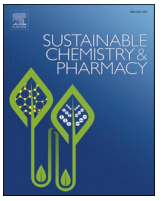
Sustainable Chemistry and Pharmacy 48 (2025) 102237

Contents lists available at ScienceDirect

Sustainable Chemistry and Pharmacy

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



Phosphorus recovery via vivianite precipitation in anaerobic digestion and fermentation processes: A comprehensive review

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ARTICLE INFO

Handling Editor: Borhane Mahjoub

Keywords:
Dissimilatory iron-reducing bacteria
Iron reduction
Iron phosphate
Phosphorus recovery
Sewage sludge
Water resource recovery facilities

ABSTRACT

Phosphorus recovery is gaining importance due to its supply risk. Wastewater treatment plants (WWTPs) are sinks of phosphorus from municipal and industrial discharges, making them ideal sites for recovery. In WWTPs, the dosage of $FeCl_3$ favours spontaneous formation of vivianite ($Fe_3(PO_4)_2{\cdot}8H_2O$). The optimal Fe:P molar ratio and pH are 2.5:1 and 7–9, respectively. These conditions can achieve phosphate recoveries as vivianite of 70–90 % after the anaerobic digestion (AD) stage. Nonetheless, excessive addition of iron ions and/or vivianite formation in AD can hinder organic matter degradation and lower biogas yields. Anaerobic fermentation (AF) and seeding have enhanced phosphorus recovery yields. The former mobilises more phosphorus and iron into the soluble fraction, while the latter promotes larger crystal sizes by reducing the supersaturation demand. Vivianite precipitation is a promising technology for phosphorus recovery due to its potential applications in industry and agriculture, all while supporting the circular economy. This literature review provides a comprehensive overview of current knowledge on vivianite precipitation in WWTPs, including detection and quantification methods. It also identifies key disadvantages of vivianite formation in WWTPs and provides valuable recommendations for future research.

1. Introduction

Phosphorus (P) is an essential resource mainly obtained from phosphate rock, which has become increasingly scarce due to rising fertiliser demand from the world's growing population (Shi et al., 2021). More than 80 % of phosphorus is used in agricultural applications (Law and Pagilla, 2019). Phosphate rock reserves are unevenly distributed worldwide, and the European Union (EU) has limited phosphate rock reserves and relies on imports from other countries. Morocco controls 75 % of world's phosphate rock reserves, with around 70 % of phosphate supply coming from the disputed region of West Sahara (Chrispim et al., 2019; Shi et al., 2021). Around 20 Mt of phosphate rock are extracted each year, a trend that could deplete reserves within the next 50–100 years (Wu et al., 2019). In 2014, the European Commission released a revised list of 20 critical raw materials, which included phosphate rock (European Commission, 2020). The list was updated in 2017 with the addition of 7 more materials, including phosphorus (Horváth et al., 2017).

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https://doi.org/10.1016/j.scp.2025.102237
Received 7 July 2025; Received in revised form 19 September 2025; Accepted 6 October 2025

Phosphorus rock and phosphorus remain classified as critical raw materials in the latest report (European Commission, 2020).

Phosphorus emissions converge in wastewater treatment plants (WWTPs), where phosphorus is mainly present as phosphate ions (PO_4^{3-}-P). Recovering this phosphorus could meet 15−20 % of global phosphorus demand (Yuan et al., 2012). Consequently, phosphorus recovery in WWTPs represents a potential solution to its depletion. Moreover, phosphorus recovery in WWTPs would reduce PO_4^{3-}-P concentrations in discharges, thereby minimising the risk of eutrophication in the receiving water bodies. The most widespread technologies for phosphorus removal in WWTPs are (i) chemical phosphorus removal (CPR) using aluminium and iron salts and (ii) enhanced biological phosphorus removal (EBPR) based on microbial transformation (Wilfert et al., 2015). In CPR, iron and aluminium salts are added during primary or secondary clarifier to remove phosphorus, where they also act as coagulants. Iron salts are more widely used than aluminium salts due to their lower cost (Wilfert et al., 2015). These iron salts can precipitate with phosphorus as vivianite.

Vivianite precipitates are present in the WWTP sludge, especially in digested sludge, due to anaerobic conditions. Its potential recovery could promote the circular economy, while simultaneously reducing mineral encrustation in WWTPs (Prot et al., 2021; Wilfert et al., 2018). Vivianite can be applied in various industries, serving multiple purposes, such as a precursor in Li-ion secondary batteries (Satyavani et al., 2016) and as a fertiliser (De Santiago et al., 2013). Notably, higher phosphate recoveries in WWTPs can be obtained via vivianite precipitation because a large percentage of phosphorus accumulates in the sludge (60 % of PO_4^{3-}-P with respect to the total phosphorus) compared to struvite precipitation from anaerobic digestion (AD) supernatants (30−40 % of PO_4^{3-}-P with respect to the total phosphorus) (Wu et al., 2019). Various lab-scale studies have confirmed the viability of recovering phosphorus via vivianite precipitation in WWTPs (Cao et al., 2019; Heinrich et al., 2023; Wang et al., 2023).

Vivianite was detected in WWTPs with CPR using ferrous iron. Wilfert et al. (2015) reported that before the anaerobic digestion (AD) stage, 43 % of the total iron was present as vivianite, while after AD, this percentage increased to 60−67 %. Furthermore, if there is an excess of iron during the AD stage, up to 80−90 % of the phosphorus in digested sludge can be present as vivianite (Wijdeveld et al., 2022). Vivianite precipitation is an emerging process for phosphorus recovery in WWTPs. The main factors influencing vivianite precipitation are the Fe:P molar ratio, pH, and sulphate or sulphur content (Amin et al., 2024). According to Heinrich et al. (2023), vivianite production in digested sludge increases with higher iron content. The optimal pH range reported for vivianite formation is 6–8 and 6−7 by Cao et al. (2019) and Eshun et al. (2024), respectively. pH values close to 6 have facilitated the investigation of vivianite precipitation during anaerobic fermentation (AF). Furthermore, the release of phosphorus and iron from the sludge is higher at acidic pH conditions (Cao et al., 2019; Hu et al., 2022; Wen et al., 2022; Wu et al., 2020a).

Some recent reviews in the literature that address the topic of phosphorus recovery via vivianite precipitation in WWTPs. These reviews primarily focus on the following topics: (i) formation mechanisms and natural occurrence of vivianite, (ii) factors affecting vivianite precipitation, (iii) iron-phosphorus interaction in wastewater, (iv) technique to identify and quantify vivianite, and (v) applications of vivianite in the environmental field (Chen and Song, 2022; Rothe et al., 2016; Wilfert et al., 2015; Wu et al., 2019; Yuan et al., 2021; Zhang et al., 2022). Nevertheless, there are relevant topics that have not been addressed in detail, including the formation of vivianite during AD and AF stages, and the effect of vivianite and iron ions on biogas production.

This literature review provides a comprehensive analysis of phosphorus recovery as vivianite in the stages of AD and AF in WWTPs. The review was carried out using the PRISMA® methodology and aims to elucidate several scientific and technological aspects, including the characteristics, formation conditions, potential applications and techniques to quantify of vivianite in WWTPs. This review also includes a bibliometric analysis of vivianite research.

2. Methodology

A systematic review was carried out using the PRISMA® methodology (Urrútia and Bonfill, 2010) considering peer-review papers published between 1967 and 2024. Search equations that included Boolean operators (i.e. AND, OR) were developed (Table 1) and subsequently executed in SCOPUS® database. After removing duplicates, a total of 132 publications were identified, and their metadata were downloaded in CSV format for further review in Excel®. The title, keywords, and abstract were then reviewed to check whether the paper was related to vivianite precipitation in WWTPs. This process narrowed the selection down to 52 publications. Following a thorough review of their full content, all 52 publications were selected for detailed analysis in this review.

Table 1
Search equations used to find relevant publications in SCOPUS®.

ID	Search Equation	Results
A	vivianite AND phosphorus AND wastewater AND sludge OR supernatant AND “anaerobic fermentation” OR “anaerobic digestion” OR co-fermentation	26
B	vivianite AND phosphorus AND wastewater AND sludge OR supernatant AND “anaerobic fermentation” OR “anaerobic digestion” OR co-fermentation AND “magnetic separation”	2
C	vivianite AND phosphorus AND wastewater AND “anaerobic fermentation” OR “anaerobic digestion” OR co-fermentation	28
D	vivianite AND phosphorus AND “anaerobic fermentation” OR “anaerobic digestion” OR co-fermentation	58
E	vivianite AND phosphorus AND “anaerobic fermentation” OR “anaerobic digestion” OR co-fermentation AND sludge OR supernatant	55
F	vivianite AND phosphorus AND “anaerobic fermentation” OR “anaerobic digestion” OR co-fermentation AND sludge OR supernatant AND “mineral precipitation”	1
G	vivianite AND phosphorus AND wastewater OR “wastewater treatment plant”	106

2.1. Main countries and researchers in vivianite research

The publications were analysed through Excel® and Bibliometrix® software (Fig. 1), where the intensity of the colour indicates the percentage of publications published in each country. Moreover, all files were downloaded in RIS format to uploaded then into the VosViewer® bibliometric software to create a co-occurrence map of authors (Fig. 2). This approach facilitated the identification of the connections between vivianite and main researchers on this topic.

As depicted in Fig. 1, China is the leading country in vivianite research, contributing 63 % of the publications reviewed. The Netherlands is the second contributor to vivianite research with 13 % of the publications. The significant disparity in research output between these two countries and others suggests that vivianite research is either in its early stages or has not been as thoroughly explored in other parts of the world. Accordingly, international research collaborations could provide more knowledge and advance the development of this technology.

Fig. 2 shows the co-occurrence map of authors, which revealed four distinct clusters distinguished by colours (green, yellow, blue, and purple). This analysis also allowed to identify the main authors, and the research institutes engaged in this field. Authors with more than 4 publications are: (i) Xin Wang from Nankai University (7 papers, blue cluster), (ii) Mark C.M. Van Loosdrecht from Delft University of Technology (6 papers, green cluster), (iii) Wu Yang from Hohai University (6 papers, yellow cluster), (iv) Li Nan from Tiajin University (5 papers, blue cluster), (v) Wang Shu from Tiajin University (5 papers, blue cluster) and (vi) Leon Korving from the European Centre of Excellence of Sustainable Water Technology (5 papers, green cluster). The blue and red clusters have a high influence on authors from China, the green cluster shows authors from The Netherlands, and the purple and yellow clusters show relationships between authors from China and The Netherlands. Fig. 2 facilitates an understanding of the collaborative networks and the intellectual landscape of vivianite research, showing how knowledge and research efforts are distributed and interconnected.

2.2. Keywords in timescale in vivianite research

The VosViewer® bibliometric software was used to create a co-occurrence map of keywords (Fig. 3), which facilitates the identification of the connections between vivianite and related terms. Vivianite precipitation in WWTPs has gained significant attention over the last five years, emerging as a novel research topic and laying the foundation for future research and application. The co-occurrence map of keywords indicates that the most important word in this topic is *phosphorus*, followed by *vivianite* and *sewage* (Fig. 3). These three keywords are interrelated, indicating that phosphorus can be recovered as vivianite in sewage. In Fig. 3, the colour scale is used to show the timescale for the development of various concepts. Fig. 3 shows that initially *vivianite* (*ferric phosphorus)* precipitation was studied in sewage sludge anaerobic digesters. Then, the *phosphorus recovery* as vivianite gained interest. The addition of different sources of *iron* to facilitate vivianite recovery in WWTPs was also studied. The added iron could be introduced either as *ferrous* (Fe^{2+}) or *ferric* (Fe^{3+}) ions. Currently, studies mainly focus on *anaerobic fermentation* because it operates at lower pH values compared to anaerobic digestion. Lower pH values favour the release of phosphorus from inorganic and organic compounds. Recently, the *microbial community* in sludge has been studied, particularly the presence of iron reducing bacteria, because iron reduction is important for vivianite formation.

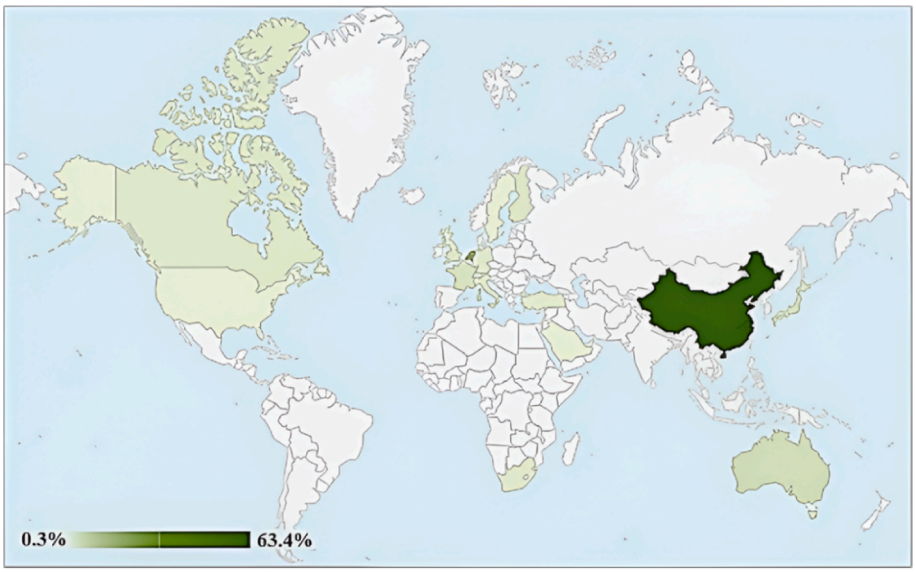

Fig. 1. World map illustrating the distribution of publications by country. The colour scale represents the percentage of publication, with higher intensity indicating a higher number of publications.

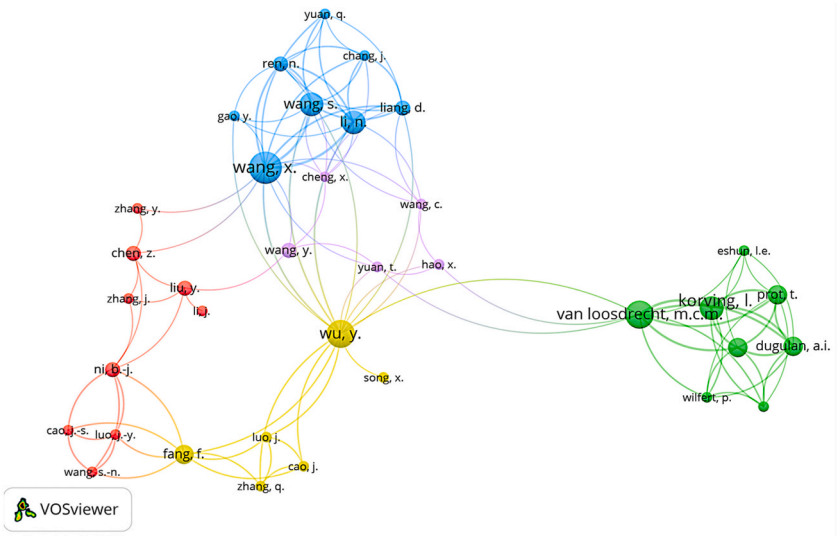

Fig. 2. The co-occurrence map of authors from 2019 to 2024. Each colour identifies the main collaborations between authors.

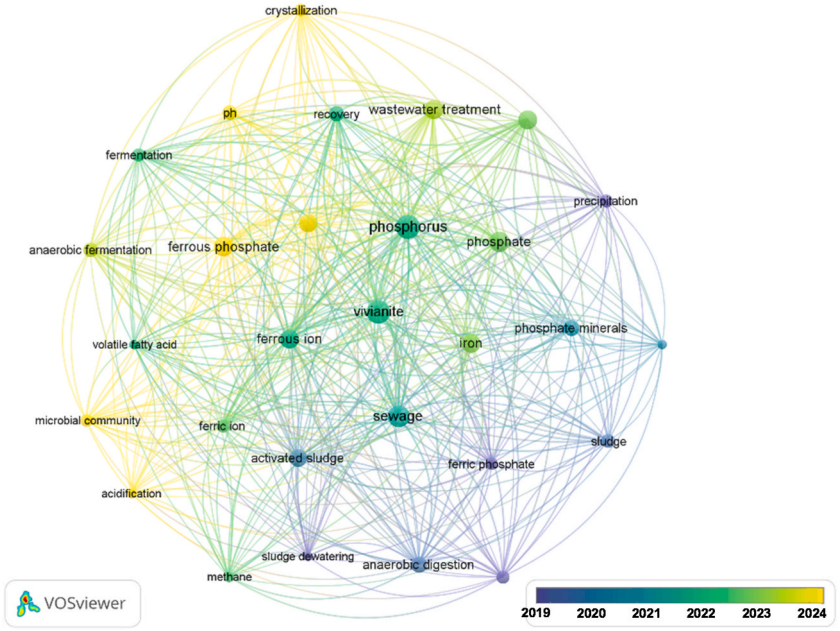

Fig. 3. The co-occurrence map of keywords from 2019 to 2024. The colour scale indicates the period of appearance for each of keywords.

3. Context on the recovery of vivianite

3.1. Vivianite

Vivianite ($Fe_3(PO_4)_2{\cdot}8H_2O$) is a hydrated iron phosphate mineral commonly found in natural environments. Vivianite precipitation naturally occurs under anaerobic conditions (reducing environment) that have a high iron and phosphate content, such as river sediments and muds, canals and lakes (Chen and Song, 2022). The formation enthalpy and Gibbs energy of vivianite at 298.2 K are -5217 kJ·mol^{-1} and -4439 kJ·mol^{-1}, respectively (Ogorodova et al., 2017). These values suggest that thermodynamically the reaction of vivianite formation is spontaneous.

Vivianite is colourless in its original state, but it changes colour when exposed to oxygen and/or light (Chen and Song, 2022; Prot et al., 2020). Vivianite can exhibit hues of blue, green, or black, depending on the oxidation degree of Fe^{2+} (Chen and Song, 2022). These hues of blue were used as pigment in paintings in Europe in the early sixteenth century (Cruz et al., 2018).

Vivianite is sparingly soluble in water and remains stable in absence of oxygen and under non-sulphidic conditions. Its precipitation requires a minimum Fe:P molar ratio of 1.5:1 (Eq. (1)) and a pH of 7–9 (Jowett et al., 2018; Wilfert et al., 2015). Vivianite has a paramagnetic behaviour, with an average magnetic susceptibility of $1.05{\cdot}10^{-6}$ $m^3{\cdot}kg^{-1}$ (Minyuk et al., 2013). This property can facilitate its recovery using magnetic extraction techniques (Prot et al., 2020).

In WWTPs, vivianite is predominantly found in digested sludge, where the Fe^{2+} and PO_4^{3-}-P concentrations increase and exceed the solubility product ($K_{sp} = 10^{-36}$) (Bradford-Hartke et al., 2021; Wilfert et al., 2018). The precipitation process involves the stages of nucleation and crystal growth, both of which are influenced by factors such as pH, Fe:P molar ratio, temperature, microbial activity to reduce iron, the presence of competing ions and the presence of external solids as seeds (Wang et al., 2023).

$$3\ Fe^{2+}(aq) + 2\ PO_4^{3-}(aq) + 8H_2O(l) \rightarrow Fe_3(PO_4)_2{\cdot}8H_2O(s) \quad \text{(Eq. 1)}$$

3.2. Potential uses

Vivianite is utilised and researched for several applications, primarily as a fertiliser, but also as a heavy metal reducer in soils and sediments, as a catalyst for degrading emerging pollutants, and to produce secondary lithium-ion batteries.

Vivianite contains PO_4^{3-}-P and Fe, making it a suitable slow-release fertiliser for crops (Díaz et al., 2010; Wu et al., 2019). Fodoué et al. (2015), who assessed the effect of vivianite on bean plants, concluded that it could be used as an alternative of phosphates fertiliser. Fodoué et al. (2015) also showed that vivianite had a positive effect in the ramifications of stem, densification and extension of leaves and bean yield. Vivianite can also be used as an iron fertiliser to address iron deficiency, which causes chlorosis (yellowing) in plants, a common issue in calcareous soils (Abadía et al., 2011; De Santiago et al., 2013). Iron fertilisers are typically grouped into synthetic Fe-chelates (e.g. iron chelate of ethylenediamine di-2-hydroxyphenyl acetate ferric (FeEDDHA)) and inorganic Fe-compounds (e.g. $Fe_2(SO_4){\cdot}7H_2O$, Fe oxides and hydroxides) (Abadía et al., 2011; Díaz et al., 2010). Synthetic Fe-chelates remain soluble across a wide pH range, making them effective in calcareous soils. However, they are expensive and mainly used in high-value crops. In contrast, inorganic Fe-fertilisers are more affordable, but their use in calcareous soil is inefficient because high pH levels convert them into insoluble compounds (Abadía et al., 2011). Vivianite has proven to be an effective iron fertiliser due to its high iron content and ability to dissolve in calcareous soils. This dissolution is facilitated by the carboxylate chemicals generated by roots and the poorly crystalline Fe^{3+} oxides resulting from the Fe^{2+} oxidation of vivianite (De Santiago et al., 2013; Díaz et al., 2010; Rosado et al., 2002). Rosado et al. (2002) demonstrated that vivianite can reduce iron chlorosis in olive trees grown in calcareous soils. Díaz et al. (2010) and De Santiago et al. (2013) compared the effectiveness of vivianite and FeEDDHA in correcting iron chlorosis. In strawberry plants, Díaz et al. (2010) reported that vivianite was as effective as FeEDDHA in remediating leaf iron chlorosis and also had a positive effect on the number of leaves and shoot length. In grapes plants, De Santiago et al. (2013) showed that vivianite was more effective than FeEDDHA remediating leaf iron chlorosis and the number of leaves. Nonetheless, the roots and shoots were larger with FeEDDHA. De Santiago et al. (2013) also indicated that the addition of vivianite with compost improved root and shoot growth, being as effective as FeEDDHA.

Vivianite can also be used as a heavy metal reducer in soils, effectively mitigating pollutants such as cobalt (Co), mercury (Hg), strontium (Sr), and uranium (U) (Etique et al., 2021; Veeramani et al., 2011). Etique et al. (2021) added vivianite in soil as electron

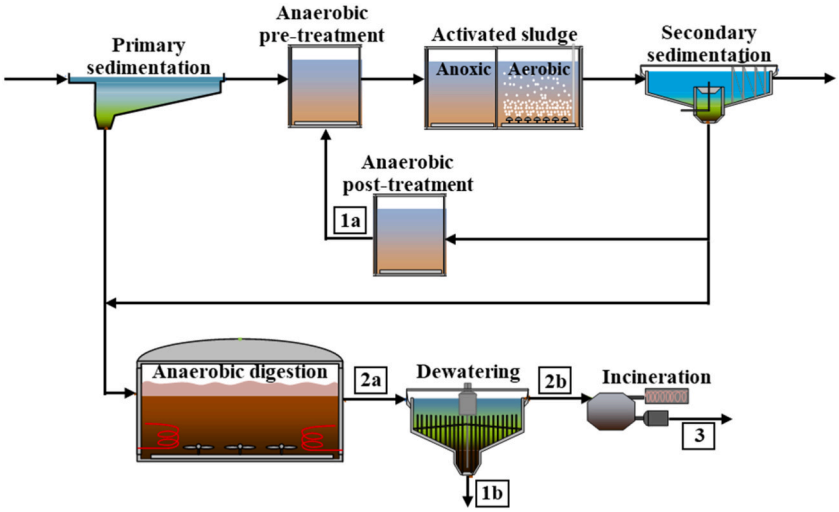

Fig. 4. WWTP with enhanced biological phosphorus removal adapted from Desmidt et al. (2015), identifying locations for phosphorus recovery: (1a) effluent from anaerobic fermentation of return activated sludge, (1b) supernatant from digested sludge dewatering, (2a) digested sludge, (2b) digested sludge cake from dewatering and (3) sludge ash after incineration.

donor and demonstrated that the reduction of Hg^{2+} to Hg^0 occurred quickly and efficiently under anoxic conditions when the Fe^{2+}:Hg^{2+} molar ratio was greater than or equal to 1:1. Veeramani et al. (2011) showed that vivianite favoured the reduction of U^{6+} to monomeric U^{4+} due to electron transfer from Fe^{2+} to U^{6+}. In environment science, Yi et al. (2022) showed the catalytic capabilities of vivianite to activate persulfate, produce reactive oxygen species for the removal of tetracycline antibiotics using LED UV, visible, and solar light. Another application of vivianite is as an iron-phosphate in the synthesis of lithium iron phosphate ($LiFePO_4$) for the production of Li-ion secondary batteries (Wu et al., 2019), where $LiFePO_4$ serves as the cathode material (Satyavani et al., 2016).

4. Vivianite precipitation in WWTPs

4.1. Phosphorus in WWTPs

WWTPs treat municipal and industrial sewage from their catchment area. WWTPs remove organic and inorganic pollutants in sewage using a combination of physical, chemical and biological processes (Desmidt et al., 2015). In sewage, phosphorus comes from various sources including human excretions (50 % from human urine), household waste, phosphorus-based detergents and industrial discharges (Simbeye et al., 2023).

Phosphorus recovery can be achieved from various sources including wastewater, sewage sludge, and sludge ash. In WWTPs with EBPR (Fig. 4), phosphorus can be recovered in the effluent of an anaerobic chamber fermenting return activated sludge (1a) or in the AD supernatant (1b). Other points for PO_4^{3-}-P recovery in WWTP include digested sludge (2a) and thickened digested sludge after dewatering (2b). Phosphorus can also be recovered from bottom ashes from sludge incineration (3). Phosphorus recovery from sewage sludge or sludge ash has been reported to reach up to 80 % (Cao et al., 2019; Desmidt et al., 2015), while recovery from wastewater can range from 40 to 50 % depending on the influent characteristics (Garcia-Belinchón et al., 2013). The phosphorus concentration in AD supernatants in WWTPs depend on the phosphorus removal process implemented. WWTPs with a chemical phosphorus removal process have PO_4^{3-}-P concentrations below 75 mg PO_4^{3-}-P·L^{-1}, while WWTPs with an enhanced biological phosphorus removal process have PO_4^{3-}-P concentrations ranging between 75 and 300 mg PO_4^{3-}-P·L^{-1} (Garcia-Belinchón et al., 2013).

In the water line of the WWTPs, the PO_4^{3-}-P concentration is reduced through precipitation, biological assimilation, and/or binding with coagulants. The phosphorus concentration in the liquid stream decreases while simultaneously increasing its concentration in the sludge. Within the EU, it is estimated that around 370 kt·$year^{-1}$ of phosphorus are present in WWTP sludge (Prot et al., 2019; Van Dijk et al., 2016), predominantly as Fe–P compounds and phosphorus bound to biomass (Heinrich et al., 2023). This bound phosphorus can be released from waste activated sludge (WAS) through various mechanisms: (i) Fe^{3+} reduction of P Fe^{3+} compounds under anaerobic conditions by dissimilatory iron-reducing bacteria (Chen and Song, 2022), (ii) action of chelating substances such as oxalate or citrate, which chelate iron and release PO_4^{3-}-P, (iii) presence of anions such as bicarbonate or hydroxide, which desorb PO_4^{3-}-P from iron oxides and precipitate with iron, (iv) pH changes that release PO_4^{3-}-P from Fe–P precipitates, and (v) degradation of organic matter (Wilfert et al., 2015).

Cui et al. (2024) showed that during the AD stage, organic phosphorus was transformed into inorganic phosphorus (inorganic compounds containing PO_4^{3-}-P). The inorganic phosphorus content increased as the AD process progressed, reaching percentages of 70–80 % of the total phosphorus content in the sludge. The authors stated that organic phosphorus was first released as soluble phosphorus and subsequently precipitated with the available cations, forming inorganic phosphorus salts that were trapped in the sludge matrix. The addition of iron to anaerobic digesters favours the formation of P–Fe compounds such as vivianite.

4.2. Iron in WWTPs

Iron concentration in WWTPs influents range 0.5–1.5 mg·L^{-1} (Wilfert et al., 2015). The primary sources of iron are the infiltration of iron-rich groundwater into the sewer system and the presence of iron in human excreta (Wilfert et al., 2018). During the treatment process, the iron concentration may increase due to the dosage of iron salts, which can be used for several purposes, including (i)

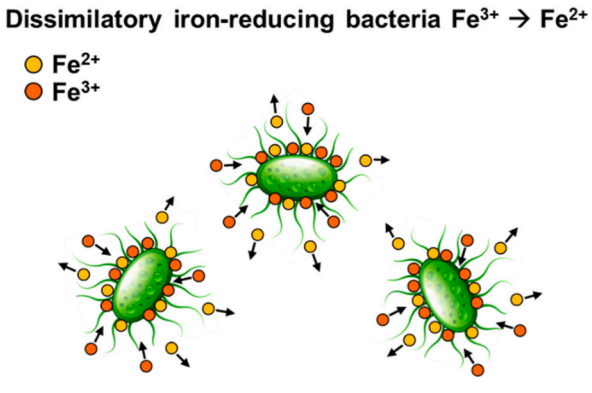

Fig. 5. Dissimilatory iron-reducing bacteria under anaerobic conditions.

facilitating phosphorus removal through immobilisation in precipitable compounds, (ii) acting as a coagulant to improve sludge dewaterability, and (iii) limiting hydrogen sulphide concentration in biogas (Cao et al., 2019; Heinrich et al., 2023; Wilfert et al., 2015).

Among the iron-based flocculants, $FeCl_3$ is the most widely used flocculant in WWTPs (Cao et al., 2019). $FeCl_3$ has an acidic behaviour when hydrolysed in water (Chen and Song, 2022). $FeSO_4$ is also used mainly due to its cost-effectiveness in comparison to $FeCl_3$ (Cao et al., 2019; Heinrich et al., 2023). According to Chen and Song (2022), $FeSO_4$ is priced at 0.055 $\$\cdot kg^{-1}$, while $FeCl_3$ is prices at 0.262 $\$\cdot kg^{-1}$. Another advantage of $FeSO_4$ is that it does not require reduction to Fe^{2+} for vivianite precipitation. However, $FeSO_4$ addition led to the formation of Fe–S compounds and the reduction of sulphate to sulphide in anaerobic environments. These factors reduce the iron availability, decrease vivianite yield, and reduce the amount of organic matter for methane production (Heinrich et al., 2023; Prot et al., 2020). In contrast, $FeCl_3$ requires reducing Fe^{3+} to Fe^{2+} for vivianite precipitation, but its addition does not introduce sulphates into the anaerobic digester. Amin et al. (2024) and Wilfert et al. (2018) indicated that $FeCl_3$ is effectively reduced from Fe^{3+} to Fe^{2+} in clarifiers, thickeners and anaerobic digesters, making Fe^{2+} the dominant oxidation state. Dissimilatory iron-reducing bacteria are responsible for reducing Fe^{3+} to Fe^{2+} (Fig. 5) (Rothe et al., 2016). This is relevant because the availability of Fe^{2+} controls vivianite formation.

4.3. Vivianite precipitation

As discussed in Section 4.1. and 4.2., vivianite precipitation in the sludge can occur spontaneously due to the presence of phosphorus and iron at various stages of the WWTP. The authors would like to clarify that the terms “anaerobic fermentation” and “anaerobic digestion” do not refer to the same process. The concept of “anaerobic fermentation” refers to a process aiming the accumulation of low molecular weight organic molecules (e.g. carboxylic acids and alcohols) by limiting the growth of methanogenic archaea. The term “anaerobic digestion” refers to a process that aims to increase methanogenic archaea activity for biogas production (Perez-Esteban et al., 2022).

4.3.1. Anaerobic digestion

In digested sludge, the main forms of phosphorus are P–Fe solid compounds (20–60 %), phosphorus bound to organic matter (5–45 %), and minor proportion phosphates bound to carbonates (≤10 %) (Heinrich et al., 2023). The inorganic compounds commonly found in digested sludge include quartz, calcite, and vivianite. However, struvite, enstatite, albite, microcline, and halite can also be found (Heinrich et al., 2023). The proportion of phosphorus in the form of vivianite is variable and depends on the WWTPs influent and operating conditions. Vivianite can precipitate at a neutral pH that is within the AD pH range. According to Wilfert et al. (2015), vivianite is the predominant phosphorus component in both digested sludge and wasted activated sludge. Heinrich et al. (2023), who evaluated 16 WWTP, showed that the highest phosphorus content as vivianite in digested sludge was found in WWTPs with a high iron concentration and a low sulphur concentration. In another WWTP, Amin et al. (2024) reported that the transformation of Fe^{3+} to Fe^{2+} occurs in clarifiers and thickeners before the sludge is fed into the anaerobic digesters. This is relevant because the availability of Fe^{2+} controls vivianite formation in anaerobic digesters (Amin et al., 2024; Heinrich et al., 2023).

Yuan et al. (2020) showed that adding $FeCl_3$ (500 $mg\cdot L^{-1}$) to the anaerobic digester reduced by 95.4 % the phosphorus concentration, resulting in a concentration of 3.4 mg $PO_4^{3-}\cdot L^{-1}$. In Yuan et al. (2020), vivianite was the dominant precipitate containing

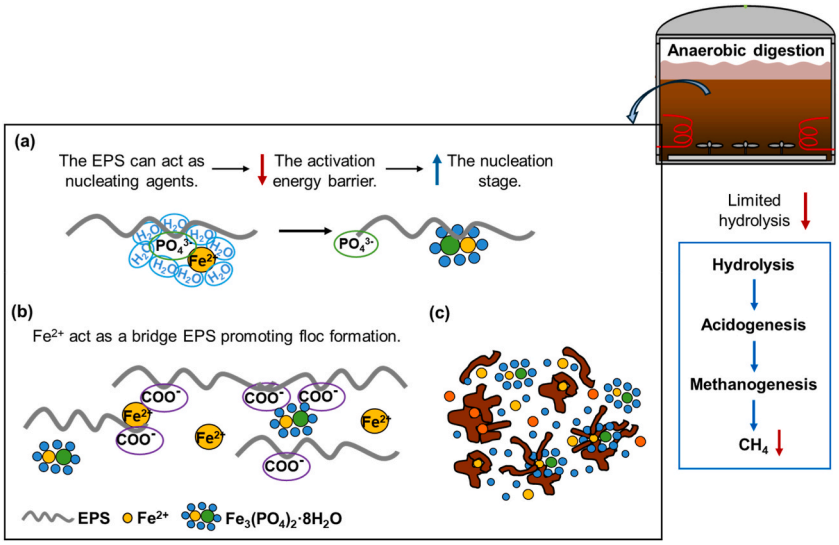

Fig. 6. Interferences of vivianite precipitation in anaerobic digesters: (a) interference of vivianite with EPS, (b) interference of Fe^{2+} with EPS and (c) interference of organic matter with Fe^{2+}, Fe^{3+} and vivianite.

phosphorus. The methane production in the anaerobic digester was not affected by the addition of $FeCl_3$ or formation of vivianite. Prot et al. (2020) doubled the Fe dosage at the WWTP in the Netherlands, where $FeSO_4$ was dosed in the aerated tank to remove chemical oxygen demand (COD) and phosphorus. The increase in iron favoured the yield and kinetics of vivianite precipitation in the AD. The methane production yield in the AD was not affected in accordance with Yuan et al. (2020).

In contrast, Wang et al. (2022) showed that the presence of vivianite decreased the methane yield in the AD process. The study was carried out in biochemical methane potential (BMP) assays, where vivianite was added externally and not formed in the digester as in Yuan et al. (2020) and Prot et al. (2020). Specifically, the cumulative methane yield in the control digester after 30 days was 104 $mL{\cdot}g^{-1}$ of VS (volatile solids), whereas the presence of vivianite decreased the cumulative methane yield to 94, 82 and 77 $mL{\cdot}g^{-1}$ VS at vivianite concentrations of 100, 300, 500 mg $P{\cdot}L^{-1}$, respectively. Wang et al. (2022) showed that vivianite limits the degradation of tightly bound extracellular polymeric substances (EPS), as vivianite and iron combines with certain organic functional groups, restricting the release and degradation of these organic compounds. EPS contain polysaccharides and proteins that may have phosphate groups, giving a negative charge to the biofilm matrix and interacting with cations such as Fe^{2+}; this interaction can lead to the formation of vivianite (Fig. 6 (a)) (Hao et al., 2022). Furthermore, in the precipitation of vivianite, the EPS can serve as nucleating agents, reducing the activation energy barrier and thus facilitating the nucleation step on the surface of the EPS (Hao et al., 2022). Divalent cations, such Fe^{2+}, can act as a bridge between the negatively charged carboxyl groups (COO^-) of the EPS, promoting floc formation and not their degradation (Fig. 6 (b)). These factors limit the hydrolysis stage, where complex organic matter degrades into soluble organic matter, thereby reducing the amount of acetate and hydrogen available for methane production. Cui et al. (2024) showed that organic compounds interact with Fe^{2+} and/or vivianite, reducing the availability of Fe^{2+} or the formation of vivianite (Fig. 6 (c)).

Hao et al. (2022) reported *Rhodoferax ferrireducens* as the main genus among dissimilatory iron-reducing bacteria in AD, which uses acetate as electron donor. The acetoclastic methanogens also utilise acetate for methane production, leading to competition for this substrate. This competition can either decrease the production of methane or lower the rate of ferric reduction (Hao et al., 2022). Hao et al. (2022) and Wang et al. (2022) showed that vivianite formation and/or iron addition can negatively affect methane production. However, it should be noted that WWTP already have a system for chemical phosphorus removal through the addition of iron, which leads to the formation of vivianite. Further research is needed to evaluate the impact of vivianite presence and formation on AD performance.

The use of seeds in the crystallisation stage promotes larger crystal sizes by lowering the thermodynamic demand in the metastable zone (Amjad et al., 2023). Additionally, certain seed materials like carbon nanotubes in vivianite crystallisation enhance electron transfer between the mineral and the microorganisms, or provide a larger contact area between PO_4^{3-}-P and Fe^{2+} (Wu et al., 2023). Wu et al. (2023) studied magnetic biochar with iron as seed material in AD, using iron oxyhydroxide oxide (FeOOH) at a Fe:P molar ratio of 1.5:1 as the iron source. They showed that the addition of magnetic biochar with a concentration of 0.52–0.75 $g{\cdot}g^{-1}$ VS (volatile solids) enriched both dissimilatory iron-reducing bacteria and methanogenic communities, promoting Fe^{3+} reduction and methane production. Specifically, the addition of magnetic biochar increased the PO_4^{3-}-P recovery yield by 45 % and the methane yield by 27 %. The dosage of magnetic biochar provided a large surface area, increasing the aggregation sites of small vivianite particles (the vivianite particle size increased from 32 to 102 μm). This study justified the increase in methane production to the release iron ions that facilitated the decomposition of long-chain fatty acids and improved the metabolic activity of microorganisms. However, magnetic biochar concentrations greater than 0.75 $g{\cdot}g^{-1}$ VS hindered vivianite formation and methane production due to the increase in humic acid and EPS, in agreement with Wang et al. (2022) and Cui et al. (2024).

He et al. (2022) investigated the formation of vivianite in a batch anaerobic digester dosing carbon nanotubes (CNTs). The authors demonstrated that CNTs addition promoted the electron transfer between Fe^{3+} and dissimilatory iron-reducing bacteria, leading to a 17 % increase in vivianite precipitation compared to the control experiment without CNTs. Initially, the efficiency of vivianite precipitation decreased due to the destruction of dissimilatory iron-reducing bacteria cell membranes, which are needed to reduce Fe^{3+} to Fe^{2+}. This led to an 83 % lower iron reduction compared to the control experiment without CNTs. However, over time, dissimilatory iron-reducing bacteria secreted EPS that formed bioflocs, helping them to withstand physical punctures by CNTs. The study added a CNTs concentration of 1 $g{\cdot}L^{-1}$ and measured the percentage of dissimilatory iron-reducing bacteria at 36 and 48 h, which increased by 79 and 98 %, respectively.

Li et al. (2020) investigated the fate of phosphorus during an oxidation pre-treatment before AD. They used potassium ferrate (K_2FeO_4) at a concentration of 70 $mg{\cdot}g^{-1}$ SS (suspended solids). Their results indicated a significant release of organic matter into the

Table 2
Processes to favour vivianite precipitation in anaerobic digesters.

Process	Initial PO_4^{3-}-P concentration ($mg{\cdot}L^{-1}$)	pH	Fe:P molar relation	Seed	PO_4^{3-}-P recovery (%)	Crystal size (μm)	Source
Biogas recirculation with $FeCl_3$	70	6	1.5:1	–	97	50-100 to 300–700 μm	Yuan et al. (2020)
Pre-oxidation with K_2FeO_4	100	–	–	–	80	–	Li et al. (2020)
Crystal seed dosing	372	7.3	1.6:1	Carbon nanotubes	44	–	He et al. (2022)
Crystal seed dosing	68	7.1	1.5:1	Magnetic biochar	45	32–102 μm	Wu et al. (2023)

supernatant, which was subsequently anaerobically degraded. The pre-treatment increased the phosphorus concentration in liquid-phase up to 100 mg PO_4^{3-}-P·L^{-1} as both organic and inorganic phosphorus were released. The pre-treatment also provided enough iron to facilitate vivianite precipitation. During the AD process, Fe^{3+} was reduced to Fe^{2+} and 80 % of phosphorus was precipitated as vivianite. The pre-oxidation process enhanced the proportion of phosphorus and the formation of vivianite, with vivianite increasing from 16 to 21 mg·g^{-1} SS and improved volatile suspended solids (VSS) degradation by 44.2 % in the AD process.

The results presented by Li et al. (2020) are promising to increase phosphorus recovery and AD yields, as well as the use of seed materials. However, a techno-economic analysis is needed to support its efficiency. Further research on pre-treatments and seed addition should also consider the limitations stated by Wang et al. (2022) and Cui et al. (2024), who noted that the presence of iron and vivianite limits the degradation of organic matter during the digestion process. Table 2 provides a summary of the different experiments conducted to promote vivianite precipitation in anaerobic digesters.

4.3.2. Anaerobic fermentation

The formation of volatile fatty acids (VFAs) during anaerobic mixed-culture fermentation decreases the pH of the medium, thereby enhancing the release of iron and phosphate from the sludge (Cao et al., 2019). Subsequently, the pH of the AF process supernatant can be adjusted to 7 to precipitate vivianite. This strategy allows the phosphorus recovery as vivianite in a precipitation reactor instead of being incorporated in the digested sludge where separation is more challenging.

The phosphorus release during AF is generally positively impacted by acid or alkali treatments. Cao et al. (2019), Li et al. (2021), and Hu et al. (2022) studied the influence of pH on the release of iron and phosphorus from waste activated sludge during fermentation. Cao et al. (2019) added a Fe:P molar ratio of 1.5:1 using $FeCl_3$, followed by pH adjustments using NaOH and HCl. Results showed that at pH 3, the percentages PO_4^{3-}-P and Fe^{2+} released from sludge were 85.7 and 78.8 %, respectively. The microbial community analysis revealed that the *Clostridiaceae* family comprised 40.3 % of the bacterial population, which played a pivotal role in the Fe^{3+} reduction. Under these conditions, over 83 % of phosphorus could be recovered as vivianite in a precipitation reactor adjusting the pH to 7−8. Li et al. (2021) performed fermentation experiments at different pHs (2, 3, 4, 5, 10, 11 and 12) where the release of PO_4^{3-}-P was greater than 59.0 %. Vivianite precipitation was carried out by adding a Fe:P molar ratio of 1.5:1 at a pH of 7 in the supernatant of experiments at pHs 5 and 11 with an initial PO_4^{3-}-P concentration of 312 and 284 mg PO_4^{3-}-P·L^{-1}, respectively. These pH conditions in the fermentation supernatant favoured the purity of the vivianite, as very acidic pHs favoured the release of heavy metals and very basic pHs the precipitation of hydroxyapatite. Phosphorus recovery was greater than 99 %, reaching phosphorus concentrations of 0.5 mg PO_4^{3-}-P·L^{-1}. Hu et al. (2022) investigated the impact of pH on iron reduction during fermentation to precipitate vivianite. The iron source in this experiment was amorphous iron oxyhydroxide (FeO(OH)). Three experiments were conducted: (i) a control experiment at pH 7.2 and without iron addition, (ii) an experiment at pH 3 and with iron addition (Fe:P molar ratio of 1.5:1), and (iii) an experiment at pH 10 and with iron addition (Fe:P molar ratio of 1.5:1). The iron reduction rates were higher at pH 3 and 10 compared to pH 7, with maximum increases of 1.9 and 1.7 times, respectively. The amount of iron reduced was also higher at pH 3 and 10 compared to pH 7 by 17.5 % and 12.0 %, respectively. The higher performance at pH 3, was related to the presence of *Clostridium sensusensu*, an iron-reducing bacteria. These results are consistent with those reported by Cao et al. (2019) at pH 3. Hu et al. (2022) also indicated that the phosphorus precipitation with iron increased in the supernatants obtained at pH 3 and 10 compared to pH 7, with increases of 50.0 and 33.7 %, respectively. These increases were attributed to the higher concentration of Fe^{2+} and PO_4^{3-}-P. The three studies showed that fermentation at acidic pHs favours phosphorus release. However, Li et al. (2021) reported that fermentation under alkaline conditions (>10) favours VFA production and sludge degradation, while lowering the dissolution of heavy metals that may late precipitate. Nonetheless, alkaline pH values also promote hydroxyapatite formation, thereby decreases phosphorus concentration and its subsequent recovery. An improvement in the degradation of organic matter could counteract interactions between certain functional groups of organic matter and vivianite and/or iron. Further evaluation of parameters under these conditions could show better yields in the precipitation of phosphorus and the production of VFAs.

Cao et al. (2023) studied the influence of pH and Fe:P molar ratio on vivianite size in a synthetic fermentation supernatant. The average particle sizes of vivianite were 22.9, 25.8 and 24.1 μm at pH of 6.5, 7.5 and 8.5, respectively. This behaviour was explained by the stages of nucleation and crystal growth. As pH rises, supersaturation increases moving from the metastable zone to the labile zone. Particle growth is favoured in the metastable zone, while in the labile zone, a high supersaturation degree promotes nucleation and limits particle growth (Cao et al., 2023). At Fe:P molar ratios of 1.2:1, 1.5:1, 1.8:1 and 2.1:1, the corresponding particle sizes were 24.2, 25.8, 26.3 and 27.4 μm, respectively. These results indicated that increasing Fe:P molar ratio favoured the growth of vivianite particles. Nonetheless, the four Fe:P molar ratios studied are close to the stoichiometry of vivianite.

Some researchers have focused their studies on the co-fermentation process. Co-fermentation is the simultaneous fermentation of two or more substrates to enhance VFA production (Perez-Esteban et al., 2022). Wu et al. (2020a, 2020b), who co-fermented waste activated sludge (WAS) and food waste (FW), investigated the effect of WAS:FW ratio, pH, and iron addition on the co-fermentation process. In their first study, Wu et al. (2020b) used four WAS:FW ratios (100:0, 90:10, 80:20, and 70:30 %, based on dry weight). The best WAS:FW ratio for phosphorus recovery as vivianite was 70:30 % of WAS:FW, allowing an 83 % phosphorus recovery without pH control. In their second study, Wu et al. (2020a) carried out five experiments: (i) 100 % WAS, without pH control or $FeCl_3$ addition, (ii) 70:30 % WAS:FW, without pH control or $FeCl_3$ addition, (iii) 100 % WAS, without pH control and with $FeCl_3$ addition (Fe:P molar ratio of 1.5:1), (iv) 70:30 % WAS:FW, without pH control and with $FeCl_3$ addition (Fe:P molar ratio of 1.5:1), and (v) 70:30 % WAS:FW, with pH control at 4.5 and $FeCl_3$ addition (Fe:P molar ratio of 1.5:1). The results showed that the addition of FW and/or iron increased the concentration of Fe^{2+}, PO_4^{3-}-P, and VFAs in the fermentation liquor. Food waste provided readily biodegradable organic matter to the acidogenic bacteria to produce VFAs, which generation decreased the pH of the media and promoted the dissolution of compounds with Fe^{2+} and PO_4^{3-}-P. The best conditions for releasing Fe^{2+} and PO_4^{3-}-P and subsequent vivianite precipitation were a WAS:FW ratio of

Table 3
Processes for vivianite recovery from anaerobic fermentation.

Process	Initial PO_4^{3-}-P concentration ($mg{\cdot}L^{-1}$)	pH	Fe:P molar relation	Seed	PO_4^{3-}-P recovery (%)	Crystal size (μm)	Source
Optimise iron source and pH for P recovery	184	3.0, 5.0, 10.0 and 12.0	1.5:1	–	82.6	–	Cao et al. (2019)
Co-fermentation of a mixture of WAS and food waste	260	Fermentation: 4.53 Precipitation: 7.0	1.5:1	–	82.9	–	Wu et al. (2020a)
Crystal seed dosing	319	5.5–6.0	1.5:1	Spong& iron	83.2	–	G. Wu et al. (2021)
Fermentation (Acid/alkali)	312 285	Fermentation: 5.0/11.0 Precipitation: 7.0	1.5:1	–	>99	–	Li et al. (2021)
Fermentation (Acid/alkali)	28.7	3.0 and 10.0	1.5:1	–	pH 3: 80.1 pH 10: 72.3	pH 3: 10 μm pH 10: 5 μm	Hu et al. (2022)
Pre-oxidation with K_2FeO_4	57.3	8.0	0.33:1	–	32.4	–	Wen et al. (2022)
Crystal seed dosing	52.6	7.8	1.74:1	Quartz sand	–	19.6 μm–39.4 μm	Wang et al. (2023)

70:30 %, no pH control, and $FeCl_3$ addition at a Fe:P molar ratio of 1.5:1. WAS:FW co-fermentation reached a pH of 4.5 without using pH control, indicating that chemical reagents to acidify the medium were not required. Subsequently, the pH of the fermentation supernatant was adjusted to 7.0, resulting in vivianite precipitation. The PO_4^{3-}-P recovery as vivianite was 82.9 %, with a purity of 95.2 % (Wu et al., 2020a).

The addition of seeds in fermentation experiments has also been evaluated to improve vivianite precipitation yields. Wu et al. (2021) first studied phosphorus recovery as vivianite without seed addition. They conducted different lab-scale experiments, studying the effect of pH (ranging from 3 to 6) on PO_4^{3-}-P precipitation. The results showed that PO_4^{3-}-P precipitation as vivianite was enhanced by increasing pH, with the highest PO_4^{3-}-P recovery reaching 98 % at pH 6. However, the obtained particle size was between 30 and 50 μm. Wu et al. (2021) indicated that these particle sizes were too small to be separated from the digested sludge. To promote bigger particle size, Wu et al. (2021) used sponge iron ($4\ g{\cdot}L^{-1}$) as seed. The iron sponge aims to improve vivianite precipitation by (i) acting as a seed and reduce the nucleation step, (ii) improving the magnetic capacity of the precipitate, and (iii) being a source of iron in the process. The results showed that PO_4^{3-}-P recovery was 83.2 % and the particle size increased to 300 and 700 μm, 10 times larger than the results without adding seeds (Wu et al., 2021). The separation of vivianite from the digested sludge improved due to the magnetic properties of sponge iron, using a rubidium magnet. Wang et al. (2023) used quartz sand as a seed material to improve vivianite precipitation. The addition of quartz sand increased PO_4^{3-}-P recovery and the average particle size by reducing the supersaturation demand. The smaller particles of quartz sand had a larger surface area, which developed an ion adsorption layer that improved interaction with the solution and promoted crystal growth and attachment. The authors reported that adding quartz sand with a particle size of 25–50 μm at concentration of $4\ g{\cdot}L^{-1}$ increased PO_4^{3-}-P recovery as vivianite by 4.3 % and the particle size from 19.6 to 39.4 μm. The addition of the quartz sand also increased the vivianite content in the precipitate by 12.5 %.

Wen et al. (2022) conducted a pre-treatment using potassium ferrate (K_2FeO_4), where the sludge was pre-oxidated before the fermentation process. The addition of K_2FeO_4 ($0.14\ g\ Fe^{6+}{\cdot}g^{-1}$ TSS) increased the soluble COD from 1517 to 17621 $mg{\cdot}L^{-1}$ and the PO_4^{3-}-P concentration from 57 to 750 mg PO_4^{3-}-$P{\cdot}L^{-1}$. The high capacity of potassium ferrate as an oxidizing agent accelerated the disintegration of EPS and the release of soluble organic matter into fermentation liquor favouring VFAs production during fermentation process. The pre-treatment also increased the proportion of microorganisms that promoted the hydrolysis and acidification stages as *Bacteroidetes*, *Firmicutes*, and *Proteobacteria*. The abundance of *Bacteroides* increased with increasing K_2FeO_4 and promoted the production of VFAs. Vivianite formation was favoured up to K_2FeO_4 concentrations of $0.6\ g\ Fe^{6+}{\cdot}g^{-1}$ TSS. Higher concentrations led to a reduced detection of vivianite in the precipitates, as well as a decline in iron-reducing bacteria, including *Dechloromonas* and *Geobacter*. *Geobacter,* in particular, was stated to promote vivianite precipitation, resulting in a 20−48 % increase in vivianite formation in its presence. Table 3 provides a summary of the different experiments conducted to favour vivianite precipitation after waste fermentation.

5. Detection and quantification of vivianite in WWTPs samples

5.1. Detection of vivianite

Vivianite was identified in the Milwaukee WWTP (USA) by Seitz et al. (1973), who reported its magnetic properties, which can be used to separate vivianite from dried sludge through magnetic separation. A sample was taken and analysed by X-ray diffraction (XRD) from which vivianite was identified and semi-quantified. Vivianite represented around 1 % of the total weight of the dried sludge. Frossard et al. (1997) showed that 60−67 % of total iron in its oxidised form in digested sludge was incorporated as vivianite, while in the undigested sludge iron in its oxidised form represented 43 % of total iron. Frossard et al. (1997) introduced scanning electron microscopy (SEM) and Mössbauer spectroscopy analysis to detect and quantify vivianite in digested sludge.

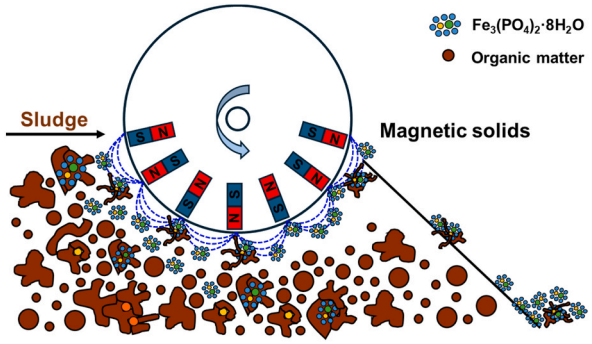

Fig. 7. Magnetic drum separator applied to the separation of vivianite from digested sludge.

Wilfert et al. (2016) evaluated the presence of vivianite in two WWTPs from The Netherlands: one utilising CPR with iron salts, and the other utilising EBPR supported by iron salts dosage. They quantified vivianite concentration in the sludge before and after AD. In both WWTPs, phosphorus was concentrated in the solid fraction of the digested sludge. However, the PO_4^{3-}-P bound to iron as vivianite at the WWTP with a CPR system was 40–50 % of total phosphorus, while the WWTP with an EBPR system yielded between 10 and 30 % of total phosphorus. It should be noted that the CPR system added 11 times more iron than the EBPR system. In a following study, Wilfert et al. (2018) investigated the presence of vivianite in seven WWTPs in Europe (2 EBPR and 5 CPR systems), all of which were equipped with anaerobic digesters. The selected WWTPs utilised various iron coagulants with different oxidation states (Fe^{2+} and Fe^{3+}) at different Fe:P molar ratios. Wilfert et al. (2018) showed that vivianite was the most abundant phosphate-containing mineral in digested sludge. An Fe:P molar ratio of 2.5:1 favoured the formation of vivianite, which represented 70−90 % of total phosphorus in the digested sludge. Regardless of the initial iron source, Fe^{2+} was the main oxidation state of iron in the digested sludge. The presence of Fe^{2+} before and after AD was about 50 and 85 %, respectively.

Fig. 7 illustrates a magnetic drum separator used to recover metallic elements from sludge such as vivianite. Magnetic drum separators consist of permanent magnets, grids, filters, and drums that rotate in the same direction as the sludge flow, causing metallic particles to move forward (Metso, 2010). The high concentrations of vivianite in the digested sludge are driving the development of new equipment using magnetic fields for its recovery. Prot et al. (2019) developed a lab-scale magnetic separator (type Jones). The device consisted of two steel plates with seven vertical teeth measuring 4 cm height and 1.5 mm length. A magnetic field is formed between the ridges, which are separated by 2 mm. The solid separated by the magnetic separation to 1.3 T had a content between 52 and 62 % of vivianite, 20 % of organic matter, <10 % of quartz, and small proportion of siderite. Wijdeveld et al. (2022) conducted a pilot-scale study of vivianite recovery in a WWTP from The Netherlands, using a magnetic separator commonly utilised in the mining industry with a digested sludge flow of 0.5–1.0 $m^3 \cdot h^{-1}$. The separator utilised a magnetic field with an intensity up to 1 T over a steel rod, creating multiples sites of high field gradient. The rods attracted paramagnetic vivianite particles. The separator used pulses to agitate the sludge and maintain the particles in loose state, facilitating the attraction of the particles to the rods. The magnetic separator significantly enhanced the separation of vivianite when the digested sludge was recirculated three times, increasing the recovery from 30 to 80 %. Wijdeveld et al. (2022) also showed that vivianite concentration increased with a higher iron dosage, equivalent to a PO_4^{3-}-P recovery of 18 and 54 %, respectively. Most studies have focused on high-intensity magnetic separation, which consumes significant amounts of energy. However, Gao et al. (2024) studied low-intensity magnetic separation, where scrap iron was used as a source of iron in the precipitation of vivianite. The scrap iron used had zero-valence iron at the centre of its structure and three-valence iron on the surface (mineral phase: akaganeite), forming an Fe(III)[Fe(0)] structure. On the one hand, vivianite precipitated on the surface of the undissolved iron scrap, which acted as both as an iron source and as a nucleating agent. On the other hand, the resulting precipitate had zero-valent Fe at its centre, which improved magnetic separation and allowing low-intensity magnetic separation with a magnetic field of 0.3 T. Gao et al. (2024) reported an energy saving in the separation process by using scrap iron, which reduced magnetic intensity by more than three times.

5.2. Quantification of vivianite

The main challenge in detecting and quantifying vivianite in WWTPs samples is the presence of impurities (e.g. organic matter, biofilm) and the oxidation vivianite during the sampling, drying and analysis stages. Vivianite oxidation can be prevented or minimised by using anaerobic drying conditions and by storing the sludge samples at low temperatures to decrease microbial activity (Wilfert et al., 2018). Prot et al. (2020) indicated that light and oxygen can oxidise vivianite. Contrariwise, Amin et al. (2024) concluded that vivianite samples were not oxidised as the percentage of Fe^{2+} remained constant after one year. The sample storage process by Amin et al. (2024) involved centrifuging the sludge to separate the supernatant. The resulting centrifuged sludge was then placed in a bottle, which was purged with nitrogen for 1−2 days until the sludge was fully dried. They suggested that vivianite undergoes oxidation during sampling, where Fe^{2+} in vivianite is oxidised to Fe^{3+} until equilibrium is reached, and the reaction stops over time.

The most used techniques to detect and quantify vivianite are X-ray diffraction and Mössbauer spectroscopy (Heinrich et al., 2023;

Prot et al., 2022; Wang et al., 2019; Wilfert et al., 2016). XRD analysis detects the crystalline mineral phases of the sample, while the amorphous phases are not detected. Wilfert et al. (2016) and Prot et al. (2022) considered XRD analysis a semi-qualitative technique when analysing sludge samples since the amorphous Fe–P compounds are not identified. Mössbauer spectroscopy detects and quantifies the elements and their oxidation states in both crystalline and amorphous phases. Mössbauer spectroscopy allows the distinction between Fe^{2+} and Fe^{3+}, providing their respective percentages, which can be used to quantify the presence of vivianite. The main limitations of this technique are: (i) the possible oxidation of vivianite during analysis, and (ii) the used of specialised instrumentation (Wang et al., 2021).

Other techniques used in vivianite research to detect and quantify include scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDS), inductively coupled plasma optical emission spectroscopy (ICP-OES), IR-absorption and Raman spectroscopy, thermogravimetric analysis (TGA), and sequential extraction (Heinrich et al., 2023; Prot et al., 2019; Wang et al., 2021; Wilfert et al., 2018). SEM-EDS is used to study the morphology and determine the elemental composition of different spots of the sample. Based on the elemental composition, the analysis identifies and characterises the morphologies of vivianite and other components (Wang et al., 2021). ICP-OES is used to determine the concentration of different elements in a sample. In vivianite studies, it is particularly important to measure Fe, P, Ca, Mg and heavy metals (Prot et al., 2019). IR-absorption and Raman spectroscopy are used to identify the functional groups of the components. The bands corresponding to Fe^{3+}-OH and PO_4^{3-} can be found in sludge samples containing vivianite, while the band of Fe^{2+}-OH is not detectable (Zhang et al., 2022). TGA analysis measures the weight loss percentage of the volatile compound of each mineral phase as the temperature increases (Fernández et al., 1999). According to Prot et al. (2019), vivianite losses its eight waters when the samples is heated from 40 to 550 °C at a heating ramp of 10 °C·min^{-1} under argon atmosphere. Specifically, seven waters are lost when the samples reach 200 °C, while the last water molecule is lost between 200 and 550 °C. Quantification of water loss could be used to quantify vivianite in samples. However, the calcination of organic materials and dehydration of other mineral phases also occurs within the 200−550 °C range, complicating the accurate quantification of vivianite. For instance, struvite, which naturally precipitates in some WWTPs, is composed of six waters and ammonium. Aguilar-Pozo et al. (2024) demonstrated that all six waters and ammonium in struvite were lost before 300 °C. It is important to mention that TGA analysis can be performed under an inert gas atmosphere, which would prevent oxidation of vivianite in the analysis. Finally, a sequential phosphate extraction method to quantify vivianite was developed by Gu et al. (2016) in lake sediments. This method was employed by Wang et al. (2021) in sludge samples. The sequential phosphate extraction method quantifies phosphorus bound to vivianite without interferences from phosphorus bound to P–Fe^{3+} compounds. To quantify vivianite an extra extraction step using an aqueous solution of 0.2 wt% at 2,2 ′-bipyridine in 0.1 M KCl. The extraction is based on the complexation of 2,2′-bipyridine ("Bipy") with Fe^{2+} dissolved from vivianite. The consumption of Fe^{2+} from vivianite to form the $[Fe(Bipy)_3]^{2+}$ complex shifts the equilibrium of vivianite towards its dissolution, releasing its phosphates, which are subsequently measured by spectrophotometry (Gu et al., 2016; Wang et al., 2021). Numerous methods have been utilised to detect and quantify vivianite since no single method has been established.

6. Future research

Most of the publications analysed in this literature review on vivianite precipitation in WWTPs are based on lab-scale experiments. One measure that helps assess the maturity level of a specific technology is the technology readiness levels (TRLs). These levels are categorised into three groups: (i) the technology is conceived and validated at the lab-scale (TRLs 1–4), (ii) the technology is tested at pilot-scale, in an environment with characteristics similar to real-world conditions (TRLs 5–6), and (iii) the technology is implemented and validated at full scale, i.e., under real operational conditions (TRLs 7–9). Vivianite precipitation technology in WWTPs currently has a low TRL, although research on this technology has increased in recent years. The current TRLs is estimated at 4 (between 3 and 5) due to the scarcity of pilot-scale studies and the limited research on industrial-scale implementations. This review also highlights the opportunity for international collaboration to share scientific knowledge and promote the implementation of vivianite precipitation in WWTPs. The following knowledge gaps have been identified as priorities for future research:

- Anaerobic digestion in WWTP aims to degrade organic matter and produce methane-rich biogas. The potential negative impact of vivianite and iron on AD reported by some authors on methane production could limit the feasibility of vivianite precipitation in anaerobic digesters. However, several studies have reported positive impacts of iron dosage on AD performance (Bardi et al., 2023; Hao et al., 2017). A better understanding of the impact of vivianite and iron concentrations on AD performance is needed.
- Fermentation at acidic pH is increasingly studied to produce vivianite. However, fermentation under alkaline conditions (> pH 10) also favours VFA production, sludge degradation and phosphorus release. There are few studies at alkaline pHs, however, enhanced degradation of organic matter could counteract interactions between certain functional groups of organic matter and vivianite and/or iron. Further evaluation under these conditions could unlock higher yields in the production of vivianite and VFAs.
- Anaerobic co-fermentation experiments using sewage sludge and food waste have shown higher VFA yields, a decrease in pH without chemicals dosage, an higher P-PO_3^- concentrations. However, the number of studies is limited. Investigating other co-substrates rich in phosphorus, such as dairy waste, could be an opportunity to increase VFA yields and PO_4^{3-}-P recovery as vivianite.
- Research should explore more eco-friendly and cost-effective sources of iron, including those derived from industrial by-products and residues, such as steel industry waste. The use of alternative iron sources supports circular economy principles. Key research priorities include: (i) characterisation of the waste source, (ii) evaluation of the availability and solubility of iron, (iii) assessment of its chemical behaviour (acidic, basic, or neutral), and (iv) investigation of the impact of particle size on the precipitation and dissolution process, among other factors.

- Quantification of vivianite remains a significant challenge. To ensure accurate measurements, the oxidation kinetics of Fe^{2+} to Fe^{3+} in vivianite should be further investigated. Kinetic characterisation would allow the quantification of Fe^{2+} and Fe^{2+} over time. A combination of various analytical techniques (XRD, XRF, TGA, and Mössbauer spectroscopy) along with equilibrium and calcination reactions, could be used to develop new procedures for more accurate quantification. For example, Aguilar-Pozo et al. (2024) accurately quantified the percentage of struvite in the precipitate obtained using a combination of XRD, XRF and TGA, and calcination reactions.
- Magnetic separators, widely used in the mining industry, could enhance the recovery of vivianite from sludge in WWTPs. Collaboration between the mining and the wastewater sectors may facilitate the adaptation of this technology to improve vivianite separation efficiency.

7. Conclusions

Vivianite precipitation is a promising technology for phosphorus recovery in WWTPs. The dosage of iron (mainly $FeCl_3$ and $FeSO_4$) in the activated sludge and anaerobic digestion systems favours vivianite precipitation, where Fe^{2+} is the main oxidation state of iron regardless of the iron source. The presence of dissimilatory iron-reducing bacteria in anaerobic digestion and anaerobic fermentation reduces Fe^{3+} to Fe^{2+}, enhancing and controlling vivianite precipitation. Phosphorus recovery as vivianite can reach 70−90 %, with an optimal Fe:P molar ratio of 2.5:1 and pH of 7–9. Acidogenic (co-)fermentation units typically operate at an acidic pH, which favour PO_4^{3-}-P and iron release from sludge, allowing subsequent vivianite precipitation at pH 7.

Vivianite appears as an attractive route for phosphorus recovery in WWTPs. However, methane production in anaerobic digestion could be compromised by (i) reduced availability of soluble organic matter, and (ii) competition for acetate between dissimilatory iron-reducing bacteria and methane-producing archaea. Furthermore, the interaction of organic matter with iron ions and vivianite particles limit their availability for vivianite formation or particle growth.

X-ray diffraction and Mössbauer spectroscopy are the two most used techniques to identify and quantify vivianite. However, the presence of impurities and the oxidation of vivianite difficult the reliability and accuracy of these analyses. Vivianite can be separated from sludge using a magnetic separator and valorised in industrial and agricultural applications.

CRediT authorship contribution statement

V.B. Aguilar-Pozo: Writing – original draft, Visualization, Validation, Methodology, Investigation, Formal analysis, Conceptualization. **P. Tamayo:** Writing – original draft, Investigation, Formal analysis, Conceptualization. **M. Casallas-Ojeda:** Writing – original draft, Visualization, Methodology. **E. Siscar:** Writing – review & editing, Conceptualization. **X. Fonoll:** Writing – review & editing, Supervision. **J.M. Chimenos:** Writing – review & editing, Validation, Supervision, Funding acquisition, Conceptualization. **S. Astals:** Writing – review & editing, Validation, Supervision, Funding acquisition, Conceptualization.

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 was supported by the Grant RTC2019-007257-5 funded by MICIU/AEI/10.13039/501100011033, and by "European Union NextGenerationEU/PRTR". The gran PDC2022-133669-I00, also funded by the Spanish Ministry of Science and Innovation. The Agència de Gestió d'Ajuts Universitaris i de Recerca (AGAUR) contributed through Ms. Verónica B. Aguilar-Pozo predoctoral grant (2022 FI_B 00032). Miguel Casallas-Ojeda is grateful to the Universidad de La Sabana for the funding his PhD studies through the Carlos Jordana distinction (2020-II). The authors would like to thank the Catalan Government for the quality accreditation given to both research groups of the University of Barcelona (2021 SGR 00708 and 2021 SGR 00234). DIOPMA (2021 SGR 00708) is a certified agent TECNIO in the category of technology developers from the Government of Catalonia.

Data availability

Data will be made available on request.

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