was higher under oxic conditions, the ratio between the removed As and oxidized Fe was higher under anoxic conditions (61 µgAs/mgFe) than under oxic conditions (26 µgAs/mgFe). This result is in-line with earlier studies, indicating that step-wise Fe^{2+} oxidation and precipitation improved As removal by adsorption and/or co-precipitation (Annaduzzaman et al., 2021;

Casentini et al., 2016; Roberts et al., 2004). It appears that the freshly formed HFO flocs in the anoxic storage containers were more efficient for As removal under low pH (6.9), compared to the pre-formed HFO and high pH (7.5) during oxic storage (Kim and Nriagu, 2000; Mercer and Tobiason, 2008; Senn et al., 2018). The As(III) oxidation results for storage with bio-carriers was similar to the experiments conducted without bio-carriers, both for the oxic and anoxic conditions (Fig. 3, S3). This observation underlines that on the first experimental day, surface-related biological processes did not contribute to the As(III) conversion, and As(III) oxidation could be considered as abiotic.

2.3.3 Effect of long-term operation on Fe^{2+} oxidation

The changes in ORP and Fe^{2+} concentration for the various containers over the experimental period of 30 days are shown in Fig. 4. Throughout the experimental periods, the Fe^{2+} concentration during oxic conditions remained low and constant at 0.2(±0.05) mg/L, and ORP values remained constant too, at 130(±10) mV (Fig. 4a). However, during anoxic storage, both in the presence and absence of bio-carriers, ORP, and Fe^{2+} oxidation increased gradually over the 30 days (Fig. 4c,d). Where in the anoxic storage containers without bio-carriers, on the first day, the ORP remained stable over 8 hours, the ORP drifted from -100 mV to -46 mV and from -23 mV to 49 mV on days 5 and 30, respectively (Fig. 4c). During anoxic storage, in the presence of bio-carriers, the ORP drifted from -110 mV on day 1 to -15 mV and -18 mV on days 5 and 30 correspondingly (Fig. 4d). The detected increase in ORP over time during anoxic storage might have resulted from the oxidation of Fe^{2+} (Yue et al., 2016).

During anoxic storage the Fe^{2+} oxidation rate between 1 and 8 hours after filling increased with time from 0.12(±0.01) mg/L/h on the first day to 0.17(±0.02) mg/L/h on day 30. This is probably due to bacterial growth since it is known that at low DO concentrations, biological Fe^{2+} oxidation is faster than abiotic oxidation (Vollrath et al., 2012). In addition, the oxidation rate upon filling (during the first 10 minutes) increased as well, potentially explained by Fe^{2+}/Fe-(hydro)oxide and biofilm enhanced surface-related Fe^{2+} oxidation (Tian et al., 2017; van Beek et al., 2015). The combination of heterogeneous and biological Fe^{2+} oxidation led to an overall drop in Fe^{2+} concentration during anoxic storage to an average of 0.94(±0.05) mg/L on day 30 after 8 hours, from 1.39(±0.1) mg/L on the first day.

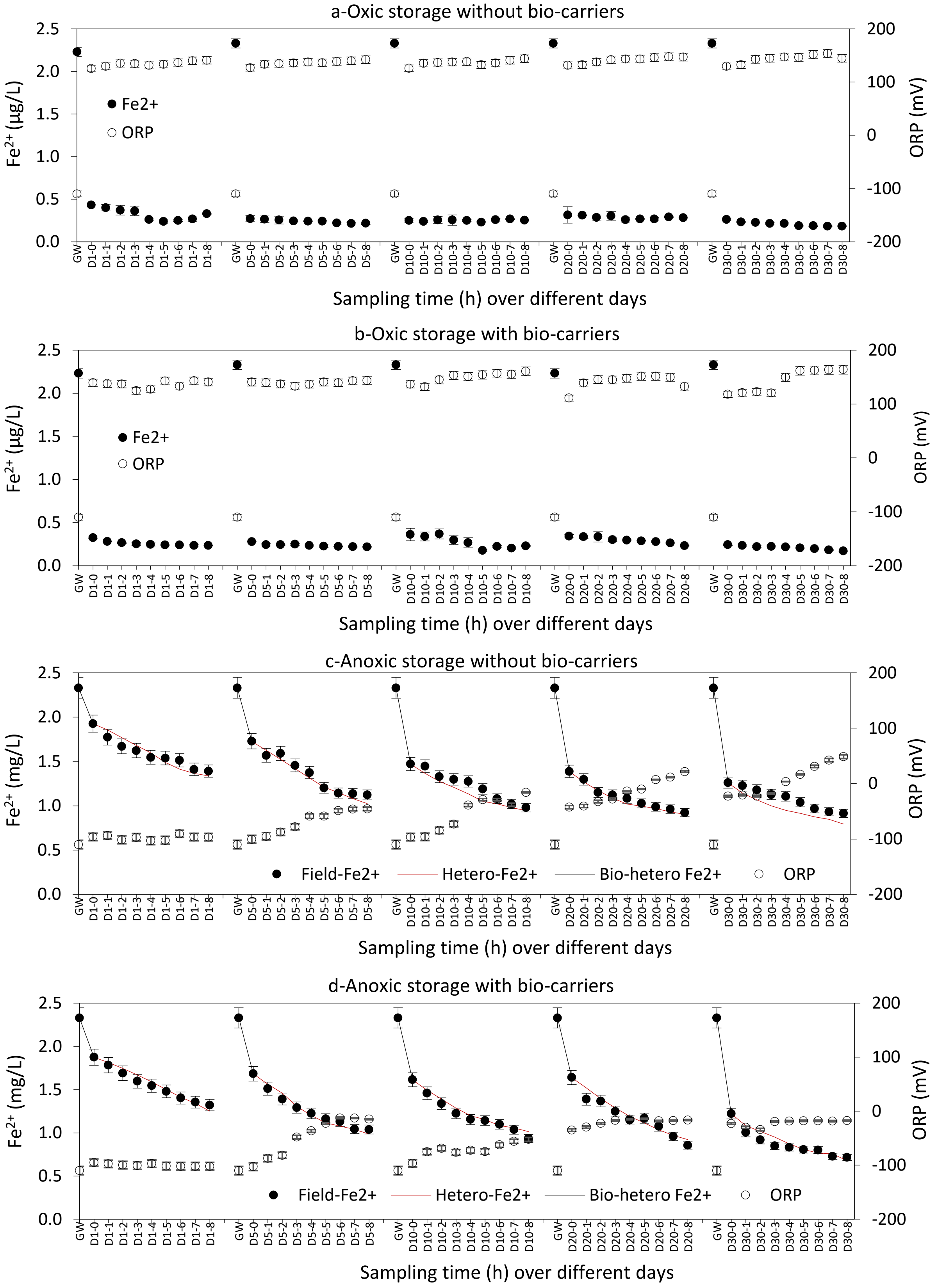


Fig. 4. ORP and Fe^{2+} variation over the experimental periods for oxic storage containers (a) without and (b) with bio-carriers; and anoxic storage containers (c) without and (d) with bio-carriers. The error bars represent the standard deviations.

2.3.4 Effect of long-term operation on As(III) oxidation and removal

Arsenic speciation over the 30 experimental days in the oxic and anoxic storage containers without bio-carriers are depicted in Fig. 5, and the results for the bio-carriers containing containers are detailed in Fig. S4. The As(III) oxidation during oxic storage was considerably higher after 30 days than during anoxic storage. During oxic storage in the containers with bio-carriers, the remaining As(III) concentration decreased from 97 μg/L on day 1 to 64 μg/L on day 30. The detected As(III) oxidation rate (13±5 μg/L/h) during oxic storage at day 30 might have resulted from the high DO concentration (Shumlas et al., 2016) and the favorable high pH (7.5) (Wan et al., 2011). In addition, the growth of As(III) oxidizing bacteria over the days in the containers could also have contributed to the increased As(III) oxidation (Ghosh et al., 2018). The removal of As after the first 8 hours on day 1 was 54(±5) μg/L, increased to 100(±10) μg/L at day 5 and remained constant afterward. This higher and constant removal from day 5 onwards, was possibly caused by the accumulation of HFO flocs (Annaduzzaman et al., 2021).

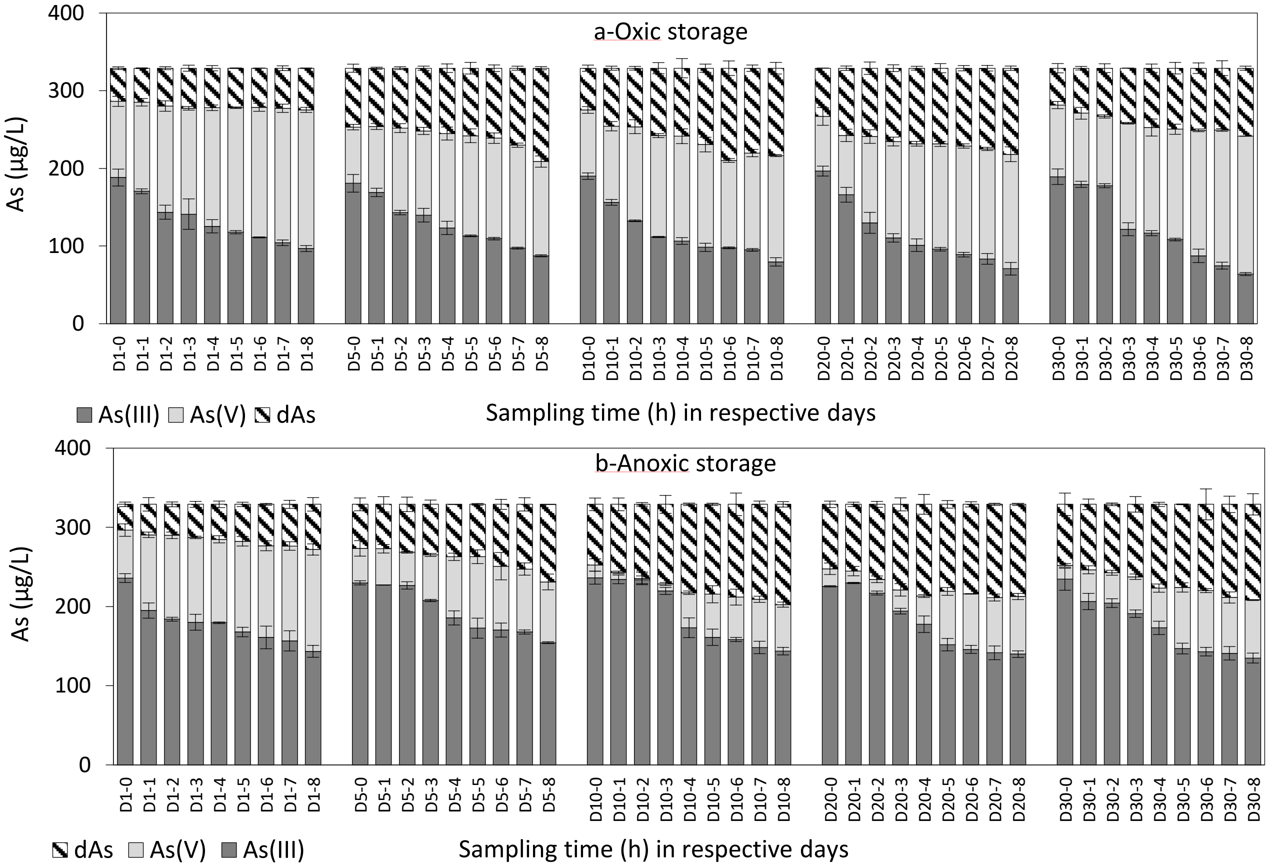


Fig. 5. Oxidation of As(III) and removal over the experimental time at respective days for the (a) oxic, and (b) anoxic storage containers without bio-carriers. The error bars represent the standard deviations.

During anoxic storage, the As(III) oxidation rate also remained nearly stable throughout the 30-day experimentation (Fig. 5b). The oxidation of As(III) was most likely due to the continuous Fe^{2+} oxidation over time. The removal of produced As(V) was more effective during anoxic storage compared to oxic storage, and further improved over the 30 experimental days. The As removal per gram of oxidized Fe increased from 61(±5) µg of As on day 1 to 80(±10) µg of As on day 30 during anoxic storage, where during oxic storage the maximum 45(±5) µg of As removal was achieved after 30 days. Apart from the continuous *in-situ* HFO flocs formation and the favorable low pH (6.7) for As(V) adsorption (Klas and Kirk, 2013; Wan et al., 2011) in anoxic storage, both the oxic and anoxic storage containers that contained bio-carriers showed 20(±5) µg/L higher As(III) oxidation and 17(±5) µg/L higher As removal, respectively, (Fig. S4) compared to the containers without bio-carriers over the experimental period of 30 days, indicating biotic influences, as further discussed below.

2.3.5 Effect of long term operation on NH_4^+, NO_3^-, and PO_4^{3-} concentration

The groundwater NH_4^+, NO_3^-, and PO_4^{3-} concentrations were on average 0.96 mg/L, 0.39 mg/L, and 2.15 mg/L, respectively (Table 1). During both oxic and anoxic storage, oxidation of NH_4^+ was observed after 10 days (Fig. 6a). The decrease in NH_4^+ concentration during oxic storage resulted from the commencement of biological ammonium oxidation (Koch et al., 2019; van Kessel et al., 2015), leading to an increasing NO_3^- concentration from 0.25±0.1 mg/L to 0.73(±0.10) mg/L. However, during anoxic storage without bio-carriers, the NH_4^+ concentration decreased with only 0.15(±0.05) mg/L (Fig. 6a) over the entire experimental 30 days, where the concentration of NO_3^- after 10 days increased from 0.25(±0.05) mg/L to 80(±0.05) mg/L (Fig. 6b). Both the bio-carriers containing containers (oxic and anoxic) showed a ±5% higher decrease in NH_4^+ concentrations which resulted in ±9% elevated NO_3^- formation (Fig. S5a,b) compared to the containers without bio-carriers. The nitrification process, although starting-up slowly, was not hindered by the slow/partial Fe^{2+} oxidation in the anoxic containers.

The concentrations of PO_4^{3-} dropped drastically during oxic storages: from its source (ground)water concentration of 2.15 mg/L to an average of 0.65(±0.05) mg/L (Fig. 6c). This decrease in PO_4^{3-} concentration during oxic storage with and without bio-carriers, compared to anoxic storage, justified its removal with HFO flocs originated from rapid (2.03 mg/L) Fe^{2+} oxidation (Fig. 4a). Over 8 hours of observation, the PO_4^{3-} removal remained constant (±3%), likely due to the lack of new HFO floc formation. However, during anoxic storage the PO_4^{3-} removal followed the slow/step-wise Fe^{2+} oxidation and removal process (Annaduzzaman et al., 2021): over 30 days and after 8 hours PO_4^{3-} decreased from an initial concentration of 2.03(±0.05) mg/L to an average of 1.2(±0.19) mg/L, where Fe^{2+} concentration decreased from an initial concentration of 1.88(±0.1) mg/L to 1.66(±0.14) mg/L.

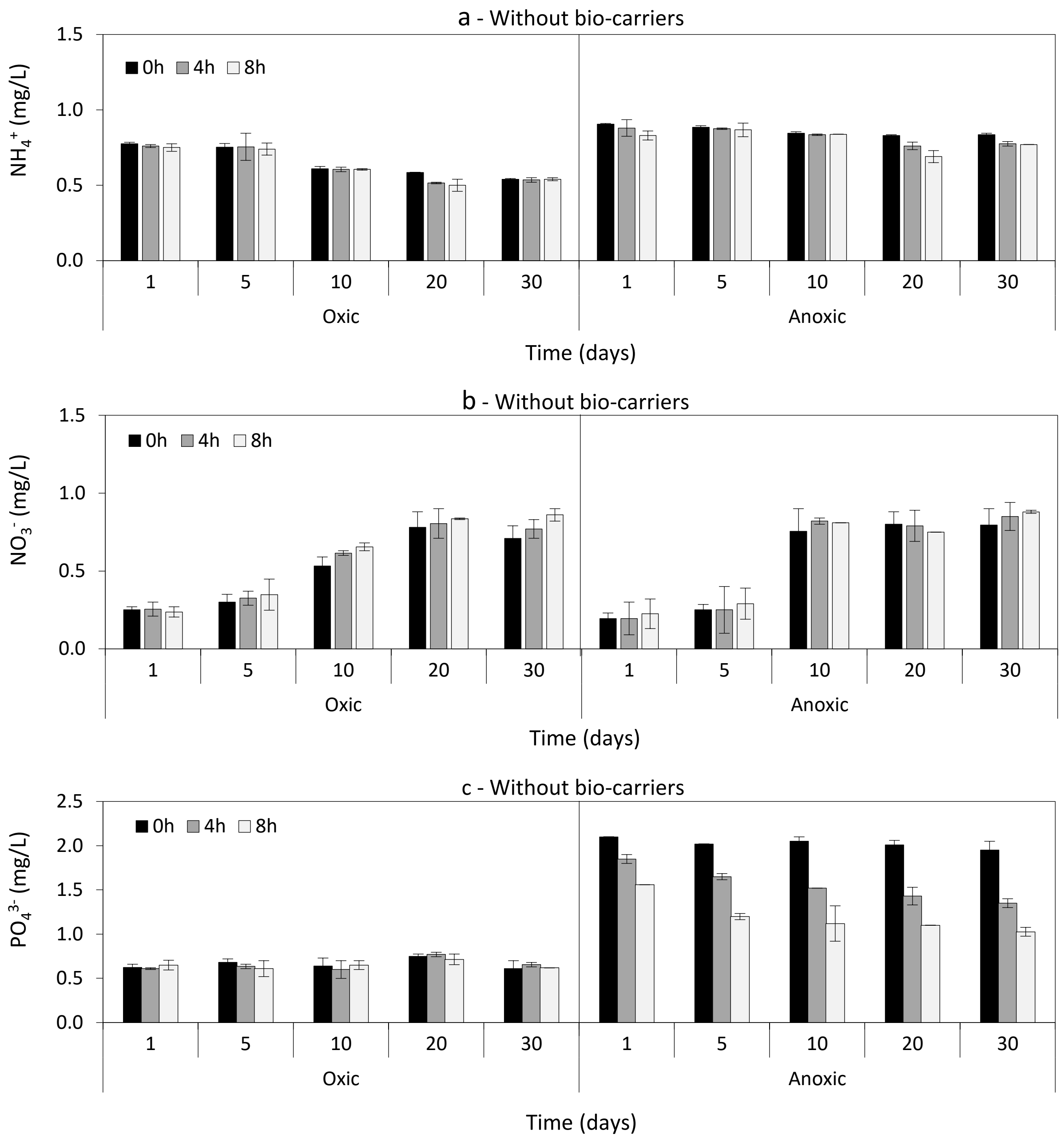


Fig. 6. The concentration of (a) NH_4^+; (b) NO_3^- and (c) PO_4^{3-} at different sampling times (1, 4, and 8 hours) over the experimental period of 30 days of the oxic and anoxic storage containers in the absence of bio-carriers. The error bars represent the standard deviations.

2.3.6 Microbial communities in the container's biomass

The metagenomics analysis of the microbial community from the oxic and anoxic container walls showed the presence of various microbial activities. A predominance of Gram-negative bacteria family, specifically Proteobacteria groups such as *Comamonadaceae, Hydrogenophilaceae, Rhodocyclaceae* was observed (Fig. S6). Gram-negatives are usually dominant in water bodies, especially in the subterrestrial systems and such predominance has been reported in other studies from the Ganges-Brahmaputra-Meghna Delta region before (Chakraborty et al., 2020; Ghosh et al., 2014). Germination of spores and abundance of Gram positives (such as *Geodermatophilaceae, Actinopolysporaceae, Saccharopolyspora, Bacillus, Aeromicrobium, Oceanobacillus*) were found on the walls of containers with oxic water only.

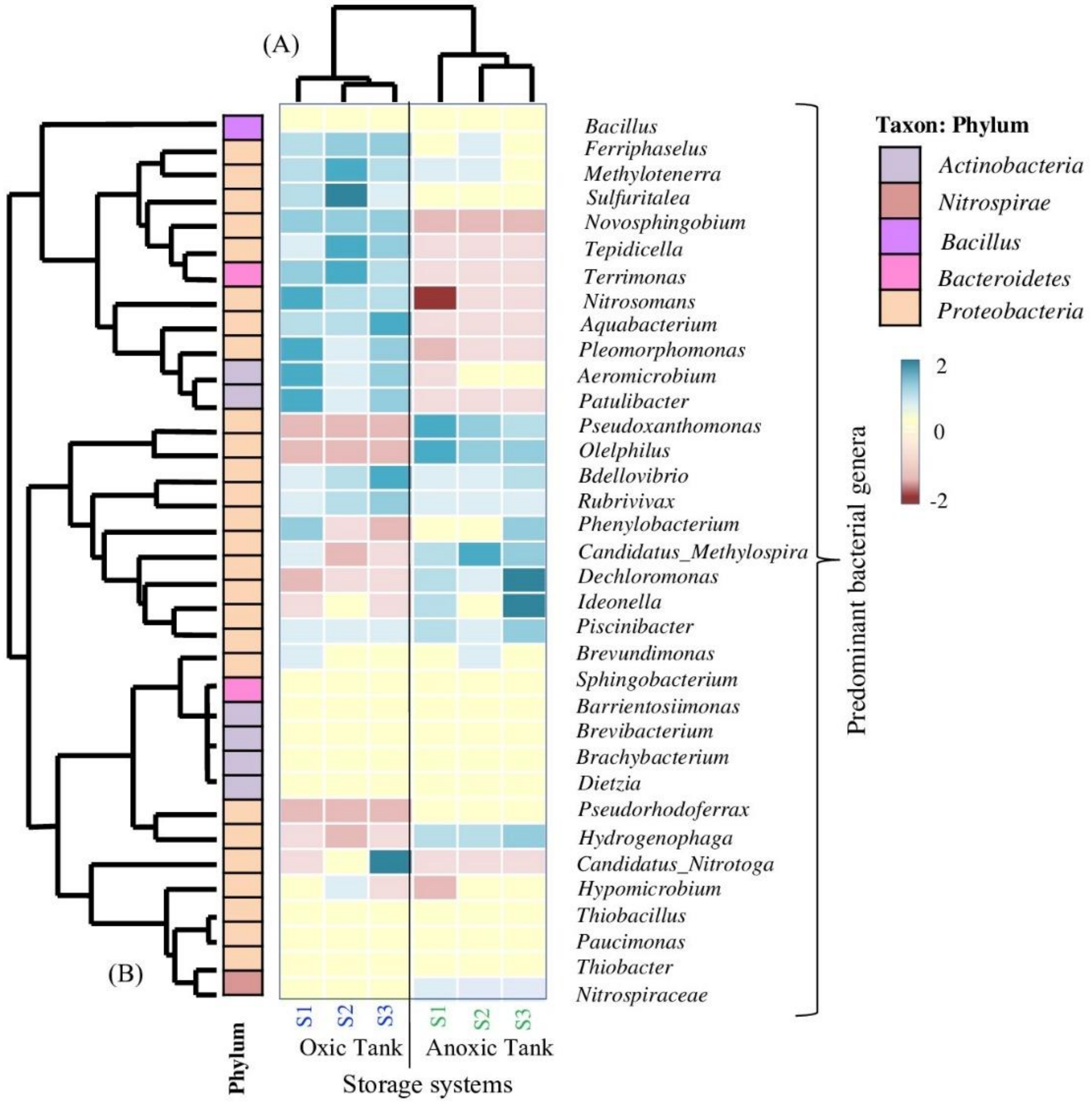


Fig. 7. (A) The samples for generating the metagenomic libraries are clustered based on Weighted Unifrac distance in a UPGMA cluster tree. (B) The predominant common 35 bacterial genera were used to generate a taxonomic heat map and understand their distribution in different setups, where the gradient indicates the distance between the raw score and the mean of the standard deviation. Samples from the oxic storage containers are represented in blue and from the anoxic storage containers are represented in green.

The metagenomic library datasets from the oxic storage containers (S1, S2, S3) and anoxic storage containers (S1, S2, S3) were clustered and are presented in Fig. 7. In the oxic storage containers, after an incubation period of 30 days, the presence of the bacterial species *Pseudorhodoferrax, Thiobacter, Sideroxydans, Gallionella, Patulibacter, Pedomicrobium, Tepidicella,* and *Acidibacillu*s were observed. These bacteria are known to accelerate Fe^{2+} oxidation (Meijler et al., 2002). However, no or limitedly available Fe^{2+} in the oxic storage containers does not imply the notion that these bacteria were involved in Fe^{2+} oxidation only.

In the anoxic storage containers, different chemolithotrophic Fe^{2+} oxidizing bacterial genus was found except for *Pseudorhodoferrax,* which was available in both the oxic and anoxic storage containers. The identified possible chemolithotrophic Fe^{2+}-oxidizers in the anoxic storage containers were *Nitrosomonas, Rhodobacter, and Sphingobacterium* (Table S1). Besides Fe^{2+} oxidation and flocculation, the abundance of Fe-oxidizers along with thiosulfate oxidizers like *Thermithiobacillus, Paucimonas, Thiobacillus, Dyella, Acidibacillus* might also lead to acidification and lowering of pH (Fisher et al., 2008; Ilgrande et al., 2018). This pH decreases further supported a higher As removal by adsorption with the freshly formed HFO flocs in the anoxic storage container.

The absence of the As(III) oxidizing bacterial genus in the anoxic storage containers indicated that the observed As(III) oxidation was probably controlled by continuous and slow/step-wise Fe^{2+} oxidation. However, the observed stable As(III) oxidation during oxic conditions might have been associated with detected *aioA* gene expression of the As(III) oxidizing bacterial groups (Fig. 7), such as - *Sideroxydans, Gallionella, Hydrogenophaga* (de Vet et al., 2011; Ghosh et al., 2018). In addition, the bacterial population on the wall of the container under anoxic conditions was characterized by a higher abundance of *Nitrospirae*, (*Nitrospiraceae*) compared to oxic conditions (Fig. 7), suggesting a possible enhancement of nitrification (Bryce et al., 2018; Koch et al., 2019). Furthermore, the presence of ammonia-oxidizing groups like *Nitrosomonas, Chitinivorax, Legionella, Brevibacterium*, and the absence of nitrite oxidoreductase producing bacterial groups like *Nitrobacter*, may result in possible nitrite (intermediate NO_2^-) production (Ilgrande et al., 2018). The NO_3^- production from NH_4^+ could also attribute to the high rate of nitrate reduction coupled (*Massilia, Candidatus, Paracoccus, Pseudorhodoferrax, Comamonadceae, Hydrogenophaga, Methylomonas*) with dissimilatory Fe^{2+} oxide reduction in the storage containers (Shaw et al., 2020). Overall, the microbial processes fortify additional As removal during the incubation and slow oxidation period in the anoxic storage containers.

2.4 Conclusion

The conventional practice of aeration before storage, where rapid and complete Fe^{2+} oxidation takes place, results in poor As removal despite the presence of sufficient native-Fe^{2+} in the source water. The current study hypothesized that the novel concept of anoxic storage will delay the groundwater native-Fe^{2+} oxidation, and consequently, the in-situ HFO flocs formed would allow for higher As sorption per unit Fe in opposition to the conventional oxic storage. The oxic and anoxic storage container experiments were conducted in pilot scale in the presence and absence of bio-carriers, over 30 days with natural (ground)water containing Fe^{2+} (2.33 mg/L), As (>300 µg/L), and other contaminants like PO_4^{3-} (2.15 mg/L) and NH_4^+ (0.96 mg/L). It was found that application of anoxic storage enhanced As removal from groundwater, containing ≥300 µg/L of As and 2.33 mg/L of Fe^{2+}, in Rajshahi, Bangladesh. Although the oxidation of Fe^{2+} and As(III) during oxic storage was considerably faster, the As/Fe removal ratio was higher during anoxic storage (61-80±5 µg As/mgFe) compared to the oxic storage (45±5 µgAs/mgFe). This higher As removal efficacy could not be attributed to the speciation of As, since As(V) concentrations were higher during oxic storage, due to more favorable abiotic (As(III) oxidation by O_2 and Fenton-like intermediates) and biotic (As(III) oxidizing bacteria, e.g., *Sideroxydans, Gallionella, Hydrogenophaga)* conditions. The bio-carriers containing storage containers (oxic and anoxic) improved only 15% of As oxidation and removal compared to the without bio-carriers containing storage containers. Therefore, the improved performance in the anoxic containers was likely as a consequence of the continuous, in-situ hydrous ferric oxide floc formation in this flow-through system, as well as the favorable lower pH (6.9) aiding higher sorption capacities for the gradually formed As(V).

2.5 Acknowledgment

This study was supported by the NWO-WOTRO funded DELTAP project. All the research assistants from RUET, Rajshahi University, and EPRC are highly acknowledged for their support during the experimentation in Rajshahi, Bangladesh. The authors also thank the landowner Md Sirajul Islam, and his family, without their support, this work would not be possible as the work required to stay for the whole day over the entire experimental period. Finally, the authors are thankful to Nadia van Pelt for her invaluable help with English grammar revision.

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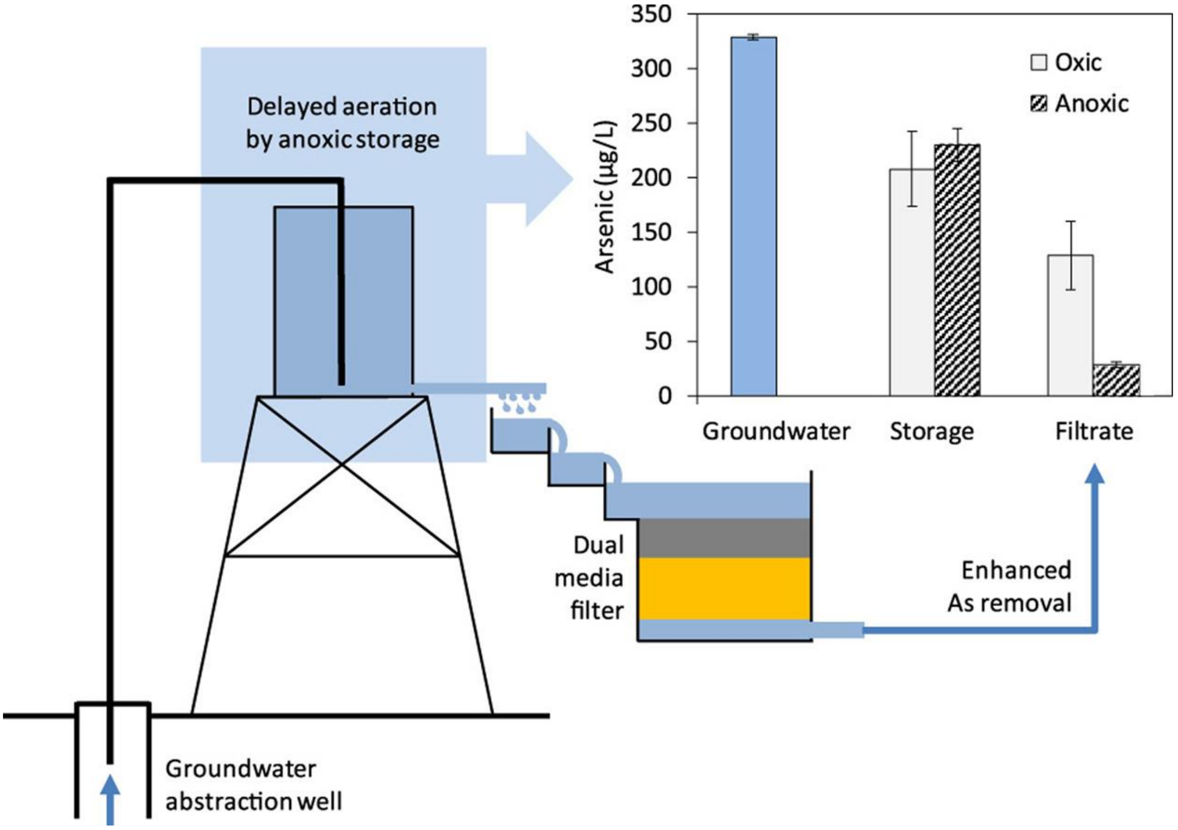
Chapter 3

Arsenic removal from iron-containing groundwater by delayed aeration in dual-media sand filters



This chapter is based on:

Md Annaduzzaman, Luuk C. Rietveld, Bilqis Amin Hoque, Md Niamul Bari, Doris van Halem. (2021). Arsenic removal from iron-containing groundwater by delayed aeration in dual-media sand filters, Journal of Hazardous Materials, Volume (411), 124823.
https://doi.org/10.1016/j.jhazmat.2020.124823

Abstract

Generally, abstracted groundwater is aerated, leading to iron (Fe^{2+}) oxidation to Fe^{3+} and precipitation as Fe^{3+}-(hydr)oxide (HFO) flocs. This practice of passive groundwater treatment, however, is not considered a barrier for arsenic (As), as removal efficiencies vary widely (15-95%), depending on Fe/As ratio. This study hypothesizes that full utilization of the adsorption capacity of groundwater native-Fe^{2+} based HFO flocs is hampered by rapid Fe^{2+} oxidation-precipitation during aeration before or after storage. Therefore, delaying Fe^{2+} oxidation by the introduction of an anoxic storage step before aeration-filtration was investigated for As(III) oxidation and removal in Rajshahi (Bangladesh) with natural groundwater containing 329(±0.05) µgAs/L. The results indicated that As(III) oxidation in the oxic storage was higher with complete and rapid Fe^{2+} oxidation (2±0.01 mg/L) than in the anoxic storage system, where Fe^{2+} oxidation was partial (1.03±0.32 mg/L), but the oxidized As(V)/Fe removal ratio was comparatively higher for the anoxic storage system. The low pH (6.9) and dissolved oxygen (DO) concentration (0.24 mg/L) in the anoxic storage limited the rapid oxidation of Fe^{2+} and facilitated more As(V) removal. The groundwater native-Fe^{2+} (2.33±0.03 mg/L) adsorbed 61% of As in the oxic system (storage-aeration-filtration), whereas 92% As removal was achieved in the anoxic system.

Keywords: Anoxic Storage; Arsenic removal; Sand filtration; Drinking water treatment

3.1 Introduction

Groundwater arsenic (As) contamination is a severe drinking water quality problem and a threat to human health in Bangladesh and other countries (Chakraborti et al., 2013; Smedley and Kinniburgh, 2002). Chronic exposure to As-contaminated drinking water has resulted in tens of millions of people suffering from skin lesions, hyperkeratosis, melanosis, skin cancer, and cancer of internal organs (Guo et al., 2013; Li et al., 2012; Luzi et al., 2004). The World Health Organization (WHO) recommends that As concentrations in drinking water should not be more than 10 µg/L (Smith et al., 2000). However, according to Bangladesh Drinking Water Standard (BDWS), the recommended value for As in drinking water is 50 µg/L. Nevertheless, groundwater in an extended area of Bangladesh contains As concentrations higher than those recommended values (Haque et al., 2018; Perez and Francisca, 2013; Rosso et al., 2011), and sometimes, it even exceeds 1500 µgAs/L (Cavalca et al., 2019; Nordstrom, 2002). In reducing groundwater, at near-neutral pH, As exists in the thermodynamically stable form as arsenite or As(III) (H_3AsO_3) (Cullen and Reimer, 1989; Smedley and Kinniburgh, 2002), while, in oxidizing conditions, arsenate or As(V) is the predominant species ($H_2AsO_4^-$, $HAsO_4^{2-}$) (Lafferty et al., 2010; Villalobos et al., 2014). Various treatment technologies, including adsorption, coagulation/flocculation, chemical precipitation, lime softening, ion-exchange, and membrane filtration have been studied to remove As from water (Amen et al., 2020; Meng et al., 2001; Niazi et al., 2018; Pio et al., 2015; Roberts et al., 2004; Shakoor et al., 2019; Su and Puls, 2001; Zhang et al., 2010). However, these options are energy-intensive, and/or, consume chemicals that make the treatment methods expensive (Hoque et al., 2006, 2004; Hossain et al., 2014). In addition, commonly available treatment systems are complicated to operate and maintain, needing regular parts' replacement and aftermarket services that are expensive and skilled personnel who may not be locally available (Delaire et al., 2017). As a consequence, these technologies are not sustainable in the long run in vulnerable communities (Hossain et al., 2015, 2014).

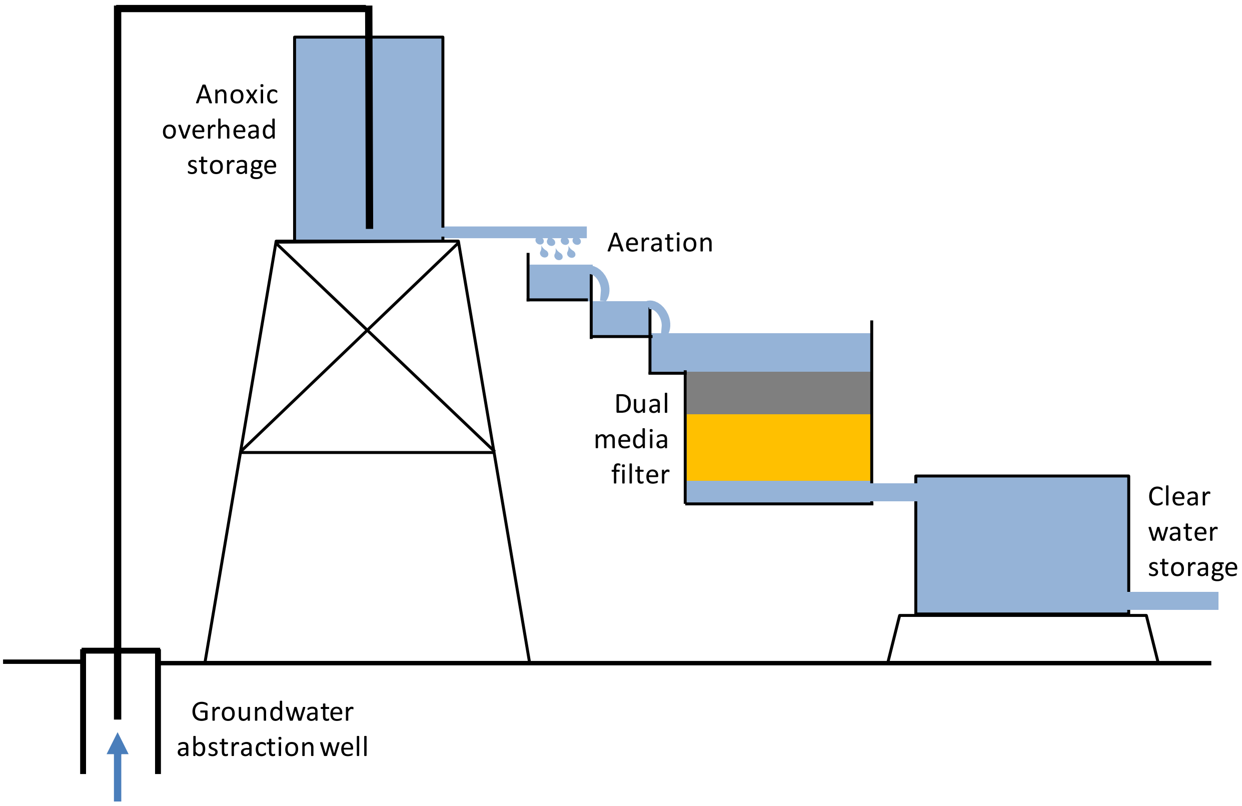


Fig. 1. The concept of delayed aeration by application of an anoxic storage container before aeration and dual-bed filtration.

Therefore, there is a need for simple, economical, and energy-efficient alternatives, utilizing locally available materials and less or no use of additional chemicals (Hering et al., 2017; Katsoyiannis et al., 2015; Senn et al., 2018). Passive groundwater treatment consists of aeration, followed by single or multiple filtration steps (Morrison et al., 2002; Roberts et al., 2004) without using chemicals, as shown in Fig. 1. Aeration frequently consists of cascades or spray aerators, followed by gravitational filtration through a submerged filter bed. Traditionally, passive groundwater treatment is used for the removal of Fe^{2+}, ammonium (NH_4^+), and manganese (Mn^{2+}) (Bruins et al., 2014; Katsoyiannis et al., 2008b; Vries et al., 2017). However, this treatment method is not considered a robust barrier for As, as its removal efficiencies typically vary widely between 15% to 95% (Gude et al., 2016; Lowry and Lowry, 2002; Sorlini and Gialdini, 2010), depending on the water chemistry (Sorlini and Gialdini, 2014). Co-removal of As with groundwater native-Fe is reported to be only possible if As concentration is low (<50 µg/L) (Gude et al., 2018a; Katsoyiannis et al., 2015) and the Fe to As ratio is sufficiently high (Annaduzzaman et al., 2018; Biswas et al., 2012; Sharma et al., 2016). Furthermore, studies by Holm and Wilson (2006) showed that despite having groundwater native-Fe^{2+} of >1.5 mg/L, only 20-25% (8-10 µg/L) of As could be removed. This was also the case in Lowry and Lowry's (2002) study that showed aeration and storage of Fe2+ containing groundwater, facilitated only partial As removal with hydrous ferric oxide (HFO) flocs. Roberts et al. (2004) also revealed that 50-55 mg/L of Fe^{2+} was required to achieve <50 µg/L As in the treated solution from 500 µg/L of As in a single-step Fe^{2+} oxidation system, while in a step-wise Fe^{2+} oxidation system, only 20-25 mg/L of Fe^{2+} was sufficient to have an efficiency of over 90% As removal. All of these studies underline that the ratio of Fe to As played a major role in the As removal process.

Equilibrium adsorption studies of As on Fe oxides show that although both As(III) and As(V) have an affinity for Fe oxides (Dixit and Hering, 2003; Han et al., 2016; Hug and Leupin, 2003; Luzi et al., 2004; Voegelin and Hug, 2003), during Fe^{2+} oxidation and subsequent fresh HFO formation, the removal capacity for As(V) is much higher (Hering et al., 2017; Manning et al., 2002; Mercer and Tobiason, 2008). The removal of As(III) is more efficient through co-precipitation, while As(V) removal is related to surface complexation/precipitation with HFO flocs (Tian et al., 2017). Therefore, in order to develop passive groundwater treatment into an efficient system for As removal by HFO flocs, it is critical to promote the presence of As in the oxidized state during onset Fe^{2+} oxidation.

In this study, it was hypothesized that by delaying the oxidation of groundwater native-Fe^{2+}, the available adsorption capacity of the freshly formed HFO flocs can be utilized better for sufficient As removal. Therefore, anoxic storage before aeration and filtration was applied to allow step-wise Fe^{2+} oxidation. This novel oxidation sequence was compared against a conventional oxic storage system, to study the influence on As removal efficiency by delayed/step-wise oxidation followed by aeration and dual-media sand filtration. Moreover, in this treatment system, locally available filter materials were used without additional adsorbents/chemicals. The study was conducted in Rajshahi (Bangladesh), using naturally As-contaminated groundwater (329±0.05 µg/L) in the presence of other inorganic groundwater contaminants (e.g., Fe^{2+}, PO_4^{3-}, NH_4^+).

3.2 Materials and methods

3.2.1 Water Quality

The pilot-scale experiments were conducted using As contaminated groundwater in Uttar Kazirpara village in Paba Upazila of Rajshahi district, Bangladesh. Table 1 provides the relevant water quality parameters of used natural groundwater. The groundwater was in a reducing/anoxic state and abstracted from 50(±1) m depth using an electric submersible pump (GAZI, Bangladesh).

Table 1. Raw groundwater quality in the shallow well that used as an influent for the pilot experiments.

Water Quality Parameters	Unit	Raw Groundwater
pH	[-]	6.94±0.08(SD)
Dissolved Oxygen (DO)	mg/L	0.07±0.06(SD)
Oxygen Reduction Potential (ORP)	Mv	-110±4(SD)
Electrical Conductivity (EC)	µS/cm	675±6(SD)
Temperature	°C	26.7±1(SD)
As(total)	µg/L	329±0.05(SD)
As(V)	µg/L	39±0.02(SD)
As(III)	µg/L	290±0.02(SD)
Iron (Fe^{2+})	mg/L	2.33±0.03(SD)
Manganese (Mn)	µg/L	600±0.04(SD)
Magnesium (Mg)	mg/L	13.93±0.22(SD)
Calcium (Ca)	mg/L	69.96±1.07(SD)
Ammonium (NH_4^+)	mg/L	0.96±0.02(SD)
Nitrate (NO_3^-)	mg/L	0.39±0.02(SD)
Silicate (SiO_4^{4-})	mg/L	28.5±2.04(SD)
Phosphate (PO_4^{3-})	mg/L	2.15±0.03 (SD)

3.2.2 Experimental set-up

The experimental set-up consisted of four identical dual-media filter columns to run the two parallel experiments in duplicate (Fig. 2). The As(III) oxidation and removal were investigated with two different storage conditions from the same source water: (1) conventional oxic storage and (2) anoxic storage. The oxic storage container was equipped with a spray aerator placed 35 cm above the container, whereas the anoxic storage container had an inlet at the bottom of the container – preventing any atmospheric contact. On the first day, the systems were allowed to overflow for 5 minutes to remove atmospheric oxygen. On the subsequent days, groundwater was added to the remaining stored water (about one-third of the volume), to refill the storage systems.

After storage, the water was aerated by letting it drip into the column from the pipeline, which was placed 35 cm above the top of the supernatant level of the column (Fig. 2). Each column has a diameter of 10 cm and a height of 120 cm. The columns were filled with 40(±2%) cm anthracite (0.6-0.9 mm) on top followed by 50(±2%) cm of quartz sand (0.3–0.75 mm) at the bottom. The quartz sand (known as

Domar sand) is commonly used in construction, and gravel packing of the screen during tubewell installation. The Domar sand was bought from locally available shops. Before starting the experiment, the filter columns were extensively backwashed until the supernatant was visually clear. The experimental flowrate was set to 9 L/h to achieve a filtration velocity of 1 (±10%) m/h. The supernatant water level was kept at 15-20 cm above the filter bed, when the level rose beyond 20 cm due to filter clogging, backwashing was done.

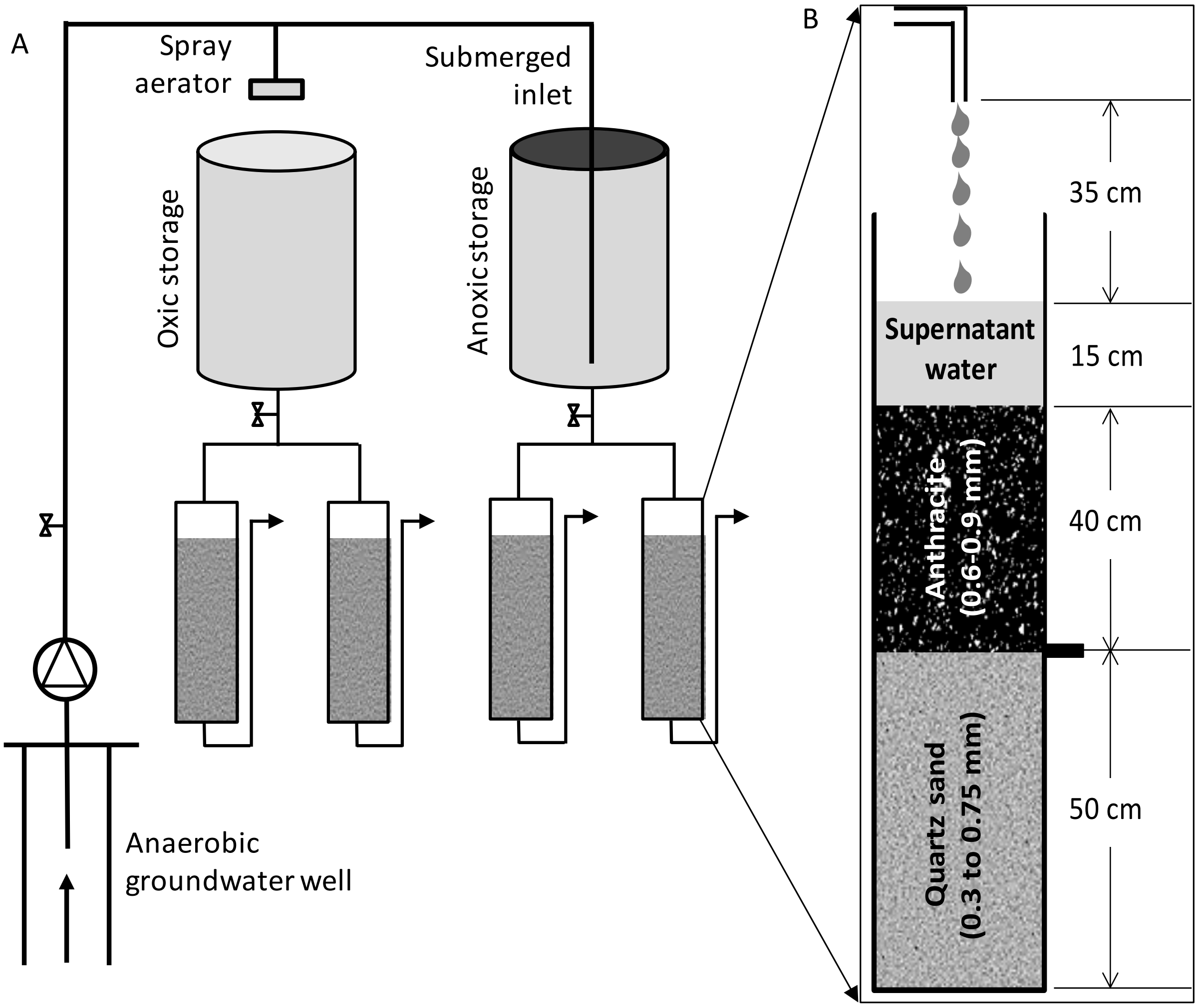


Fig. 2. Schematic overview of the dual-media sand filtration set-up. The anaerobic groundwater was exposed to atmospheric oxygen by a spray aerator before the oxic storage, whereas, the submerged inlet was used to fill the anoxic storage to avoid aeration. The pre-stored water was aerated by letting it drip into the column from the pipeline from 35 cm above the column top. The dual-media column experiments were performed in duplicates for each storage system.

Backwashing was executed with a 20% expansion of the filter bed using stored water and continued until the supernatant water was visually clear (±20 min). No chemicals were used during the experiments. Throughout the experimental period of 30 days, the column was continuously fed with water and covered to protect the water from direct sunlight exposure. The water quality of the different storage containers, supernatant, anthracite filtrate and column filtrate were compared for 30 days, and all experiments were performed in duplicates.

3.2.3 Sampling and analytical procedure

The parameters pH, dissolved oxygen (DO), oxidation-reduction potential (ORP), and temperature (T) were directly measured on-site during sample collections using WTW electrodes (SenTix 940, FDO®925, SenTix ORP 900, and Terracon 925, respectively). Samples were collected on days 1, 5, 10, 20, and 30. The filtered and unfiltered 15 ml water samples were collected in polypropylene transparent 15 ml centrifuge tubes (Sigma Aldrich) and the relevant samples were acidified immediately in the field for preservation until further analysis. The samples were acidified with ultrapure HNO_3 acid (ACS reagent, 70%; Formula weight 60.01 g/mol; Sigma Aldrich) that made up for 1.5% of the total solution. Furthermore, 250 ml filtered (0.45 µm) and non-acidified water samples were collected in 250 ml polypropylene laboratory-grade water vials for determining ammonium (NH_4^+), nitrate (NO_3^-), and phosphate (PO_4^{3-}) concentrations. All filtered samples were filtered using a polyether-sulfone 0.45 µm filter (25 mm, VWR). Arsenic and Fe was analyzed using Inductively Coupled Plasma Mass Spectrometry (ICP-MS) in the water laboratory at the Delft University of Technology, the Netherlands. The concentration of NH_4^+, NO_3^-, and PO_4^{3-} were determined from 250 ml filtered samples at Rajshahi Regional Laboratory, Department of Public Health Engineering (DPHE), Bangladesh.

The speciation of As(III) was conducted using the ion-exchange resin Amberlite® IRA-400 chlorite (Sigma Aldrich), by pushing 100 ml filtered (0.45 µm filter) water through a 60 ml syringe which contained 30 ml ion-exchange resin. After resin filtration, the remaining As concentrations were considered to be uncharged As(III) (Gude et al., 2016; Karori et al., 2006). The concentration of As(V) was calculated by deducting As(III) from the total As concentration obtained from the 0.45 µm filtered sample as mobile, dissolved As.

3.2.4 Data analysis

The data analyses were conducted using one-way analysis of variance (ANOVA) with a confidence level of 95% (α = 0.05) for the statistical validation of the removal efficiency of As, Fe, NH_4^+, and PO_4^{3-} during different filtration steps. The obtained duplicate data from each step and condition (oxic and anoxic) were used in duplicate assays from each sampling day (n=5) over the experimental 30 days. The data were presented in the form of mean with their standard deviations. The p-value (probability value) from the ANOVA test was used to determine the significant difference between the duplicate results from the two different operational conditions (oxic and anoxic storage) followed by aeration and RSF steps. The analyzed p-value was consistently below 0.05 for As, Fe, $NH_4^{+,}$ and PO_4^{3-} removal at different operational conditions and filtration steps, meaning the removal was statistically significant.

3.3 Results and discussion

3.3.1 Fe^{2+} oxidation in the storage systems

The pH, DO, ORP, and Fe^{2+} concentrations in the oxic and anoxic storage systems are presented in Fig 3. The natural groundwater pH, DO, and ORP were stable at 6.94(±0.2), 0.07(±0.06) mg/L, and -110(±4) mV, respectively (Table 1). Due to aeration before storage in the oxic system, the pH, DO, and ORP increased to 7.5(±0.1), 6.21(±0.2) mg/L, and 50(±14) mV, correspondingly, since CO_2 was stripped (i.e., pH increase) and O_2 was added during aeration (Rahman, 2017). Furthermore, the aeration facilitated rapid oxidation of Fe^{2+} to Fe^{3+} and form HFO flocs. This was to be expected as the kinetics of homogeneous Fe^{2+} oxidation at pH 7.5 and high DO is fast ($t_{1/2}$: roughly 2-3 min) (Katsoyiannis et al., 2008a, 2008b; Morgan and Lahav, 2007). The total Fe concentration in the oxic storage system dropped slightly in the course of experiments and varied between 1.97 to 2.19 mg/L (Fig. 3d), which can be explained by the settling of HFO flocs in this non-stirred storage system. The 2.08 mg/L oxidized Fe^{3+} roughly corresponded to the consumed DO of 0.30 mg/L, which was calculated based on the 1:4 stoichiometry of the Fe^{2+} oxidation reaction with DO (Stumm and Lee, 1961), illustrating that DO was the electron acceptor under the oxic conditions.

In the anoxic storage, the continuously low pH, DO, and ORP resulted in limited Fe^{2+} oxidation. However, the pH and DO remained low over days, whereas ORP increased slowly with increasing Fe^{2+} oxidation to Fe^{3+}. The pH and DO were found to be 6.86(±0.04), 0.24(±0.1) mg/L, respectively, but ORP drifted from -96.7 mV on the first day to -45.7 mV, -15.8 mV, 21.7 mV, and 48.6 mV on days 5, 10, 20 and 30, correspondingly (Fig. 3c). From the graphs, the observed increase in pH, DO, ORP and Fe^{2+} on day 5 compared to day 1 could have resulted from the dilution effect of newly added water with remaining stored water (one-third of the volume). Due to the stable operation of the systems over days, the measurements stabilized from day 5-10 onwards (Fig. 3a,c). The oxidation of Fe^{2+} also increased over time from 0.64 mg/L of oxidized Fe^{3+} on the first day to 0.9 mg/L on day 30, where the Fe^{2+} oxidation rate in the anoxic storage was 0.8 mg/Lh and 0.12 mg/Lh on day 1 and 30 correspondingly.

During the filling of the anoxic storage, the introduction of DO into the abstracted groundwater could not be fully avoided, which probably led to partial oxidation of Fe^{2+}. However, the acceleration of Fe^{2+} oxidation over days in the anoxic storage is likely linked to either accumulation of Fe^{3+} hydroxides that catalyze the oxidation reaction (heterogeneous Fe^{2+} oxidation; van Beek et al., 2015) or development of a Fe^{2+} oxidizing biofilm (biological Fe^{2+} oxidation) (de Vet et al., 2011; Lin et al., 2012; Uddin et al., 2019). Nevertheless, Fe^{2+} oxidation in the anoxic system was indeed suppressed throughout the experimental period, allowing for delayed/step-wise oxidation.

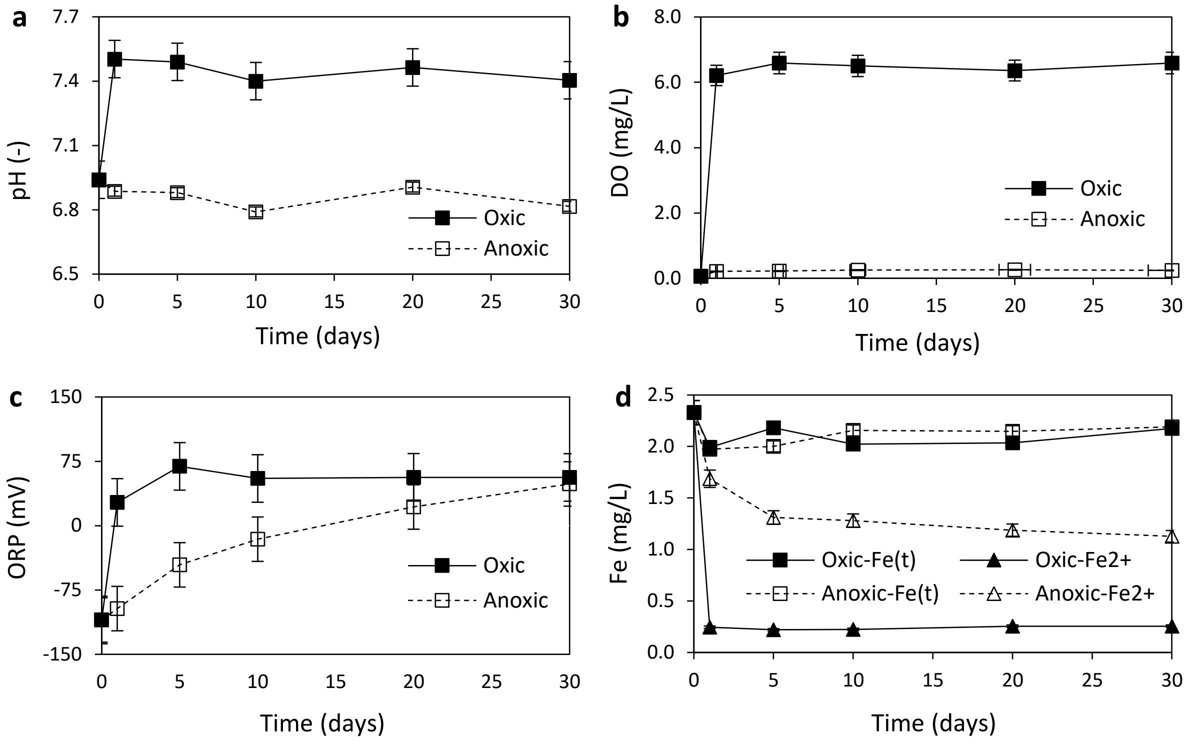


Fig. 3. (a) pH, (b) DO (c) ORP changes, and (d) the average concentration of Fe^{2+} and Fe(total) in the oxic and anoxic storage systems during the 30-day experimental period. The error bar represents the standard deviation.

3.3.2 As(III) oxidation and removal in the storage systems

Arsenic concentration and speciation in the oxic and anoxic storage systems are presented in Fig. 4. Partial As(III) oxidation and As removal were observed in both storage systems with slightly more oxidation and removal in the oxic storage. The groundwater contained 329(±0.05) µg/L of total As, with 290(±0.02) µg/L being As(III). On the first day of operation, the oxic storage system contained 267 µg/L of total As, in which As(III) was 216 µg/L (Fig. 4a); the anoxic system contained 280 µg/L of total As and 240 µg/L of As(III) (Fig. 4b). After 5-10 days, the operational mode was considered to be stable (see the previous section), also reflected in the stabilization in As(III) concentrations after 10 days, with an average As(III) concentration of 72(±7) µg/L and 171(±8) µg/L in the oxic and anoxic storage respectively (Fig. 4).

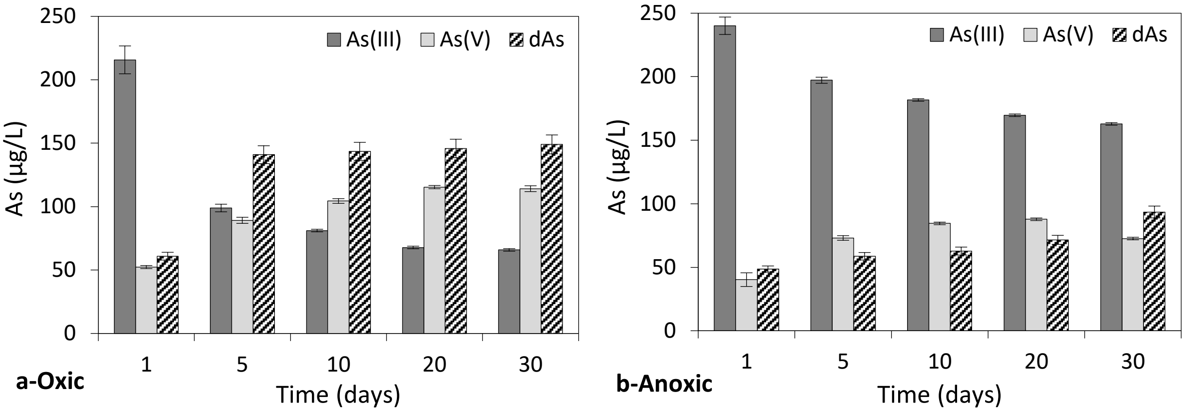


Fig. 4. Arsenic species (As(III), As(V), and removed As) and their average concentration in the duplicate (a) oxic and (b) anoxic storage system. The error bar represents the standard deviation.

The elevated average As(V) concentration of 95 µg/L (min. 52 µg/L to the max. 115 µg/L) in the oxic storage system indicates the high level of As(III) oxidation under aerated conditions, which may be due to various oxidation processes, such as enhanced homogeneous oxidation (Bissen and Frimmel, 2003; Shumlas et al., 2016), biological As^{3+} oxidation (Cavalca et al., 2013; Quéméneur et al., 2008), oxidation by reactive intermediates (˚OH, H_2O_2, and O_2˚) formed during Fe^{2+} oxidation and/or Fenton-like (Fe(IV) based) reactions (Ciardelli et al., 2008; Hug et al., 2001; Hug and Leupin, 2003; Roberts et al., 2004; Sahai et al., 2007). The higher As removal in the oxic storage, compared to the anoxic storage, is likely to be a consequence of produced HFO flocs that bind both As(III) and As(V). The findings are in agreement with studies by Holm (2002), and Mercer and Tobiason (2008), who found that higher in-situ HFO flocs formation in the oxic storage during aeration resulted in higher As removal. After the first 5 days, the As removal in the oxic storage was nearly constant at 145(±2) µg/L, probably because an equilibrium was established between suspended and settled HFO flocs, while the latter did not further contribute to As removal. Over the experimental 30 days, it was observed that both Fe^{2+} and As(III) oxidation increased slightly, which could be induced by microbial activities (Gude et al., 2018b; Shafiquzzaman et al., 2008; van Beek et al., 2015, 2012).

In the case of the anoxic storage system, the low DO level (<0.25 mg/L) limited homogeneous As(III) oxidation (Bissen and Frimmel, 2003; Shumlas et al., 2016), rapid Fe^{2+} oxidation and formation of abundant reactive intermediates (e.g., ˚OH, H_2O_2, and O_2˚), thus hampering As(V) formation. However, the observed As(III) concentration seemed to be slightly dropping over 30 days, likely due to the increase in Fe^{2+} oxidation over time (Fig. 4b). When calculating the ratio between oxidized Fe^{3+} and removed As on day 30, the amount of removed As per gram of Fe was higher in the system with anoxic storage (80(±4) µgAs/mgFe^{3+}) than in the conventional oxic storage (60(±5) µgAs/mgFe^{3+}), with a p-value of less than 0.05. The lower removal ratio in the oxic storage was in agreement with previous findings, where it has been stated that at pH above 7.0, As(V) removal with HFO flocs decreased considerably, due to lowering the positive surface charge, compared to systems with low pH (Dixit and Hering, 2003; Katsoyiannis and Zouboulis, 2002; Senn et al., 2018; Wilkie and Hering, 1996). Other studies also revealed that freshly formed HFO flocs in anoxic systems are more efficient for As removal as opposed to pre-formed HFO flocs in the traditional oxic storage systems (Kim and Nriagu, 2000; Senn et al., 2018).

3.3.3 Fe and As oxidation-removal after aeration

Over the experimental period of 30 days, after both the oxic and the anoxic storage, the groundwater was aerated by dipping from 35 cm above the filter bed. The dissolved Fe^{2+}, Fe^{3+}, As(III), and As(V) concentrations before and after aeration is shown in Fig. 5. After aeration before feeding the filtration units, the pH, DO and ORP for the oxic storage system was 7.7(±0.07), 6.7(±0.1) mg/L, and 61(±0.6) mV respectively and for the anoxic storage system, the pH, DO, and ORP was 7.4(±0.04), 5.83(±0.02) mg/L, and 45.7(±0.6) mV, correspondingly. The oxic storage water contained 2.08(±0.07) mg/L of total Fe, wherein 89% was HFO flocs (>0.45 µm), indicating no/limited Fe^{2+} was available for oxidation during the aeration before column feeding.

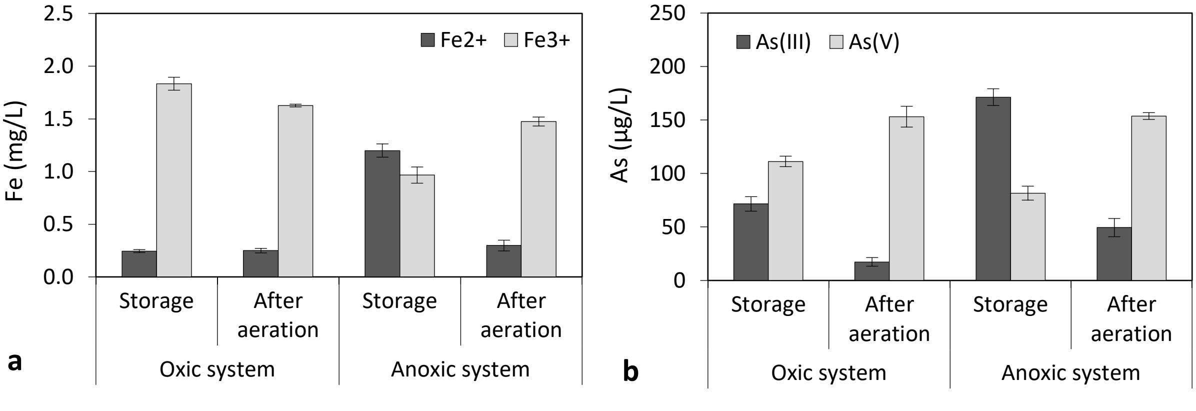


Fig. 5. The (a) Fe^{2+} and Fe^{3+}; and (b) As(III) and As(V) species (average) concentration in the oxic and anoxic storage system and after aeration before the filter bed. The error bar represents the standard deviation of duplicate column experiments.

In the anoxic system, however, the introduction of O_2 during aeration before column feeding resulted in oxidation of the 1.20 mg/L of residual Fe^{2+} from anoxic storage (Fig. 5a). Subsequently, Fe^{3+} hydrolyzed to filterable/insoluble (0.45 µm membrane filter) Fe^{3+} (HFO) flocs. Along with Fe^{2+}

oxidation, 120 µg/L of additional As(III) oxidation was also observed after this aeration step (Fig. 5b). In the oxic system, 55 µg/L of As(III) was also oxidized during the second aeration step, while Fe^{2+} was not present anymore, probably as a result of homogeneous As(III) oxidation by DO or bacterial processes that could be developed over time (Gude et al., 2018b; Shumlas et al., 2016). During filtration, a supernatant water level of 15-20 cm was maintained to provide a hydraulic head and a saturated filter bed. The water sample was collected from the supernatant water, which was in contact with the top layer of the filter bed, providing a potential carrier for bacteria and promoting biological oxidation of As(III), as earlier reported by Katsoyiannis and Zouboulis (2004b) and Gude et al. (2018b). The aeration step prior to filtration, thus aided in partial As(III) oxidation and As removal in both oxic and anoxic systems. However, the system with anoxic storage showed a higher As removal than the oxic storage system ($p<0.05$), probably due to the presence of newly, in-situ formed active HFO flocs (Mercer and Tobiason, 2008; Senn et al., 2018; Wilson et al., 2004). The removed As after aeration (supernatant) of the oxic and the anoxic system was 12 µg/L (7%) and 50 µg/L (25%), respectively. This also confirmed the findings of the work of Roberts et al. (2004), who stated that multiple additions of Fe^{2+} lead to more As(III) oxidation and removal compared to a higher and single Fe^{2+} dose.

3.3.4 Fe and As removal in the filter bed

The dissolved Fe, As(III), and As(V) concentrations in the filtrate is shown in Fig. 6. For both the systems with oxic and anoxic storage, Fe removal was quick and efficient to result in 97% removal in the top anthracite layer. Independent of the storage systems before aeration-filtration, the filtrate Fe concentration was consistently lower than 0.3 mg/L (Fig. 6a), and thus below the WHO drinking water standard. Although the column influent concentrations of Fe^{2+}/Fe^{3+} and As(III)/As(V) were similar for both systems, As removal was considerably more effective in the columns that followed anoxic storage. The filtrate As concentration in the anoxic system was 28 µg/L, whereas in the oxic system it was 128 µg/L ($p<0.05$) (Fig. 6b). Hering et al. (1996), proposed that the varied As removal with in-situ and pre-formed HFO flocs results from their surface charge differences. According to model predictions by Holm (2002), the removal capacity of As by in-situ HFO flocs can be 3.8 times higher than that of preformed HFO flocs. Other studies also indicate that the increase in surface site density of in-situ formed HFO flocs (0.7 mol site/molFe) is higher than the pre-formed HFO flocs (0.205 mol site/molFe) (Fuller et al., 1993; Mercer and Tobiason, 2008). Furthermore, the lower filtrate pH (7.1) in the anoxic system compared to the oxic system (pH of 7.7) could be another reason for more As removal with adsorptive HFO flocs. The lower pH in the anoxic system slowed the HFO flocs formation (Gude et al., 2016; Katsoyiannis et al., 2008a; Zhang et al., 2019), and probably helped to increase the positive surface charge of HFO flocs, and thereby improved As removal (Wilkie and Hering, 1996). According to

Mercer and Tobiason (2008), for 90% As removal in an ideal scenario, the required Fe:As ratio is about 9 and 6 at pH 7.3 and 6.2 respectively, where Holm's (2002) study mentioned that the pH difference by two units can increase or decrease As removal from 10 to 90%.

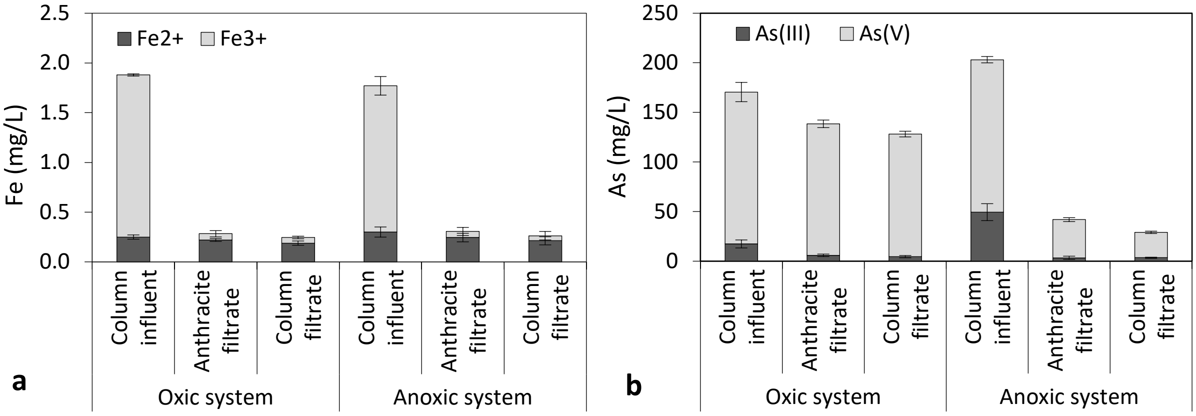


Fig. 6. The column influent, anthracite filtrate, and column filtrate (a) Fe^{2+} and Fe^{3+}; and (b) A(III) and As(V) species (average) concentration for the system with oxic and anoxic storage. The error bar represents the standard deviation of duplicate column experiments.

Apart from HFO floc filtration, the filter bed probably also functioned as a bio-filter for As(III) oxidation by AsOB (Gude et al., 2018b; Shafiquzzaman et al., 2008). In both storage systems, the residual As(III) that enters the filter bed was fully oxidized to As(V) in the anthracite layer perhaps by the presence of AsOB in the filter bed (Gude et al., 2018b). They also indicated that the penetration of freshly or in-situ formed HFO flocs into the filter bed for the anoxic system facilitates more As(V) adsorption compared to pre-formed HFO flocs penetration for the oxic system (Amstaetter et al., 2010; Hohmann et al., 2010; Wang et al., 2008). Similar to Gude et al. (2016), the rapid removal of HFO flocs in the first layer resulted in the low As removal in the bottom sand layer (3-7 µg/L).

3.3.5 Ammonium, nitrate, and phosphate removal

Over the experimental period of 30-day, the concentrations of NH_4^+ and NO_3^- in different treatment steps of the system with oxic and anoxic storage are shown in Fig. 7. In groundwater, the NH_4^+ and NO_3^- concentrations were, on average, 0.96(±0.02) mg/L and 0.39(±0.02) mg/L, respectively (Table 1). After the first five days, the concentration of NH_4^+ decreased in the oxic system due to the onset of biological nitrification, resulting in NO_3^- concentration increase by aerobic oxidation of NH_4^+ (Koch et al., 2019). The lack of DO in the anoxic storage system limited the NH_4^+ oxidation process, consequently, 0.79(±0.05) mg/L of NH_4^+ remained in the storage system. After 5-10 days, the oxidation of NH_4^+ was observed to commence in the filter bed for both the oxic and anoxic systems, as can be observed from the lowering of NH_4^+ and increase in NO_3^- concentration in the filter bed (anthracite) (de Vet et al., 2011; Koch et al., 2019; van Kessel et al., 2015). However, the results did not imply a 1:1 NH_4^+ conversion to NO_3^- (N-Balance), probably meaning that the nitrification process was not complete, resulting in (intermediate) nitrite (NO_2^-) production. However, it may be concluded that the nitrification process, although delayed in start-up, was not hampered by the step-wise Fe^{2+} oxidation sequence in the anoxic system.

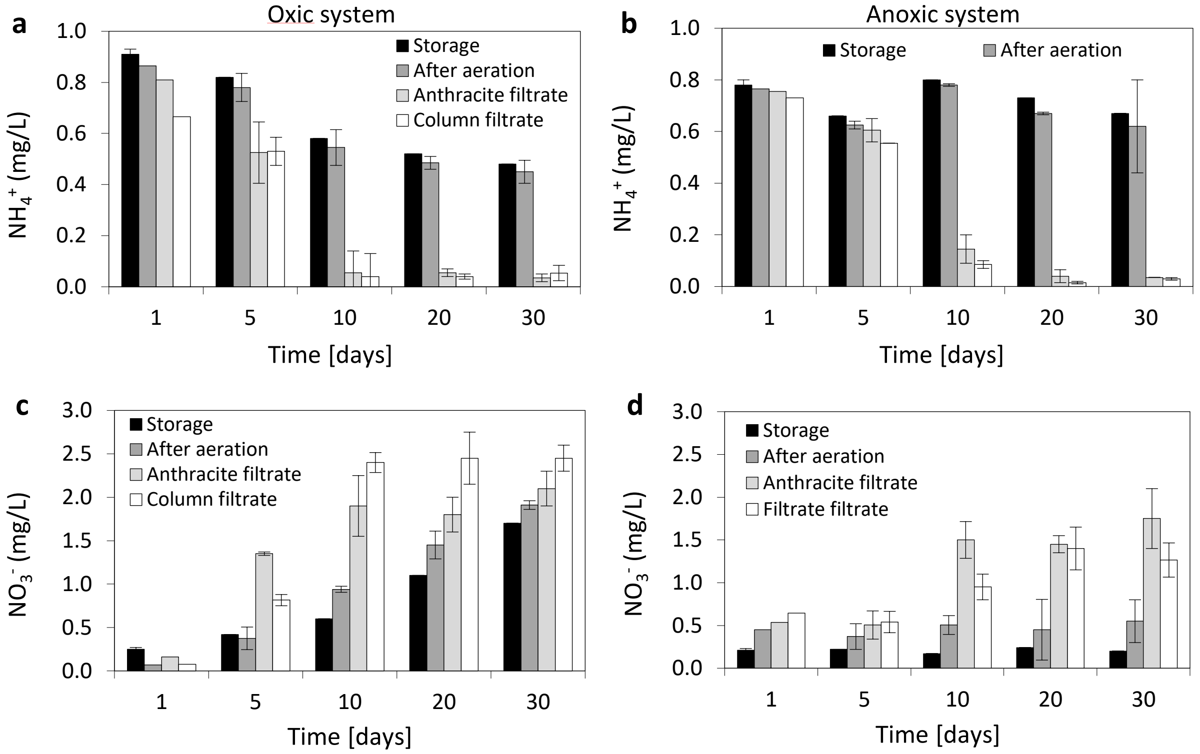


Fig. 7. The average concentration of (a-b) NH_4^+ and (c-d) NO_3^- at different treatment steps of the system with oxic (a, c) and anoxic (b, d) storage respectively. The error bar represents the standard deviation of duplicate dual-media sand filtration column experiments.

The PO_4^{3-} concentrations in the stored water and different treatment steps over time are depicted in Fig. 8. In the groundwater, the PO_4^{3-} concentration was 2.15(±0.03) mg/L, which dropped to an average of 0.76(±0.05) mg/L in the oxic storage system (Fig. 8a). However, in the anoxic storage system, PO_4^{3-} concentration remained high at 1.68(±0.22) mg/L (Fig. 8b). The large decrease of PO_4^{3-} concentration in the oxic storage system, compared to the anoxic storage system ($p<0.05$), can be explained by co-precipitation with HFO flocs (Guan et al., 2009; Voegelin et al., 2010) originating from rapid Fe^{2+} oxidation. In the anoxic storage followed by aeration-filtration, the PO_4^{3-} removal follows the step-wise

Fe^{2+} oxidation. PO_4^{3-} was partially removed during anoxic storage (0.47±0.18 mg/L) and aeration (1.14±0.06 mg/L) before filtration (Fig. 8b). The removal of PO_4^{3-} was also observed at different layers of the filter bed (aerated water vs. anthracite filtrate vs. column filtrate), indicating ongoing adsorption of PO_4^{3-} onto HFO flocs. The concentration of PO_4^{3-} further decreased in the column filtrate to 0.38(±0.07) mg/L and 0.30(±0.05) mg/L from anthracite filtrate concentration of 0.45(±0.06) mg/L and 0.43(±0.04) mg/L respectively for the oxic and anoxic systems.

3.4 Considerations for application

The suitability of the As co-precipitation with naturally present Fe^{2+} by anoxic storage followed by aeration-sand filtration system was evaluated in Bangladesh based on the five criteria proposed by WHO (2013), which are effectiveness, appropriateness, acceptability, cost, and implementations.

In Bangladesh, people prefer using tubewells to other drinking water options due to low operation and maintenance costs, and water accessibility around the year (Hossain et al., 2014). With the proposed treatment method, it is possible to achieve As removal without using any additional chemicals. Moreover, it uses only locally available materials and works with an existing groundwater source. Previous studies suggested Fe/As ratios over 40 (mg/mg) would be required to reduce As levels below 50 µg/L (Meng et al., 2002; Ware, 2013) with passive treatment. The present study indicates that delayed aeration-oxidation of Fe^{3+} could be a promising method for As removal with Fe/As ratios as low as 10 (mg/mg). However, from a waste management perspective, it is recommended to apply this treatment scheme on a larger scale. Although the combination of anoxic storage with aeration-filtration requires a low As/Fe ratio, still As-containing sludge is being produced which needs to be disposed of. At the concentrations found during this study, As-containing Fe sludge can be used in brick industries or concrete masonry work (Rouf and Hossain, 2003). Prior to the application of this novel technology, it is recommended to further investigate the influence of groundwater matrices and varying operational parameters, which might impact As removal efficiency.

3.5 Conclusion

This study aimed to investigate the influence on As removal efficiency by delayed aeration using an anoxic pre-storage system followed by aeration and dual-media sand filtration. This novel treatment sequence was compared against conventional aeration-filtration for groundwater containing total As of 329 µg/L, with 290 µg/L being As(III) and 2.33 mgFe^{2+}/L. The obtained step-wise Fe^{2+} oxidation with anoxic pre-storage enhanced As removal to 92%, compared to only 61% in the conventional oxic system. It is suggested that this was due to the formation of fresh HFO flocs during step-wise oxidation in the anoxic system that removed more As than the pre-formed HFO flocs in the oxic system. Moreover, Fe^{2+} oxidation did not compromise the removal of other groundwater contaminants like NH_4^+, and PO_4^{3-}. Therefore, this study demonstrated that with anoxic storage, passive treatment is an effective barrier against As(III) with Fe/As ratios much lower (<10 mg/mg) than previously determined (>40 mg/mg). Consequently, the combination of anoxic storage followed by aeration and sand filtration can be used as a cost-effective and chemical-free alternative for removing As(III) from groundwater under field-relevant conditions.

3.6 Acknowledgment

This study was supported by the DELTAP project funded by the NWO-WOTRO research grant. The authors acknowledge all research assistants from RUET, Rajshahi University, and EPRC in the pilot-scale experimentation in Rajshahi Bangladesh for their help and logistic supports during the intensive fieldwork. The authors also wish to thank landowner Md Sirajul Islam and his family, for allowing work to be done on their premises for the whole day over the entire experimental period. Without their support, this study would not have been possible.

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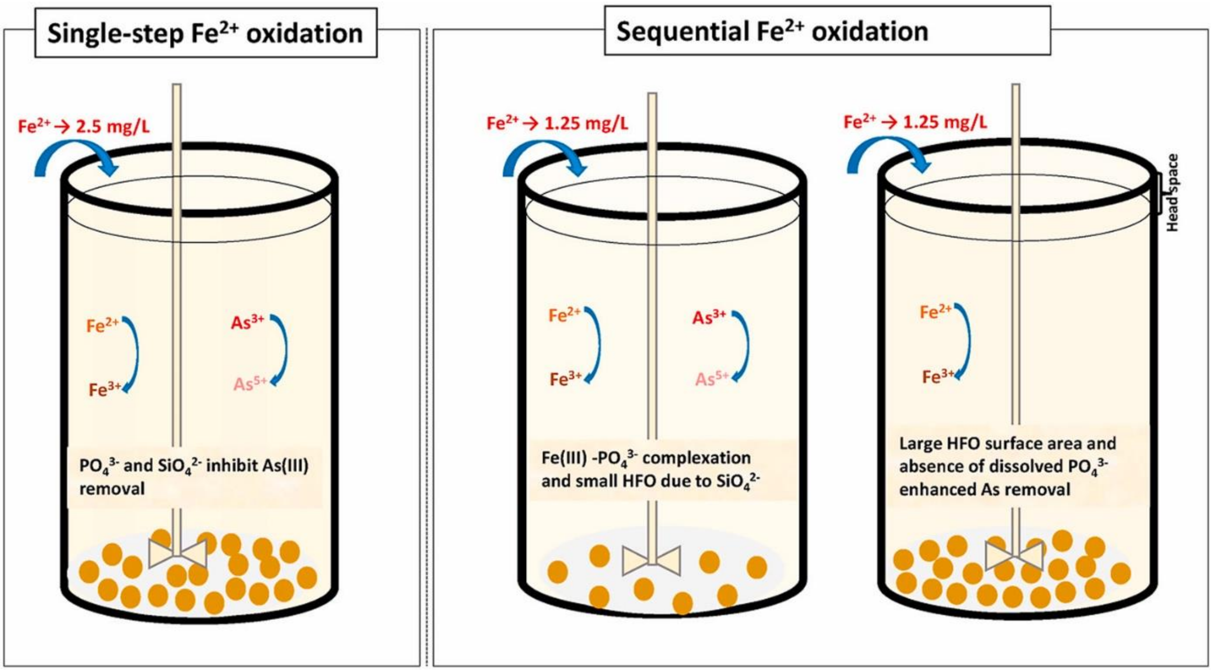
Chapter 4

Sequential Fe^{2+} oxidation to mitigate the inhibiting effect of phosphate and silicate on arsenic removal



This chapter is based on:

Md Annaduzzaman, Luuk C. Rietveld, Bilqis Amin Hoque, Doris van Halem, (2022). Sequential Fe^{2+} oxidation to mitigate the inhibiting effect of phosphate and silicate on arsenic removal, Groundwater for Sustainable Development, Volume 17, 100749, https://doi.org/10.1016/j.gsd.2022.100749

Abstract

Sequential iron (as Fe^{2+}) oxidation has been found to yield improved arsenic (as As(III)) uptake than the single-step oxidation. The objective of this study was to gain a better understanding of interactions with phosphate (PO_4^{3-}) and silicate (SiO_4^{2-}) during sequential Fe^{2+} and As(III) oxidation and removal, as these are typically found in groundwater and known to interfere with As removal. The laboratory experiments were performed using single and multi-step jar tests with an initial As(III/V), Fe^{2+}, PO_4^{3-}, SiO_4^{2-} concentrations, and pH of 200 µg/L, 2.5 mg/L, 2 mg/L, 16 mg/L and 7.0, respectively representing the targeted natural groundwater in Rajshahi district, Bangladesh. The sequential Fe^{2+} and As(III) oxidation in the multi-step jar tests indicated that the PO_4^{3-} hindrance on As removal in the first Fe^{2+} oxidation step was compensated for in the second. Moreover, smaller Fe flocs (<0.45 µm) were observed in the presence of SiO_4^{2-}, potentially providing more surface area during the second Fe^{2+} oxidation step leading to better overall As removal. Altogether it may be concluded that controlling the As(III) and Fe^{2+} oxidation sequence is beneficial for As removal compared to single-step Fe^{2+} oxidation, both in the presence and absence of PO_4^{3-} and/or SiO_4^{2-}.

Keywords: Arsenic; Iron; Groundwater; Oxidation; Water Treatment.

4.1 Introduction

Groundwater contamination with arsenic (As) is a global concern due to its adverse health effects. The contamination of As in drinking water in the Bengal Delta Plain, including Bangladesh and West Bengal, India, is considered one of the major natural disasters of the 21st century (Chakraborty et al., 2015; Harvey et al., 2005; Ahmed et al., 2004; Hossain et al., 2014; Kapaj et al., 2006). Regular consumption of arsenic-contaminated water beyond the standards may lead to chronic diseases such as skin lesions, skin, bladder and kidney cancer, peripheral vascular disease, neurological effects, hypertension, and cardiovascular disease (Huaming et al., 2013; Li et al., 2012; Luzi et al., 2004). The World Health Organization (WHO) reported that about 200 million people depend on As contaminated drinking water, and approximately 20% of mortalities may be ascribed to As contaminated drinking water in Bangladesh and West Bengal of India every year (Jakariya, 2007). The World Health Organization (WHO) recommends As values in drinking water below 10 µg/L (WHO, 2011), whereas 50 µg/L is the maximum allowable limit in many high-risk countries, including Bangladesh and India. However, groundwater in an extended area of Bangladesh could have As concentrations beyond these recommended values, even exceeding 1500 µgAs/L (Haque et al., 2018; Rosso et al., 2011; Zecchin et al., 2019). Therefore, the As contaminated groundwater used for drinking requires treatment prior to supply and/or consumption.

The available treatment technologies, including adsorption, chemical precipitation, ion exchange, membrane filtration, and nanofiltration (NF), are efficient for arsenate [As(V)] removal, but not for arsenite [As(III)] (Bai et al., 2016; Lytle et al., 2007). The reason is that, in reducing groundwater at circumneutral pH, As(III) exists as thermodynamically stable and non-ionized H_3AsO_3 (Cullen and Reimer, 1989; Hou et al., 2017) and is thus difficult to remove by adsorption processes. In contrast, As(V) is the predominant species in oxidizing conditions and exists as negatively charged $H_2AsO_4^-$ and $HAsO_4^{2-}$ and can thus be adsorbed to adsorbents (e.g., Fe-oxides) (Lafferty et al., 2010; Meng et al., 2000; Villalobos et al., 2014). Therefore, oxidation of As(III) to As(V) is required for effective As removal, either by chemical oxidants or natural processes (Gude et al., 2018; Hu et al., 2012; Pio et al., 2015; Ryu et al., 2017). However, the use of chemical oxidants is energy-intensive, costly, and increases the complexity of the treatment methods.

Arsenic co-precipitation with Fe is a well-known treatment method implemented in many countries (Ahmed, 2001; Li et al., 2012; Sharma et al., 2016; Sorensen and McBean, 2015; Tian et al., 2017). However, despite having sufficient Fe/As ratio for as removal in As-affected shallow groundwater (Annaduzzaman et al., 2018, Biswas et al., 2012), native-Fe based As removal is not considered as a effective barrier for As removal. Importantly, the removal efficiency of As using hydrous ferric oxides (HFO), such as ferrihydrite (Hagstroem, 2017), is highly efficient; however, over time, the transformation of poorly crystalline HFO flocs to more crystalline precipitates (e.g., hematite or goethite) reduces As removal efficiency (Huo et al., 2017). Recent studies have suggested that As co-precipitation with freshly formed HFO flocs can be 3.8 TO 4.1 times more efficient than pre-formed HFO flocs or more stable Fe-oxides (Hering et al., 1996; Holm, 2002; Ryu et al., 2017), e.g., during oxidation of groundwater native-Fe^{2+} into HFO flocs (Annaduzzaman et al., 2021b; Klas and Kirk, 2013; Sorensen and McBean, 2015). Fe^{2+} oxidation is also known to stimulate As(III) oxidation by Fenton-like chemical reactions and the formation of reactive oxidation species (ROS) (Hug et al., 2001; Hug and Leupin, 2003), contributing to more effective As uptake.

However, the source water composition heavily influences As removal efficiency with Fe^{2+} mediated HFO flocs. The groundwater of Bangladesh also contains high concentrations of PO_4^{3-} (0.2-18 mg/L) and SiO_4^{2-} (6-54 mg/L), which is not desirable in drinking water (Meng et al., 2001). The WHO does not have any standard for PO_4^3- and SiO_4^{2-}, but Bangladesh Drinking Water Standard for PO_4^{3-} is 6 mg/L (Hug et al., 2008). Furthermore, phosphate (PO_4^{3-}) and silicate (SiO_4^{2-}) are the most common hindering oxyanions for As removal with HFO flocs (Kanematsu et al., 2013; Li et al., 2012; Meng et al., 2000; Van Genuchten et al., 2012). Although PO_4^{3-} and As(V) have similar affinities to HFO flocs surfaces (Liu et al., 2001; Sahai et al., 2007), As removal with HFO may considerably be reduced as PO_4^{3-} is generally present in higher concentrations than As (Kanematsu et al., 2013; Li et al., 2012). In addition, Guan et al. (2009) stated that at a pH ranging from 4 to 5, the presence of 10 mg/L SiO_4^{2-} does not affect As removal by Fe-oxides (Möller and Sylvester, 2008); however, at higher pH, ranging from 6 to 9, As removal decreases by 5 to 53%, respectively. Other authors have mentioned that with the presence of 10 mg/L SiO_4^{2-} (Meng et al., 2000) and 2 mg/L of PO_4^{3-} (Chanpiwat et al., 2017), As removal per mg of Fe dropped from 90% to 28% and 35%, respectively. Apart from competition on adsorption sites, the presence of PO_4^{3-} also influences the structure, composition, and identity of HFO flocs, where SiO_4^{2-} explicitly affects the size of HFO, thus affecting As removal (van Genuchten et al., 2014).

Some authors have reported that sequential Fe^{2+} dosages and oxidation could be beneficial for As removal (Roberts et al., 2004; Senn et al., 2018). Roberts et al. (2004) revealed that in the presence of 30 mg/L SiO_4^{2-} and 3 mg/L PO_4^{3-}, the sequential Fe^{2+} addition and oxidation only required 20-25 mg/L of Fe^{2+} for achieving a filtrate As concentration of <50 µg/L, from an initial As concentration of 500 µg/L, whereas, single-step addition and oxidation required 50-55 mg/L of Fe^{2+}. However, these studies were conducted in the laboratory considering high As, Fe, PO_4^{3-} and SiO_4^{2-} levels, which is not common in most situations. Our previous pilot-scale studies revealed that sequential oxidation of groundwater native-Fe^{2+} using anoxic storage followed by aeration filtration facilitated high As removal (80 µgAs/mgFe) compared to the oxic storage system (45 µgAs/mgFe) (Annaduzzaman et al., 2021b, 2021a). Therefore, it is hypothesized that the preference of Fe^{3+}- PO_4^{3-} complexation and PO_4^{3-} removal over As in the first Fe^{2+} oxidation step could improve overall As removal in the following Fe^{2+} oxidation step. Thus, this novel study was conducted to understand the As removal interactions with PO_4^{3-} and/or SiO_4^{2-} during sequential Fe^{2+} oxidation conditions at an initial pH of 7.0 in the laboratory jar tests considering targeted groundwater conditions in Bangladesh.

4.2 Materials and methods

4.2.1 Experimental procedure

The experiments were conducted in two series: (1) single-step jar tests to simulate direct oxidation of Fe^{2+} and (2) multi-step jar tests to simulate sequential Fe^{2+} oxidation. **Table 1** provides an overview of the executed experiments. Experiments were performed using 1.5 L tap water in beakers (Pyrex 2L jar), and As(III/V), PO_4^{3-} and SiO_4^{2-} stock solutions were added to meet the desired concentrations of 200 µg/L, 2.0 mg/L, and 16.0 mg/L, respectively, while the paddles (VELP JLT6) were mixing at 150 rpm. Subsequently, the pH was adjusted using concentrated HNO_3 or NaOH to 7.0, which was around >8.0 after chemical introduction. After pH adjustment, the prepared stock solution was added to make up a Fe^{2+} concentration of 1.25 or 2.5 mg/L. The duration of the single-step jar tests was 2 h, and 10 ml filtered (0.45 µm and 0.2 µm (VWR)), and unfiltered water samples were collected at 0, 10, 30, 60, 90, and 120 min from 3-5 cm from the (top) water surface during paddles mixing.

Table 1. Experimental overview for the single and multi-step jar test experiments to simulate single-step and sequential Fe^{2+} oxidation in the presence of As(V), As(III), PO_4^{3-}, and/or SiO_4^{2-}.

Single-Step Jar Test		
Fe^{2+} + SiO_4^{2-}	Fe^{2+} + As(III) + SiO_4^{2-}	Fe^{2+} + As(V) + SiO_4^{2-}
Fe^{2+} PO_4^{3-}	Fe^{2+} + As(III) + PO_4^{3-}	Fe^{2+} + As(V) + PO_4^{3-}
Fe^{2+} + As(III)	Fe^{2+} + As(III) + SiO_4^{2-} + PO_4^{3-}	Fe^{2+} + As(V) + SiO_4^{2-} + PO_4^{3-}
Fe^{2+} + As(V)		

Multi-Steps Jar test			
Fe^{2+} + As(III)	Fe^{2+} + As(III) + PO_4^{3-}	Fe^{2+} + As(III) + SiO_4^{2-}	Fe^{2+} + As(III) + SiO_4^{2-} + PO_4^{3-}

The multi-step jar tests consisted of two steps Fe^{2+} addition and oxidation. Each step duration was 60 min, and 10 ml water was sampled (both filtered and unfiltered) from the jars during each step at 0, 10, 30, and 60 min. The samples were immediately acidified for preservation and elemental quantification later by laboratory elemental analysis.

During the single-step jar test, 2.5 mgFe^{2+}/L was dosed to oxidize Fe and As, precipitate Fe, and As removal. In the multi-step jar tests, Fe^{2+} was dosed twice at a concentration of 1.25 mg/L in the first step and after As(III) oxidation step for sequential Fe^{2+} oxidation. The second Fe^{2+}-oxidation step was intended to replicate the aeration-filtration condition, similar to sequential oxidation in pilot-scale studies (Annaduzzaman et al., 2020a). Before the second Fe^{2+} dosing, 20 mg/L of 12.5% Cl containing NaOCl solution was added after 60 minutes of the first step to oxidize the remaining As(III) concentration and observed another 60 minutes to simulate total As(III) oxidation in practice by, e.g., biological processes in sand filters. This would therefore allow for determining the residual As(V) adsorption capacity of the precipitated HFO flocs from the previous step (first step). Subsequently, pH was readjusted to 7.0, followed by the second 1.25 mg/L of Fe^{2+} dosing. All the experiments were performed in triplicate and reported averages with standard deviations. The removed As was calculated by subtracting dissolved As from its initial concentrations. The reported units for removed As, Fe, $PO_4^{3-}$and SiO_4^{2-}were µg/L, percentile (%), mg/L, or combinations.

4.2.2 Chemicals and preparation

Stock solutions for 0.5 g/L of As(III) and As(V) were prepared daily using $NaAsO_2$ (*Fluka Analytical* - #SZBF1400V) and $Na_2HAsO_4.7H_2O$ (SIGMA *Life Science* - #SLBN2835V), respectively. Similarly, the individual stock solutions for 1.0 g/L of Fe^{2+}, PO_4^{3-}, and SiO_4^{2-} were prepared by dissolving $FeSO_4.7H_2O$ (SIGMA *Life Science* - #SLBT0884), Na_3PO_4 (SIGMA *Life Science* - #MKCB7570), and $Na_2SiO_3.5H_2O$ (SIGMA *Life Science* - #71746) correspondingly. The prepared stock solutions were stored with a 1M ultra-pure HNO_3 solution (Sigma Aldrich) (pH <3) to prevent chemical reactions. A laboratory-grade

12.5% Cl containing sodium hypochlorite (NaOCl) solution (Brenntag – #CAS7681-52-9) was used to oxidize the remaining As(III) in the multi-step jar tests.

4.2.3 Sampling and analytical procedure

The pH, Dissolved Oxygen (DO), Oxygen Reduction Potential (ORP), and Temperature (T) were measured using WTW electrodes (SenTix 940, FDO®925, SenTix ORP 900, and Terracon 925, respectively) over the experimental period. Fe, PO_4^{3-}, SiO_4^{2-}, and As concentrations were quantified from the collected 10 ml acidified water samples (both unfiltered and filtered) using Inductively Coupled Plasma Mass Spectrometry (ICP-MS- Alanlytik Jena model PlasmaQuant MS) in the WaterLab of Water Management Department at the Delft University of Technology, the Netherlands. Filtering of the water samples was done through a polyether-sulfone 0.45 µm filter (Ø-25 mm, VWR) and 0.20 µm (Ø-25 mm, VWR) filter to determine the varied HFO floc size and impact on As removal. Once As(III) was dosed, an additional sample was taken to quantity remaining As(III) species. Furthermore, the oxidation and removal process was completed (95%) within the first 60 minutes and reached chemical stability. Therefore, the data were reported for the first 60 minutes only for single-step and multi-step jar tests. The adsorption/removal efficiency was validated using pseudo-first-order, pseudo-second-order kinetic models and the PHREEQC geochemical hydro-equilibrium computer-based model explained in the Supplementary Information (SI).

4.2.4 Arsenic speciation

The As(III) speciation was conducted using an ion-exchange resin, Amberlite® IRA-400 chlorite (SIGMA Aldrich). The 100 ml filtered (0.45 µm filter) sample was re-filtered using a 60 ml syringe that contained 30 ml ion exchange resin. The remaining As concentration in the resin filtrate represented the uncharged As(III) species (Annaduzzaman et al., 2021b; Gude et al., 2018, 2016; Karori et al., 2006). The resin filtrate As(III) concentration was deducted from the 0.45 µm filtered As concentration to determine the dissolved As(V).

4.2.5 Data analysis

The one-way variance (ANOVA) analyses were conducted with a confidence level of 95% (α = 0.05) for the statistical validation of the removal efficiency. The data points from each jar test were used in triplicate assays from each sampling point (n=3) for the performed jar experiments. The data were presented in a mean with their standard deviations. The p-value (probability value) from the ANOVA test was used to determine the significant difference among triplicate results. The consistent lower p-value (<0.05) for As, Fe, PO_4^{3-} and SiO_4^{2-} removal at different experimental conditions, which means that the removal was statistically significant.

4.3 Results and discussion

4.3.1 As(III) and As(V) removal by single-step Fe^{2+} oxidation

Fig. 1 represents the removal of total As during the control experiments under single-step Fe^{2+} oxidation in the absence of PO_4^{3-} and SiO_4^{2-}. The control jar tests contained an initial 200 µg/L of As(III) or As(V) and either 2.5 mgFe^{2+}/L or 1.25 mgFe^{2+}/L. Symbols present the data points, and the lines represent the pseudo-second-order kinetic model-based As removal.

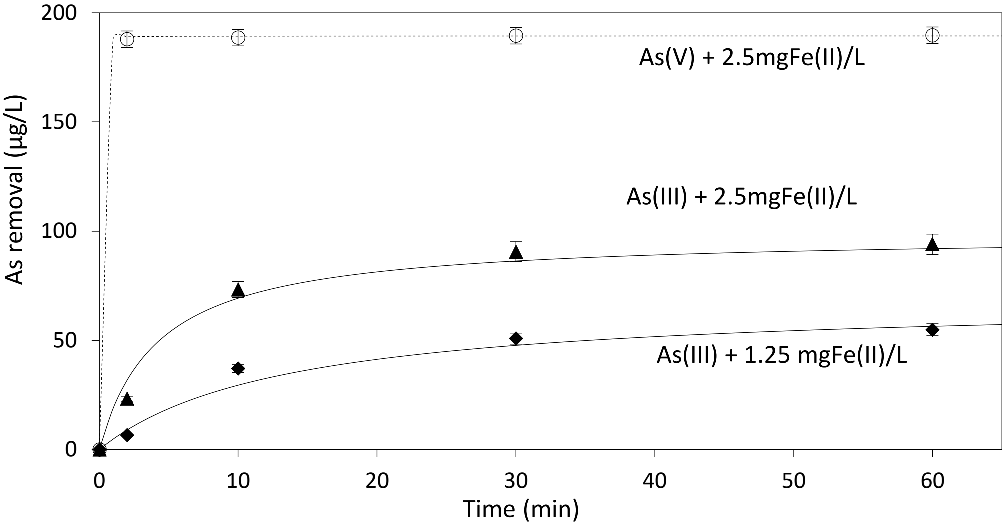


Fig. 1. The As removal in the single-step control jar experiments (without PO_4^{3-} and SiO_4^{2-}). Solid and open symbols depict the experimental As(III) and As(V) removal, respectively. The line depicts the Pseudo-second-order kinetic model based As removal. Initial concentrations were 200 µg/L As(III/V), 1.25 mg/L and 2.5 mg/L Fe^{2+}. Error bars indicate the standard deviations of the measurements.

The initial DO, ORP, and T in the jar tests were 7.9±0.8 mg/L, 267±25 mV, and 20±2°C, respectively, which were kept constant (within ±5%) during the experimental duration with a p-value of <0.05. The As(III) removal stabilized after approximately 30 min to 50-55 µg/L and 90-94 µg/L for the jar containing 1.25 mgFe^{2+}/L and 2.5 mgFe^{2+}/L, respectively . After complete Fe^{2+} oxidation (<2 min), only minor As(III) oxidation is to be expected. As such, the decrease in As(III) concentration over time was likely caused by its direct adsorption to HFO (Han et al., 2016) and increased equilibrium pH to 7.7±0.1 from the initial pH of 7.0. Roberts et al. (2004) also found that As(III) oxidation was limited to 200-250 µg/L (40-50%) during batch experiments, containing 500 µg/L of As(III) and 5-50 mgFe^{2+}/L. When we dosed As(V), however, As removal was 190±2 µg/L (95%) within 2 min after dosing 2.5 mgFe^{2+}/L (see Fig. 1). Afterward, no further adsorption of As(V) was observed, illustrating that As(V) removal was limited by the HFO adsorption capacity and not by the kinetics of adsorption. Based upon the removal in the As(V) experiments, the maximum As removal capacity for the single-step aeration was 76 µgAs/mgFe ($p<0.05$), similar to the previously found 70-80 µgAs/mgFe (Annaduzzaman et al., 2021b; Katsoyiannis et al., 2008; Roberts et al., 2004). When As was present as As(III), the available capacity of HFO for As uptake was only utilized for 38 µgAs/mgFe ($p<0.05$).

For both As(III) and As(V), the observed As removal from the jar tests were found to be best fitted with pseudo-second-order kinetic model compared to the pseudo-first-order model (detailed in SI), which is in line with previous studies (Song et al., 2019; Wang et al., 2014; Zhang et al., 2019). The model rate constant k_2 was found to be $1.34X10^{-3}$ mg.µg^{-1}.min^{-1} and $6.04X10^{-3}$ mg.µg^{-1}.min^{-1}, for As(III) with 1.25 µg/L and 2.5 mg/L of Fe^{2+}, respectively, whereas for As(V) with 2.5 mg/L of Fe^{2+} the model rate constant k_2 was $7.15X10^{-2}$ mg.µg^{-1}.min^{-1}. The observed rate constant k_2 for As(V) adsorption was higher than As(III), indicating that the As(V) removal was faster than that of As(III). Similar results were also attained in previous studies for As(III) and As(V) adsorption by Fe based adsorbent, e.g., ferrihydrite (Pena et al., 2005), nanocrystalline titanium dioxide (Stumm, 1997), and Fe- modified bone char (Begum et al., 2016).

4.3.2 Effect of PO_4^{3-} and SiO_4^{2-} on As removal by single-step Fe^{2+} oxidation

The results in **Fig. 2** indicate that in the presence of PO_4^{3-} or SiO_4^{2-}, As(III) and As(V) removal decreased compared to the control experiments. For the PO_4^{3-}-containing single-step jar tests, the removal of As(III) and As(V) after 60 min was 40 µg/L and 173 µg/L, respectively ($p=<0.05$). For the SiO_4^{2-}-containing systems, the As(III) and As(V) removal was 82 µg/L and 184 µg/L, respectively, which was in line with earlier studies into the competition of PO_4^{3-} and SiO_4^{2-} with As onto precipitating Fe-oxides (Chanpiwat et al., 2017; Holm, 2002; Roberts et al., 2004; Senn et al., 2018; Voegelin et al., 2010). The removal of As also followed pseudo-second-order kinetics, meaning removal was chemisorption, where the model rate constant k_2 for the PO_4^{3-} containing system was $9.68X10^{-3}$ mg.µg^{-1}.min^{-1}, and $1.23X10^{-2}$ mg.µg^{-1}.min^{-1}, for As(III) and As(V), respectively. For the SiO_4^{2-}-containing system, the rate-constant k_2 was $1.03X10^{-2}$ mg.µg^{-1}.min^{-1} and $1.41X10^{-2}$ mg.µg^{-1}.min^{-1} for As(III) and As(V) respectively.

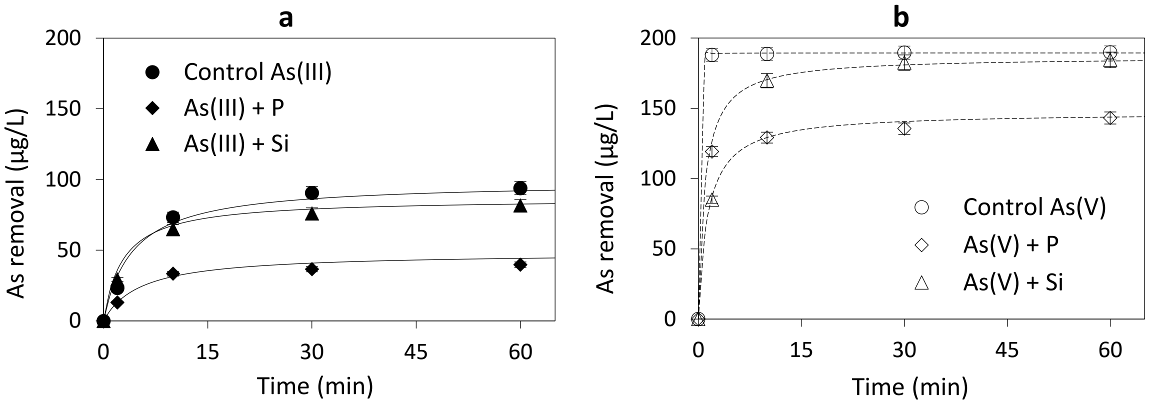


Fig. 2. Arsenic removal in single-step jar experiments either in the presence of PO_4^{3-} (noted as P) or SiO_4^{2-}(noted as Si). The experimental (a) As(III) and (b) As(V) removal are represented by solid and open symbols, respectively. The (solid and broken) lines depict the pseudo-second-order kinetic model. The initial concentrations were 200 μg/L As(III/V), 2.5 mg/L Fe^{2+}, 2 mg/L PO_4^{3-} and 16 mg/L SiO_4^{2-}. Error bars indicate the standard deviations of the measurements.

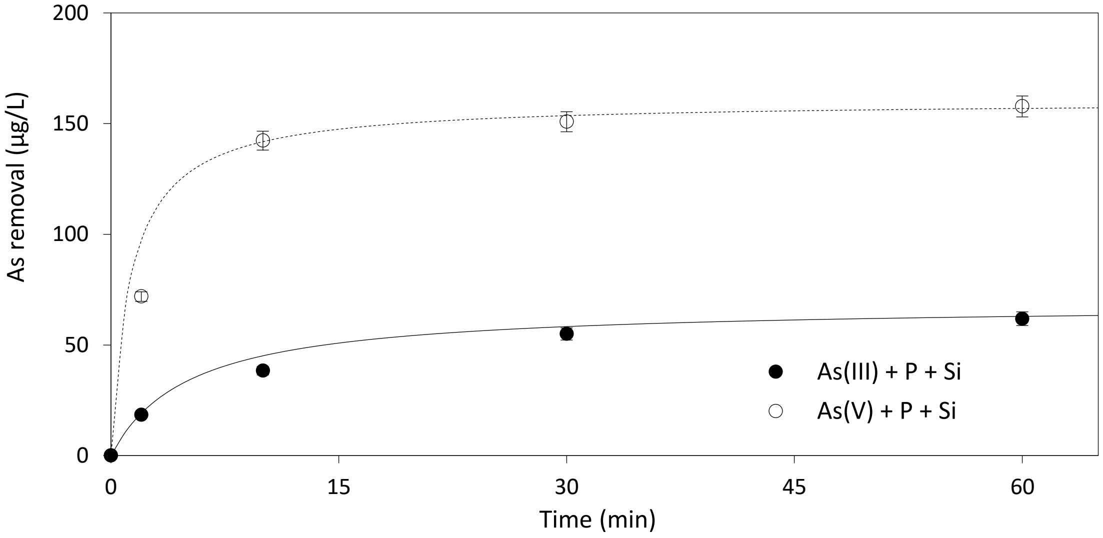


Fig. 3. Arsenic removal in the single-step jar experiments in the presence of both PO_4^{3-} (noted as P) and SiO_4^{2-}(noted as Si). The experimental As(III) and As(V) removal are represented by solid and open symbols, respectively. The line graphs depict the pseudo-second-order kinetic model-based As removal. The initial concentrations were 200 μg/L As(III/V), 2.5 mg/L Fe^{2+}, 2 mg/L PO_4^{3-} and 16 mg/L SiO_4^{2-}. Error bars indicate the standard deviations of the measurements.

The presence of both PO_4^{3-} and SiO_4^{2-} showed a substantial decrease in the removal efficiency of As(III) and As(V) in the single-step Fe^{2+} oxidation system (**Fig. 3**). After 60 min, the removal was 62 μg/L and 157 μg/L for A(III) and As(V), respectively ($p<0.05$). Under similar conditions, Davis et al. (2014) reasoned that the formation of ferrihydrite polymerization might be interrupted by PO_4^{3-} and SiO_4^{2-}, which could affect overall As removal. In the system with both PO_4^{3-} and SiO_4^{2-}, As removal was higher than in the presence of PO_4^{3-} only, indicating that SiO_4^{2-} might partially compensate for the inhibitory effects of PO_4^{3-} on As removal, which was also reported by Su and Puls (2001). **Fig. 4** presents the HFO floc sizes for the experiments with and without PO_4^{3-}, in the presence of SiO_4^{2-} and As(III)/As(V). It can be observed that in the presence of PO_4^{3-}, the floc sizes, measured as removal by 0.45 and 0.2 µm filters, are particularly smaller within the first 2 min, indicating PO_4^{3-}-SiO_4^{2-}-Fe interaction from the start of the reaction followed by gradual growth of these flocs. In the presence of SiO_4^{2-} the flocs were the smallest (<0.2 µm), which might have reduced the PO_4^{3-} effect on overall As removal because of a larger specific adsorption surface area. The PHREEQC model study indicated the required Fe/As ratios (g/g) for 95% As removal was 30-55, either in the absence and presence of PO_4^{3-} and SiO_4^{2-}, with the initial As(III), where for As(V) containing jar system the ratio was 11-20 (Table S1) and the experimental Fe/As ratio was 10-24%.

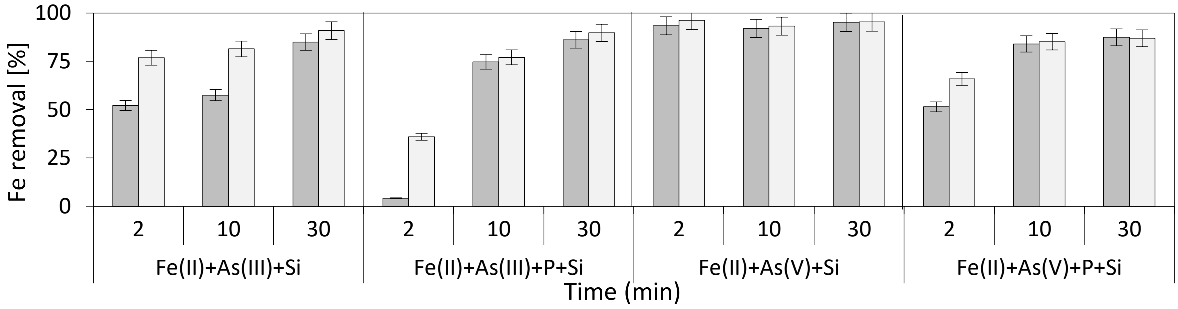


Fig. 4. Percentile Fe removal by 0.45 µm (light grey) and 0.20 µm (dark grey) filter at t=2, 10, and 30 min for SiO_4^{2-}-containing jar tests. The error bars represent the standard deviation of the triplicate measurements.

4.3.3 Sequential oxidation of Fe^{2+} and As(III)

Fig. 5 represents the As(III) removal after sequential oxidation of Fe^{2+} and As(III) either in the presence or absence of PO_4^{3-} and/or SiO_4^{2-}. In these experiments, the Fe^{2+} concentration of 2.5 mg/L was introduced in two sequential steps before and after dosing the oxidant (20 mg/L NaOCl) for As(III) oxidation. In between dosing, enough time (60 min) was reserved for the complete oxidation of As(III) and removal of oxidized As(V) by residual adsorption capacity previously HFO flocs. The oxidation of the first 1.25 mgFe^{2+}/L yielded an As(III) removal of 55 µg/L for the control experiments (without PO_4^{3-} and SiO_4^{2-}) and 52, 26, and 40 µg/L for SiO_4^{2-}, PO_4^{3-}, and both PO_4^{3-} and SiO_4^{2-}, respectively ($p<0.05$). The addition of the oxidant in the As(III) oxidation step after the first Fe^{2+} oxidation step led to the instant oxidation of As(III) to As(V) (data in SI), showing a residual adsorption capacity of the previously precipitated HFO flocs for As(V) of 64 µg/L in the control experiments. This residual As(V) adsorption capacity was lower in the presence of PO_4^{3-} and/or SiO_4^{2-}, namely between 14-41 µg/L. The overall As uptake by the first Fe^{2+} dosing, followed by the As(III) oxidation step, was 119 µgAs/mgFe ($p<0.05$) in the absence of $PO_4^{3-}$and SiO_4^{2-}, and 93, 40 and 61 µgAs/mgFe when SiO_4^{2-}, PO_4^{3-}, and both PO_4^{3-} and SiO_4^{2-} were added, respectively. The uptake of As by HFO was thus 2-3 times more effective in the absence of PO_4^{3-} than in the presence of PO_4^{3-}. This underlines the previously reported PO_4^{3-} competition for HFO sites and changing the HFO structures (Davis et al., 2014; He et al., 1996; Lytle and Snoeyink, 2002), resulting in the unavailability of HFO adsorption sites for dissolved As(V).

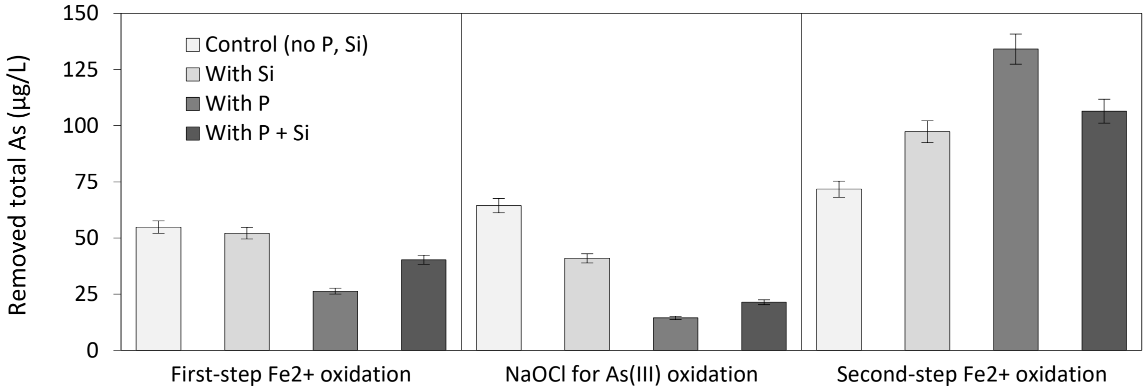


Fig. 5. Total As removal in each step of the sequential addition of 1.25 $mgFe^{2+}/L$, 20 mg/L NaOCl and 1.25 $mgFe^{2+}/L$ to a solution containing 200 µg/L As(III) with and without 2 mg/L PO_4^{3-} (noted as P) and/or 16 mg/L SiO_4^{2-} (noted as Si).

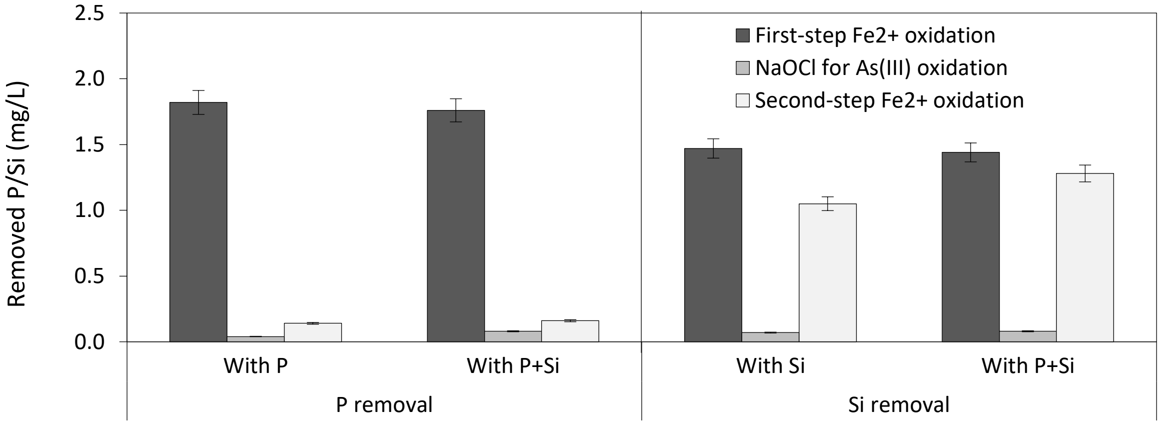


Fig. 6. Total PO_4^{3-} (noted as P) and SiO_4^{2-}(noted as Si) removal after the sequential addition of 1.25 $mgFe^{2+}/L$, 20 mg/L NaOCl and 1.25 $mgFe^{2+}/L$ to a solution containing 200 µg/L As(III) and 2 mg/L PO_4^{3-} and/or 16 mg/L SiO_4^{2-}.

Fig. 6 shows that PO_4^{3-} removal was approaching 90% in both experiments after dosing the first 1.25 mg/L Fe^{2+}. The uptake of As(V) after oxidant dosing was slightly better in the presence of both PO_4^{3-} and SiO_4^{2-} than PO_4^{3-} only, which is in line with earlier observations that SiO_4^{2-} might, partially, compensate for the inhibitory effect of PO_4^{3-} (Su and Puls, 2001). Robert et al. (2004) studies reported that under sequential Fe^{2+} oxidation, the required Fe/As ratio for 95% As removal was 40-50 (mg/mg) instead of 80-90 (mg/mg) in the single-step oxidation process. However, our previous natural groundwater-based pilot-scale studies revealed that under step-wise aeration-oxidation, 10 (mg/mg) of Fe/As ratio could be sufficient for As removal (Annaduzzaman et al., 2021a). Consequently, this laboratory-based Sequential Fe^{2+} oxidation study revealed that the required Fe/As ratio of 10-15 (mg/mg) could be sufficient to reach As concentration below 50 µg/L either in the presence/absence of PO_4^{3-} and SiO_4^{2-}. With the introduction of the remaining 1.25 mg/L of Fe^{2+} in the second step, a substantial amount of available As(V) was removed by the newly formed HFO flocs (Fig. 5), particularly in the presence of PO_4^{3-}. Obviously, the starting conditions for this final step were not the same in all jars, e.g., As(V) concentrations were lowest for the control and highest in the presence of PO_4^{3-}. Nevertheless, the initial hindrance observed due to PO_4^{3-} is apparently compensated during the second Fe^{2+} dosing, due to the removal of PO_4^{3-} during the first Fe^{2+} dosing.

4.4 Conclusion

The objective of this study was to gain a better understanding of interactions with phosphate (PO_4^{3-}) and silicate (SiO_4^{2-}) during sequential Fe^{2+} and As(III) oxidation, as these are typically found in groundwater and known to interfere with As removal. The research was conducted in single and multi-step jar tests with initial As(III/V), Fe^{2+} concentrations, and pH of 200 µg/L, 2.5 mg/L, and 7.0, respectively, representing the targeted groundwater in Bangladesh. The sequential Fe^{2+} and As(III) oxidation in the multi-step jar tests indicated that the hindrance by PO_4^{3-} in the first Fe^{2+} oxidation step was compensated for in the second. Moreover, smaller Fe flocs (<0.45µm) were observed in the presence of SiO_4^{2-}, potentially providing more surface area during the second Fe^{2+} oxidation step leading to better overall As removal. The present study specifies that the sequential Fe^{2+} could be a promising method for As removal with Fe/As ratios as low as 10-15 (mg/mg) either in the presence/ absence of PO_4^{3-} and SiO_4^{2-}. Altogether it may be concluded that controlling the As(III) and Fe^{2+} oxidation sequence is beneficial for As removal in the presence and absence of PO_4^{3-} and/or SiO_4^{2-}. However, before applying this sequential Fe^{2+} oxidation method for As removal, further investigation is recommended considering other contaminant effects.

4.5 Acknowledgment

This study was supported by the DELTAP project funded by the NWO-WOTRO research grant (W07.69.205). The authors also acknowledge the Water Treatment Research course student groups from the Water Management Department, TU Delft, for their support during Laboratory Study. Finally, the authors are thankful to Nadia van Pelt for her invaluable help with English grammar revision.

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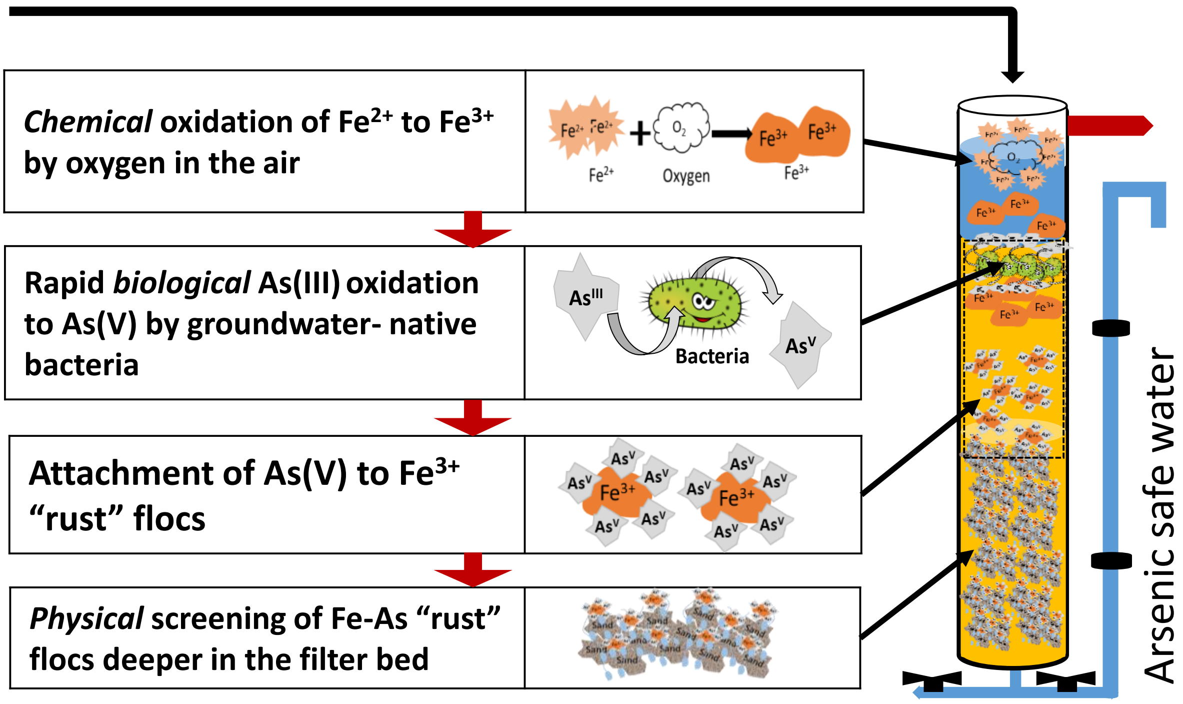
Chapter 5

Arsenic removal with biofilters using groundwater-native iron from different wells in Bangladesh



This chapter is based on:

Md Annaduzzaman, Luuk C. Rietveld, Devanita Ghosh, Bilqis Amin Hoque, Doris van Halem, (2022). Arsenic removal with biofilters using groundwater-native iron from different wells in Bangladesh, will (under review).

Abstract

Arsenic (As) removal by precipitating iron (Fe) is found to be effective, however, the applicability under varying groundwater conditions should be known for further upscaling. Therefore, we aimed to study the interaction between Fe, As, phosphate, and manganese during anoxic storage followed by sand filtration, using natural groundwater, containing low to high concentrations of As (<60 - >300 µg/L), Fe^{2+} (2.4-5.4 mg/L), phosphate (2-4 mg/L) and manganese (280-600 µg/L), in the As-affected areas of Rajshahi, Bangladesh. The experiments were conducted using anoxic storage of groundwater followed by dual-bed (for high As concentration) and single-bed (for low As concentration) sand columns, respectively, to investigate if the systems were effective in As removal without dosing chemicals, only depending on locally available materials and crafts. This study proved that independent of locations or source (ground)water composition, the use of anoxic storage before aeration followed by aeration-filtration produces in-situ HFO flocs by delayed/step-wise Fe^{2+} oxidation and contributed to high (>94%) As removal without compromising the removal of phosphate and manganese. In addition, while the community dynamics depended on the regional water composition, microbial communities supported As removal. Irrespective of the As concentrations in the groundwater, heterotrophic As(III) oxidizers, such as *Sediminibacterim, Sideroxydans, Dyella, Pseurhodoferax, Hydrogenophaga, Methylovulum, Geobacter,* were identified. Therefore, it can be assumed that the use of anoxic storage of groundwater could facilitate the delayed/step-wise Fe^{2+} oxidation through surface-related and/or biological processes, which would be beneficial in the subsequent aeration-(sand) filtration steps for better As removal.

Keywords: Arsenic removal, Native iron, Groundwater, Sand filter, Drinking water treatment

5.1 Introduction

Arsenic (As) contamination in groundwater is a worldwide concern for its adverse health effects upon continued consumption, even at low concentrations. Chronic exposure to As contaminated drinking water has been depicted in tens of millions of people suffering from skin lesions, hyperkeratosis, melanosis, cancer of the skin and internal organs (Hou et al., 2016; Huaming et al., 2013; Li et al., 2012). About 50-55 million people in Bangladesh are exposed to As levels beyond the World Health Organization (WHO) guideline of 10 µg/L, while, considering Bangladesh Drinking Water Standard (BDWS) of 50 µg/L, the exposed population number is about 20-22 million (BBS/UNICEF, 2015, 2011; Jamil et al., 2019). A large part of Bangladesh thus has As concentrations in groundwater above those recommended values, and concentrations sometimes even exceed 1500 µgAs/L (Cavalca et al., 2019; Haque et al., 2018; Nordstrom, 2002; Rosso et al., 2011). The available treatment technologies, including adsorption, chemical precipitation, ion exchange, membrane filtration, and nanofiltration (NF), are typically efficient for arsenate (As(V)) removal, but not for arsenite (As(III)) (Bai et al., 2016; Begum et al., 2016; Lytle et al., 2007). In anaerobic groundwater at circumneutral pH, As(III) exists as thermodynamically stable and non-ionized H_3AsO_3 (Cullen and Reimer, 1989; Hou et al., 2017a, 2017b) and thus difficult to remove by charge-based adsorption processes. In contrast, As(V) is the predominant species in oxidizing conditions and exists as negatively charged $H_2AsO_4^-$ and $HAsO_4^{2-}$ and can thus more easily be adsorbed to adsorbents such as iron (Fe)-oxides (Lafferty et al., 2010; Meng et al., 2000; Villalobos et al., 2014). Therefore, oxidation of As(III) to As(V) is required for effective As removal, either by chemical oxidants or by natural processes (Dodd et al., 2006; Gude et al., 2017; Pio et al., 2015; Ryu et al., 2017).

Arsenic co-precipitation with Fe is a well-known treatment method implemented in many countries (Ahmed, 2001; Li et al., 2012; Sharma et al., 2016; Sorensen and McBean, 2015; Tian et al., 2017), and the removal efficacy of As using Fe oxides, such as magnetite (Wang et al., 2008), ferrihydrite (Hagstroem, 2017), goethite (Amstaetter et al., 2010; Farquhar et al., 2002), and zero-valent iron (Kanel et al., 2006; Wang et al., 2017), has been studied extensively. The oxidized Fe^{3+} solids have a large specific surface area and has a robust adsorption affinity for inorganic As(V) species (Wan et al., 2011).

The slow oxidation of As(III) by dissolved oxygen (DO) has resulted in the use of various chemical oxidants (e.g., chlorine, permanganate, and ozone) for more rapid As(III) oxidation before subsequent removal. However, the use of chemical oxidants is energy-intensive, costly, and increases the complexity of the treatment methods. Also, from previous studies it was concluded that external or groundwater native-Fe^{2+} oxidation can also be effective for As(III) oxidation, e.g. by Fenton-like chemical reactions and the formation of reactive oxidation species (ROS) (Hug et al., 2001; Hug and Leupin, 2003). In other studies it was found that groundwater indigenous bacteria (Arsenic Oxidizing Bacteria; AsOB) can support As(III) oxidation during various treatment steps (Dey et al., 2016; Hering et al., 2017; Liao et al., 2011), such as in overhead storage containers (Annaduzzaman et al., 2021a) and during filtration (rapid sand filter (RSF); Gude et al., 2018b).

Passive groundwater treatment for Fe, ammonium (NH_4^+), and manganese (Mn^{2+}) removal consists of aeration followed by single or multiple filtration steps (Katsoyiannis et al., 2008; Morrison et al., 2002; Vries et al., 2017) without using chemicals (**Fig. 1**). However, this method is not appropriate for As removal, as its removal efficacy can vary between 15-90%, depending on water composition (Gude et al., 2016; Lowry and Lowry, 2002; Sorlini and Gialdini, 2014, 2010). Moreover, studies by Holm and Wilson (2006) suggested that, despite the presence of sufficient groundwater native-Fe^{2+} (>1.5 mg/L) (Annaduzzaman et al., 2018; Biswas et al., 2012), the As removal can be limited up to only 20–25% (8–10 µg/L). Similarly, Lowry and Lowry (2002) revealed that aeration prior to storage facilitated one-step rapid and complete native-Fe^{2+} oxidation before As(III) oxidation, and thus resulted in relatively low As removal.

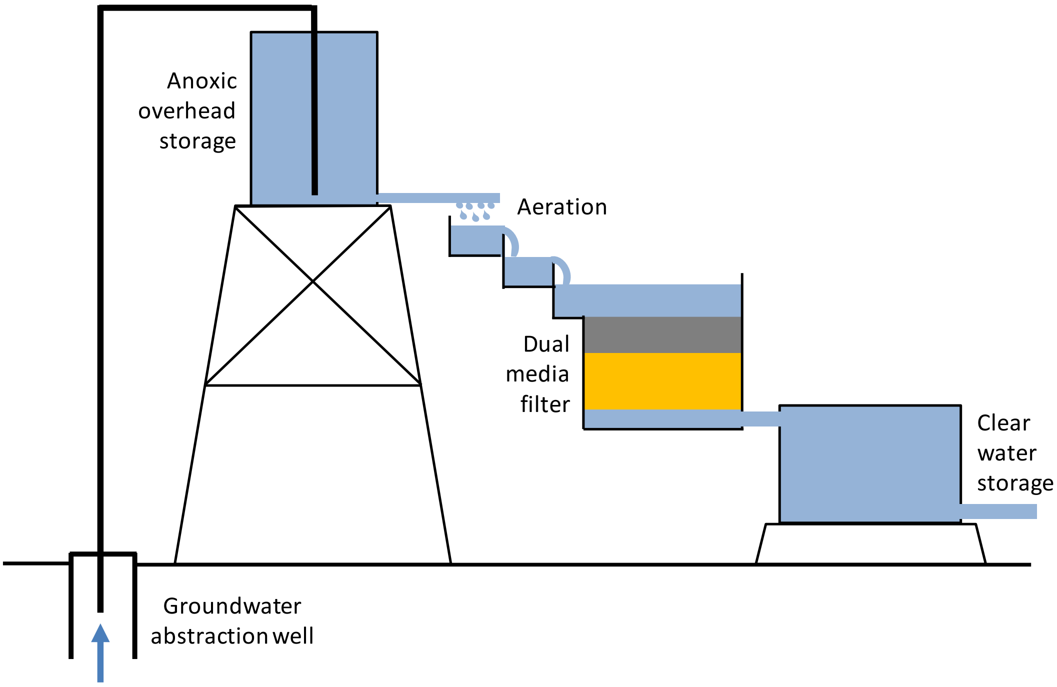


Fig. 1. The concept of delayed aeration by applying an anoxic storage container before aeration and dual-bed filtration (Annaduzzaman et al., 2021b).

However, Roberts et al. (2004) concluded that 90% As removal could be achieved in step-wise Fe^{2+} oxidation using half of the total Fe^{2+} required in single-step oxidation. Previous studies by our groups revealed that anoxic storage followed by aeration and sand filtration allowed for this step-wise Fe^{2+} oxidation, which indeed facilitated As(III) oxidation and consequent removal of oxidized As(V) with freshly formed hydrous ferric oxide (HFO) flocs (Annaduzzaman et al., 2021a, 2021b, 2021c). Although, this treatment concept was found to be effective during previous studies, the applicability under varying groundwater conditions should be known for further upscaling. The present study intended to determine the interactions between Fe, As, PO_4^{3-} and Mn after aeration and in sand filtration using natural groundwater containing low (50±5 µg/L) and high (>300 µg/L) concentrations of As and varying Fe^{2+} (2.4-5.4 mg/L), PO_4^{3-} (2-4 mg/L) and Mn^{2+} (280-600 µg/L) concentrations. This novel treatment method was piloted using three different natural groundwater in As-affected areas of Rajshahi, Bangladesh. The experiments were conducted using dual-bed (for high As) and single-bed (for low As) sand columns to study if the systems behave the same for As removal without dosing chemicals but making only use of locally available materials and crafts. Furthermore, the study included the identification of microbial community composition on the filter materials and its possible role in enhancing Fe and As oxidation during filtration.

5.2 Materials and methods

5.2.1 Water Quality

The study was conducted at pilot scale with high and low As contaminated natural groundwater in the villages Uttar Kazirpara (location 1) and Durgapur (Location 2a and 2b) in Paba Upazila of Rajshahi district, Bangladesh, respectively. The villages Kazirpara and Durgapur are 17 km apart, where locations 2a and 2b in Durgapur were about 500 m apart. **Table 1** shows the used natural groundwater quality parameters from respective locations. Using submergible electrical pumps (Gazi, Bangladesh), the reducing/anoxic groundwater was pumped from 50±5 m depth and stored in overhead (anoxic) storage containers without allowing aeration.

Table 1. The used groundwater quality as an influent for the pilot-scale rapid sand filters.

Parameters	Units	Location 1	Location 2a	Location 2b
pH	[-]	6.94	6.88	6.99
Dissolved oxygen, DO	mg/L	0.07	0.09	0.11
Oxygen reduction potential, ORP	mV	-110	-134	-140
Electrical conductivity, EC	µS/cm	675	683	809
Temperature, T	°C	26.7	27.8	27.6
Arsenic, As(total) (*As: Fe ratio-mg:mg*)	µg/L	329 *(0.14:1)*	49 *(0.01:1)*	59 *(0.02:1)*
Arsenite, As(III)	µg/L	290	39	48
Arsenate, As(V)	µg/L	39	10	11
Iron, Fe^{2+}	mg/L	2.33	5.32	3.6
Manganese, Mn	µg/L	600	373	288
Phosphate, PO_4	mg/L	2.15	3.96	2.69
Magnesium, Mg	mg/L	13.93	31.64	28.45
Calcium, Ca	mg/L	69.96	58.38	45.68
Silicate, SiO_4	mg/L	28.5	26.94	21.93

5.2.2 Sand filter design

The experimental pilot-scale sand filtration column setup consisted of three identical columns at each location. The As(III) oxidation and removal were studied with anoxic storage followed by aeration and dual bed (location 1) and single-bed (location 2) sand filtration. The overhead storage was filled with anoxic groundwater using an inlet at the bottom of the container to prevent any intentional aeration by atmospheric contact. At the start of the experiments, the storage systems were thoroughly disinfected using 35% (w/w) hydrogen peroxide (H_2O_2) (Sigma-Aldrich) prior to use. On day 1, the storage containers were overflowed for an additional 5 minutes to remove atmospheric oxygen. On the following days, groundwater was added to the remaining stored water (nearly one-third of volume) to refill and overflowed for additional 5 minutes.

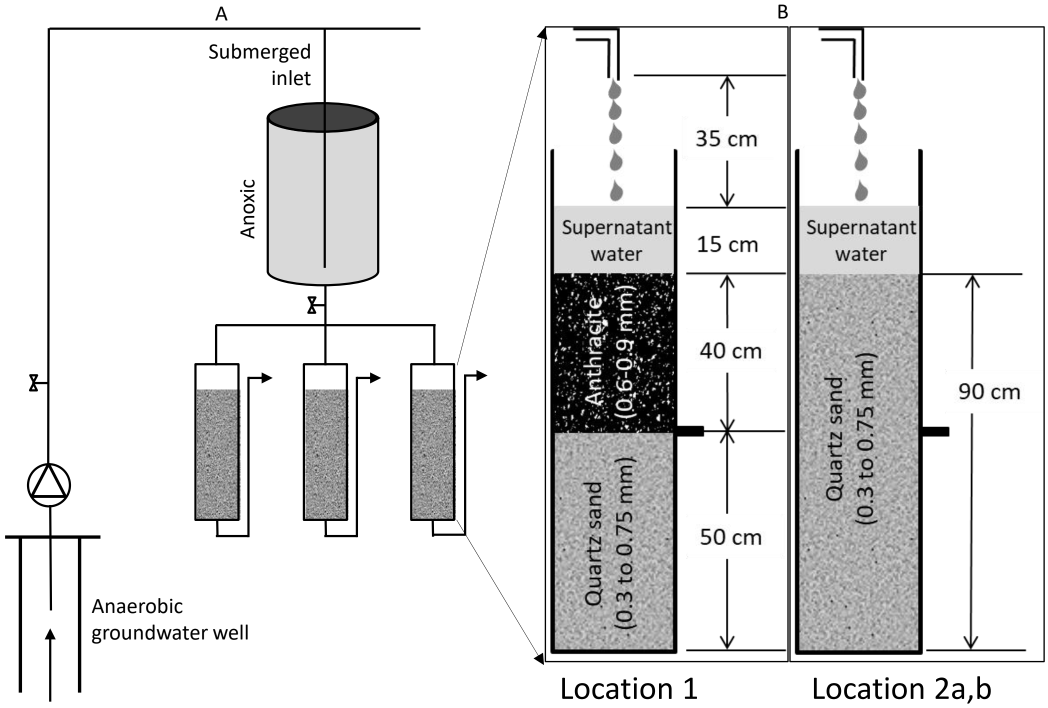


Fig. 2. Schematic overview of the dual-media sand filtration setup. The storage containers were filled with anoxic groundwater using a submerged inlet at the container's bottom to avoid atmospheric aeration. The pre-stored water was aerated by dripping into the column from the pipeline placed 35 cm above the column top. The dual-media (Location 1) and single bed (Location 2a, b) sand column experiments were performed in triplicate.

The column feeding was performed by anoxic stored water dripping from the pipeline, placed 35 cm above the supernatant water (**Fig. 2**). Each column had a diameter of 10 cm and a height of 120 cm. The dual bed filter columns at location 1 were installed with 40 cm anthracite on top, followed by 50 cm of quartz sand at the bottom, and the used groundwater contained a high concentration of As (>300 µg/L). Due to the high As/Fe ratio (0.14:1 mg/mg), it was assumed that the courser anthracite layer on top could allow for deep penetration of formed HFO flocs and thus increasing the contact time with As and, thereby, enhancing As removal. The filter column at location 2 (a, b) only contained quartz sand with a bed height of 90 cm, while As concentrations of the used groundwater were low (<60 µg/L). The quartz sand, known as Domar sand, commonly used for gravel packing the tube well screen, was collected from locally available shops.

Before experimentation, the columns were comprehensively backwashed until the supernatant was clear. The flowrate of 9 L/h was fixed to achieve a filtration velocity of 1 m/h. 15-20 cm supernatant water level above the filter bed was maintained, and once the water level rose beyond 20 cm by filter clogging, backwashing was performed by allowing 20% filter bed expansion until the supernatant became visually clear (±20 minutes). The backwash frequency (2-3/week) varied depending on the Fe concentration of the incoming water. The columns were continuously fed with stored water and protected from direct sunlight exposure during the entire experimental period. The water quality at the various treatment steps was analyzed over the experimental 30 days, i.e. in the storage containers, after aeration (supernatant of the filter column), in the middle of the filter (40 cm from the top), and in the columns' filtrate.

5.2.3 Sampling and analysis

pH, oxygen-reduction-potential (ORP), dissolved oxygen (DO), Electrical conductivity (EC), and temperature (T) were measured using WTW electrodes (SenTix 940, SenTix ORP 900, FDO925, Terracon 925, TetraCon 700, respectively). To do so, a tube was connected to a sampling point and placed at the bottom of an overflowing 2 L jar containing the WTW electrodes. Water samples were collected from the bottom of the jar using a 60 ml syringe to avoid contamination by atmospheric oxygen. The 15 ml filtered, and unfiltered water samples were collected in transparent polypropylene 15 ml centrifuge tubes (Sigma Aldrich). A polyethersulfone 0.45 µm filter (25 mm, VWR) was used for water filtering. Both filtered and unfiltered samples were immediately acidified with ultrapure HNO_3 acid (ACS reagent, 70%; Formula weight 60.01 g/mol; Sigma Aldrich) to make up 1.5% of the solution and to preserve the samples until elemental analysis. Iron, As, P, and Mn were analyzed from the collected 15 ml filtered and unfiltered samples using Inductively Coupled Plasma Mass Spectrometry (ICP-MS; Alanlytik Jena model PlasmaQuant MS) in the WaterLab at the Water Management Department of the Delft University of Technology, the Netherlands.

5.2.4 Arsenic speciation

As speciation was conducted using an ion-exchange resin, Amberlite® IRA-400 chlorite (SIGMA Aldrich). A 100 ml filtered (0.45 µm filter) water sample was re-filtered using a 60 ml syringe that contained 30 ml ion exchange resin. The remaining As concentration in the resin filtrate represented the uncharged As(III) species (Gude et al., 2018b, 2016; Karori et al., 2006). The resin filtrate As(III) concentration was deducted from the 0.45 µm filtered As concentration to determine the dissolved As(V) species.

5.2.5 Microbial sampling and analyses

To analyze the microbial community dynamics, the biomass from the column sand (top) was collected from Locations 1 and 2a and stored at -80˚C. From these samples, around 0.25 g of biomass was used for DNA extraction using the DNeasy UltraClean microbial kit (Qiagen) at Rajshahi University, Bangladesh. Afterwards, the DNA samples were used for metagenomics analysis at Novogene Hongkong, China. The cetyl-trimethylammonium bromide/sodium dodecyl sulfate (CTAB/SDS) method followed by 1% agarose gel horizontal electrophoresis was used to extract and detect the total environmental DNA from the samples. The environmental DNA samples were used for metagenomic analyses with a further dilution of 1 ng/µL. The polymerase chain reactions (PCR)-amplification of V3 region of 16S rRNA genes was performed using the universal primers 341F (5′- CCT ACG CGA GGC AGC AG -3′) and 517r (5′- ATT ACC GCG GCT GCT GG -3′) (Muyzer et al., 1993), using Phusion® High-Fidelity PCR Master Mix (New England Biolabs) at Novogene Hongkong, China. The PCR products were detected using SYBR green in a 2% agarose gel electrophoresis and purified with the Qiagen Gel Extraction Kit (Qiagen, Germany). The Illumina HiSeq paired-end raw reads were generated with NEBNext® UltraTM DNA Library Prep Kit and quantified via Qubit and qPCR.

The Illumina HiSeq paired-end raw reads were checked for quality (Base quality, base composition, GC content) using the FastQC tool (Andrews et al., 2010). The QIIME (Version: 1.9.1) pipeline (Caporaso et al., 2010) was used to select 16S RNA, clustering, and OTU picking followed by taxonomic classification based on the SILVA database and statistical analysis. The chimeric sequences were removed from the libraries using the de-novo chimera removal method UCHIME implemented in the tool VSEARCH. Pre-processed reads from all samples were pooled and clustered into Operational Taxonomic Units (OTUs), based on their sequence similarity using the Uclust program (similarity cutoff = 0.97). A representative sequence was identified for each OTU and aligned against the SILVA core set of sequences using the PyNAST program (Caporaso et al., 2010). The representative sequences of the OTUs were also used to predict KEGG orthodoxy (KO) abundances using PICRUSt2 (Langille et al., 2013), and microbial pathways were inferred. The eight metagenomic library datasets were clustered from the collected biological sand samples of piloted columns at location 1 (Anoxic Column B1T1), and location 2a (A1, A1R1, A2, A2R1, A3), based on the arithmetic mean of weighted Unifrac distance using Unweighted Pair Group Method (UPGMA). An unrooted Neighbor-Joining (NJ) tree of the 35 predominant and common bacterial 16S rRNA sequences was built using the software MEGA X version 11. All raw sequencing data related to this project are submitted to the NCBI BioProject: PRJNA673456 (https://www.ncbi.nlm.nih.gov/bioproject/PRJNA673456).

5.2.6 Data analysis

The statistical validation of Fe, As, PO_4^{3-}, and Mn^- removal at the different treatment steps was executed by one-way analysis of variance (ANOVA), considering a confidence level of 95% (α=0.05). The triplicate data from each step were used in assays from each sampling day. The data presented here were the mean from the triplicate samples with their standard deviations. The p-value (probability value) from the ANOVA test was used to determine the significant difference between the anoxic storage results, followed by the aeration and RSF steps. The analysed p-value was constantly below 0.05 for Fe, As, PO_4^{3-}, and Mn removal at the different treatment steps, indicating statistically significant removal of these contaminants.

5.3 Results and Discussion

5.3.1 Fe^{2+} oxidation in the storage containers

The DO, pH, ORP, and Fe^{2+} concentrations in the storage containers are presented in **Fig. 3**. The DO, pH, ORP, and Fe^{2+} of the natural groundwater were 0.07 mg/L, 6.94, -110 mV and 2.33 mg/L; 0.09 mg/L, 6.88, -134 mV and 5.32 mg/L; and 0.17 mg/L, 7.08, -140 mV and 3.6 mg/L for Location 1, 2a and 2b, respectively (**Table 1**). The pH and DO remained low over time (<0.2 mg/L; sub-oxic) (**Fig. 3a**), whereas ORP increased slowly with partial Fe^{2+} oxidation and the formation of Fe^{3+}-oxides (i.e., HFO flocs) (**Fig. 3b**). The pH dropped slightly to 6.7±0.03 from the initial pH of 6.8±0.03, and the ORP increased to 48, 31, and 22 mV at locations 1, 2a and 2b, correspondingly, from a groundwater ORP of -128±15 mV. Similar to previous findings, the oxidation of Fe^{2+} in the (anoxic) storage containers was inhibited throughout the experimental period, allowing for delayed/step-wise oxidation (Annaduzzaman et al., 2021b). The trace amount of DO intrusion, while filling the storage container, led to partial Fe^{2+} oxidation on day 1. However, its oxidation was accelerated during the following days, which was likely associated with Fe^{3+} hydroxide accumulation that supported heterogeneous Fe^{2+} oxidation (van Beek et al., 2015) and/or the formation Fe^{2+} oxidizing biofilm (de Vet et al., 2011; Lin et al., 2012; Uddin et al., 2019), which finally resulted in an overall drop in Fe^{2+} concentrations in the storage containers from 1.80, 3.32, and 2.8 mg/L on the first day to 1.09, 2.19, and 1.17 mg/L after the experimental period for locations 1, 2a, and 2b, respectively (**Fig. 3b**).

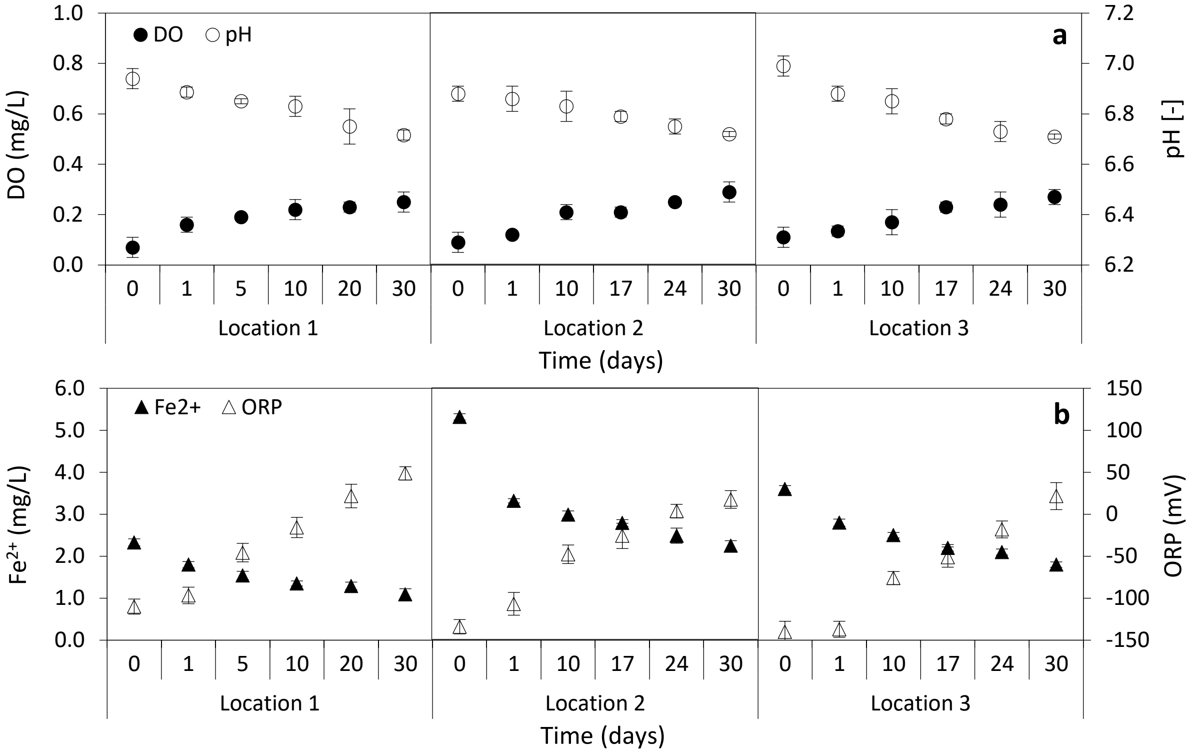


Fig. 3. (a) pH, DO, and (b) ORP and Fe^{2+} changes in the storage containers over the experimental period. The error bar represents the standard deviations.

5.3.2 As(III) oxidation and As removal in the storage containers

Arsenic species over the experimental duration of 30 days in the storage containers before aeration and RSF filtration at locations 1, 2a, and 2b are presented in **Fig. 4**. Partial As(III) oxidation and As removal were observed in all storage at respective locations. The total As concentrations in groundwater for location 1 was 329 µg/L (high) and for locations 2a, and 2b were <60 µg/L (low), with As(III) concentrations of 290 and 43±4 µg/L respectively. After the first day, the total dissolved As concentrations in the storage containers for location 1 was 268 µg/L, and 44±1 µg/L for location 2a, and 2b, while the As(III) concentrations were 235 and 34±1 µg/L for locations 1 and 2a and 2b, respectively.

Similar to previous findings (Annaduzzaman et al., 2021a), after 5-10 days, stable operational conditions in the storage containers resulted in As(III) concentrations of 40(±10)% of the original groundwater content (**Fig. 4**). The low (or suboxic) DO conditions probably resulted in partial/slow Fe^{2+}oxidation and the presence of Fe^{3+} induced, heterogeneous As(III) oxidation (Amstaetter et al., 2010; Tian et al., 2017; Wang and Giammar, 2015). However, the limited Fe^{2+} oxidation and the limited formation of ROS (e.g., $^{\circ}OH$, H_2O_2, and O_2°) could have hampered As(III) oxidation. However, it is not to be expected that AsOB were developed in the anoxic storage containers during the period of 30 days. The low pH (Fig. 3a) could have assisted in better As(V) removal with precipitating HFO flocs in the storage system, due to an increased positive surface charge on HFO flocs and hence increased removal of the negatively charged As(V). The calculated Fe^{3+}/As removal ratio after the experimental period of 30 days was within the same range of 80(±10) (μgAs/mgFe^{3+}), with a p-value of less than 0.05, as reported previously (Annaduzzaman et al., 2021b).

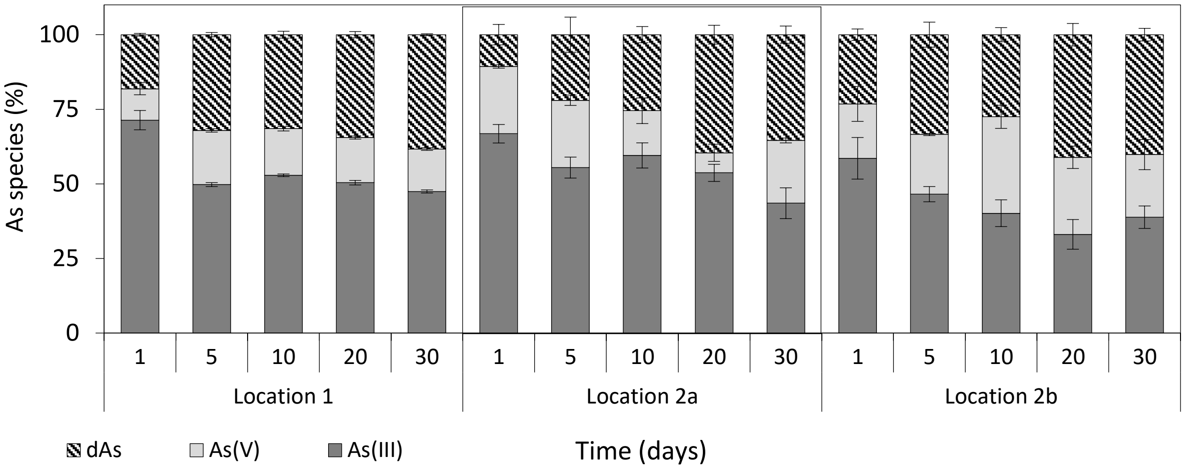


Fig. 4. Arsenic species (As(III), As(V), and removed As) and their average concentration in the storage containers. The error bar represents the standard deviation.

5.3.3 Fe and As oxidation and removal after aeration

The dissolved Fe^{2+}, Fe^{3+}, As(III), and As(V) concentrations before and after aeration are presented in **Fig. 5**. After the anoxic storage containers, the groundwater was aerated by dripping from 35 cm above the RSF filter bed over 30 days. The aeration before column feeding increased the pH, DO, and ORP to 7.5(±0.15), 6.6(±0.2) mg/L, and 55(±5) mV, respectively. This increased DO enhanced remaining Fe^{2+} oxidation from the storage containers and formed *in-situ* HFO flocs, where the remaining Fe^{2+} was below 0.3 mg/L (Fig. 5a).

Along with Fe^{2+} oxidation, As(III) oxidation of 69, 12, and 7 μg/L was found at locations 1, 2a and 2b, respectively, possibly resulting from homogeneous As(III) oxidation by DO, bacterial processes, *in-situ* formation of ROS during Fe^{2+} oxidation, or a combination of these processes. The maintained 15-20 cm supernatant water level, which was in contact with the filter bed's top layer, possibly provided a carrier for bacteria to promote biological As(III) oxidation (Gude et al., 2018b; Katsoyiannis and Zouboulis, 2004). In the supernatant, the removed As was 16, 10, and 13 μg/L at the locations 1, 2a, and 2b, respectively. This also confirmed the earlier findings, revealing that step-wise/delayed Fe^{2+} oxidation and *in-situ* HFO flocs formation enhances As(III) oxidation and As removal (Annaduzzaman et al., 2021a,b,c; Roberts et al., 2004).

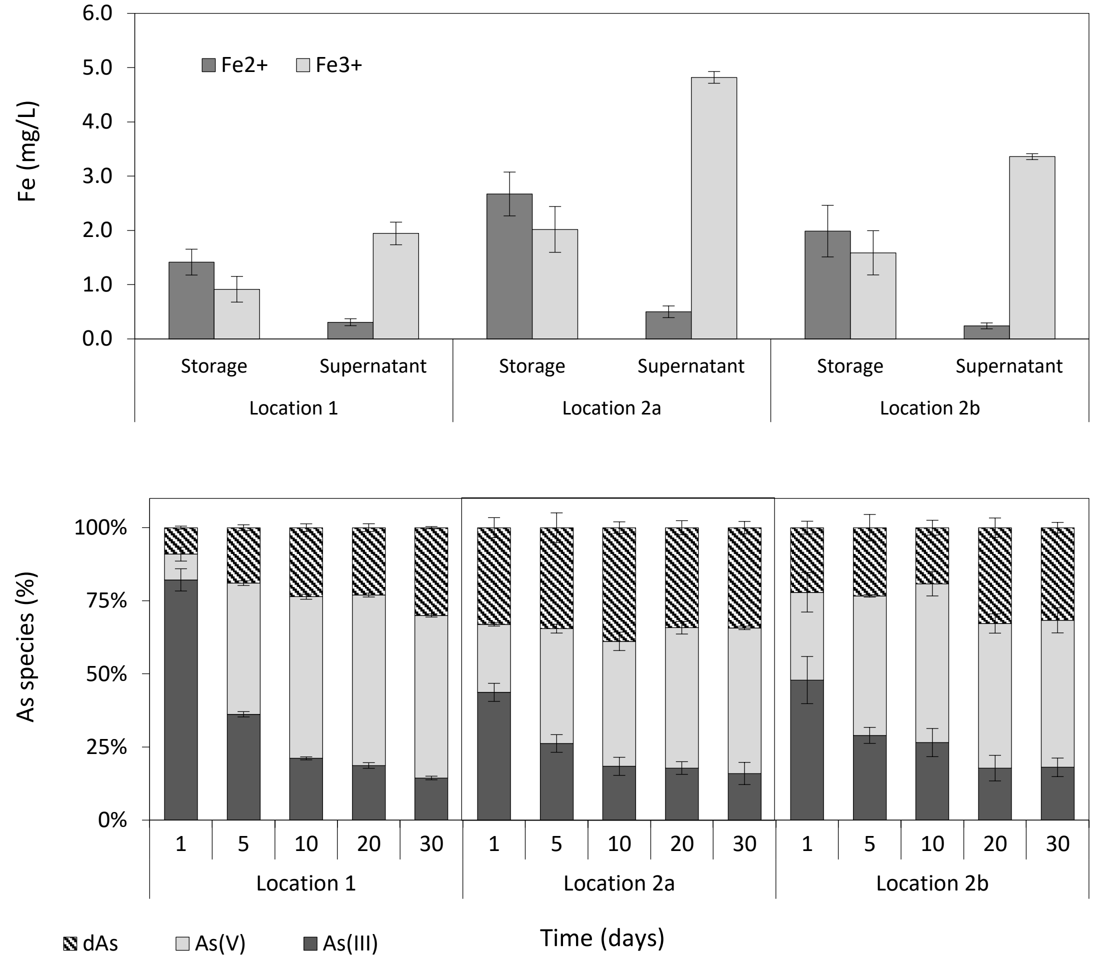
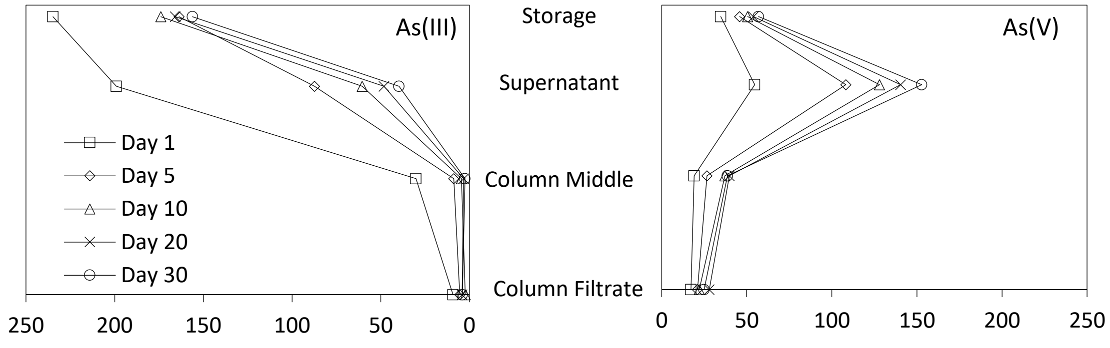


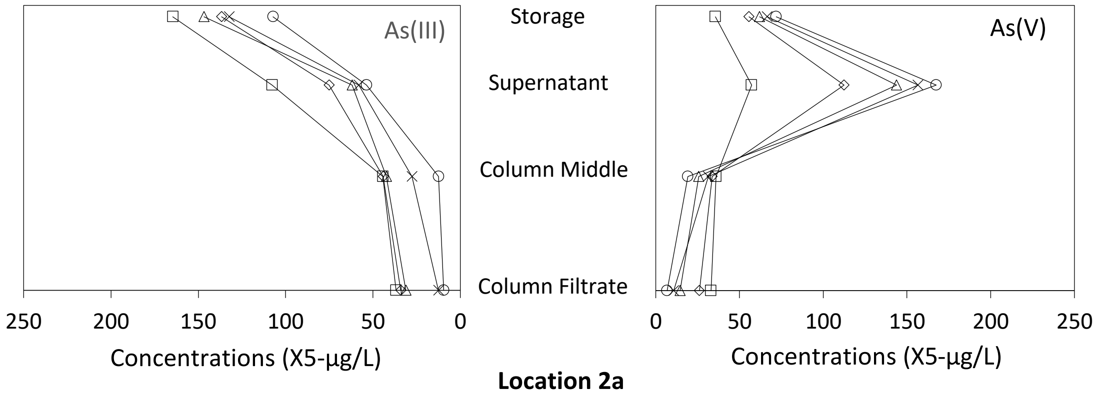
Fig. 5. The average (a) Fe^{2+} and Fe^{3+}; and (b) percentile As(III), As(V) and removed As in the supernatant (after aeration) before RSF. The error bar represents the standard deviation of the measurement.

5.3.4 Fe and As removal in the filter bed

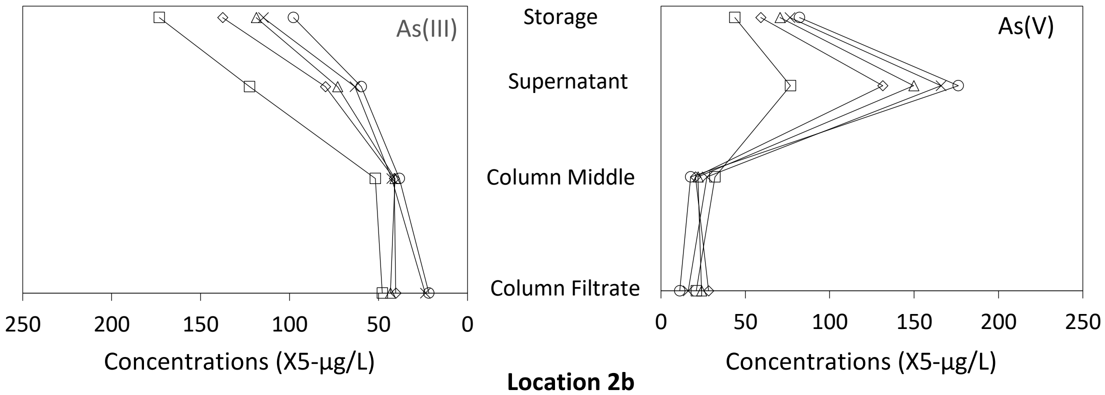
The dissolved concentration of As(III), and As(V) in the storage containers (as a reference), in the supernatant water, in the middle of the column (40 cm from the top of the filter bed), and in the filtrate are shown in **Fig. 6**. It can be observed that independent of the type of filter bed (dual/single-bed) and concentrations, the removal of Fe at all locations was fast and effective (>98% removal) within the top layer (of 40 cm) of the filter bed, with a p-value of less than 0.05. The groundwater Fe/As ratio at location 1 was 7.08 (mg/mg), and 108 (mg/mg) and 61 (mg/mg) for location 2a and 2b, respectively. The findings at location 1, with filtrate pH of 7.6(±0.1), are in agreement with Mercer and Tobiason (2008), who stated that for an As removal of over 90% at pH of 7.3, the required Fe/As ratio should be about 9 In addition, the As removal at location 1 is much higher than that for the conventional aeration before storage (oxic storage) followed by aeration-filtration, using groundwater with the same Fe/As ratio. Apart from HFO floc formation and filtration, the filter bed could also have acted as a bio-carrier for AsOB based As(III) oxidation (Gude et al., 2018b; Shafiquzzaman et al., 2008). The increase in As(V) concentration in the supernatant over time indicates possible microbial growth. The freshly, *in-situ* formed HFO flocs probably infiltrated deep into the filter bed stimulating As(V) adsorption, being more effective than conventional practices of oxic storage followed by aeration-filtration, where to pre-formed HFO flocs penetrate in the filter bed (Amstaetter et al., 2010; Hohmann et al., 2010; Wang et al., 2008).



Location 1



Location 2a



Location 2b

Fig. 6. The remaining concentration of A(III) and As(V) in the storage system; column supernatant, column middle and column filtrate of the sand filters at a depth of 90, 50 and 0 cm, respectively: on the x-axis As concentration (µg/L); on the y-axis sampling points of the filtration system.

5.3.5 Manganese and phosphate removal

The percentile total Mn and PO_4^{3-} removal over the treatment steps for the experimental period of 30 days is shown in **Fig. 7**. The groundwater Mn concentrations were 600, 382, and 288 µg/L at the locations 1, 2a, and 2b, respectively. After 30 days of operation for locations 1, 2a and 2b, the total Mn removal gradually increased to 21%, 33% and 38%, respectively (**Fig. 7a**). Previous studies have revealed that Mn removal in sand filtration systems require an extended period of operation (more than 60 days) for effective performance, as its removal depends on biological and surface-catalytic processes (Gude et al., 2018a, 2018b; Jeż-Walkowiak et al., 2014; Tobiason et al., 2016).

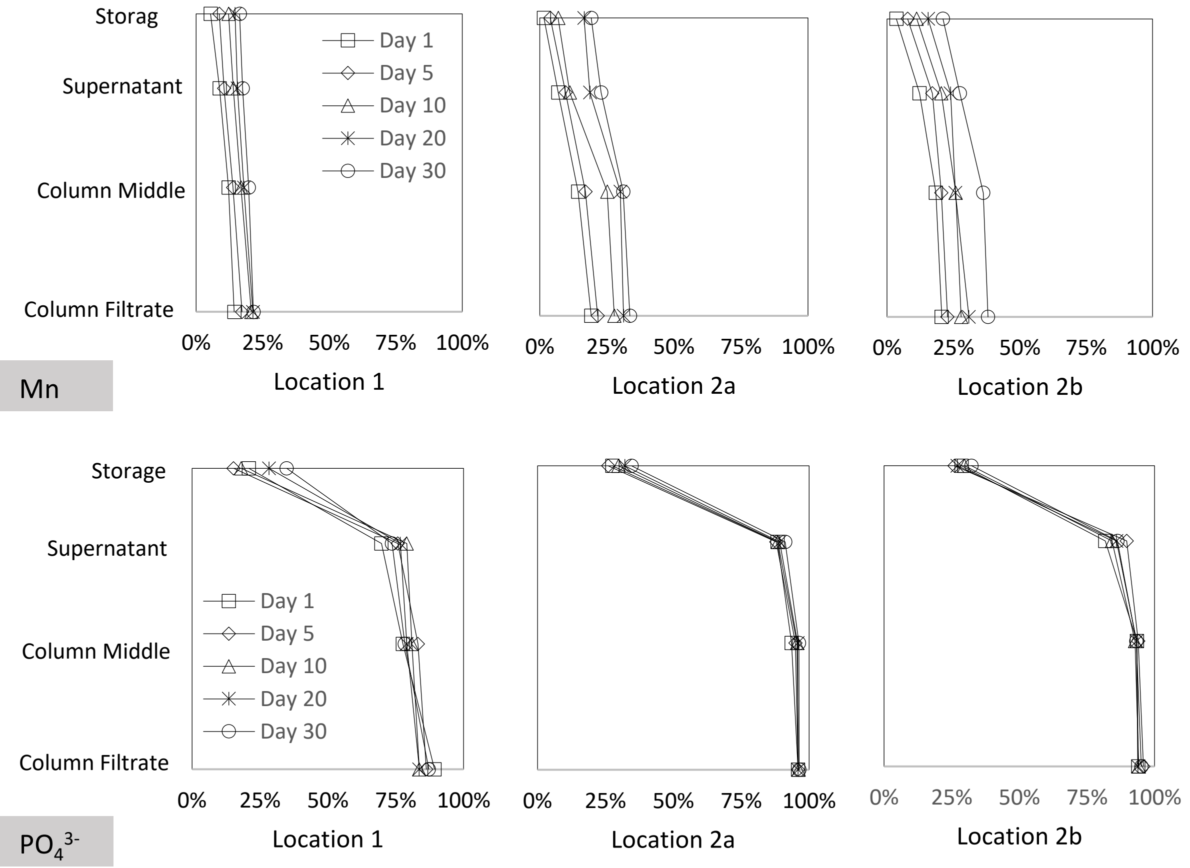


Fig. 7. The dissolved concentrations and removal of (a) Mn and (b) PO_4^{3-} at different treatment steps. The error bar represents the standard deviation of the measurements.

The groundwater PO_4^{3-} concentrations at locations 1, 2a, and 2b were 2.15, 3.96, and 2.69 mg/L, respectively, and decreased to 1.7, 2.9, and 1.9 mg/L (Fig. 6b), correspondingly, in the storage containers. The limited DO level in the storage containers only allowed for partial Fe^{2+} oxidation, which, thus, resulted a little PO_4^{3-} precipitation with Fe^{3+}. However, the PO_4^{3-} removal reached up to 83±7% in the supernatant after aeration, and removal of PO_4^{3-} continued inside the filter bed to reach effluent concentrations of less than 0.25 mg/L (94±2% removal) at all three locations (**Fig. 7b**). The removal of PO_4^{3-} in this filtration system can be explained by co-precipitation with HFO flocs (Guan et al., 2009; Voegelin et al., 2010), which is generated by rapid Fe^{2+} oxidation before column feeding.

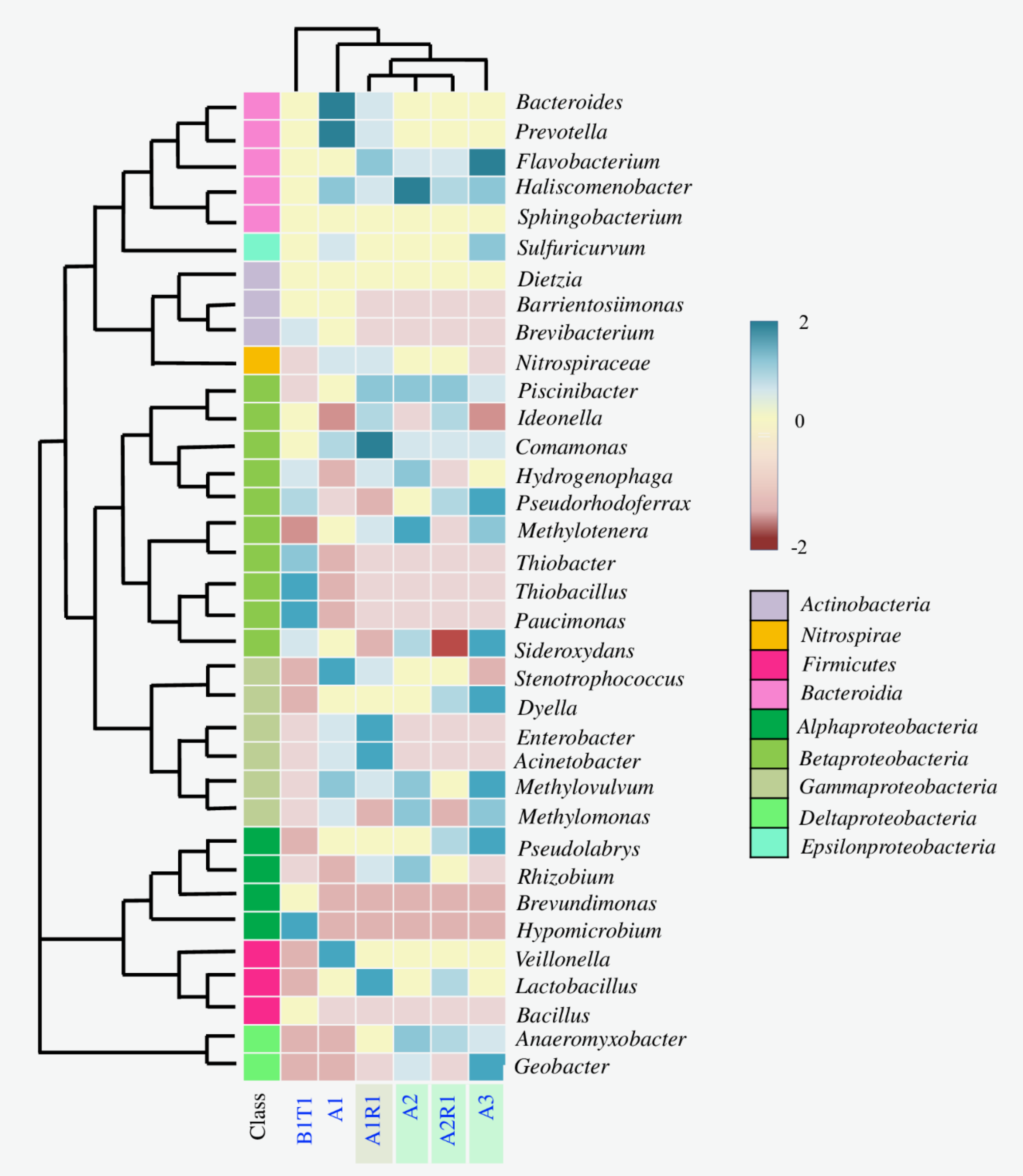


Fig. 8. The samples for generating the metagenomic libraries were clustered based on Weighted Unifrac distance in a UPGMA cluster tree. The predominant, common 35 bacterial genera were used to generate a taxonomic heat map and understand their distribution in different column setups, where the gradient indicates the distance between the raw score and the standard deviation mean. Samples from the column filter materials of location 1 location 2a are labelled in blue and green respectively.

5.3.6 Microbial communities in the filter bed

The eight metagenomic library datasets, generated from the sand samples collected from the anoxic columns at location 1 (column B1T1) and location 2a (column A1, A1R1, A2, A2R1, A3), were clustered and presented in **Fig. 8**. The clustering clearly indicates the branching out of the library B1T1, suggesting the contrast in microbial community diversity parameters of location 1 in comparison to Location 2a. The average number of operational taxonomic units (OTUs) in metagenomics libraries analysed for each of these samples was 1082 for B1T1 and were 587, 609, 630, 468, 607 for the libraries A1, A1R1, A2, A2R1, A3 respectively. The results suggest that the filter bed (detailed in **Table 1**) at location 1 had a higher microbial diversity compared to the less As contaminated water of location 2, indicating an effect of natural selection causing horizontal gene transferring on microbial communities (Ghosh et al., 2014).

In the anoxic columns from location 1, a relatively low abundance of Fe(II) and As(III) oxidizing microbial groups was observed compared to abundance in the upstream anoxic storage containers that have been reported previously (Annaduzzaman et al., 2021a). This could be due to the partial pre-oxidation of As(III), that resulted in accumulation of pre-oxidized As(V) in the storage containers of Location 1. This induced the growth of a microbial community in the filter column, which has a greater abundance of As(V) reducers than upstream (*Nitrosomonas, Sulfuritalea, Rhodoferrax*). However, probably, the remaining As(III) induced the growth of As oxidizers such as *Sideroxydans, Comamonas and Pseudorhoferrax* (Zavarzina et al., 2020), resulting in gradual reduction in As(III) in the supernatant (**Fig. 5**). These metabolic processes probably also supported the formation of Fe dependent biofilm formation by microbial groups such as *Pseudorhodoferrax, Patulibacter, Sphingobacterium, Tepidicella*. Some of the nitrate dependent Fe-oxidisers, such as *Brachybacterium, Rhodoferrax, Acidimicrobiales, CL500_29 marine*, also oxidize Mn. Moreover, an increased thiosulfate oxidation can be observed due to the abundance of the chemolithotrophic iron and the thiosulfate oxidizers *Thermithiobacillus, Paucimonas, Thiobacillus, Dyella, Acidibacillus,* which possibly lowered the pH during filtration (**Fig. 3**).

A contrasting picture was observed in the columns of location 2a (Fig. 9), where a predominance of methylotrophs like *Methylocystis, Candidatus_Nitrotoga, Methylotenera, Methylovulum, Methylomonas,* and *Longilinea* was observed. Thiosulfate oxidizers, observed in columns of location 1, were absent at location 2. Since, thiosulfate oxidation can inhibit methanogenesis, the absence of these groups resulted in the predominance of methanogenic bacterial communities (Oremland and Polcin, 1982). A low abundance of heterotrophic As(III)/Fe(II) oxidizers like *Sediminibacterim, Sideroxydans, Dyella, Pseurhodoferax, Hydrogenophaga, Methylovulum, Geobacter,* along with a low abundance of chemolithotrophic Fe-oxidizers like *Nitrosomonas, Pseudorhodoferrax, Rhodobacter,* *Sphingobacterium, Ideonella* was found. PiCRUST analysis suggested that metabolic processes could hamper flocculation of HFO in the column, compared to the columns studied from Location 1 (**Fig. 5**). The symbiosis between the Fe-oxidizers and Fe dependent biofilm forming microbial groups like *Pseudorhodoferrax, Commamons, Sphingobacterium, Tepidicella*, playing a vital role in subsequent Fe-flocculation. From the above, it can thus be concluded that growth of microbial groups with varying abundances supported As and Fe- oxidation, depending on the water composition.

5.4 Conclusion

This study aimed to examine the As removal capacity of anoxic storage followed by aeration and sand filtration considering varying groundwater composition. Furthermore, the interaction among Fe, As, PO_4^{3-} and Mn after aeration and in sand filtration were studied, considering low (40-60 µg/L) and high (>300 µg/L) concentrations of As and varying concentrations of Fe^{2+}, PO_4^{3-} and Mn. This novel treatment method was compared at three different locations, using groundwater in Rajshahi, Bangladesh, and using locally available materials and crafts without dosing chemicals. It was found that, independent of location, in-situ formed HFO flocs by delayed/step-wise Fe^{2+} oxidation contributed to high (>94%) As removal without compromising the removal of PO_4^{3-} and Mn. In addition, microbial communities assisted oxidation of As(III) and Fe^{2+}, while community dynamics depended on the water composition. Irrespective of the As concentrations in the groundwater composition, heterotrophic As(III) oxidizers, such as *Sediminibacterim, Sideroxydans, Dyella, Pseurhodoferax, Hydrogenophaga, Methylovulum, Geobacter,* were identified. Therefore, it can be concluded that the use of anoxic storage of groundwater could facilitate the delayed/step-wise Fe^{2+} oxidation through surface-related (heterogeneous) and/or biological processes, which would be beneficial for subsequent aeration-filtration steps for better As removal, which could be a cost-effective and chemical-free alternative for removing As(III) from contaminated groundwater, like in Bangladesh.

5.5 Acknowledgment

This study was supported by the Dutch Science Council, NWO-WOTRO Urbanising Deltas of the World. The authors acknowledge all research assistants from RUET, Rajshahi University, and staff from EPRC for their help and support during the pilot-scale studies in the remote areas of the Rajshahi district in Bangladesh. The authors also wish to thank landowners of three investigated locations for allowing work on their premises for the whole day over the entire experimental period; without their support, this study would not have been possible.

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Chapter 6

Conclusions and Recommendations

6.1 Overall conclusion

Passive groundwater treatment for iron, ammonium, and manganese removal consists of aeration followed by single or multiple filtration steps without using chemicals. However, this passive method is not appropriate for As removal, since its removal efficacy can vary between 15-90%, depending on groundwater composition. The commonly practiced aeration prior to storage facilitates rapid and complete Fe^{2+} oxidation before As(III) oxidation, which hampers the overall As removal efficacy. Consequently, the conventional processes require additional chemical oxidants/adsorbents to remove As. In this thesis, the use of anoxic storage of groundwater followed by aeration-filtration is described to achieve delayed/step-wise Fe^{2+} oxidation, which promote As(III) oxidation and subsequent removal of oxidized As(V) with freshly formed hydrous ferric oxide (HFO) flocs. This thesis included pilot-scale studies using natural groundwater (in Bangladesh) and locally available materials and crafts without external chemicals. The piloted natural groundwater contained low (40-60 µg/L) to high (>300 µg/L) levels of As and Fe^{2+} concentration of 2.33-5.5 mg/L. Furthermore, a laboratory investigation was performed to understand the effects of various contaminants (PO_4^{3-} and SiO_4^{2-}) on As removal during sequential Fe^{2+} oxidation. The results revealed that removals of up to 92% could be achieved without the dosing of (external) oxidants or chemicals. In addition, the results indicated that the removal of Fe, PO_4^{3-},NH_4^+, and Mn were not compromised. In the following more detailed conclusions on the processes during anoxic storage and filtration are given and the interaction between Fe, PO_4^{3-},NH_4^+, and Mn is discussed.

6.2 Anoxic storage to delay Fe^{2+} oxidation

The slow and partial Fe^{2+} oxidation in the anoxic storage containers resulted in a lower pH, dissolved oxygen (DO) concentration (semi-oxic), and oxidation-reduction potential (ORP), compared to the oxic storage containers. The trace amount of DO intrusion while, filling the storage container, led to partial Fe^{2+} oxidation on the first day of the experiment. However, its oxidation accelerated over the days of the experiment, which was likely associated with Fe^{3+} hydroxide accumulation that supported heterogeneous Fe^{2+} oxidation and/or biofilm-based Fe^{2+} oxidation. The identified chemolithotrophic Fe^{2+} oxidizing bacterial genera in both the oxic and the anoxic storage containers were *Sideroxydans, Comamonas, Pseudorhoferrax, Phingobacterium, Tepidicella, Brachybacterium, Rhodoferrax, CL500_29 marine, Geobacter,* and *Gallionella.* Biofilm growth might also have led to acidification and lowering of pH, which resulted in an increased positive surface charge of formed HFO flocs and enhanced negatively charged As(V) removal.

Arsenic removal was higher in the oxic storage containers than the anoxic storage containers. The aeration step before storage in the oxic system allowed for complete Fe^{2+} oxidation, whereas, in the anoxic system, Fe^{2+} partially oxidized to Fe^{3+} (HFO) flocs. This complete Fe^{2+} oxidation also assisted in increasing the As(V) concentration e.g. by Fenton-like reaction-based As(III) oxidation. The higher *in-situ* HFO flocs formation in the oxic storage then resulted in higher As(V) removal than in the anoxic storage. However, the As/Fe removal ratio was higher in the anoxic storage (80±5 µgAs/mgFe) compared to the oxic storage (45±5 µgAs/mgFe). The slow Fe^{2+} oxidation process in anoxic storage containers allowed for an extended interaction time of the As with formed HFO flocs and promoted As(III) oxidation and As(V) removal.

6.3 The value of filtration

The introduction of O_2 during aeration, after the anoxic storage and before the filter column, resulted in oxidation of the residual Fe^{2+} (±1.69 mg/L) and additional (120±10 µg/L) As(III) (**Chapter 2**). This observed As(III) oxidation after aeration is expected to be both abiotic (i.e., radicals formed during oxidation of residual Fe^{2+}) and biotic, since the maintained 15-20 cm supernatant water level was in contact with the filter bed's top layer, providing a possible carrier for bacteria to promote biological As(III) oxidation.

In the oxic system, also a considerable As(III) (55±5 µg/L) oxidation was observed after aeration in the supernatant **(Chapter 2)**. However, in this case, Fe^{2+} was not present anymore, making it likely that only biotic processes were responsible for As(III) oxidation. Indeed, it was observed that As oxidizing bacteria (AsOB) rapidly accumulated in the (oxic) storage container (**Chapter 2**) and the (sand) filter bed (**Chapter 5**). The abundance of *Sideroxydans, Comamonas, Pseudorhoferrax*, *Sediminibacterim, Sideroxydans, Dyella, Pseurhodoferax, and Hydrogenophaga,* showed that AsOB based As(III) oxidation was present in both filtration (bed) systems and in both systems, the residual As(III) was fully oxidized to As(V) in the top layer of the filter bed.

Arsenic removal was higher in the filter bed compared to the supernatant, which was probably due to the accumulation of freshly formed HFO flocs in the filtration bed, promoting adsorption of As. Iron removal was effective for both the oxic and anoxic systems, resulting in a 97% Fe removal in the top layer of the filter bed. The rapid HFO flocs removal in the top filter layer resulted in the low As removal in the bottom sand layer (3-4 µg/L) as a very small fraction of HFO flocs penetrate into the deep filter bed to remove more As. The filter bed, placed after the anoxic storage showed a higher As removal, because, firstly, the residual Fe^{2+} oxidation during aeration of the (anoxic) stored water supported the formation of *in-situ* HFO flocs, which are more effective in As removal than pre-formed HFO, and secondly, the lower pH (7.1) in the anoxic system, compared to the pH (7.5) in the oxic system, could have assisted in As removal by HFO. The lower pH in the anoxic system allowed for slow HFO flocs formation, and an increase in the positive surface charge of the HFO flocs and thereby enhancing As removal.

6.4 Overcoming the inhibitory effect of PO_4^{3-}

As concluded above, sequential iron (as Fe^{2+}) oxidation has yielded better As uptake than single-step Fe^{2+} oxidation. However, the source water composition can influence the As removal efficiency with HFO flocs, e.g. by the presence of PO_4^{3-} and SiO_4^{2-} (silicate). **Chapter 4** represents the results based on laboratory studies on step-wise/sequential Fe^{2+} oxidation towards more efficient As(III) oxidation and removal in the presence of PO_4^{3-} and SiO_4^{2-}. The results illustrated that As removal with precipitating HFO flocs, under the studied conditions, was indeed affected by the presence of groundwater native PO_4^{3-} and SiO_4^{2-}, because of the competition for HFO binding site. However, the sequential Fe^{2+} and As(III) oxidation in the multi-step jar tests indicated that the PO_4^{3-} hindrance on As removal in the first Fe^{2+} oxidation step (anoxic storage) was compensated for in the second step (aeration-filtration). Moreover, smaller Fe flocs (<0.45 µm) were observed in the presence of SiO_4^{2-} in the first step, potentially providing more surface area during the second step, leading to even a better overall As removal. Altogether, it may be concluded that controlling the As(III) and Fe^{2+} oxidation sequence was beneficial for As removal, compared to single-step Fe^{2+} oxidation, both in the presence and absence of PO_4^{3-} and SiO_4^{2-}.

6.5 Lessons learnt from application in Bangladesh

The novel concept for removing arsenic from groundwater by applying anoxic pre-storage was tested in Bangladesh with natural groundwater and was found to be effective without the addition of chemicals and/or adsorbents. As such, the concept can considerably impact arsenic mitigation in reducing aquifers worldwide, even with as low as Fe/As ratio of 10. A field prototype of a household sand filter system was tested in Bangladesh, based on the results from the pilot-scale studies, presented in the thesis. The filter was made using local materials, such as bamboo sticks, recyclable 5-liter (plastic) water bottles, 2 liter Coca-Cola bottles, sand, pipes, and connectors. In addition, local expertise and crafts were used to assemble the installation. The performance of the prototyped filters indicated its potential as a cheap and safe alternative for arsenic-safe drinking water production from contaminated groundwater. However, the optimization of the filtration system considering filtration velocity, the height of filter bed, filter materials, and grain sizes, in relation to variation of groundwater composition, remain to be studied. Moreover, although the combination of anoxic storage followed by aeration-filtration requires a low As/Fe ratio, still As-containing sludge is being produced, which needs to be disposed, and proper waste management should thus be provided.

Chapter 7

Summary

Groundwater arsenic (As) contamination is a severe drinking water quality problem and threatens human health in Bangladesh and other countries. Chronic exposure to As-contaminated drinking water has resulted in tens of millions of people suffering from skin lesions, hyperkeratosis, melanosis, skin cancer, and cancer of internal organs. The World Health Organization (WHO) recommends that As concentrations in drinking water should not be more than 10 µg/L. However, according to Bangladesh Drinking Water Standard (BDWS), the recommended value for As in drinking water is 50 µg/L. Nevertheless, groundwater in an extended area of Bangladesh contains As concentrations higher than those recommended values, and sometimes, it even exceeds 1500 µgAs/L. Various treatment technologies, including adsorption, chemical precipitation, ion exchange, membrane filtration, nanofiltration (NF), and reverse osmosis (RO) have been studied to remove As from water. However, these options are typically energy-intensive and/or consume chemicals that make the treatment methods expensive. In addition, commonly available treatment systems are complicated to operate and maintain, needing regular parts' replacement and aftermarket services, and skilled personnel who may not be locally available. Consequently, these technologies are not sustainable on the long run in vulnerable communities. Therefore, there is a need for simple, economic, and energy-efficient alternatives, utilizing locally available materials and crafts without the need for chemical dosing.

Passive groundwater treatment, consisting of aeration, followed by single or multiple filtration steps, is used for the removal of iron, ammonium, and manganese. However, this treatment method is not effective for As removal, as its removal efficiencies widely vary, between 15% to 95%, depending on the water composition. Co-removal of As with groundwater native-Fe is reported to be only possible if the As concentration is low (<50 µg/L), despite having a sufficiently high Fe to As ratio, mainly due to the As oxidation state, as As(III), in these aquifers. Equilibrium adsorption studies of As on Fe oxides show that, although both As(III) and As(V) have an affinity for Fe oxides, the removal capacity for As(V) by freshly forming Hydrous Ferric Oxides (HFO) is much higher than for As(III). Even though the production of reactive oxidation species during Fe^{2+} oxidation is known to cause As(III) oxidation, the overall removal of these reduced As species is limited during aeration-filtration. Moreover, as formerly observed, the rise in pH during aeration (i.e., flushing out of CO_2) increases the negative surface charge on HFO flocs and decreases As removal potential. Therefore, in this thesis, it was hypothesized that the step-wise/delayed oxidation of groundwater native-Fe^{2+} by introducing anoxic (pre-)storage could

promote As(III) oxidation and removal of As(V) to meet the WHO and regional standards. This thesis included pilot-scale studies using natural groundwater (in Bangladesh) and locally available materials and crafts without dosing chemicals. The piloted natural groundwater contained low (40-60 µg/L) to high (>300 µg/L) concentrations of As and Fe^{2+} concentration of 2.33-5.5 mg/L. Furthermore, a laboratory study was performed to understand the effect of PO_4^{3-} and SiO_4^{2-} on As removal during sequential Fe^{2+} oxidation.

Oxic and anoxic storage container experiments (**Chapter 2)** indicated that applying anoxic storage could enhance As removal from groundwater. Although the oxidation of Fe^{2+} and As(III) during oxic storage was considerably faster, the As/Fe removal ratio was higher during anoxic storage (80±5 µgAs/mgFe) compared to the oxic storage (45±5 µgAs/mgFe). This higher As removal efficacy could not be attributed to the speciation of As, since As(V) concentrations were higher during oxic storage, due to more favorable abiotic (As(III) oxidation by O_2 and Fenton-like intermediates) and biotic (As(III) oxidizing bacteria, e.g., S*ideroxydans, Gallionella, Hydrogenophaga*) conditions. Bio-carriers containing storage containers (oxic and anoxic) enhanced As oxidation and removal by ±20% compared to storage containers without bio-carriers. Experiments conducted in a pilot treatment system, including anoxic storage followed by aeration-(sand) filtration (**Chapter 3**), revealed that the obtained step-wise Fe^{2+} oxidation, as well as the favorable lower pH (6.9) with anoxic pre-storage, enhanced As removal to 92%, compared to only 61% in the conventional oxic system. It is suggested that this was due to the formation of fresh HFO flocs during step-wise oxidation in the anoxic system that removed more As than the pre-formed HFO flocs in the oxic system (**Chapter 5**). Moreover, Fe^{2+} oxidation did not compromise the removal of other groundwater contaminants like Mn, NH_4^+ and PO_4^{3-}. In addition, this study demonstrated that with anoxic storage, passive treatment is an effective barrier against As(III) with Fe/As ratios much lower (<10 mg/mg) than previously determined (>40 mg/mg). Furthermore, sequential/step-wise Fe^{2+} and As(III) oxidation experimental studies (**Chapter 4**) indicated that the PO_4^{3-} hindrance on As removal in the first Fe^{2+} oxidation step was compensated for in the second. Moreover, smaller Fe flocs (<0.45 µm) were observed in the presence of SiO_4^{2-}, potentially providing more surface area during the second Fe^{2+} oxidation step leading to better overall As removal with Fe/As ratios as low as 10-15 (mg/mg), either in the presence/ absence of PO_4^{3-} and SiO_4^{2-}.

The overall conclusion from the thesis, therefore, is that anoxic storage combined with aeration and sand filtration could be a cost-effective and chemical-free alternative for removing As from groundwater under field-relevant conditions and can be considered for large scale application to provide As-safe drinking water in affected communities (e.g., Bangladesh).

Chapter 8

Samenvatting

Grondwaterverontreiniging door arseen (As) is een ernstig drinkwaterkwaliteitsprobleem dat de gezondheid bedreigt van mensen in Bangladesh en andere landen. Door chronische blootstelling aan As verontreinigd drinkwater hebben tientallen miljoenen mensen last van huidproblemen, hyperkeratose, melanomen, huidkanker en kanker van de inwendige organen. De Wereldgezondheidsorganisatie (WHO) adviseert een maximale As-concentratie in drinkwater van 10 µg/L, de Bangladesh drinkwaterstandaard (BDWS) adviseert een bovengrens van 50 µg/L As. Welke standaard je ook volgt, het grondwater in een groot deel van Bangladesh bevat As-concentraties hoger dan deze advieswaarden, soms zelfs hoger dan 1500 µg As/L. Er is onderzoek gedaan naar verschillende waterzuiveringstechnologieën om As uit water te verwijderen, onder andere naar adsorptie, chemische precipitatie, ionenuitwisseling, membraanfiltratie, nanofiltratie (NF) en omgekeerde osmose (RO). Een nadeel van deze opties is dat zij energie-intensief zijn en/of afhankelijk zijn van chemicaliën die deze zuiveringsmethoden duur maken. Bovendien zijn algemeen verkrijgbare zuiveringssystemen ingewikkeld om te gebruiken en te onderhouden, en vereisen ze regelmatige vervanging van onderdelen, ondersteunende diensten en bekwaam personeel dat mogelijk niet lokaal beschikbaar is. Dientengevolge zijn deze technologieën in kwetsbare gemeenschappen geen duurzame oplossing. Er is behoefte aan eenvoudige, betaalbare en energiezuinige alternatieven, waarbij gebruik wordt gemaakt van lokaal beschikbare materialen en vakmanschap en zonder gebruik van chemicaliën. Voor de verwijdering van ijzer, ammonium en mangaan wordt een passieve grondwaterbehandeling toegepast. Na beluchting volgen enkele of meerdere filtratiestappen. Deze behandelingsmethode is echter niet effectief voor het verwijderen van As. De verwijderingsefficiëntie van As varieert, afhankelijk van de samenstelling van het drinkwater, van 15% en 95%. Het gelijktijdig verwijderen van As met natuurlijk in grondwater aanwezig ijzer (Fe) is, voor zover bekend, alleen mogelijk bij een lage As-concentratie (<50 µg/L), zelfs met een voldoende hoge Fe/As-verhouding. Dit is voornamelijk vanwege de As-oxidatievorm in de watervoerende lagen; As (III). Studies naar evenwichtsadsorptie van As en Fe-oxiden wijzen uit dat zowel As(III) als As(V) een affiniteit hebben voor Fe-oxiden, maar dat de verwijderingscapaciteit voor As(V) door het vers vormen van waterhoudende Fe-oxiden (HFO) veel hoger is dan voor As(III). Hoewel bekend is dat de productie van reactieve oxidatievormen tijdens Fe^{2+}-oxidatie As(III)-oxidatie als gevolg heeft, is de algehele verwijdering van deze gereduceerde As-vormen beperkt tijdens beluchting-filtratie.

Bovendien is in eerder onderzoek waargenomen dat de stijging van de pH tijdens beluchting (dat wil zeggen: het wegspoelen van CO_2) zorgt voor een verhoogde negatieve oppervlaktelading op HFO-vlokken en voor een vermindering van het verwijderingspotentieel van As. De hypothese die daarom in dit proefschrift onderzocht wordt is dat de stapsgewijze/vertraagde oxidatie van natuurlijk Fe^{2+} uit grondwater door het introduceren van zuurstofarme (voor-)opslag de As(III)-oxidatie en verwijdering van As(V) zodanig kan bevorderen dat de As concentratie voldoet aan de WHO en regionale adviesnormen. Dit proefschrift omvat pilotstudies waarbij gebruikt is gemaakt van natuurlijk grondwater (in Bangladesh) en lokaal beschikbare materialen en vakmanschap en zonder gebruik te maken van chemicaliën. Het gebruikte natuurlijke grondwater bevatte lage (40-60 µg/L) tot hoge (>300 µg/L) concentraties As en Fe^{2+} concentraties van 2,33-5,5 mg/L. Daarnaast is er laboratoriumonderzoek uitgevoerd om het effect van PO_4^{3-} en SiO_4^{2-} op As-verwijdering tijdens opeenvolgende Fe^{2+}-oxidatie beter te begrijpen.

Experimenten met drinkwateropslag in containers met en zonder zuurstof (hoofdstuk 2) maakten duidelijk dat het toepassen van zuurstofarme opslag de verwijdering van As uit grondwater zou kunnen verbeteren. Hoewel de oxidatie van Fe^{2+} en As(III) in de zuurstofrijke opslagcontainer aanzienlijk sneller was, was de As/Fe-verwijderingsverhouding hoger in de zuurstofarme opslagcontainer (80±5 µgAs/mgFe) dan in de zuurstofarme opslagcontainer (45±5 µgAs/mgFe). Deze hogere As-verwijderingsefficiëntie kon niet worden toegeschreven aan de vorming van nieuwe vormen van As, aangezien As(V)-concentraties hoger waren in de zuurstofrijke opslagcontainer, als gevolg van gunstigere abiotische (As(III)-oxidatie door O_2 en Fenton-achtige tussenproducten) en biotische (As (III) oxiderende bacteriën, bijv. *Sideroxydans, Gallionella, Hydrogenophaga*) omstandigheden. Bio-carriers in opslagcontainers (zowel zuurstofrijk als zuurstofarm) verbeterde de As-oxidatie en verwijdering met ±20% in vergelijking met opslagcontainers zonder bio-carriers. Experimenten uitgevoerd in een testsysteem met zuurstofarme opslag gevolgd door beluchting-(zand)filtratie (Hoofdstuk 3), toonden aan dat de verkregen stapsgewijze Fe^{2+} oxidatie en ook de gunstige lagere pH (6,9) in de zuurstofarme vooropslag, de As-verwijdering verhoogde tot 92%, een verbetering ten opzichte van de 61% in het conventionele zuurstofrijke systeem. Dit kan veroorzaakt worden door de vorming van verse HFO-vlokken tijdens stapsgewijze oxidatie in het zuurstofarme systeem die meer As verwijderden dan de voorgevormde HFO-vlokken in het zuurstofrijke systeem (hoofdstuk 5). De oxidatie van Fe^{2+} bracht verder de verwijdering van andere grondwaterverontreinigingen, zoals Mn, NH_4^+ en PO_4^{3-}, niet in gevaar. Deze studie toonde verder aan dat passieve behandeling met zuurstofarme opslag een effectieve barrière vormt tegen As(III), met Fe/As-verhoudingen die veel lager zijn (<10 mg/mg) dan eerder bepaald (>40 mg/mg). Verder geven experimentele studies waarbij gebruik werd gemaakt van opeenvolgende/stapsgewijze Fe^{2+} en As(III) oxidatie (Hoofdstuk 4) aan dat de belemmerende werking van PO_4^{3-} op As verwijdering in de eerste Fe^{2+} oxidatiestap gecompenseerd wordt in de tweede. Ook werden kleinere Fe-vlokken (<0,45 m) waargenomen bij aanwezigheid van SiO_4^{2-}, wat mogelijk meer oppervlakte oplevert tijdens de tweede Fe^{2+}-oxidatiestap. Dit leidt weer tot een betere algehele As-verwijdering met Fe/As-verhoudingen van slechts 10-15 (mg/ mg), hetzij in aanwezigheid/afwezigheid van PO_4^{3-} en SiO_4^{2-}. De algemene conclusie van het proefschrift is daarom dat zuurstofarme opslag in combinatie met beluchting en zandfiltratie een kosteneffectief en chemicaliënvrij alternatief zou kunnen zijn voor het verwijderen van As uit grondwater onder relevante omstandigheden in het veld en dat deze methode kan worden overwogen voor grootschalige toepassing om gemeenschappen getroffen door As-verontreiniging van As-veilig drinkwater te voorzien (bijv. Bangladesh).

Chapter 9

Acknowledgments

I am grateful to Almighty Allah for giving me the opportunity to pursue my PhD degree. With His blessings, I was able to complete this PhD thesis, which was, at times, quite challenging.

I am thankful to many people for their support and contribution during my PhD candidateship in my works at the field, laboratory, and office.

First and foremost, I would like to express my heartfelt gratitude to my supervisor and promotor, Associate Prof. Dr. Ir. Doris van Halem, for this PhD research opportunity and allowing me to join your esteemed research group. Your tremendous support from the very beginning to the very last moment of this research timeframe played a vital role in this success story. I feel extremely fortunate to have had the chance to work under your excellent leadership and learn from your abundant scientific and project-management knowledge.

I also want to express my sincerest gratitude to my other promotor, Prof. Dr. Ir. Luuk Rietveld for being beside me along this journey. I am thankful for your continuous encouragement and valuable input on the experiment, the guidelines that you provided, and your critical review of this thesis.

Furthermore, I also want to thank my supervisor Prof. Dr. Eng. Bilqis Amin Hoque, Environmental Population and Research Centre (EPRC) in Dhaka, Bangladesh. Without your local support and connections with Department of Public Health Engineering (DPHE), Government of Bangladesh, NGOs and other relevant organizations, the conducted field work would have been difficult. I am thankful to Dr. Sufia Khanam, Jahid Shipon, Sohel Rana, and Samiul Hoque from EPRC for their support and assistance during my stay in Bangladesh and field studies.

I would also like to thank Prof. Dr. Ashok Ghosh and his research group for their contributions during my one-month intensive field studies in Bihar, India. Furthermore, I want to acknowledge and thank Prof. Dr. Md Niamul Bari from Rajshahi University of Engineering and Technology (RUET), Prof. Dr. Khaled Hossain from Rajshahi University, and Ex. Engr. Rokonujjaman from Department of Public Health Engineering (DPHE), Bangladesh for your logistical and research contributions during my field studies in Rajshahi, Bangladesh. Your local support during the pilot scale column studies and biological investigation contributed expressly to this research and its applicability in arsenic mitigation.

Annemarie Mink, if I don’t mention your name, this section will remain incomplete. Working with you was a joy throughout my PhD journey. You were not only a hard-working colleague, but a dear friend who always looked out for the team. It has been an honour to work alongside you in our research in the field of safe drinking water and its accessibility to all. Thank you for everything you did to make my PhD candidateship at TU Delft so memorable.

Also, I want to extend my deepest gratitude to my TU Delft friends- Jink Gude, Bayardo, Risalat, Adiba, Daniel, Mrinal, Shreya, Devanita, Marijet, Santosh, David de Rider, Nan, Sofie Mona, Erik and many others who made my days at TU Delft some of the most enjoyable ones in my life. I would also like to acknowledge the Delft Bangladeshi Student Community who made sure we had enough get-togethers to keep my homesickness at bay.

I am grateful to the Integrated Programme of WOTRO Science for Global Development of the Netherlands Organization for Scientific Research (NWO) for funding my PhD research in TU Delft, the Netherlands.

I would like to express my gratitude to all the committee members of my PhD thesis: Dr. Ir. J.C.J. Gude, Prof. Dr. R. Hofmann, Prof. Dr. Ir. J.P. van der Hoek, Prof. Dr. K.M.U. Ahmed, Prof. Dr. Ir. M.K. de Kreuk and Prof. Dr Bilqis Amin Hoque for their significant scientific inputs in my research.

I want to thank the Sanitary Engineering Section, Department of Water Management, Faculty of Civil Engineering and Geosciences, Delft University of Technology, the Netherlands for hosting me during my PhD research period. I would like to express my gratitude to Mariska van der Zee for your positive spirit and conducting exhaustive administrative paperwork during my tenure.

I would like to express my sincerest gratitude to my current managers, Nicholas Doucette, and Trevor Hille, from QM Environmental for accommodating my needs to complete the PhD thesis. Without Nick and Trevor’s logistical support, it would be more than stressful to complete the thesis from all the way here in Toronto, Canada.

I would like to express my immense love and gratitude to my beloved parents, parents-in-law, my loving sisters and sisters-in-law, brothers, my extended family, and friends for their endless love, inspiration, and motivation. I would like to convey my special gratitude to my brother Engr. Md Yousuf Ali, who inspires me to work sincerely, honestly, and most importantly- selflessly every day. He is not only my brother, but he is also my mentor and my guardian, who urges me to keep aiming for the stars. It was he who urged me to continue with post-grad studies. I wish you could be here with me at my Graduation ceremony.

Most importantly, to my wife Dil Afroz Rosa, thank you from the bottom of my heart for making so many sacrifices for me. During this PhD journey, we had to maintain a long-distance relationship for a long period of time, which was immensely tough. It would not have been possible for me to complete my PhD without your endless love, unconditional support, patience, and prayers. You proved the proverb right that I now so strongly believe in- *“Behind Every Successful Man Is a Strong Woman.”* Thank you for being with me through all the ups and downs.

Chapter 10

Curriculum vitae

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CAREER STATEMENT

After completing my BSc in Civil Engineering in 2009, I was admitted for my MSc in Environmental Engineering and Sustainable Infrastructure at the Department of Land and Water Resources Engineering, KTH Royal Institute of Technology, Sweden. During my MSc thesis, I examined and validated the 'Effectiveness of tubewell platform color as screening tool for arsenic and manganese in drinking water wells in a research project entitled "Sustainable Arsenic Mitigation (SASMIT). In 2012, I received the European Union's FP7 Fellowship for my Licentiate of Engineering (LiE) study KTH International Groundwater Arsenic Research Group. During my LiE study, I investigated the '*Chitosan biopolymer as an adsorbent for drinking water treatment-Investigation on arsenic, uranium, and thorium*.' Currently, I am at finishing my PhD degree from the T.U. Delft Global Drinking Water research group at the Delft University of Technology, the Netherlands, led by Dr. Ir. Doris van Halem, in November 2021. I moved to Toronto with a permanent residence (P.R.) in Canada in December 2020 and remotely worked on PhD dissertation writing. My research focuses on '*Bio-based groundwater filter - arsenic removal using groundwater native-iron*.'

My academic research career covered surface water, groundwater, aquifer sediment sampling, trace/heavy elements screening, and mitigations. In addition to these, the extensive investigations, analysis, and uses of different laboratory, pilot-scale, and large-scale field applications have helped me to develop insight into water/soil chemistry and develop low-cost drinking water treatment methods using locally available resources in the water-scarce region. Furthermore, I have also developed working skills on numerous modeling tools, such as Geochemical Modeling (e.g., speciation modeling, surface complexation modeling) by Visual MINTEQ and PHREEQC. Therefore, my foundations for further research are not only limited to surface water and groundwater chemistry, remediation, water quality, treatment, and supply, but also data collection and analysis, (waste)water/contaminated site management, and time-based R&D projects executions. Furthermore, understanding the environmental fate and transport mechanisms that govern the behaviour of contaminants in the freshwater environment.

I look forward to continuing my career in academia to implement and develop my experience in Environment/water technologies towards viable socio-economic management methods. I value strong work ethics and honour accountability. I have been a dedicated student supervisor, and as an extrovert, I enjoy conducting and organizing research workshops and discussion forums.

PROFILE AND KEY ACCOMPLISHMENTS

- Member for IWA, IWA-YWP Canada (PD), PEO, OWWA, AWWA, OSPE, ISGSD, CAWQ, TUD-Water for Impact
- Environmental/water Engineer with 10+ years' international (Europe and Asia) experience in consulting – water quality and quantity control, remediation, process design, and application
- PhD and two advanced level degrees (M.Sc. and Lic) in Environmental Science and Engineering focused on sediment and groundwater chemistry, water treatment, quality, supply, and management
- Developed cost-free arsenic and manganese screening tool based on (tube)well platform color

- Conceptualized and Implemented Do-It-Yourself (DIY) laboratory for developing household water treatment and safe water storage systems in rural communities
- Completed 15+ soil, wastewater, and drinking water projects feasibility and environmental evaluation
- Expert in water quality, pipeline design, cost estimation, scheduling, material requisitions, and quotations
- 20+ technical reports, manuals, and journal and conference articles publications and presentations
- P. Eng. in Ontario is under review, Holding driving license 'G' with a good driving record
- Hands-on solid experience in multidisciplinary project management, collaboration, and coordination with NGOs, stakeholders, and Governments policymakers
- Proficient in MS Office, Suite, and Projects, data analysis, interpretation, modeling, and planning programs
- Experienced in teaching and BSc and master's project (thesis) supervision
- Organized, technically skilled, detailed and solution-oriented, problem-solving, and ethical

EDUCATION

Doctor of Philosophy in Water Management (Treatment) 12 July 2022
Water Management Department, Delft University of Technology, the Netherlands
Thesis: Enhancing arsenic removal from Bangladesh groundwater by controlled iron oxidation in filters
Advisors: Dr. Ir. Doris van Halem and Prof. Dr. Ir. Luuk C. Rietveld

Licentiate of Engineering in Land and Water Resource Engineering 2015
Department of Sustainable Development, Environmental Science and Engineering, KTH Royal Institute of Technology, Sweden
Advisors: Prof. Dr. Prosun Bhattacharya and Prof. Dr. Mustafa Ersoz

Master of Science in Environmental Engineering and Sustainable Infrastructure 2012
Department of Sustainable Development, Environmental Science and Engineering, KTH Royal Institute of Technology, Sweden
Supervisor: Prof. Dr. Prosun Bhattacharya and Prof. Kazi Matin Ahmed

Bachelor of Science in Civil Engineering 2009
Department of Civil Engineering, Rajshahi University of Engineering & Technology, BGD

PROFESSIONAL EXPERIENCES AND ACHIEVEMENTS

Water Treatment Technician, QM Environmental, Toronto, ON, Canada 12/2021–Present

- Performed assessments, design, drawing, cost estimations, specifications, contract documents, bids, and proposals writing for water treatment based on client's specifications
- Managed Municipal projects (water) including scope, schedule, and budget and client relationships
- Monitored pre- and post-treated water quality and performance of the treatment system
- Supervised and mentoring junior engineers, technologists, and designers on field and office work
- Performed feasibility studies, preliminary and detailed designs of water infrastructure projects including bulk water pipelines, reservoirs, water treatment plants and distribution networks
- Supervised the production of irrigation systems design, drawings, materials acquisitions, cost evaluations, infield system installation and application
- Performed field environmental health and safety by monitoring air quality (VOCs) and spill management
- Maintained surface water management including drainage system dewatering to support excavation
- Performed water quality monitoring before and after pre-treatment ponds and feeding to plant
- Developed to daily operational, project plans, and participate in deliverable level planning with PM
- Project site control, including preparation of safe zones, lay down areas, stockpile areas, hot zones of PortLands Flood protection projects
- Coordinated the physical activities of employees, subcontractors, and suppliers for all site activities

- Assured all site resource (labor, machinery, materials, sub-contractors' etc.) are effectively utilized and monitored to achieve timely completion of projects
- Supervised, administered, and managed construction works with emphasis on scope, time, cost, risk, resources, and quality management

Project Coordinator, Mobilinx, Hurontario LRT project, Mississauga, ON, Canada 09/2021–12/2021

- Designed and applied water distribution network along the Hurontario street for LRT 'Mega' project
- Supervised field and administrative work, including project management information and documentation
- Tracked Project progress using Procore Project Management and SitePhotos program
- Tracking and reporting of production quantities and equipment utilization, cost, schedule, and milestones
- Coordinated and managed onsite utilities, including material delivery and quality control
- Led the Safety and Quality control by adhering to and promoting plans, policies, and procedures
- Maintained strong relationships with clients, engineers, and stakeholders for business development

Senior Research Engineer, Luleå University of Technology, Sweden 01/2016 – 05/2016

- Processed and analyzed laboratory-based research data
- Planned, designed, and implemented different work packages and applications in field and laboratory
- Disseminated among different partners, field team, research group, and stakeholders
- Assessed and applied different methods for arsenic-contaminated soil/site remediation and management
- Communicated and maintained a relationship with various industrial and academic research partners

Environmental Specialist, EPRC, Bangladesh 06/2015–12/2016

- Monitored water project specification and construction quality by ensuring work and health safety
- Applied pre and post constructions site assessment to improve service and product quality
- Developed and applied the WASH model to minimize water-borne diseases in flood-prone areas
- Demonstrated outstanding interpersonal skills by effective communication and proactive response Provided optimization alternatives for water usage and supply under project budget and schedule
- Adjusted and coordinated with changing office and management system to improve services

Environmental Engineer, KTH Royal Institute of Technology, Sweden 12/2012–05/2015

- Developed sediment color-based arsenic and manganese safe water well installation in polluted sites
- Invented tubewell platform color-based arsenic and manganese screening tool in affected areas
- Recognized as a skilled trainer for field and laboratory soil and water samples collection and analysis
- Performed 400+ borehole drillings, well installations, sediment, and water sampling, storage, and analysis
- Managed Engineers, investigators in the field, laboratory, and in-office system design and application
- Developed and applied manual and troubleshooting of laboratory and field analysis equipment

Structural Engineer, Magnum Engineering and Construction Limited, Bangladesh 06/2009–08/2010

- Prepared AutoCAD drawings and drafts according to construction specifications and project schedules
- Coordinated and supervised over six construction projects of water infrastructure and residential building
- Tested structural planning, design, analysis, calculations, constructions, evaluation, and reporting
- Managed contracts and payment claims; supervised task forces of trainees, Engineers, field officers
- Designed cost-effective methodologies for further maintenance and resource management
- Performed data and hazard analysis, quality monitoring, modeling, and risk assessment
- Worked extensively with individuals and maintained good relations with partners and stakeholders

SCHOLARSHIPS AND AWARDS

NWO WOTRO Ph.D. Fellowship, TU DELFT, Netherlands (€ 25,000/year)	2018-2020
Lamminga Foundation Research Grants, TU DELFT, Netherlands (€ 5,000)	2016
CITG Dean's Research grants, TU DELFT, Netherlands (€ 11,000)	2017
FORMAS Research Fellowship, LTU, Sweden (SEK 150,000),	2016
EU-FP7-SME Research Fellowship, KTH, Sweden (SEK 0.7 M)	2012-2015
Linnaeus Palme Awards, KTH, Sweden (SEK 50,000)	2010-2012
Vice-chancellors Awards, RUET, Bangladesh	2005-2009

TRAINING AND DEVELOPMENTS

Engineering Connections, Toronto, Canada *ACCES Employment Services/ Humber College Institute of Technology & Advanced Learning- Introduction to Canadian Engineering Codes and Standards, Ethics, Project Management, and Workplace Communications*	2021
Worker Health and Safety Awareness in 4 Steps, MoL, Training & Skills Development	2021
Workplace Hazardous Materials Information System (WHMIS 2015)	2021
The Employee's Guide to Sustainability, LinkedIn Learning	2021
Community-enabled Lifecycle Analysis of Stormwater Infrastructure Costs (CLASIC), US-EPA	2021
Watershed Management Optimization Support Tool (WMOST), US-EPA	2021
Enhanced Aquifer Recharge: Influence of Stormwater on Groundwater Quality, US-EPA	2021
Professional Diploma in Project Management & Leadership, Shaw Academy	2020
Thermo-Scientific Microanalysis Education Workshop, The Netherlands	2014

LABORATORY AND COMPUTER SKILLS

- ICAP-6300; ICP-MS, FT-IR Spectrometry, SEM, UV-Vis spectroscopy, TGA/DTA, X-Ray Diffraction Spectroscopy, Fluorescence and ESR
- IBM SPSS Statistics-20, Microsoft Office, Auto-CAD, ArcGIS, Visual Minteq, Phreeqc, PhreePlot, BioWin

VOLUNTEER EXPERIENCE

Programming Director (elected for two years), IWA-YWP Canada Executive board	2021 - present
Coordinator, IWA-YWP Canada Waterside Chat Webinar	2020 - present
Coordinator, T.U. Delft | Global Drinking Water Group	2018 - present
Lead organizer, yearly Water and Health Workshop, T.U. Delft, Netherlands	2017 – 2019

TEACHING AND MENTORING

Course offered:

- Water and Health (MSc course), Delft University of Technology, Netherlands
- Water Treatment Research (MSc course), Delft University of Technology, Netherlands
- Fundamental to water Treatment (BSc/MSc), Delft University of Technology, Netherlands
- Management of Land and Water (MSc), KTH Royal Institute of Technology, Sweden
- Environmental Impact Assessment (MSc), KTH Royal Institute of Technology, Sweden

Student Projects Supervision:

1. ***Multi-disciplinary project:***

   Project Bangla – Safe water for Bangladesh. Water Management Department, T.U. Delft, NL.

   This project work included students from different backgrounds to integrate and apply the multi-disciplinary knowledge to develop sustainable solutions towards the existing problem in developing nations by co-creation.

   The study aimed to analyze the relationship between arsenic contamination and the local geology, monitor the drinking water quality using mobile applications, and design and construct a water treatment unit. An essential aspect of this research was to develop a monitoring and maintenance protocol to ensure a safe water supply in the future.

2. ***Masters project in Water treatment research:***
   The Influence of Silicate and Phosphate on Arsenic Removal With Iron (HFO) Flocs. Water Management Department, T.U. Delft, NL.
   This project work included three groups of students (5 per group) from the water treatment research course to investigate the effect of silicate and phosphate on arsenic removal during stepwise Fe^{2+} oxidation on laboratory scale jar tests.
3. ***BSc Thesis:***

- **M. H. Helsdingen and A. A. Karlicic (2017)**: Iron-based Arsenic Removal in Bangladesh - A way towards safe drinking water in rural Bangladesh. Water Management Department, T.U. Delft, NL.
- **T. Ahmed and R. Ahmed (2018):** Native iron-based arsenic and manganese removal in rapid sand filters. Dept. Of Civil Engineering, Rajshahi University of Engineering and Technology, Bangladesh.
- **E. Kraaijeveld (2018).** Effect of Phosphate on Arsenic removal - Production of safe drinking water in Bangladesh. Water Management Department, T.U. Delft, NL.

FUNDED RESEARCH PROPOSALS

- **“Water & Health: Re-inventing the arsenic filter for safe drinking water in Bangladesh.”** T.U. Delft Global Initiative, the Netherlands 2017, Euro 11,000.
- **“As-Mn-Fe oxidation and adsorption mechanisms in rapid sand filters.”** T.U. Delft Global Initiative, the Netherlands 2018, Euro 15,000.
- **“Development of affordable adsorbent systems for arsenic and fluoride removal in the drinking water sources in Tanzania (DAFWAT).”** with Prof. Prosu Bhacharya and Rajabu Hamisi Mohamed, KTH Royal Institute of Technology, Swedish International Development Cooperation Agency (Sida) 2015-2020, SEK 16 million.

PEER-REVIEWED JOURNALS AND PUBLISHED THESIS

1. **M. Annaduzzaman**, L.C. Rietveld, B.A. Hoque, and D. van Halem (2022). Sequential Fe^{2+} oxidation to mitigate the inhibiting effect of phosphate and silicate on arsenic removal. *Groundwater for Sustainable Development.* V 17, 100749.
2. **M. Annaduzzaman**, L.C. Rietveld, D. Ghosh, B.A. Hoque, and D. van Halem (2021). Anoxic storage to promote arsenic removal with groundwater-native iron. *Water Research.* 202-117404.
3. **M. Annaduzzaman**, Luuk C. Rietveld, B.A. Hoque, M.N. Bari, and D. van Halem (2020). Arsenic removal from iron-containing groundwater by delayed aeration in dual-media sand filters. *Journal of Hazardous. Materials.* 124823.
4. **M.N. Bari, M.M.A Hannan, M.Z Alam, M. Annaduzzaman (2019).** Critical issues of current medical waste management practice in Rajshahi city and its improvement strategies. J*ournal of Environmental Treatment Techniques.* V7(3): 316-323.
5. **M. Annaduzzaman**, P. Bhattacharya, A. Biswas, M. Hossain, K.M. Ahmed, and D. van Halem (2018). Arsenic and manganese in shallow tubewells: validation of platform color as a screening tool in Bangladesh. *Groundwater for Sustainable Development (6). pp. 181–188.*
6. B.K. Pramanik, **M. Annaduzzaman**, F. Suja, and S.M. Zain, (2016). Effect of biological and coagulation pre-treatments to control organic and biofouling potential components of U.F. membrane in the treatment of lake water. *Environmental Technology.* pp. 1-23.
7. **M. Annaduzzaman,** L.C. Rietveld, D. Ghosh, B.A. Hoque, and D. van Halem (2022). Arsenic removal with biofilters using groundwater-native iron from different wells in Bangladesh. *(In review- ES&T).*
8. **Annaduzzaman, M.** (2015). Chitosan biopolymer as an adsorbent for drinking water treatment – Investigation on arsenic and uranium. *TRITA-LWR LIC-2015-02, 26p.*

9. **Annaduzzaman, M.**, (2012). Effectiveness of Tubewell platform color as a screening tool for arsenic and manganese in drinking water wells: An assessment from Matlab region Southeastern Bangladesh. *TRITA LWR Degree Project 12:35-32p.*

CONFERENCE ABSTRACTS AND PRESENTATIONS (PRESENTER UNDERLINED)

1. **M. Annaduzzaman (2021)**. Development and fate of different arsenic mitigation options in Bangladesh. AOGS 18th Annual Meeting-Virtual Conference, Agust 01-06, 2021.
2. **M. Annaduzzaman**, L.C. Rietveld, B.A. Hoque, and D. van Halem (2021). As(III) oxidation and removal with groundwater native Fe^{2+} in the biological rapid sand filter. AOGS 18th Annual Meeting-Virtual Conference, Agust 01-06, 2021.
3. **M. Annaduzzaman**, L.C. Rietveld, B.A. Hoque, and D. van Halem (2021). Arsenite oxidation and removal by delayed Fe^{2+} oxidation in the presence of phosphate. *IWA-YWP Canada, June 24-24, 2021.*
4. **M. Annaduzzaman**, L.C. Rietveld, B.A. Hoque, and D. van Halem (2020). Sequential ferrous iron oxidation for arsenic removal from phosphate-containing groundwater. *8th International Congress and Exhibition on Arsenic in the Environment, Wageningen, June 2020, Netherlands.*
5. **M. Annaduzzaman**, L.C. Rietveld, B.A. Hoque, and D. van Halem (2019). As(III) oxidation in contaminated groundwater with biological rapid sand filter columns in Rajshahi, Bangladesh. *IWA Water and Development Congress & Exhibition Colombo, Sri Lanka, 1-5 December 2019.*
6. **M. Annaduzzaman,** L.C. Rietveld, and D. van Halem (2019). Fecal contamination of drinking water in the arsenic-affected area of rural Bihar: tubewell and storage container survey. *7th International Congress and Exhibition on Arsenic in the Environment (AS 2018), July 1-6, 2018, Beijing, P.R. China. ISBN 978-1-138-48609-6: pp. 502-503.*
7. **M. Annaduzzaman**, D. van Halem L.C. Rietveld, P. Bhattacharya, K.M. Ahmed, and B.A. Hoque (2017). Development of arsenic and iron screening tool based on shallow drinking water tubewells platform color. Benelux-Young water professionals, regional conference, Ghent 2017, Belgium.
8. P. Bhattacharya, F. Mtalo, R.R. Mato, and **M. Annaduzzaman** (2015). Geogenic contaminants in the groundwater in the rift valley of Tanzania- the case of arsenic and fluoride. 2015 GSA Annual meeting in Baltimore, Maryland, USA. Vol. 47(7): 690.
9. Rosborg, P. Bhattacharya, and **M. Annaduzaman** (2015). Finns mineralerna finns kvar efter behandling av dricksvatten med Chitosan för eliminering av en rad föroreningar? Tredje nationella Dricksvattenkonferensen, Forum för kunskap och diskussion om dricksvatten, 14–15 April 2015, Uppsala.
10. **M. Annaduzzaman**, P. Bhattacharya, M. Ersoz, and Z. Lazarova (2014). Arsenic Removal Viability from Contaminated Water Using Chitosan Biopolymer as an Adsorbent Derived from Shrimp or Crab Shells. 2014 GSA Annual Meeting & Exposition, Vancouver, British Colombia, Canada.
11. **M. Annaduzzaman**, P. Bhattacharya, M. Ersoz, and Z. Lazarova (2014). Characterization of chitosan biopolymer and arsenate removal during drinking water treatment. 5th International Congress of Arsenic in the Environment (As2014), Buenos Aires, Argentina (11-16 May), 2014.
12. **Md Annaduzzaman**, I. Owusu-Agyeman and A.Malovany (2012). Microbial fuel cells: a new source of renewable energy from wastewater treatment. 1st International Conference on Advances in Civil Engineering (ICACE), December 2012, CUET, Chottogram, Bangladesh

PROFESSIONAL ACTIVITIES/MEMBERSHIPS

- International Water Association (IWA),
- IWA-Young Water professional, Canada Chapter
- TU Delft|Global Drinking Water
- Asia Oceania Geosciences Society (AOGS)
- Geological Society of America (GSA),
- International Society of Groundwater for Sustainable Development (ISGSD),
- KTH-International Groundwater Arsenic Research Group (GARG)

SCIENTIFIC JOURNAL REVIEWER/GUEST EDITOR

- Water Research
- Journal of Hazardous Materials
- Waste Management
- Groundwater for Sustainable Development
- International Journal of Environmental Research
- Journal of Drinking Water Engineering and Science
- International Journal of Water and Wastewater Treatment
- International Congress on Arsenic in the Environment (bi-yearly conference)

REFERENCES

1. **Dr. Ir. Doris van Halem,** *Associate Professor,* Drinking water Treatment, Sanitary Engineering Section, Department of Water Management, Faculty of Civil Engineering, and Geosciences, Delft University of Technology. Tel. +31 (0) 15 27 85838; E-mail: D.vanHalem@TUDelft.nl
2. **Dr. Ir. Luuk C. Rietveld,** *Professor,* Drinking Water & Urban Water Cycle Technology, Department of Water Management, Faculty of Civil Engineering and Geosciences, Delft University of Technology. Tel. +31 (0) 15 27 84732; E-mail: L.C.Rietveld@tudelft.nl
3. **Dr. Prosun Bhattacharya,** Professor, Groundwater Chemistry, KTH-International Groundwater Arsenic Research Group (GARG), Dept. of Sustainable Development, Env. Science and Engineering (SEED), KTH Royal Institute of Technology, Stockholm, Sweden. Tel. +46 8 790 73 99; E-mail: prosun@kth.se