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Efficient formation of vivianite without anaerobic digester: Study in excess activated sludge

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ABSTRACT

It was recently discovered that vivianite ($Fe_3(PO_4)_2.8H_2O$) could be magnetically extracted from digested activated sludge which opened a new route for phosphorus recovery (Wijdeveld et al. 2022). While its formation in digested sludge is regularly reported, it is not yet studied for fresh, undigested activated sludge. In particular, the extent to which vivianite could form during sludge storage is missing. The current research showed that iron reduction was completed after 2–4 days of anaerobic storage, and the vivianite appeared to form quickly from the pool of reduced iron made available. After sludge thickening at the wastewater treatment plant (30 h retention time), around 11% of the iron was vivianite. With subsequent 1–3 days of anaerobic storage, this fraction increased to 50–55%. After this storage, almost all the vivianite that could potentially form did form. This research concluded that efficient vivianite formation can be achieved without a sludge digester, showing phosphorus recovery potential from undigested sludge via vivianite recovery. Besides, the recovery of vivianite from undigested sludge presents advantages like the reduction of the sludge to dispose of and mitigation of the vivianite scaling formation.

1. Introduction

Phosphorus is an essential element for all living organisms. It is crucial in the energy metabolism (ATP), is vital for DNA and membrane lipid synthesis, and forms bones [21]. The way phosphorus is produced nowadays through mining is not environmentally friendly, and the resources are depleting [34]. The global reserves of phosphorus are estimated at 71 * 10^9 metric tons, 70% of which being in Morocco and Western Sahara [8]. In 2014 it was estimated that 180–190 million tons of phosphate rock are mined each year [8]. Since Europe has no phosphorus reserves, its depletion is economically disadvantageous due to future scarcity and dependence on the countries bearing the phosphate rock [27]. Society heavily relies on phosphorus, mainly because of its essential role in the agricultural and food production sector, although a fraction is also used in industrial processes [50]. Around 80% of the mined phosphorus is used in the fertilizer industry [43]. A large fraction of the phosphorus ends up in the food, and after consumption, in the wastewater. Removal of phosphorus at Wastewater Treatment Plants (WWTP's) is essential since discharging too much phosphorus in surface water leads to eutrophication and harmful algal growth, causing hypoxia [38]. Around 90% of the phosphorus in the influent of the WWTPs ends up in the sludge, which is, therefore, an interesting secondary source for phosphorus mining [7].

Phosphorus recovery from ash at central sludge mono-incinerations is well-developed and presents an interesting recovery of 60–90% [10]. However, decentralized phosphorus recovery would offer numerous advantages like better sludge dewatering, transportation costs reduction, and potentially reduced phosphorus scaling formation at the WWTP [40]. Phosphorus recovery through struvite ($NH_4MgPO_4.6H_2O$) crystallization was one of the first decentralized methods developed where struvite can be used as a slow-release fertilizer [28]. A disadvantage of the struvite recovery approach is the limited phosphorus recovery, approximately 10–30% of the phosphorus in the influent [46]. Moreover, this strategy is only applicable for WWTP's using Enhanced

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Biological Removal (EBPR).

Iron is commonly dosed in WWTP's using Chemical Phosphorus Removal (CPR) since it can remove phosphorus to a very low level. It is also beneficial for reducing hydrogen sulfide (H_2S) formation in biogas [11] and improve the flocculation of the sludge [46]. The form of the precipitated iron phosphates has hardly been studied. Wilfert et al. [47] showed that vivianite ($Fe_3(PO_4)_2.8H_2O$) was omnipresent in the sludge after anaerobic digestion. If the quantity of iron is high enough, vivianite can bear up to 70–90% of the phosphorus present in digested sludge [48]. An increase of iron dosing in the waterline to minimize phosphate in the effluent showed quick and efficient vivianite formation in the digester [31]. Thanks to its paramagnetic properties' vivianite can be recovered from digested sludge via magnetic separation [30,39], a technology that is currently scaled up. This technology could recover more than 60% of the phosphorus from the influent wastewater at pilot scale [49].

Vivianite has been widely reported as the dominant phosphate mineral in digested sludge [12,30,31,35,47,48] (Zhang, [54]). Its formation in waste activated sludge (WAS) before digestion was more rarely discussed. Studies involving sludge before digestion mainly considered vivianite as a way to recover phosphorus after its release from WAS by pH modification [4,18,51]. Some studies mentioned the presence of vivianite in sludge before digestion, mainly in surplus sludge [31,39,44,48]. Still, these studies mainly focused on vivianite formation in digested sludge. Iron reduction in activated sludge kept under anaerobic conditions has already been studied [26,33]. Recently, Wang et al. [44] showed that the iron reduction was well-advanced after a day of storage in anaerobic conditions and that some vivianite could already form in this timeframe.

Iron reduction in iron-rich sludge kept under anaerobic conditions (like in digesters) is suspected to be the main trigger for vivianite formation [1,31,44,54]. However, the anaerobic residence time that is required for the optimum formation of vivianite is still unclear. Some research focused on the formation of vivianite in undigested sludge [6] or septic water [1,54], but the majority of the studies were carried on digested sludge so far [12,30,31,35,47,48] (Zhang, [54]). Indeed, sludge has a long anaerobic residence time (20–30 days) in a digester, which is favorable for vivianite formation.

However, many WWTP's are not equipped with a digester while still dosing a high amount of iron. Therefore, it is crucial to study the possibility of vivianite recovery at WWTP's without digester since it represents an important part of the WWTP's. It may also be necessary concerning future developments related to resource recovery where organic substances (PHA, Kaumera) are produced from sewage sludge instead of producing biogas [2,46]. The current study investigates the correlation between iron reduction in thickened sludge and possible vivianite formation. At the moment, vivianite extraction is mainly proposed for digested sludge because previous research showed that vivianite formation is complete. This would limit vivianite extraction to plants with a digester. Previous research [44] however suggested that Fe reduction is quick and that therefore vivianite formation in sludge may not need long residence times. This research aims to assess the feasibility of vivianite formation during short anaerobic residence times so that recovery may also be possible in plants without a digester. The iron reduction kinetics in excess sludge dosed with iron salts was first investigated before looking at the correlation with vivianite formation. Finally, the opportunities for phosphorus recovery opened by this study were discussed.

2. Material and methods

2.1. Sludge samples

Thickened sludge from the WWTP Hoensbroek, operated by Waterschapsbedrijf Limburg (The Netherlands), was collected 30 min before the start of each experiment. The sludge was sampled from a tap downstream from the thickener. At this installation, 150 kg Fe/year is dosed as $FeClSO_4$ in the aeration tank for phosphorus removal to achieve a phosphorus level of around 0.4 mg/L in the effluent. The surplus sludge goes to a thickener with a solid's residence time of approximately 15 h under regular operation but was 30 h during the sampling period. In this thickener, external sludge from WWTP Abdissenbosch is added. The thickened sludge is then dewatered by centrifugation and transported for disposal. There is no sludge digester in WWTP Hoensbroek.

2.2. Method of lab experiments

Three experiments were carried out: a blank with no extra iron addition, a run with the addition of $FeCl_3$, and one with $FeCl_2$. The dosage of $FeCl_3$ or $FeCl_2$ was calculated on the sludge composition for all the phosphorus to precipitate as vivianite potentially. The quantity of iron added was calculated considering that iron will first precipitate as FeS and only then as vivianite as suggested in Prot et al. [31]. Unfortunately, the sludge's composition changed right before the experiments' start due to an unexpected higher thickening time of 30 h instead of 15 h meaning. This should not influence the main findings of this research but only the fact that not all the phosphorus will be converted as vivianite due to the lack of iron dosed.

Thickened sludge was poured until the brim in a 1 L sealed bottle and kept under constant stirring at 1000–1200 rpm and at room temperature for the experiments' duration. Iron salts were added immediately after the initial sampling, as one increment of 50 mL under strong stirring. Samples were taken at: 0 (before iron addition), 0.5, 1, 2, 4, 8, 24, 48, 72, 96, 168, 216 and 264 h. Note that the sludge had a residence time of 30 h in the thickener, so the actual anaerobic residence time of a sample is 30 h more than its sampling time. The difference between the approach in this study and digested sludge samples are the lower temperature (10–20 °C versus 38–40 °C for digestion) the shorter anaerobic storage time (1–2 days versus 20–30 days for digestion) and the absence of digested sludge inoculum. The conditions in the current experiments were fermentative and not methanogenic.

For each sample, pH and ORP were measured, and three homogenized sludge samples are taken:

- 25 mL of sludge was poured into a pre-weight aluminum tray and dried at ambient temperature. The solid content was determined, and a fraction of the sample was used for elementary composition analysis (Microwave digestion followed by ICP-OES). The samples were always dried at ambient temperature since higher temperatures can provoke the crystal water's evaporation in vivianite, potentially damaging its structure [30].
- 15 mL of sludge was centrifuged for 12 min at 4000 rpm, and the centrate was filtered with a 0.45 μm hydrophilic filter. The phosphate and iron (Fe^{2+} and Fe^{3+}) concentrations in the centrate were immediately measured with Hach-Lange kits (LCK 321). The cake was dried at ambient temperature and stored for microscope, XRD, and Mössbauer spectroscopy analyses.
- 4 mL of sludge was added to 16 mL of 0.5 M HCl solution for the iron extraction, based on protocols described in Rasmussen and Nielsen [33] and Nielsen et al. [26]. This solution was gently stirred for 15 min and filtered with a 0.45 μm hydrophilic filter to determine the total phosphate and Fe^{2+}/Fe^{3+} concentration in the whole sludge.

2.3. Analyses

Firstly, around 50 mg of powdered sample dried at room temperature was added in a Teflon vessel with 10 mL of ultrapure HNO_3 (64.5 – 70.5% from VWR Chemicals). The mixture was digested in an Ethos Easy digester from Milestone equipped with an SK-15 High-Pressure Rotor. It reached 200 °C in 15 min, stayed at this temperature for 15 min, and cooled down for 1 h. The digestate was diluted, and their composition was evaluated with Inductively Coupled Plasma (Perkin Elmer, type

Optima 5300 DV) equipped with an Optical Emission Spectroscopy (ICP-OES). The rinse and internal standard solution were respectively 2% of HNO_3 and 10 mg/L of Yttrium. The software Perkin Elmer WinLab32 was used for data processing.

Microscopy observations were performed on the samples dried without centrifugation to avoid embedding the crystals in the sludge matrix, making the observations challenging. The light microscope used was a Leica MZ95 equipped with a Leica DFC320 camera. The Scanning Electron Microscope (SEM) apparatus was a JEOL JSM-6480 LV equipped with an Oxford Instruments x-act SDD Energy Dispersive X-ray (EDX) spectrometer. The accelerating voltage was 15 kV for a working distance of 10 mm. Before measurements, 10 nm-layer of gold were deposited on the samples using a JEOL JFC-1200 fine coater to make the surface electrically conductive. The software used was JEOL SEM Control User Interface for the SEM and Oxford Instruments Aztec for the EDX data processing.

For XRD and Mössbauer spectroscopy measurements, the samples were centrifuged and the centrate removed before drying to avoid precipitation from the soluble ions during drying. The samples were then pulverized in a mortar for analysis. The XRD device was a Bruker D8 Advance diffractometer in Bragg-Brentano geometry with a Lynxeye position-sensitive detector, with Cu-Kα radiation, range 10–80°2θ, step size 0.008°. The Bruker DiffracSuite.EVA software vs 5.2 was used for the peak assignment and identification. Quantification was done with Profex-BGMN Rietveld software. While XRD only focuses on the crystalline fraction, Mössbauer spectroscopy detects the iron in both crystalline and amorphous forms and is, therefore, a practical way to quantify vivianite. The ^{57}Fe Mössbauer absorption spectra were collected at 300 K with a conventional constant-acceleration spectrometer using a ^{57}Co (Rh) source. The velocity calibration was carried out using an α-Fe foil while the fitting of the spectra was performed using the software Mosswin 4.0 was used [17].

3. Results and discussion

3.1. Iron reduction

It can be assumed that anaerobic conditions were present in the three samples due to consumption of the oxygen by the bacteria's present in the sludge and the absence of aeration. The ferric iron present in the liquid and the solid phase was progressively reduced. Fig. 1 shows that when no iron or only ferrous iron was added, the reduction was completed within 24 h, while it required 72 h when additional ferric iron was added. The reduction kinetics were evaluated for the time 0–24 h for the experiment without extra iron and the experiment with ferrous iron addition, and 4–72 h when ferric iron was added to only consider the timeframe when the reduction takes place. The reduction followed a first-order kinetics in the three experiments (no additional iron R^2 =0.84, ferrous addition R^2 =0.99, ferric addition R^2 =0.98, which agrees with previous studies [13,44] on the reduction of iron oxide/-hydroxides). The first-order modeling allowed the reduction rate constants' determination at 0.03, 0.04, and 0.05 h^{-1} for the experiment without additional iron, the addition of ferrous and ferric iron, respectively. Those values aligned with those of Wang et al. [44] (k = 0.05–0.06 h^{-1}), who worked with settled activated sludge. They also carried out autoclaved experiments that showed that the reduction process was 95% biological-based, which is likely to be the major trigger for iron reduction in this study as well.

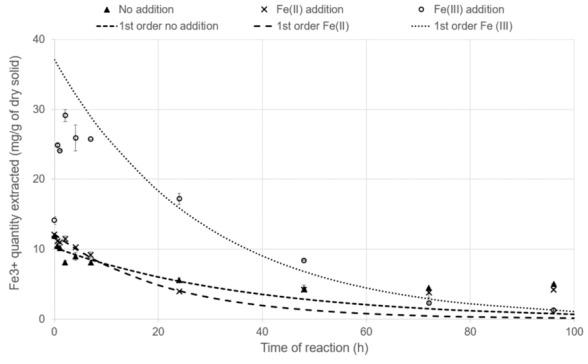

Fig. 1. Evolution of the ferric iron concentration after HCl extraction. The low initial content of Fe^{3+} can be explained by the 30 h of thickening at the WWTP before the sampling, allowing Fe(III) to be partly reduced. The dash lines represent the first-order fit and are valid until the reduction is over (0–24 h for no addition and Fe(II) addition and 4–72 h for Fe(III) addition). The data for 172 h, 216 h, and 264 h are not shown here since the Fe concentration reached a steady state by that time. The total iron content in the samples is 38, 51 and 53 mg/g of dry solids for the experiment with no addition, Fe(II) addition and Fe(III) addition.

In the current study, the initial specific iron reduction rate was 0.9 g Fe/g VS*h (VS=Volatile solids) when no iron was added. In comparison, it was 1.2 g Fe/g VS*h after both Fe(II) and Fe(III) dosing resulting in rate constants of 0.007 h^{-1} in the three cases. These rates are in the low range of the one previously observed by [26,33,44], ranging from 0.007 to 0.07 h^{-1}. The low specific rate observed in the current study can be explained by the fact that the reduction was already well-advanced when the samples were collected after 30 h of thickening (45–60% of the total iron was already Fe(II), Fig. 3). On the contrary, the samples collected in the other studies were fresh activated sludge in which Fe(II) would account for 10–30% of the total iron [33].

The reduced ferric iron was essentially from the solid phase since the soluble Fe^{3+} in all three experimental conditions stayed around 5–20 mg/L (0.15–0.6 mg/g of dry solid), which was negligible compared to the total quantity of Fe(III) reduced (Fig. 1). A part of the Fe (III) (1–3 mg/g of dry solids) persisted even after 11 days of experiments in anaerobic conditions, suggesting the presence of a minor and stable Fe (III) phase or partial oxidation of vivianite during sample manipulation. Extractions with HCl were used in this study to solubilize the iron present in the solid and study its oxidation degree. This method appeared to be suitable for this purpose since total iron recovery from the solids were 80 ± 9%, 87 ± 7%, and 86 ± 9% for the case of no iron, ferrous and ferric additions, respectively. The iron recovery after HCl extraction progressively increased with the time after which the sample was taken. Rasmussen and Nielsen [33] reported similar findings with 80–90% of recovery during HCl extraction and slightly higher recovery in sludge stored anaerobically for 2 days than in fresh sludge. This suggests that the iron species became increasingly soluble in HCl over time, which agrees with the progressive formation of vivianite and FeS_x, both soluble in HCl. In the current study, the iron compounds initially present in the thickened sludge and the Fe(III) compounds precipitated after the iron salts' addition were largely reduced in 2–4 days. It is important to note that not all iron sources are suitable for iron reduction and subsequent vivianite formation. Cheng et al. [6] showed that ferrihydrite (added to digested sludge) could be reduced within 5 days while the more stable hematite stayed inert throughout 30 days of incubation in anaerobic conditions.

The current results confirm what was already observed in a few studies involving short-term experiments: the iron reduction is relatively quick in sludge systems under anaerobic conditions. Additionally, this study reveals that the iron reduction is completed after 2–4 days, depending on the iron source used. The following section evaluates the correlation between iron reduction and vivianite formation.

3.2. Vivianite formation

In the current study, the formation of vivianite in thickened sludge was evaluated after a few days of storage under anaerobic conditions and, for some experiments, after the addition of iron salts. Vivianite could be observed in all the samples (besides in the initial thickened

sludge) by light microscope and SEM-EDX. The blue color of oxidized vivianite particles makes their identification relatively easy with a light microscope (Fig. 2). The particles observed by SEM, composed of agglomerates of needles/plates (Fig. 2), presented a similar morphology as vivianite observed in digested sludge [31,47], lake sediments [42], or synthesized vivianite [53]. The EDX scans of those particles indicated that iron and phosphorus were the main distinguishing elements present, with Fe/P molar ratios comprised between 1.3 and 1.7 (1.5 in pure vivianite).

Frossard et al. [12] reported that vivianite particles were smaller in non-digested sludge than after digestion. In the current study, the vivianite particles had a size in the range of 50–200 μm, which agrees with vivianite particles' size in digested sludge mentioned in the literature [30,48]. No significant size or morphology differences were observed depending on the time of sampling or oxidation degree of the iron salt used. Frossard et al. [12] reported that vivianite was more crystalline after digestion, while Wu et al. [52] observed that the iron phosphates were mostly amorphous in aerobic sludge with only a small fraction of vivianite. Mössbauer spectroscopy revealed that around 10% of the iron in the initial thickened sludge was vivianite. XRD did not detect any crystalline vivianite in this sample which suggests that the vivianite formed in the initial stage of anaerobic storage (after 30 h of thickening for this sample) could be amorphous or composed of tiny crystals. XRD confirmed that vivianite was present in all the other samples (Supplementary information). Additionally, the quantity of vivianite detected by XRD did not significantly increase between the time when the iron reduction was complete (24 h or 72 h according to Fig. 1) and after 168 h (Supplementary Information), which suggests that vivianite formation shortly followed iron reduction. It needs to be noted that the conclusions based on the XRD results are only made on the crystalline fraction of the sample and do not allow vivianite quantification.

3.3. Vivianite formation and iron reduction

Mössbauer spectroscopy is a powerful tool to analyze vivianite in sludge. This mineral gives two characteristic doublets, corresponding to the two sites where Fe^{2+} can be present in the vivianite structure (Fe^{2+} site A: Isomer Shift (IS) = 1.2 mm/s, Quadrupole Splitting (QS) = 2.4 mm/s and Fe^{2+} site B: IS = 1.2 mm/s, QS = 3.0 mm/s, [23,25,36]). During the present study, the samples could not be prepared under oxygen-free conditions at the WWTP site, and therefore, a part of the Fe^{2+} got oxidized [5,23]. Unfortunately, the signal of Fe^{3+} atoms in vivianite is strongly overlapping with those of FeS compounds and other Fe(III) species present in sludge, making the quantification of Fe^{3+} atoms in vivianite very complicated. We proposed in Prot et al. [31] to fit the Fe^{3+} in vivianite as a doublet with the parameters IS= 0.46 mm/s and QS= 0.63 mm/s. Still, it led to incoherent results with the current set of samples due to the higher share of oxidized vivianite (the samples in Prot et al. were protected from oxygen as much as possible). Therefore, an alternative way of fitting was used. Since all samples were exposed to oxygen for the same amount of time during drying, sample storage, and preparation, it was assumed that the vivianite was oxidized to the same degree in all the samples. Previous research on natural [9] and synthetic vivianite [36] showed that vivianite oxidation reached a (meta)stable equilibrium when around 30% of the Fe(II) was oxidized. It agrees with the measurements of dozens of our samples of synthetic vivianite and vivianite extracted from digested sludge (unpublished data). Therefore, the share of the iron present as Fe(II) in vivianite was determined with Mössbauer spectroscopy and multiply by (0.3/0.7) to obtain the share of ferric iron present in vivianite.

Mössbauer spectroscopy revealed that the share of the iron present as vivianite significantly increased from 11% in the initial thickened sludge to 50–55% in the sludge sampled after 24 h or 72 h of additional anaerobic residence time (Fig. 3). This percentage further increased by 10–15% after 168 h for the sample without iron addition and with the addition of Fe(II) salt, while it stayed constant when Fe(III) was added. The sampling time of 24 h (for no and Fe(II) addition) and 72 h (for Fe (III) addition) correspond to the moment when the iron reduction was almost completed (Fig. 1). The results show that 70–100% of the vivianite that formed after 168 h of anaerobic residence time was already formed after 24 h or 72 h. The fact that the vivianite formation was already so advanced after this time suggests that vivianite formation was strongly correlated to iron reduction. Before reaching the thickener, phosphorus is most likely adsorbed to amorphous ferric iron oxides and not present as strengite ($FePO_4$) since this mineral was never found in sludge system and was not identified in this study either. We suggest that under anaerobic conditions, both phosphorus and iron are released from the ferric (phosphate) iron oxides during the reduction process and immediately reprecipitate since the solubility of vivianite is very low. The part of the phosphorus accumulated by the polyphosphate accumulating organisms will also be released under anaerobic conditions and is expected to participate to the vivianite formation as well.

Azam and Finneran [1] and Zhang [54] already noticed that phosphorus removal in septic water led to vivianite formation. Cheng et al. [6] suspected that the Fe(III) reduction in WAS provoked vivianite formation (without solid evidence). Wang et al. [44] studied the microbial iron reduction in excess sludge and the associated kinetics. They confirmed that vivianite formed but stopped their experiment after 24 h, not getting the opportunity to evaluate the maximal potential of vivianite in undigested sludge. In the current study, the amount of vivianite formed compared to the vivianite's theoretical maximum could be calculated. Firstly, only the iron present as Fe(II) could potentially be vivianite (estimated by HCl extractions). Secondly, it was hypothesized that all the sulfur present in the sample would bind iron in a 1:1 molar ratio based on observations on digested sludge by Prot et al. [31]. If the sum of the Fe(II) present as FeS_x, as vivianite, and in solution is equal to

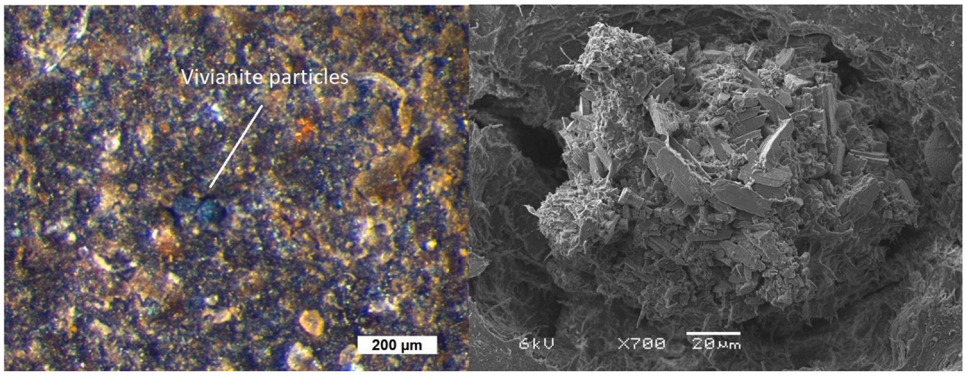

Fig. 2. Left: light microscope picture of blue vivianite crystals in the sample without extra iron addition after 24 h / Right: SEM picture of a vivianite particle in the sample without extra iron addition after 24 h.

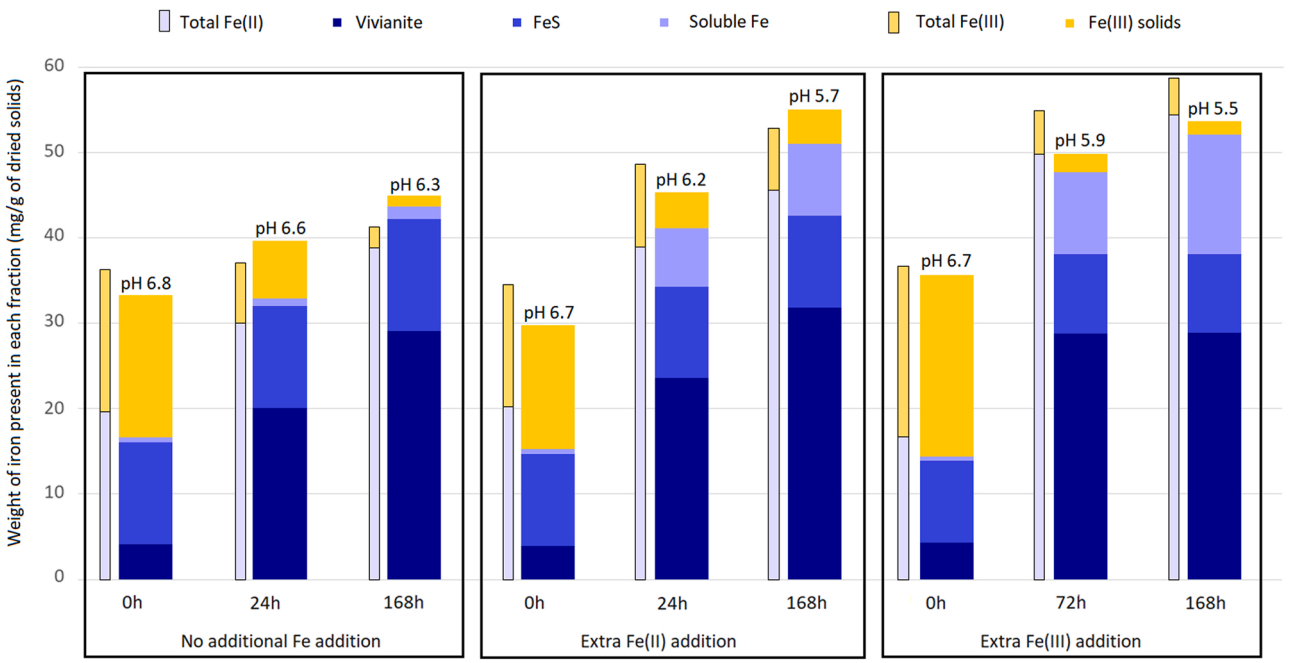

Fig. 3. Iron speciation in the seven samples analyzed. The thin bars represent the total quantity of Fe(II) and Fe(III) in the samples in mg Fe/g dried solids) and were measured by HCl extraction followed by ICP-OES. The thick bars represent the quantity of iron in each specific fraction in mg Fe/g dried solids. The quantification method for each iron fraction is described here. Vivianite: Mössbauer spectroscopy, FeS: assuming that all the sulfur in the solids bind iron in a 1:1 molar ratio, Soluble Fe: ICP-OES of the filtrate (>80% is Fe^{2+}). The vivianite quantity in the samples "0 h, no additional Fe" and "0 h, extra Fe(II)" were estimated based on the Mössbauer spectroscopy results of the sample "0 h, extra Fe(III)". Note that all the samples were under anaerobic conditions in the sludge thickener for 30 h before being sampled and used for the experiments; 0 h corresponds to 30 h of thickening at the WWTP.

the total Fe(II) obtained by HCl extraction, it indicates that there are no other Fe (II) phases. Fig. 3 shows that the sum of those 3 Fe(II) species is similar to the total Fe(II) in the samples with at least 24 h of additional anaerobic stage, suggesting that the ferrous iron present in the solids are either vivianite or FeS_x. After 30 h of sludge thickening (marked as 0 h on Fig. 3), not all the Fe(II) are accounted for (Total Fe(II)>soluble + vivianite + FeS_x), suggesting the presence of a ferrous species that could not be identified. It could be hypothesized that such specie could be a ferrous phosphate compound, intermediate to the formation of vivianite.

From these observations, it can be concluded that more than 80% of the vivianite that could form (based on the pool of Fe(II) in the samples that are not present in FeS_x) was formed as soon as the iron reduction was completed. It suggests that a sludge digester is not necessary for vivianite formation. The fact that vivianite formation is already well advanced after 24 h in the sludge with no iron addition hints that the addition of iron early in the wastewater treatment process could allow faster vivianite formation. The addition of iron in the waterline would also lead to a beneficial decrease of the soluble phosphate present in the effluent. The share of Fe(II) present as vivianite (Fe in vivianite/total Fe (II) on Fig. 3) increases from 67% to 74% (no Fe addition) and 63–71% (Fe(II) addition) between 24 h and 168 h. It suggests that even though vivianite immediately appeared after iron reduction, there is a small delay before its entire formation that could indicate the presence of an intermediate Fe(II) compound.

Around 120–130 mg/g of vivianite would form in both sludges amended with iron, hypothesizing that all the additional iron would be transformed into vivianite (calculations based on the elemental composition in Supplementary information assuming the formation of FeS and then vivianite). After 168 h, the quantity of vivianite formed was 85 mg/g of dry solids when no iron or Fe(III) was added, 97 mg/g when Fe(II) was added. This shows that only a low share of the iron added is transformed into vivianite. Fig. 3 indicates that this difference can mainly be explained by the lower pH of those sludges, resulting in 15–25% of the iron becoming soluble against less than 5% when no iron is added. Even though the additional iron is not immediately transformed into vivianite in those experiments, it does not mean that it is lost. The thickener's supernatant would be recirculated in the WWTP, diminishing the iron quantity needed for phosphorus removal in the activated sludge and vivianite formation in the thickened sludge. Alternatively, different iron sources could be used to prevent the considerable pH decrease observed in these experiments. It is important to note that after 168 h, around 50–55% of the phosphorus was bound as vivianite when no additional iron was dosed, while it accounted for 65–70% when extra iron was dosed. This increase is mainly due to the decrease in the sludge's initial phosphorus content for the samples with iron addition.

Wilfert et al. [48] showed that the amount of phosphorus present as vivianite in digested sludge increases with the Fe/P ratio. They also noticed that no pattern could be seen in surplus sludge samples. Data from four studies quantifying vivianite in undigested sludge were plotted along with the current research data to study possible correlation. The advancement of the vivianite precipitation, defined as the amount of vivianite formed compared to the maximum vivianite expected, did not show a clear pattern either, and an even larger variation in the vivianite formation advancement (Fig. 4). Some of the samples in Fig. 4 were WAS while others were surplus sludge, the second facing longer anaerobic retention times than the first. We hypothesize that these variations in vivianite content are mainly due to the different anaerobic/anoxic retention times of each sludge, strongly impacting the share of iron reduced, and thus vivianite formation. The data from the current study support this hypothesis. The share of iron present in the soluble phase (strongly depending on the pH) was not considered to calculate the vivianite formation advancement. Fig. 4 also shows that it is not rare that more than 60% of the vivianite is already formed before digestion, strengthening the fact that anaerobic digestion is not necessary to form substantial quantities of vivianite. It is important to note that the current study mostly investigated the effect of anaerobic/storage time on vivianite formation. Other differences between fermentative and methanogenic conditions like the bacterial community composition

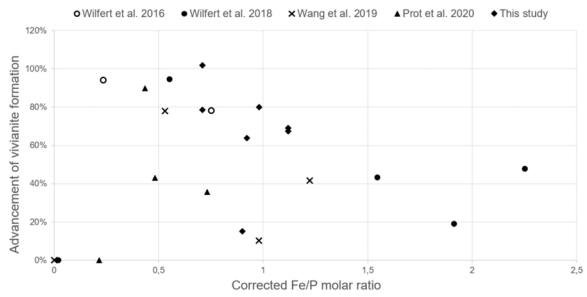

Fig. 4. Percentage of vivianite formed compared to the maximum vivianite that could form. The maximum vivianite that can form was calculated based on the sludge's elemental composition assuming that FeS forms first, immediately followed by vivianite. The corrected Fe/P molar ratio is based on the total iron minus the iron precipitating as FeS. All the samples represented in the figure are undigested sludge.

or the pH evolution may have an impact on vivianite formation and deserve a separate study.

3.4. The formation of sulfide does not provoke the destruction of the formed vivianite

Despite being out of the scope of the current research, iron-sulfur interactions are important when dealing with phosphorus recovery from iron-coagulated sewage sludge and will be briefly discussed here. The addition of sulfide to digested sludge or activated sludge provokes phosphorus release (Wilfert et al. [55]) [19]. It can also play a role in the chemical reduction of iron (Wilfert et al. [55]) [44,45]. Since FeS_x forms preferentially over vivianite during anaerobic digestion [31,35,48], it can be concluded that FeS_x is thermodynamically favored over vivianite. Therefore, there is a chance that under anaerobic conditions, as existing in excess activated sludge, the progressive reduction of sulfate to sulfide would leads to the formation of iron sulfide and the destruction the already formed vivianite.

Reduction of sulfate by sulfate reducing bacteria is a prerequisite for the formation of FeS_x and the destruction of vivianite [37]. Ingvorsen et al. [15] showed that sulfate reduction begins as soon as anaerobic conditions are present, as observed for the iron reduction in this study. The sulfate reduction is linear in the first 4–5 h after the anaerobic conditions start and only becomes exponential after this time [15]. Based on the kinetic model proposed by Ingvorsen et al. [15], more than 70% of the sulfate would already be reduced after 54 h of anaerobic exposure. This timescale matches with the observed iron reduction kinetics observed in this study (Fig. 1) suggesting that the reduction of sulfate and the formation of vivianite should happen simultaneously. Therefore, it can be hypothesized that iron sulfide formation would not happen after vivianite formation (and thus provoking vivianite's destruction), but rather at the same time. In the current study, a significant vivianite quantity was already formed after 54 h (30 h of thickening + 24 h of experiment) (Fig. 3). The fact that the vivianite quantity did not decrease after 198 h of anaerobic residence time (30 h of thickening + 168 h of experiment) (Fig. 3) reinforces this hypothesis. The relationship between vivianite and sulfide in sludge is more extensively discussed in Wilfert et al. [55] and Prot et al. [31].

3.5. The recovery of phosphorus from undigested sludge is relevant

According to the present study, a retention time of 2–4 days under anaerobic conditions in a sludge thickener or buffer tank would be sufficient for most iron to be reduced and for vivianite to form. For example, a buffer tank/fermenter could be added after the existing thickener since it presents a smaller footprint than a single thickener with a bigger retention time. The choice of working with already thickened sludge in this study was essentially to simulate the conditions that should be those of a scaled-up process. In the WWTP of Hoensbroek, the Fe/P molar ratio in the thickener is 0.9–1.0 and was increased to 1.4–1.6 during lab-scale experiments. According to vivianite's stoichiometry, a Fe/P molar ratio of 1.5 is necessary for maximal vivianite formation. Before any vivianite can form, 1 mol of iron is consumed per mole of sulfur in the sludge, assuming the same behavior as in digested sludge [31]. Considering this, the Fe/P molar ratio needed to achieve the stoichiometric formation of vivianite theoretically is 1.8 at the WWTP Hoensbroek.

According to Wilfert et al. [48], the phosphorus quantity present as vivianite is limited to 70–90%, even at a high Fe/P molar ratio. Therefore, a molar Fe/P ratio of 1.5 seems like a good alternative between a low quantity of vivianite formed and dosing excessive iron only to convert a small additional fraction of phosphorus to vivianite. If the WWTP Hoensbroek increased its iron dosage to match this ratio, it would correspond to an additional chemical cost of 45,000 € per year. Around 55% of the phosphorus would be present as vivianite based on the results of this study. Hypothesizing that the vivianite would be removed magnetically from the sludge with the same efficiency as the one shown at pilot-scale by Wijdeveld et al. [49] (80% of vivianite recovery from digested sludge), less sludge would have to be disposed of. The sludge disposal costs saving in the Netherlands would approximate 108,000 € per year to recover 460 tons of vivianite per year (corresponding to 7% of total solid reduction), compensating the additional chemical costs (detailed calculation in Supplementary Information). The operational costs and the commissioning of a larger thickener or an extra storage tank need to be considered to get a complete overview of the situation, but an entire economic study is not the scope of this research. It is worth noticing that the current approach does not involve the use of significant quantities of chemical to adjust the pH of the waste activated sludge to precipitate vivianite as in Cao et al. [4] but aims to take advantage of the spontaneous formation of vivianite in fermenting sludge.

Besides the phosphorus recovery, the additional iron dosing and 2–4 days anaerobic retention time could present other advantages. Firstly, the recirculation to the waterline of the iron-rich liquid fraction after thickening would lead to lower phosphorus in the effluent. Moreover, the additional iron earlier in the waterline would allow more time for vivianite to form whenever anaerobic/anoxic zones are encountered in the treatment, compared to dosing only in the thickener. Secondly, the reduction of the phosphorus content in the sludge is better for its valorization in cement kilns, according to Husillos Rodríguez et al. [14], which is the current disposal route Hoensbroek WWTP dewatered sludge. It should be noted that the share of phosphorus present as vivianite would be higher than 60% with the same iron dosing if the pH would be higher since the saturation index of vivianite strongly depends on the pH [20]. The addition of iron without a pH drop could be realized using other iron sources like drinking water sludge. A fermenting sludge at a pH < 6 is favorable for the production of Volatile Fatty Acids (VFA) while inhibiting methanogenesis, making it a valuable feed for biobased industries [16], for example, for the production of polyhydroxyalkanoates (PHA) [2].

It is essential to also take into consideration the effect that the iron dosing and the prolonged anaerobic retention time could have on vivianite scaling mitigation. Vivianite scaling is scarcely reported in the literature [3,22,29,41]. Still, it appears that the problem is occurring to a vast extent, according to Prot et al. [32]. It is especially the case in the WWTP of Hoensbroek, where scaling occurs in the pipeline between the thickener and the centrifuge, in the centrifuge itself, and the centrate pipe. Consequently, the centrifuge needs to be cleaned every 1–2 weeks, and the centrate pipe has to be cleaned or replaced every year. The iron reduction still ongoing after thickening appears to be an important trigger of the scaling formation [32]. The use of a longer residence time during thickening would promote vivianite formation and allow the iron reduction to be complete, which would help mitigate vivianite scaling.

4. Conclusion

During this study, iron-containing WAS was sampled after 30 h of thickening, and ferric or ferrous salts were added in some of the samples. The iron reduction and the vivianite formation were monitored in these samples. The iron reduction was completed after 2–4 days of total anaerobic storage ($k = 0.03–0.05\ s^{-1}$). The formation of vivianite was strongly correlated to the iron reduction since the share of iron present as vivianite increased from 10% (after 30 h of thickening at the WWTP) to 50–55% (after 1–3 days of additional anaerobic storage) after most of the iron was reduced. It corresponded to 75–100% of the vivianite that could potentially form, taking into account the preferential formation of FeS_x. Up to 70% of the phosphorus could be present as vivianite after additional iron dosing, even though a part of the iron was still soluble due to the pH decrease. This research's central message is that vivianite can form to a large extent not only in digested sludge but also in surplus WAS, opening the door for phosphorus recovery for WWTP not equipped with a sludge digester.

CRediT authorship contribution statement

T. Prot: Conceptualization, Methodology, Investigation, Writing – original draft, Writing – review & editing, Visualization, Supervision. **W. Pannekoek:** Methodology, Validation, Investigation. **C. Belloni:** Formal analysis, Writing – review & editing, Visualization. **A.I. Dugulan:** Formal analysis, Investigation, Visualization. **R. Hendrikx:** Formal analysis, Investigation, Visualization. **L. Korving:** Conceptualization, Methodology, Writing – review & editing, Supervision, Project administration, Funding acquisition. **M.C.M van Loosdrecht:** Conceptualization, Writing – review & editing, Supervision.

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 material

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jece.2022.107473.

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