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DOI
10.1016/j.watres.2022.118345

Publication date
2022

Document Version
Final published version

Published in
Water Research

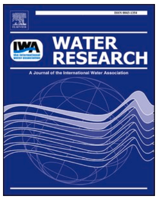
Citation (APA)
Goedhart, R., Müller, S., van Loosdrecht, M. C. M., & van Halem, D. (2022). Vivianite precipitation for iron recovery from anaerobic groundwater. *Water Research*, *217*, Article 118345. https://doi.org/10.1016/j.watres.2022.118345

Water Research 217 (2022) 118345

Contents lists available at ScienceDirect

Water Research

journal homepage: www.elsevier.com/locate/watres



Vivianite precipitation for iron recovery from anaerobic groundwater

Roos Goedhart [a,*], Simon Müller [a], Mark C.M. van Loosdrecht [b], Doris van Halem [a]

[a] Water Management Department, Faculty of Civil Engineering and Geosciences, Delft University of Technology, Stevinweg 1, Delft 2628 CN, The Netherlands
[b] Biotechnology Department, Faculty of Applied Sciences, Delft University of Technology, Van der Maasweg 9, Delft 2629 HZ, The Netherlands

ARTICLE INFO

Keywords:
Drinking water
Iron
Groundwater
Treatment
Vivianite

ABSTRACT

Iron in anaerobic groundwater is commonly removed by oxidation followed by sand filtration. This produces large volumes of iron(III)(hydr)oxide sludge with little value. Our research investigates the novel concept of anaerobic iron(II) recovery from groundwater as the valuable mineral vivianite ($Fe_3(PO_4)_2 \bullet 8\ H_2O$) by the addition of phosphate to the water. We found that vivianite precipitated both in synthetic and natural groundwater when the saturation index (SI) was higher than 4. The SI can be increased by elevating the pH, which allows for iron removal at lower concentrations. Anaerobic iron removal reached 93.7% in natural groundwater, which increased further to 99.9% after a subsequent aeration step. Vivianite precipitation followed second order kinetics with a rate constant of 2.3 $M^{-1}s^{-1}$ and the sludge volume decreased by two third compared to iron oxidation. We therefore conclude that anaerobic iron removal is a promising new approach towards sustainable groundwater treatment.

1. Introduction

The deep aquifers used for the production of drinking water are typically anaerobic and contain reduced iron (Fe^{2+}). The World Health Organization (WHO) recommends a maximum iron concentration of 0.3 mg/L in drinking water (World Health Organization, 2017), while concentrations in raw groundwater of 15 mg/L are not exceptional (Ellis et al., 2000; Kortatsi et al., 2007). Iron removal is one of the major challenges in drinking water production from anaerobic groundwater (Chaturvedi and Dave, 2012). The conventional method of iron oxidation followed by granular filtration removes iron from the water, extensively discussed by Chaturvedi and Dave (2012), Van Beek et al. (2012) and others. This produces large volumes of watery iron(III)(hydr)oxide sludge with little value; currently an inescapable by-product of the groundwater treatment.

Backwashing the filter and disposing the sludge are cost-intensive steps in the production of potable water (Sharma et al., 2001; Turner et al., 2019). In water treatment plants around the globe, 10,000 tons of sludge are estimated to be produced per day (Dharmappa et al., 1997). The reuse of waterworks sludge has been reported a key step in increasing the economic and environmental sustainability of the industry (Albrektiene et al., 2019; Babatunde and Zhao, 2007). Although some reuse opportunities of the currently produced sludge (e.g. as coagulant in wastewater treatment) are discussed by e.g. Ahmad et al. (2016), they come with several disadvantages and the pressure to find more sustainable solutions to avoid landfill disposal increases (Turner et al., 2019). The stringent regulations for waste disposal together with an ever-increasing demand for clean and safe drinking water are the drivers to find a more efficient approach to handle the iron sludge.

This research proposes a novel concept to remove iron from groundwater: anaerobic precipitation with phosphate to form the mineral vivianite. Vivianite ($Fe_3(PO_4)_2 \bullet 8\ H_2O$) is an iron(II)-phosphate mineral commonly found in reducing environments rich in iron and phosphate, such as sediments of lakes, swamps, waterlogged soils, wastewater sludge etc. (Rothe et al., 2016; Wu et al., 2019). The colourless mineral turns blue upon gradual oxidation of Fe(II). Crystal growth can occur when the mineral saturation state is above the solubility equilibrium value, the solubility product constant (K_{sp}) of vivianite is reported to be 10^{-36} (Nriagu, 1972). Al-Borno and Tomson (1994) found that the temperature has very little effect on the K_{sp} of vivianite.

Iron recovery from groundwater via vivianite crystallisation could create a compact end-product instead of the watery and voluminous iron sludge. The removal of iron in the reduced state contrasts the widely applied method of oxidation. Recently, the value of vivianite precipitation has been recognized in wastewater treatment to recover phosphate (PO_4) from the water by dosing iron (Wilfert et al., 2016; Wu et al., 2019). The hypothesis of our study was that iron can be recovered from

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* Corresponding author.
E-mail address: r.c.goedhart@tudelft.nl (R. Goedhart).

https://doi.org/10.1016/j.watres.2022.118345
Received 25 November 2021; Received in revised form 16 March 2022; Accepted 21 March 2022

groundwater as vivianite when phosphate is dosed anaerobically. Vivianite can form from Fe^{2+} with either free (Wu et al., 2019) or protonated phosphate (Liu et al., 2018):

$$3Fe^{2+} + 2\ PO_4^{3-} + 8\ H_2O \rightarrow Fe_3(PO_4)_2 \cdot 8\ H_2O \tag{1.1}$$

$$3Fe^{2+} + 2\ HPO_4^{2-} + 8\ H_2O \rightarrow Fe_3(PO_4)_2 \cdot 8\ H_2O + 2H^+ \tag{1.2}$$

$$3Fe^{2+} + 2\ H_2PO_4^{-} + 8\ H_2O \rightarrow Fe_3(PO_4)_2 \cdot 8\ H_2O + 4H^+ \tag{1.3}$$

The speciation of phosphate (Figure S.1. in Supplementary Information) depends on pH. At the pH of typical groundwater (pH 6.5–8.0), protonated phosphate dominates and the formation of vivianite will release protons. The pH dependant speciation of phosphate and iron and their total concentrations influence the saturation index (SI) of vivianite, which indicates if the mineral is supersaturated with respect to the solution. The expression of the SI is (Prot et al., 2020):

$$SI = \log \frac{IAP}{K_{sp}} \tag{1.5}$$

With the formula of vivianite $Fe_3(PO_4)_2 \bullet 8\ H_2O$ the ion activity product (IAP) becomes:

$$IAP\ =\ \left(\gamma_{Fe^{2+}} \cdot C_{Fe^{2+}}\right)^3 \left(\gamma_{PO_4^{3-}} \cdot C_{PO_4^{3-}}\right)^2 \tag{1.6}$$

In which γ is the activity coefficient of the corresponding ion in the solution (mol/L).

Studies so far have primarily focused on understanding vivianite formation pathways where microorganisms play a direct or indirect role, e.g., in sediments (Rothe et al., 2016) or wastewater treatment (Cao et al., 2019; Wang et al., 2018). However, the proposed iron removal strategy for groundwater is strictly abiotic, which makes the process conditions unique compared to previous research on vivianite formation. Consequently, known factors to influence vivianite formation such as co-occurring constituents or solution pH might be different. The main objective of this research was therefore to investigate abiotic precipitation of vivianite from anaerobic groundwater, with a particular focus on iron removal efficiencies, kinetics, and sludge volumes. To do so, experiments were conducted with natural and synthetic groundwater, under strictly anaerobic conditions. Produced solids were characterized by X-Ray Diffraction (XRD) to determine presence of vivianite.

2. Materials and methods

2.1. Synthetic and natural groundwater

The experiments were conducted with two types of water: (i) a synthetic iron solution, where 50 mL of a 0.018 M $FeCl_2 \bullet 4\ H_2O$ (Sigma-Aldrich) stock solution was added to 400 mL demineralised deoxygenated water, flushed with N_2 (impurity <200 vpm) for at least 45 min in advance, and (ii) natural groundwater collected at a groundwater treatment plant in Loosdrecht, the Netherlands. In synthetic water, the iron removal efficiency was measured for initial concentrations of 1, 10, 25, 50 and 100 mg Fe/L. In groundwater, experiments were executed with the background iron concentration (around 3.8 mg Fe/L, see Table 1). To ensure enough precipitate would form for further analysis, groundwater was also spiked with $FeCl_2$ to reach an elevated concentration of 100 mg Fe/L. To prevent air contamination of the natural groundwater samples, 1 L glass bottles (Schott DURAN®) were filled with a tube at the bottom and the water volume was replaced ten times before closing them with bromobutyl rubber stoppers secured with an open topped cap. After transportation, the bottles were stored in an anaerobic environment. Prior to the experiment, the natural groundwater was vacuum filtered with a 0.45 µm polyethersulfone membrane (Pall Supor®) in the anaerobic environment. The average composition and pH of the natural groundwater are presented in Table 1.

The phosphate and carbonate stock solutions used were prepared in the anaerobic environment by dissolving respectively Na_2HPO_4 and Na_2CO_3 to obtain a 0.018 M PO_4/CO_3 solution, in oxygen free water. All chemicals met or exceeded ACS reagent grade.

2.2. Experimental setup

A vinyl (PVC) anaerobic chamber (Coy Laboratory Products, USA) filled with a gas mixture of 5% hydrogen and 95% argon gas (impurity <200 vpm) was used for the anaerobic experiments. The chamber had an airlock and weekly regenerated palladium catalysts to secure anaerobic conditions. Water vapour was entrapped by silica beads to keep the humidity < 70% (measured by a hygrometer). All experiments were performed at room temperature of approximately 21 °C.

The approach of the experiments is presented in Fig. 1. A glass reactor with 450 mL of either the synthetic or natural groundwater was placed on a magnetic stirrer. While stirring continuously, 50 mL of the phosphate stock solution was added to achieve a 1:1 molar ratio (phosphate:iron) after which the solutions could react anaerobically. To track reaction kinetics, water samples were taken during the reaction and when no additional iron removal was observed, solids were collected for XRD. All water samples were immediately filtered through a 0.45 µm non-sterile Millex® Syringe filter with Durapore® membrane and acidified with HCl to bring the pH below 4 to prevent further reaction.

An aeration step was added (Fig. 1, right) after the anaerobic reaction, the reactor was removed from the anaerobic chamber and flushed with compressed air for 10 min. After a 50 min period, the suspension was transferred to a plastic Imhoff cone of 1 L. The volume of the liquid and sludge was measured after one day of settling and solids were collected for XRD. A set of reference experiments simulated the conventional treatment of oxidation and filtration, in which no phosphate was dosed for anaerobic iron precipitation. To compare sludge volumes, a set of experiments was conducted following the same procedure in which carbonate was anaerobically dosed instead of phosphate.

2.3. Analysis

During the experiments, the pH, oxidation–reduction potential (ORP), electrical conductivity (EC) and temperature were measured with a Multi-parameter electrode (Sension+ 5048 with MM150 multimeter, HACH) and the dissolved oxygen (DO) concentration with an optical DO sensor (WTW, FDO® 925). The concentration of DO stayed below 0.05 mg O_2/L during all experiments.

Iron concentrations and phosphate concentrations were measured with the standard phenantroline method (LCK 320 kits, HACH) for iron (II) and total iron and standard molybdenum blue method (LCK 348 kits, HACH) respectively. A HACH DR 3900 VIS spectrophotometer measured the absorbence and automatically calculated concentrations.

In the experiments in which natural groundwater was used, total iron and phosphorus concentrations were determined by inductively coupled plasma mass spectrometry (ICP-MS). The samples for ICP-MS analysis were acidified by adding 65% ultrapure HNO_3 to 1% vol.

Table 1
Composition of the natural groundwater, $n = 4$. SD = Standard deviation.

Parameter	Fe	P	Mn	Na	Mg	Si	S	Ca	pH
Conc. (mg/L)	3.81	0.18	0.12	7.78	2.16	8.26	3.39	36.18	7.39
SD	0.14	0.03	0.001	0.11	0.02	0.13	0.60	0.94	–

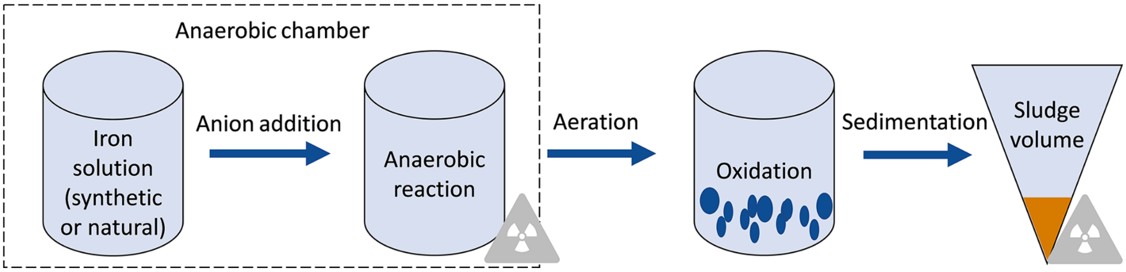

Fig. 1. Graphical representation of the experimental setup, from anaerobic precipitation in the anaerobic chamber (left) to aeration and sedimentation under ambient conditions (right). The radiation icon indicates moments of solid sampling for analysis by XRD.

XRD was applied to characterize the precipitates. The suspension was vacuum filtered with a 0.45 μm polyethersulfone membrane (Pall Supor®). For the anaerobic samples, the filter was covered in aluminium foil to prevent photo-oxidation and dried inside the anaerobic chamber for a day. Afterwards, the filter was covered with a layer of glycerol to minimise oxidation during XRD analysis open to the atmosphere. A Bruker D8 Advance diffractometer with Cu-Ka radiation was used for the XRD analysis, with coupled μ - 2μ scan 10°- 120°, step size 0.030 °2μ, counting time per step 2 s. Bruker software DiffracSuite.Eva vs 5.2 was used for the data evaluation.

2.4. Geochemical model

The saturation index of vivianite was calculated using the program Spec8 of the Geochemist's Workbench ® (GWB®) model and the standard database. The input was the measured iron and phosphate concentrations, pH and temperature.

3. Results

3.1. Vivianite precipitation in synthetic water

At initial iron concentrations above 25 mg/L, phosphate addition to the synthetic anaerobic solution removed iron from the water with a maximum recovery of approximately 79% (Fig. 2a). XRD analysis of the generated solid phases showed that only vivianite crystallised in the samples (Fig. 2b). At the lower initial concentration of 10 mg Fe/L, iron recovery remained below 35%, and for 1 mg Fe/L no iron removal was observed. The pH of the system depended on the concentration of iron and phosphate; for 1 mg Fe/L the pH was around 7.7 while it was 6.9 for an initial concentration of 100 mg Fe/L.

3.2. Vivianite precipitation in natural groundwater

Anaerobic phosphate addition to natural groundwater also resulted in iron removal by vivianite crystallisation. With the background iron concentration of around 3.8 mg/L, the anaerobic removal was 16.9%. For the spiked groundwater with an elevated iron concentration of 100 mg/L, 93.7% of iron was recovered via vivianite crystallisation (Fig. 3a). An additional oxidation step after the anaerobic reaction increased iron removal to 98.2% and 99.9% for the background and elevated iron concentrations, respectively. In both waters the efficiencies were approximately 3.5% higher than in the reference experiment of oxidation only; the addition of an anaerobic removal step improved the removal efficiencies. Vivianite was the only solid phase detected by XRD in this experiment, also after oxidation (Fig. 3b). Pictures of the blue precipitate on the filter are presented in Fig. 3c and 3d. The mass of anaerobic precipitate formed with the background iron concentration was too low to detect by XRD.

It is worth noting that to protect the samples from oxidation during XRD analysis, the anaerobic precipitates were covered with glycerol (see Section 2.3). The background signal in Fig. 2b and in the lower diffractogram of Fig. 3b are probably caused by the glycerol. The glycerol was not added to the aerobic vivianite sample shown in the upper diffractogram of Fig. 3b.

Rouzies and Millet (1993) specified that vivianite alters to metavivianite ($Fe^{2+}Fe_2^{3+}(PO_4)_2(OH)_2•6H_2O$) at 50% iron oxidation in vivianite, which can be distinguished via its altered XRD spectrum (Rothe et al., 2014). No metavivianite is detected in the solids formed during the executed experiments of iron removal in groundwater. It is therefore concluded that the iron in the formed crystals were mainly present in its reduced Fe(II) form, even when an additional oxidation step was applied.

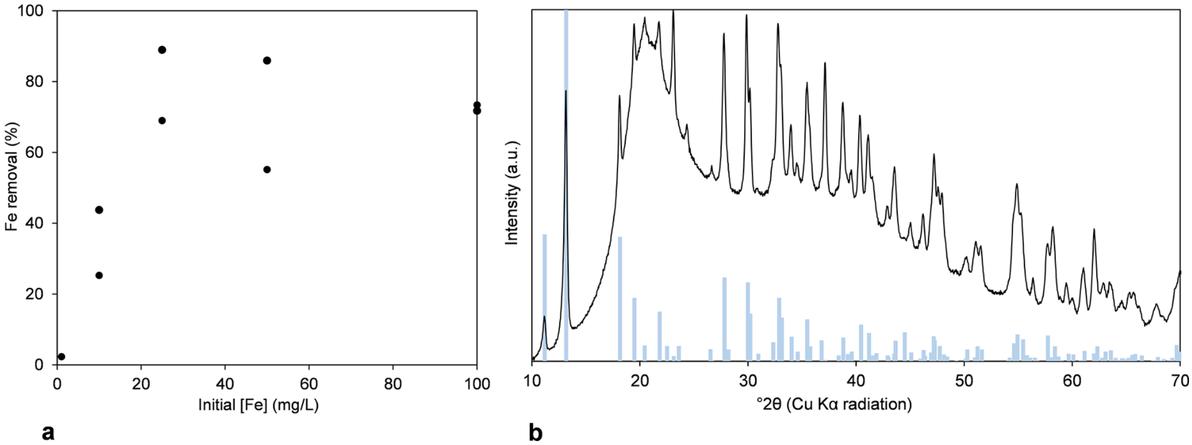

Fig. 2. a) Iron removal by vivianite crystallisation at different initial iron concentrations in synthetic groundwater. Reaction time 60 min, ratio PO_4:Fe 1:1. Data of duplo experiments given. Because of measurement error only one data point for 1 mg Fe/L. **b)** XRD pattern of the formed crystals (black line) on the filter at an initial iron concentration of 100 mg/L with the reference pattern of vivianite (blue bars).

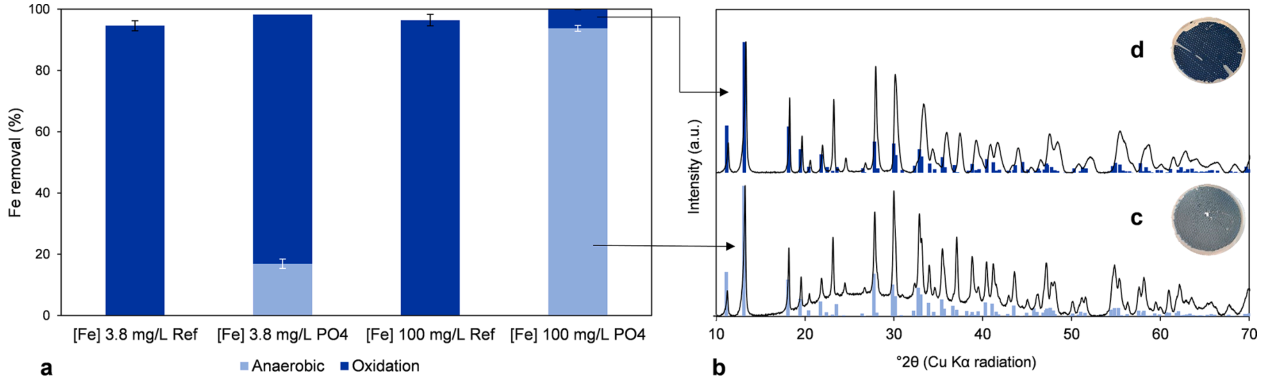

Fig. 3. **Fig 3a)** Iron removal in the reference (Ref) experiment of iron oxidation and via anaerobic (AN) vivianite precipitation by phosphate (PO4) addition followed by an oxidation (OX) step in natural groundwater with the background iron concentration (3.8 mg Fe/L) and in spiked groundwater (100 mg Fe/L). AN and OX reaction time 60 min, ratio PO_4:Fe 1:1. Error bars are SD of $n = 2$ **b)** XRD patterns of the formed crystals during the anaerobic reaction in spiked natural groundwater to which phosphate was added (bottom diffractogram) and of the same crystals after the oxidation step (upper diffractogram) including the reference pattern of vivianite (blue bars). **c)** Picture of formed anaerobic precipitate on filter and **d)** precipitate after oxidation.

3.3. Kinetics and SI

In Fig. 4, the removal kinetics (black circles) and calculated SI (blue squares) are depicted for the experiments with synthetic and natural groundwater containing an elevated initial iron concentration of 100 mg Fe/L. Iron removal stopped after 10 min in the synthetic solution, while in natural groundwater the removal continued for 60 min. A second order removal rate was found for both the iron removal in synthetic and natural groundwater (black lines). The rate constants were found to be 2.7 $M^{-1}s^{-1}$ (95% confidence interval [1.7, 3.6]) and 2.3 $M^{-1}s^{-1}$ (95% confidence interval [1.9, 2.7]) for synthetic and natural groundwater, respectively. The half-life of iron when removed via vivianite precipitation in both synthetic and natural groundwater is approximately 4 min for an initial concentration of 100 mg Fe/L.

From Fig. 4 it is apparent that the vivianite precipitation reaction stopped after reaching the approximate SI of 4 (blue dotted line in Fig. 4). In the synthetic solution, an SI < 4 is reached sooner (at minute 10) than in natural water (at minute 60), caused by stronger pH changes in the system. A pH drop from 6.9 to 5.8 occurred during the experiment with synthetic water, which was not observed in the natural groundwater due its higher alkalinity (graph in Supplementary Information, Figure S.2).

The calculated kinetics of both (homogeneous) iron oxidation with oxygen and anaerobic removal via vivianite formation are plotted in Fig. 5. The kinetics of homogeneous iron oxidation follows first-order removal with respect to Fe^{2+} at constant pH and DO. The rate law used in Fig. 5 was determined by Sung and Morgan (1980) with a rate constant of $k = 2.1 \bullet 10^{13}\,M^{-2}\,min^{-1}$ as published by Schenk and Weber (1968). The rate of iron oxidation strongly depends on pH, Fig. 5 provides the rate at groundwater-relevant pH's of 6.5, 7.0 and 7.5. The rate of vivianite precipitation is determined at pH 7, at which the half-life of iron is four times shorter than in iron oxidation at pH 7. This implies that iron recovery via vivianite precipitation has the potential to make the groundwater treatment system more efficient.

3.4. pH and iron concentration

The removal kinetics for the experiment with natural groundwater (background iron concentration of 3.8 mg Fe/L) are shown in Fig. 6. As also seen in Fig. 4, no additional removal is obtained when the SI dropped below the value of 4. The SI dropped below 4 in the first minute, while the pH of the system was around 7.7, which was higher than in the two experiments with elevated iron concentrations (see Section 3.3). It demonstrates that both the pH and the initial iron concentration influence the SI of vivianite.

Since the pH was not controlled during the experiments, the relation between SI and pH was modelled for different initial iron concentrations (Fig. 7) in synthetic water. The boundary for vivianite crystallisation was found to be at a SI of 4. For a low iron concentration of 1 mg/L the model implies that vivianite crystallisation will only occur at a pH of 8.5.

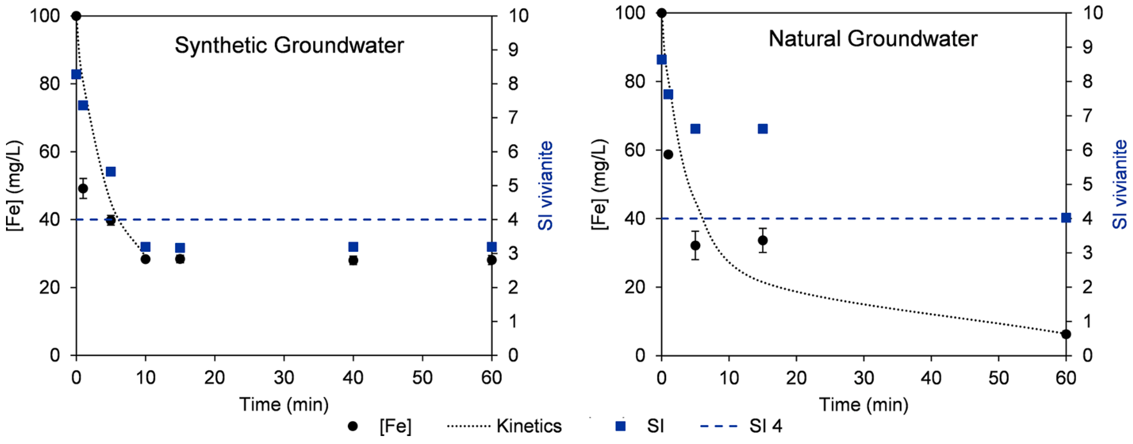

Fig. 4. *Dissolved iron concentration over time and the corresponding modelled SI of vivianite in synthetic (left) and natural groundwater (right) with an initial [Fe] of 100 mg/L. The kinetic relation is shown for points with a SI higher than 4. Kinetic relation synthetic water:* $\frac{d[Fe]}{dt} = 2.7\ [Fe]^2$ *Kinetic relation natural groundwater:* $\frac{d[Fe]}{dt} = 2.3\ [Fe]^2$. *Error bars are SD of* $n = 2$, *most [Fe] error bars too small to see.*

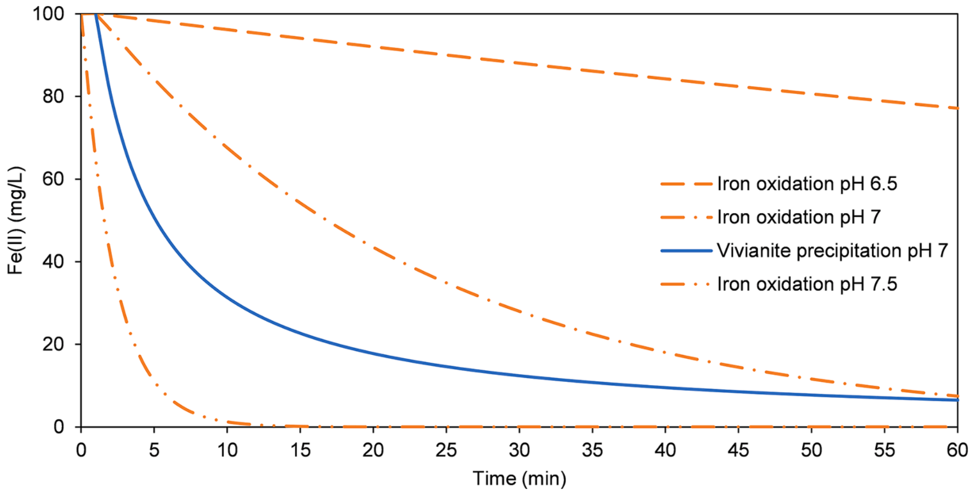

Fig. 5. Kinetics of iron removal in natural groundwater by vivianite precipitation and by iron oxidation at pH 6.5, 7.0 and 7.5. Integrated rate law iron oxidation: $[Fe(II)]=[Fe(II)]e^{k1t,}$ $k1 = k\ [OH^{-}]^{2}\bullet p_{O2,}$ $k = 2.1 \bullet 10^{13} M^{-2} atm^{-1} min^{-1}$ (Schenk and Weber, 1968). Integrated rate law vivianite precipitation: $[Fe(II)] = 1/kt + [Fe(II)]_0$ $k = 2.3\ M^{-1}s^{-1}$.

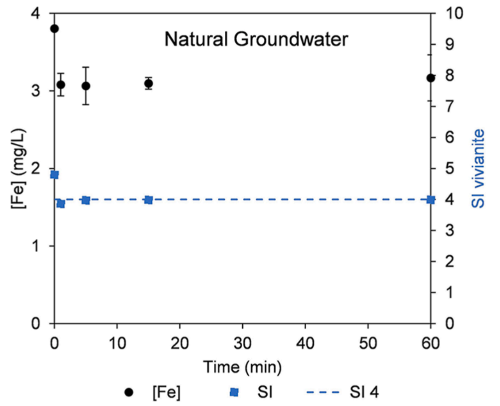

Fig. 6. Dissolved iron concentration over time and the corresponding modelled SI of vivianite in natural groundwater with the background [Fe] of 3.8 mg/L. Error bars are SD of $n = 2$, some [Fe] error bars too small to see.

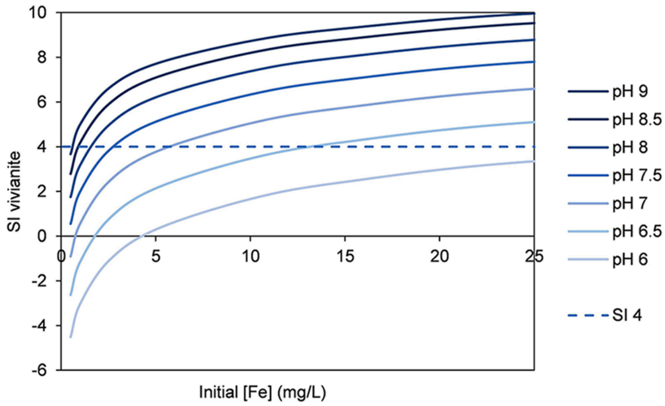

Fig. 7. The modelled saturation index of vivianite at different initial iron concentration at different pH's. Modelled with GWB® spec8, ratio PO_4:Fe 1:1 at 21 °C.

The higher iron removal in natural groundwater compared to the synthetic water can also be explained by this relationship. The alkalinity of the natural groundwater avoided a strong pH drop during vivianite formation, maintaining a higher SI.

3.5. *Sludge volume*

Fig. 8a shows that anaerobic precipitation of ferrous iron with phosphate reduces the sludge volume to a third compared to the conventional iron oxidation method. This considerable reduction was both obtained in the synthetic as in the spiked natural groundwater solution. The sludge volume formed in the groundwater without iron spiked was too small to measure. As a comparison, anaerobic carbonate addition was also tested, which increased the sludge volume approx. 6 times compared to the oxidation method. The difference in appearance and volume of the formed sludge is visible in Fig. 8b, which also illustrates that vivianite settled better than the products of iron oxidation or carbonate addition.

4. Discussion

4.1. *Conditions for abiotic vivianite crystallisation*

The anaerobic groundwater conditions were shown to be feasible for abiotic vivianite crystallisation. The removal efficiencies of iron in the experiments with anaerobic treatment followed by oxidation were approximately 3.5% higher compared to iron oxidation only. The kinetics at neutral pH are faster, the half time of iron with anaerobic precipitation is 4 times shorter compared to iron oxidation. However, this is only applicable to conditions where the SI of vivianite crystallisation exceeds 4. This finding is in line with the outcome of Liu et al. (2018), who determined that the supersaturation level at which efficient crystallisation can take place is between 4 and 11. With the geochemical model it is shown that the SI values of vivianite in the executed experiments were within this range, in which heterogeneous crystallisation is expected to take place (Li and Sheng, 2021).

In groundwater with low to moderate iron concentrations (<25 mg/L) exceeding SI 4 might be particularly challenging. A possible solution to increase the SI of vivianite is to elevate the pH, which is a common procedure in groundwater treatment. A base can be dosed alongside the phosphate or the pH can be increased by stripping CO_2 with a vacuum degasser. OH^{-} ions can however trap the free Fe^{2+}, which makes the

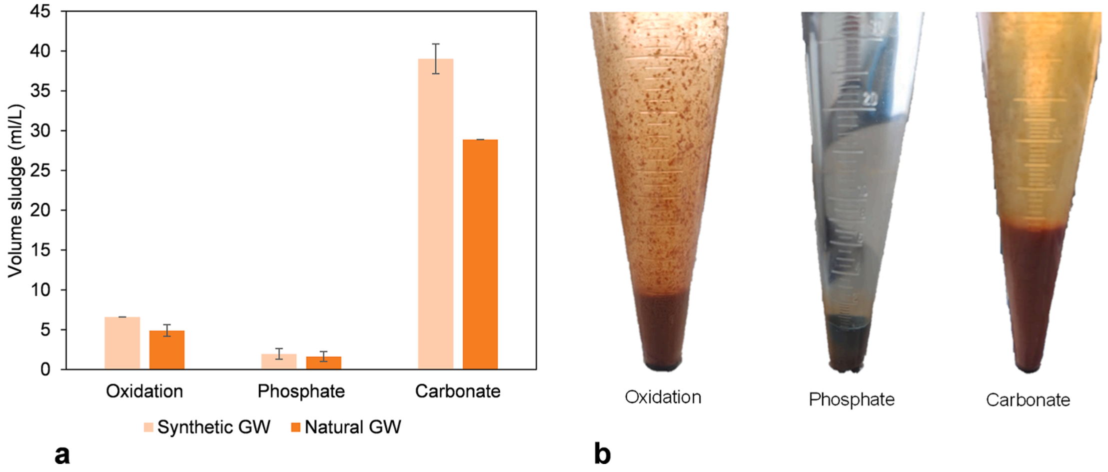

Fig. 8. a) Volume and b) appearance of sludge produced during iron oxidation (reference) and by anaerobic addition of phosphate or carbonate followed by oxidation in synthetic and natural groundwater (GW). AN and OX reaction time 60 min, [Fe] initial 100 mg/L, ratio anion:Fe 1:1. Error bars are SD of $n = 2$.

iron unavailable for vivianite precipitation (Liu et al., 2018). A more attractive method might be to lower the supersaturation demand by the addition of a seeding material, such as quartz grains (Liu et al., 2018) or sponge iron (Wu et al., 2021). Quartz is already a commonly used seeding material in groundwater treatment, e.g. in (anaerobic) pellet softening (Harms and Bruce Robinson, 1992). The addition of quartz in an anaerobic reactor before the oxidation step to offer a seeding material might therefore be a straightforward solution.

An alternative approach to increase the SI is to concentrate the iron in groundwater prior to the addition of phosphate. Anaerobic nano filtration and reverse osmosis are becoming competitive options to the conventional groundwater treatment technologies, since the quality of the produced water is high, the processes are easy to operate and a small footprint is required (Chelme-Ayala et al., 2009). However, the disposal of the concentrate is an important issue regarding membrane processes (Van der Bruggen et al., 2003), which is expected to become more difficult in the future because of stricter European legislation (Nederlof et al., 2005). Anti-scalants containing phosphate are often dosed during membrane filtration, which can cause eutrophication in the receiving waterbodies (Jong et al., 2013). Controlled vivianite formation might be a suitable alternative to remove both the iron and phosphate in the anaerobic concentrate while the resources are recovered. The concentration of iron depends on the inlet concentration and the water recovery, but the concentrate typically contains 4 to 10 times higher concentrations than the feedwater (Chelme-Ayala et al., 2009), making it suitable for vivianite precipitation.

4.2. *Vivianite recovery: scope for application*

Although vivianite is known to have a market value, its end use will depend on the grade of the vivianite obtained (Prot et al., 2019). A knowledge gap in literature can be identified on the properties of the formed vivianite in (waste) water systems (Wu et al., 2019). To investigate this will be a logical and valuable next step, which can give clarity about the value of the recovered vivianite versus the costs of the phosphate dosage and benefits of compact iron sludge. Recovery of vivianite from the water can be achieved by conventional granular filtration and periodically backwashing the filter bed. Vivianite is a paramagnetic mineral, which makes magnetic separation an alternative recovery option (Prot et al., 2019).

Important to acknowledge is that phosphate is a limited resource, making recovery of phosphate a key aspect of the approach. In the conducted experiments, phosphate was always slightly overdosed (P/Fe ratio of 1 while theoretical ratio is 0.67). In practice, residual phosphate in the produced drinking water is not desired. Identification of the optimal phosphate dosage for scaling up is therefore required, which depends on the pH (and SI) of the groundwater.

An alternative to phosphate dosage might be anaerobic iron precipitation by the addition of another anion. For example, Fe^{2+} can react with carbonate (log K 10.59 at 25 °C) and sulphide (log K 3.6 at 25 °C) (Liu et al., 2018), which can control Fe^{2+} concentrations in anaerobic aquifers (van Beek et al., 2021). We demonstrated that for anaerobic iron removal carbonate addition is possible, but this resulted in a significant increase in sludge volume. The iron-carbonate interaction might also impact iron recovery via vivianite precipitation in groundwater systems that contain high inorganic carbon concentrations. However, both Wu et al. (2019) and Liu et al. (2018) showed that iron precipitation with phosphate favours over carbonate for alkalinity up to 1000 mg/L. For sulphide, competition becomes significant at concentrations of 1.5 mM and the effect is neglectable up to 0.5 mM (Liu et al., 2018). Concentrations of sulphide in groundwater are not common to transcend this value (thermal waters rich in H_2S have a concentrations of around 0.5 mM).

The production of vivianite and the corresponding reduction in sludge volume can reduce the costs of water treatment. The treatment of backwash water is currently a major contributor to the total cost of drinking water production (Turner et al., 2019). Additionally, the production of compacter sludge reduces the transport and processing costs of the sludge. Vivianite also has an economic value in chemical and agricultural industries; it can be used as a pigment (Figueiredo et al., 2010), in lithium ion batteries (Raghupati Rao and Varadaraju, 2015), as a slow P-release fertilizer (Yaya et al., 2015) and to replenish Fe-poor soils (Rombolà et al., 2007).

The above discussed advantages and possibilities make iron removal and recovery via vivianite crystallisation an interesting approach for application in groundwater treatment plants to increase the environmental and economical sustainability of the industry. The concept is so far only tested in small batches. Given the promising results, scaling up this technology will be tested in continuous flow by the addition of an anaerobic reactor prior to the existing treatment system.

5. Conclusion

The current research successfully demonstrated the recovery of iron from anaerobic groundwater via vivianite precipitation. No longer considering iron sludge a waste but rather a new resource, our study offers a new approach in the drinking water industry. A follow up question is how the vivianite can be recovered and reused from the stream, which can make groundwater treatment a more sustainable industry. Our novel technique reduces the volume of iron sludge produced to a third compared to the conventional technique of iron oxidation, while reaching similar or higher removal efficiencies. The 4 times shorter halftime found for anaerobic iron removal at pH 7 can lead to filters with a higher throughput rate and requires less backwashing. This can contribute to the design of efficient systems, while gaining economic savings.

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.

Acknowledgements

This research is funded by NWO TTW Vitens-Dunea Sand Filtration programme (grant number: 17830). The authors would like to acknowledge the contribution of Jane Erkemeij for the ICP-MS analysis and Ben Abbas for the support with the anaerobic chamber. Furthermore, we would like to thank Ruud Hendrikx at the Department of Materials Science and Engineering at the Delft University of Technology for the XRD analyses.

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.watres.2022.118345.

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