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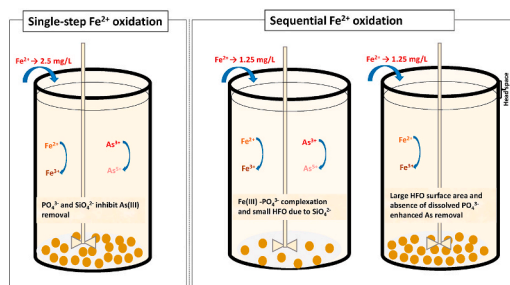
Research paper

Sequential Fe²⁺ oxidation to mitigate the inhibiting effect of phosphate and silicate on arsenic removalMd Annaduzzaman^{a,*}, Luuk C. Rietveld^a, Bilqis Amin Hoque^b, Doris van Halem^a^a Sanitary Engineering Section, Water Management Department, Delft University of Technology, the Netherlands^b Environment and Population Research Centre, Dhaka, Bangladesh

HIGHLIGHTS

- The presence of PO₄³⁻ than SiO₄²⁻ inhibited As uptake during single-step Fe²⁺ oxidation.
- Fe³⁺-PO₄³⁻ complexation and removal in the first Fe²⁺ oxidation step enhanced As removal in the second.
- SiO₄²⁻ reduced the effect of PO₄³⁻ on As removal due to larger HFO flocs surface areas.

GRAPHICAL ABSTRACT



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ABSTRACT

Sequential iron (as Fe²⁺) 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 (PO₄³⁻) and silicate (SiO₄²⁻) during sequential Fe²⁺ 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), Fe²⁺, PO₄³⁻, SiO₄²⁻ 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 Fe²⁺ and As(III) oxidation in the multi-step jar tests indicated that the PO₄³⁻ hindrance on As removal in the first Fe²⁺ oxidation step was compensated for in the second. Moreover, smaller Fe flocs (<0.45 µm) were observed in the presence of SiO₄²⁻, potentially providing more surface area during the second Fe²⁺ oxidation step leading to better overall As removal. Altogether it may be concluded that controlling the As(III) and Fe²⁺ oxidation sequence is beneficial for As removal compared to single-step Fe²⁺ oxidation, both in the presence and absence of PO₄³⁻ and/or SiO₄²⁻.

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

* Corresponding author.

E-mail addresses: M.Annaduzzaman@tudelft.nl (M. Annaduzzaman), L.C.Rietveld@tudelft.nl (L.C. Rietveld), bilqisdhaka@yahoo.com (B.A. Hoque), D.vanHalem@tudelft.nl (D. van Halem).

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(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 an 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 flocs may considerably be reduced as PO_4^{3-} is generally present in higher concentrations than As (Kanematsu et al., 2013; Li et al., 2012).

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-} .

<i>Single-Step Jar Test</i>			
$Fe^{2+} + SiO_4^{2-}$	$Fe^{2+} + As(III) + SiO_4^{2-}$	$Fe^{2+} + As(V) + SiO_4^{2-}$	
$Fe^{2+} + PO_4^{3-}$	$Fe^{2+} + As(III) + PO_4^{3-}$	$Fe^{2+} + As(V) + PO_4^{3-}$	
$Fe^{2+} + As(III)$	$Fe^{2+} + As(III) + SiO_4^{2-} + PO_4^{3-}$	$Fe^{2+} + As(V) + SiO_4^{2-} + PO_4^{3-}$	
$Fe^{2+} + As(V)$			
<i>Multi-Steps Jar test</i>			
$Fe^{2+} + As(III)$	$Fe^{2+} + As(III) + PO_4^{3-}$	$Fe^{2+} + As(III) + SiO_4^{2-}$	$Fe^{2+} + As(III) + SiO_4^{2-} + PO_4^{3-}$

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 5–53%, 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+} of 2.33 mg/L using anoxic storage followed by aeration filtration facilitated high As removal (80 µgAs/mgFe) compared to the oxic storage system (45 µgAs/mgFe), from initial As concentration of 329 µg/L (Annaduzzaman et al., 2021a, 2021b). 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.

2. Materials and methods

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 2 L 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 to 5 cm from the (top) water surface during paddles mixing.

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 $\text{mgFe}^{2+}/\text{L}$ was dosed to oxidize Fe^{2+} and As(III), 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., 2021a). Before the second Fe^{2+} dosing, 20 mg/L of 12.5% Cl containing NaOCl solution was added after 60 min of the first step to oxidize the remaining As(III) concentration and observed another 60 min 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 $\mu\text{g}/\text{L}$, percentile (%), mg/L , or combinations.

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 $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$ (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 $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (SIGMA Life Science - #SLBT0884), Na_3PO_4 (SIGMA Life Science - #MKCB7570), and $\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$ (SIGMA Life Science - #71746) correspondingly. The prepared stock solutions were stored with a 1M ultra-pure HNO_3 solution (Sigma Aldrich) ($\text{pH} < 3$) 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.

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, As, PO_4^{3-} , and SiO_4^{2-} 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 (\varnothing -25 mm, VWR) and 0.20 μm (\varnothing -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 quantify remaining As(III) species. Furthermore, the oxidation and removal process was completed (95%) within the first 60 min and reached chemical stability. Therefore, the data were reported for the first 60 min 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).

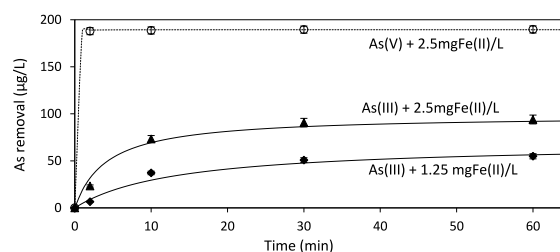


Fig. 1. The As removal in the single-step control jar experiments (without PO_4^{3-} and SiO_4^{2-}). Solid and open symbols depict the experimental As(III) and As(V) removal, respectively. The line depicts the Pseudo-second-order kinetic model based As removal. Initial concentrations were 200 $\mu\text{g}/\text{L}$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

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., 2016, 2018; 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).

2.5. Data analysis

The one-way variance (ANOVA) analyses were conducted with a confidence level of 95% ($\alpha = 0.05$) 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.

3. Results and discussion

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 $\mu\text{g}/\text{L}$ of As(III) or As(V) and either 2.5 $\text{mgFe}^{2+}/\text{L}$ or 1.25 $\text{mgFe}^{2+}/\text{L}$. Symbols present the data points, and the lines represent the pseudo-second-order kinetic model-based As removal.

The initial DO, ORP, and T in the jar tests were 7.9 ± 0.4 mg/L , 267 ± 25 mV, and 20 ± 2 $^{\circ}\text{C}$, respectively, which were kept constant (within $\pm 5\%$) during the experimental duration with a p-value of < 0.05 . The As(III) removal stabilized after approximately 30 min to 50–55 $\mu\text{g}/\text{L}$ and 90–94 $\mu\text{g}/\text{L}$ for the jar containing 1.25 $\text{mgFe}^{2+}/\text{L}$ and 2.5 $\text{mgFe}^{2+}/\text{L}$, 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 flocs (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 $\mu\text{g}/\text{L}$ (40–50%) during batch experiments, containing 500 $\mu\text{g}/\text{L}$ of As(III) and 5–50 $\text{mgFe}^{2+}/\text{L}$. When we dosed As(V), however, As removal was 190 ± 2 $\mu\text{g}/\text{L}$ (95%) within 2 min after dosing 2.5 $\text{mgFe}^{2+}/\text{L}$ (see Fig. 1). Afterward, no further adsorption of As(V) was observed, illustrating that As(V) removal was limited by the

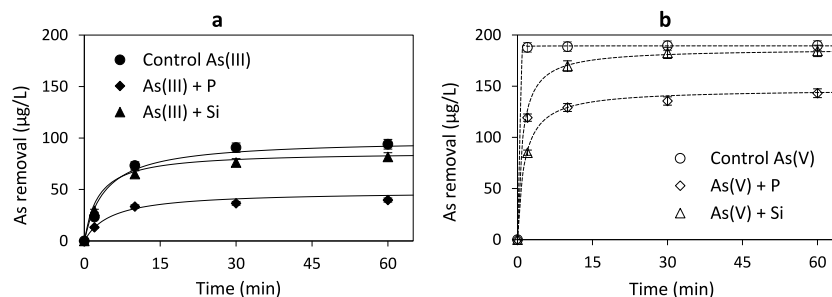


Fig. 2. Arsenic removal in single-step jar experiments either in the presence of PO_4^{3-} (noted as P) or SiO_4^{2-} (noted as Si). The experimental (a) As(III) and (b) As(V) removal are represented by solid and open symbols, respectively. The (solid and broken) lines depict the pseudo-second-order kinetic model. The initial concentrations were 200 $\mu\text{g/L}$ 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.

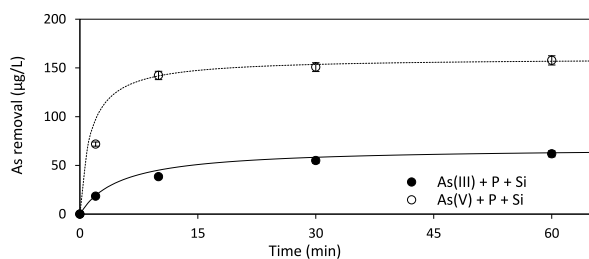


Fig. 3. Arsenic removal in the single-step jar experiments in the presence of both PO_4^{3-} (noted as P) and SiO_4^{2-} (noted as Si). The experimental As(III) and As(V) removal are represented by solid and open symbols, respectively. The line graphs depict the pseudo-second-order kinetic model-based As removal. The initial concentrations were 200 $\mu\text{g/L}$ 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.

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 $\mu\text{gAs/mgFe}$ ($p < 0.05$), similar to the previously found 70–80 $\mu\text{gAs/mgFe}$ (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 $\mu\text{gAs/mgFe}$ ($p < 0.05$).

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 $1.34 \times 10^{-3} \text{ mg } \mu\text{g}^{-1} \cdot \text{min}^{-1}$ and $6.04 \times 10^{-3} \text{ mg } \mu\text{g}^{-1} \cdot \text{min}^{-1}$, for As(III) with 1.25 $\mu\text{g/L}$ 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 $7.15 \times 10^{-2} \text{ mg } \mu\text{g}^{-1} \cdot \text{min}^{-1}$. 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).

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 $\mu\text{g/L}$ and 173 $\mu\text{g/L}$, respectively ($p < 0.05$). For the SiO_4^{2-} -containing systems, the As(III) and As(V) removal was 82 $\mu\text{g/L}$ and 184 $\mu\text{g/L}$ correspondingly, 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 $9.68 \times 10^{-3} \text{ mg } \mu\text{g}^{-1} \cdot \text{min}^{-1}$, and $1.23 \times 10^{-2} \text{ mg } \mu\text{g}^{-1} \cdot \text{min}^{-1}$, for As(III) and As(V), respectively. For the SiO_4^{2-} -containing system, the rate-constant k_2 was $1.03 \times 10^{-2} \text{ mg } \mu\text{g}^{-1} \cdot \text{min}^{-1}$ and $1.41 \times 10^{-2} \text{ mg } \mu\text{g}^{-1} \cdot \text{min}^{-1}$ for As(III) and As(V) respectively.

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 $\mu\text{g/L}$ and 157 $\mu\text{g/L}$ 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

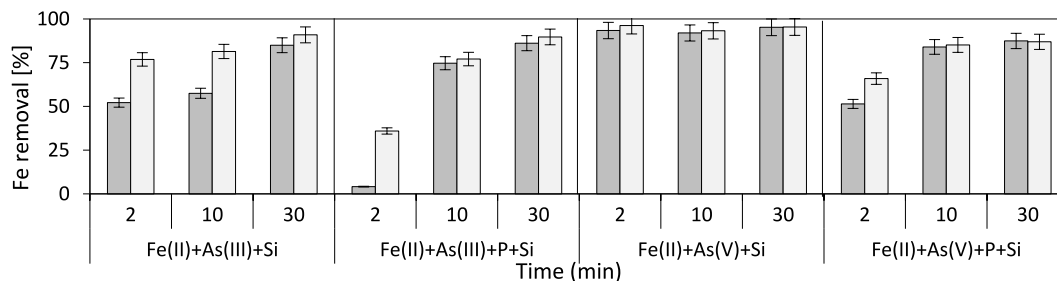


Fig. 4. Percentile Fe removal by 0.45 μm (light grey) and 0.20 μm (dark grey) filter at $t = 2, 10,$ and 30 min for SiO_4^{2-} -containing jar tests. The error bars represent the standard deviation of the triplicate measurements.

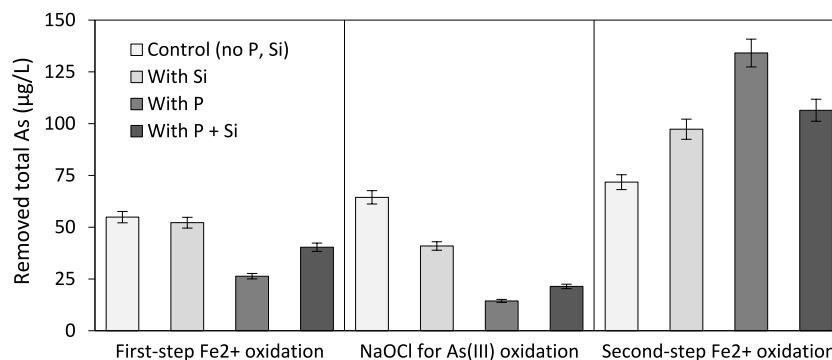


Fig. 5. Total As removal in each step of the sequential addition of 1.25 mgFe²⁺/L, 20 mg/L NaOCl and 1.25 mgFe²⁺/L to a solution containing 200 µg/L As(III) with and without 2 mg/L PO₄³⁻ (noted as P) and/or 16 mg/L SiO₄²⁻ (noted as Si).

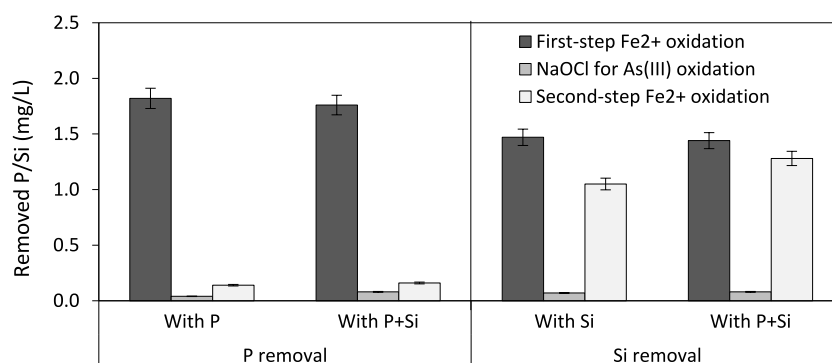


Fig. 6. Total PO₄³⁻ (noted as P) and SiO₄²⁻ (noted as Si) removal after the sequential addition of 1.25 mgFe²⁺/L, 20 mg/L NaOCl and 1.25 mgFe²⁺/L to a solution containing 200 µg/L As(III) and 2 mg/L PO₄³⁻ and/or 16 mg/L SiO₄²⁻.

removal by 0.45 and 0.2 µm filters, are particularly smaller within the first 2 min, indicating PO₄³⁻-SiO₄²⁻-Fe interaction from the start of the reaction followed by gradual growth of these flocs. In the presence of SiO₄²⁻ the flocs were the smallest (<0.2 µm), which might have reduced the PO₄³⁻ 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 PO₄³⁻ and SiO₄²⁻, 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%.

3.3. Sequential oxidation of Fe²⁺ and As(III)

Fig. 5 represents the As(III) removal after sequential oxidation of Fe²⁺ and As(III) either in the presence or absence of PO₄³⁻ and/or SiO₄²⁻. In these experiments, the Fe²⁺ 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 of previously HFO flocs. The oxidation of the first 1.25 mgFe²⁺/L yielded an As(III) removal of 55 µg/L for the control experiments (without PO₄³⁻ and SiO₄²⁻) and 52, 26, and 40 µg/L for SiO₄²⁻, PO₄³⁻, and both PO₄³⁻ and SiO₄²⁻, respectively ($p < 0.05$). The addition of the oxidant in the As(III) oxidation step after the first Fe²⁺ 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 PO₄³⁻ and/or SiO₄²⁻, namely between 14 and 41 µg/L. The overall As uptake by the first Fe²⁺ dosing, followed by the As(III) oxidation step, was 119 µgAs/mgFe ($p < 0.05$) in the absence of PO₄³⁻ and SiO₄²⁻, and 93, 40 and 61 µgAs/mgFe when SiO₄²⁻, PO₄³⁻,

and both PO₄³⁻ and SiO₄²⁻ were added, respectively. The uptake of As by HFO flocs was thus 2–3 times more effective in the absence of PO₄³⁻ than in the presence of PO₄³⁻. This underlines the previously reported PO₄³⁻ 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. 6 shows that PO₄³⁻ removal was approaching 90% in both experiments after dosing the first 1.25 mg/L Fe²⁺. The uptake of As(V) after oxidant dosing was slightly better in the presence of both PO₄³⁻ and SiO₄²⁻ than PO₄³⁻ only, which is in line with earlier observations that SiO₄²⁻ might, partially, compensate for the inhibitory effect of PO₄³⁻ (Su and Puls, 2001). Robert et al. (2004) studies reported that under sequential Fe²⁺ 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 Fe²⁺ 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 PO₄³⁻ and SiO₄²⁻. With the introduction of the remaining 1.25 mg/L of Fe²⁺ 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 PO₄³⁻. 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 PO₄³⁻. Nevertheless, the initial hindrance observed due to PO₄³⁻ is apparently compensated during the second Fe²⁺ dosing, due to the removal of PO₄³⁻ during the first Fe²⁺ dosing.

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 $\mu\text{g/L}$, 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 ($<0.45 \mu\text{m}$) 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.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.gsd.2022.100749>.

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