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Literature Review

Analysis of phosphorus recovery based on vivianite formation for practical applications

Análise da recuperação de fósforo baseada na formação de vivianita para aplicações práticas

Tengshu Chen[1]*, Xingfu Song[2]

ABSTRACT

Phosphorus (P) is considered a non-renewable resource. Owing to the increasing consumption of phosphorus in daily life, the "P crisis" is imminent. To address this crisis, it is urgent to find new phosphorus resources. This paper summarizes the research progress of P recovery based on vivianite formation from waste. Specifically, the advantages and disadvantages of optimizing the Fe source and pH in waste-activated sludge (WAS) and the co-fermentation of WAS and food waste are analyzed. Thereafter, the advantages and disadvantages of increasing the Fe dosage in full-scale wastewater treatment plants is discussed and an optimization scheme is proposed on this basis. By analyzing the advantages and disadvantages of comparative experimental results, two recovery methods are proposed to recover a large amount of P (≥ 83% total P) as high-purity vivianite (≥ 93%).

Keywords: vivianite; engineering application; P recovery.

RESUMO

O fósforo (P) é considerado um recurso não renovável. Dado seu consumo crescente na vida cotidiana, a "crise do P" é iminente. Para enfrentá-la, é urgente que novos recursos de P sejam encontrados. Este artigo resume o progresso das pesquisas sobre a recuperação de P baseada na formação de vivianita a partir de resíduos. Especificamente, são analisadas as vantagens e desvantagens de otimizar a fonte de Fe e o pH no lodo ativado residual (WAS) e a cofermentação de WAS e resíduos alimentares. Feito isso, são discutidas as vantagens e desvantagens de aumentar a dosagem de Fe em estações de tratamento de efluentes de grande escala, e com base nisso é proposto um sistema de otimização. Com a análise das vantagens e desvantagens dos resultados experimentais comparativos, dois métodos são propostos para recuperar grande quantidade de P ((≥ 83% P total) como vivianita de alta pureza (≥ 93%).

Palavras-chave: vivianita; aplicação de engenharia; recuperação de P

INTRODUCTION

Status of phosphorus recovery

Phosphorus (P) is widely found in animals and plants, and it is also one of the most abundant elements in the human body. It is an important component of human bones and teeth as well as an important component of soft tissue, especially for the formation of deoxyribonucleic acid (DNA) and ribonucleic acid (RNA) (CAO *et al*., 2019). Phosphorus is ubiquitous, and agricultural production requires it. Phosphorus mainly exists in the earth's crust in the form of phosphate rock, a non-metallic mineral resource that is difficult to regenerate. However, the distribution of phosphorus is very uneven, and the reserves are very limited. Approximately 20 million tons of phosphate materials is mined every year, and the price of phosphate materials continues to rise (CORDELL *et al*., 2011). It is worth noting that the Ministry of Electricity and Water Resources has studied the reserves and consumption of phosphorus (MEW *et al*., 2016), and they predicted that global phosphate reserves will be exhausted in the next 50–100 years, which is the reason for the surge in market quotations (CORDELL; DRANGERT; WHITE, 2009). The economic reserves of phosphorus only represent 1/3 of the basic reserves. Demand for phosphorus has increased with population growth and improvement in human living standards. According to statistical analysis, China's consumption of phosphorus materials is increasing daily, and on the basis of this trend, China's phosphate reserves will be exhausted 20 years later, followed by the "P crisis" (XIAODI *et al*., 2018).

It is precisely because phosphorus plays an indispensable role in nature and people's lives that the "P crisis" is so urgent. Although we have developed several mature recovery methods for the high-efficiency recovery of phosphorus, these methods also have their own problems. The struvite recovery method has been widely accepted as effective for phosphorus recovery, whereby P and ammonium

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ions are removed simultaneously and fixed into struvite ($MgNH_4PO_4{\bullet}6H_2O$) crystals, struvite being a commonly used slow-release fertilizer (KIM *et al.*, 2018). However, struvite crystals can only be formed under strictly controlled conditions (i.e., high phosphorus concentration, appropriate $Mg/NH_3/H_3PO_4$ molar ratio, and appropriate pH (HUG; UDERT, 2013). Generally, the concentration of Mg is much lower than that of P in wastewater, and thus it is always necessary to add an additional dose of Mg (LIU *et al.*, 2018), which reduces the economic feasibility of the technology. Moreover, the pH needs to be controlled in the range 8–9.5 for the formation of struvite, and the efficiency of the struvite recovery method for phosphorus recovery is low (10–50%). Vivianite has gradually attracted attention in recent years because of its high phosphorus recovery rate, high economic value, and broad utilization prospect. With increasing research, the characteristics of vivianite have gradually been determined. Although research on vivianite has been continuously reported in academic circles, further studies are required to elucidate the formation mechanism of vivianite and to explore crystal recovery.

The effect of temperature on the formation mechanism of vivianite has been investigated, and temperature was found to affect both the morphology of vivianite crystals (MADSEN; HANSEN, 2014) and the reduction effect of Fe(III) (CHENG *et al.*, 2017). In addition, Zhang *et al.* (2020) and Yu *et al.* (2021) explained the influence of extracellular polymeric substance (EPS) on the formation mechanism of vivianite and the addition of graphite on the promotion of crystal size. To explore the feasibility of vivianite in practical applications, Wilfert *et al.* (2018) and Prot *et al.* (2020) demonstrated the importance of adding an Fe source, and Azam and Finneran (2014) confirmed through the addition of an Fe source that vivianite can be precipitated from nutrient-rich wastewater before it leaves the on-site wastewater treatment facility. Moreover, to improve the phosphorus recovery rate and the purity of vivianite, Cao *et al.* (2019) first separated the supernatant and then recrystallized the product. Wu *et al.* (2020) further optimized the recovery experiment and co-fermented food waste (FW) and waste-activated sludge (WAS) to obtain high-purity (93.90%) vivianite with a high total phosphorus (TP) recovery rate (83.09%).

Despite the slow research progress on the recovery methods of vivianite crystals, Prot *et al.* (2020) developed a wet separation technology based on paramagnetism, specifically Jones magnetic separators, to extract magnetic components from sludge flows on a laboratory scale. The separated vivianite mixture had a purity of up to 62% and an effective TP content of 80%. Jiazhou (2020) enriched vivianite by nitrogen gas flotation and designed a hydrocyclone to separate vivianite, with low separation effect of the sludge. This may be explained by the small particle size of the vivianite produced by digestion and the interference from other P components, such as aluminum phosphorus.

Although research on vivianite has made great progress, the application of vivianite in engineering is still sparse. Because engineering applications are dependent on the combination of various reaction conditions, the experiments of Zhang *et al.* (2020) are not suitable for large-scale engineering applications, and thus can only be used as a reference for optimizing the recovery processes. At present, methods based on relatively mature technologies which thus can achieve large-scale applications include the recrystallization method of Cao *et al.* (2019), the co-fermentation experiment of Wu *et al.* (2020), and the demonstration of Wilfert *et al.* (2018) and Prot *et al.* (2020) using external iron sources in wastewater treatment plants (WWTPs) for the formation of vivianite. The following sections compare the advantages and disadvantages of these methods, including proposals for optimal countermeasures. The purpose of this study was to propose optimized processes for the formation of vivianite and improved universal methods for engineering applications. Therefore, this article comprises a summary of the basic characteristics and formation processes of vivianite, an analysis and comparison of the advantages and disadvantages of the above three mainstream engineering application technologies, and proposed optimization schemes, specifically two methods, for the recovery of phosphorus as vivianite.

Characteristics of vivianite

Vivianite ($Fe_3(PO_4)_2{\bullet}8H_2O$) was first discovered by British mineralogist John Henry Vivian (1785–1855) (ROTHE; KLEEBERG; HUPFER, 2016), so it was named vivianite. This mineral consists of single ($FeO_2(H_2O)_4$) and double ($Fe_2O_6(H_2O)_4$) octahedral groups, which are connected to each other by PO_4 groups and H_2O–H_2O hydroxyl bonds (ROUZIES; MILLET, 1993). The Fe^{2+} ion occupies two different positions in the structure. At site A, Fe^{2+} is surrounded by two oxygen atoms and four water molecules, forming an octahedral group. At site B, Fe^{2+} is surrounded by four oxygen atoms and two water molecules, forming an octahedral group. Oxygen is part of the P group (PO_4^{3-}), forming a tetrahedron (WU et al., 2019). In addition, vivianite is paramagnetic, although it undergoes a magnetic transition at a Neel temperature of 12 K (MEIJER; VAN DEN HANDEL; FRIKKEE, 1967; FREDERICHS *et al.*, 2003).

Vivianite is the end member of the iron-rich vanadium-titanium group $M_3\ (XO_4)\ _2{\bullet}8\ H_2O$, where M is divalent Mg, Mn, Fe, Co, Ni, Cu, and Zn and X is phosphorus or arsenic (FLEISCHER; MANDARINO JOSEPH, 1991); therefore, it can combine with other metal ions to form other substances. For example, baricite, the Mg analogue of vivianite, was discovered in an Fe-rich cold seep sediment off western Taiwan (HSU; JIANG; WANG, 2014). Vivianite exists in many natural environments, including river sediments (up to 20% by mass) (HEARN; PARKHURST; CALLENDER, 1983; WOODRUFF *et al.*, 1999), canals (DODD *et al.*, 2000), lakes (NRIAGU *et al.*, 1972; NEMBRINI *et al.*, 1983), and river delta mud (KONHAUSER, 1998), as well as wastewater sludge (FROSSARD; BAUER; LOTHE, 1997).

Vivianite is colorless and transparent in its original state and gradually turns green when exposed to air because of the gradual oxidation of Fe^{2+} in its crystals (ROTHE *et al.*, 2014). Depending on the degree of oxidation of Fe^{2+}, it occurs in a variety of colors, including light green, green blue, light blue, dark blue, and even black (HEARN; PARKHURST; CALLENDER, 1983; AMMARI; HATTAR, 2011;EGGER *et al.*, 2015).

In nature, Fe originates from the dissolution of iron minerals as well as from domestic sewage, industrial wastewater, aquaculture, agriculture, animals, plants, and microorganisms. In the built environment, phosphorus is found mainly in wastewater from human excrement, household waste, P-containing detergents, and industrial pollution (SMIL, 2000; LOTZE *et al.*, 2006; WITHERS; JARVIE, 2008). Phosphorus in water usually manifests as organic P, inorganic P, and poly P (MCMAHON *et al.*, 2002).

Various investigations have found that vivianite mainly exists in a reducing environment. Under anaerobic conditions, Fe^{3+} reduces to Fe^{2+} by reducing bacteria, such as dissimilatory metal-reducing bacteria (DMRB), and then Fe^{2+} combines with PO_4^{3-} produced by anaerobic microorganisms. Under certain conditions, vivianite is precipitated when the target K_{SP} is reached (NRIAGU *et al.*, 1972; WILFERT *et al.*, 2018).

In summary, vivianite is formed in the bottom sediments of natural water bodies via two processes: the conversion of organic P in organic matter to inorganic phosphate (PO_4^{3-}) and the reduction of iron ($Fe^{3+}$to Fe^{2+}). Vivianite is precipitated in the form of crystals, as shown in Figure 1 and Equations 1 to 4

$$Porg \rightarrow PO_4^{3-} \tag{1}$$

$$Fe(OH)_3 + 3H^+ + e^- \rightarrow 3H_2O + Fe^{2+} \tag{2}$$

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

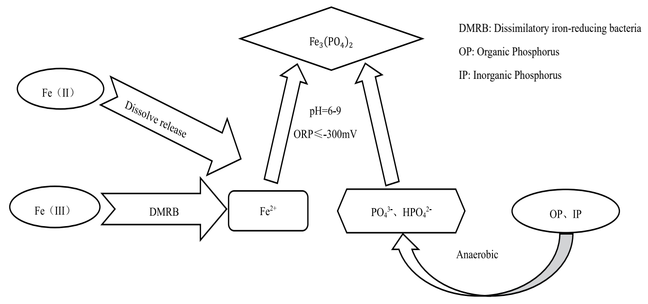
$$3Fe^{2+} + 2HPO_4^{2-} + 8H_2O \rightarrow Fe_3(PO_4)_2 \cdot 8H_2O + 2H^+ \tag{4}$$

RESEARCH PROGRESS ON PHOSPHORUS RECOVERY FROM VIVIANITE

Advantages of Fe source and pH optimization and co-fermentation

Recrystallization

Vivianite is mainly formed in a reducing environment. Cao *et al.* (2019) and Wu *et al.* (2020) crystallized vivianite in controlled environments. In both experiments, the pH was controlled and an external Fe source was used to release Fe^{2+} and PO_4^{3-} into the anaerobic fermentation solution, and the supernatant was recrystallized after separation. The advantage of this method is that the content of other ions in the solution is relatively low, and because PO_4^{3-} and Fe^{2+} are the main ionic forms, the mechanism of recrystallization is not affected by various other factors. This process is easier to control than inducing the in situ formation of azurite in the sludge. Moreover, we do not yet fully understand the various properties of the sludge, and thus there are many uncertainties in the in situ formation of azurite in the sludge. The growth of microorganisms in the sludge, pH, and various complex ions, such as Mg, Al, Zn, affect the formation of vivianite. It has been reported that a magnesium analogue called maficite is found in the sediments of an iron-rich cold spring in western Taiwan (HSU; JIANG; WANG, 2014). In addition, co-existing S^{2-} competes with PO_4^{3-} for Fe^{2+} to produce FeS preferentially (GÄCHTER; MÜLLER, 2003; O'CONNELL *et al.*, 2015). The experiment of Cao *et al.* (2019) avoided this point.



DMRB: dissimilatory iron-reducing bacteria; OP: organic phosphorus; IP: inorganic phosphorus.
Source: elaborated by the authors.

Figure 1 – Simplified vivianite formation process.

Fe source

In WWTPs, high phosphorus and low iron concentrations are common, and thus the addition of iron sources is very important for the effective formation of vivianite. This is very important in the experiments of Cao *et al.* (2019) and Wu *et al.* (2020). Generally, at low pH, most of the total water-soluble Fe in all samples is Fe^{2+} (> 95%), which facilitates the subsequent recovery of phosphorus as vivianite. In the experiment of Cao *et al.* (2019), the $FeCl_3$ dosed batch has a higher Fe^{2+} concentration than the ZVI (zero-valent iron)-dosed batch, and the time to reach the maximum Fe^{2+} concentration in the solution is the shortest. $FeCl_3$ in water is mainly hydrolyzed to form hydrous iron oxide (HFO) precipitates (CHEN *et al.*, 2019). Under anaerobic reduction conditions, Fe^{3+} is reduced by DMRB to Fe^{2+}(VUILLEMIN *et al.*, 2013), and Fe^{2+} mainly exists in the form of $Fe(OH)_2$ precipitates, which are easier to dissolve under acidic conditions (ZOU *et al.*, 2017) and are converted into the ionic state and released into the solution. In addition, because $FeCl_3$ is acidic when hydrolyzed in water, as shown in Equation 5, it also accelerates the dissolution of precipitates, as shown in Equation 6. Although in the experiment of Cao *et al.* (2019) ZVI is also selected as an additional Fe source, $FeCl_3$ batches obviously have a higher Fe^{2+} release than ZVI batches under the same conditions, for example, under the same pH3 condition. The reason for this result is the dissolution of ZVI in an acidic environment (LIU; WANG, 2019). However, in a weakly acidic environment, the dissolution rate of ZVI is relatively low, resulting in a relatively low Fe^{2+} concentration in the aqueous solution, as shown in Equation 7. Therefore, $FeCl_3$ is a better choice than zero-valent Fe.

$$Fe^{3+} + 3H_2O \rightarrow Fe(OH)_3 + 3H^+ \tag{5}$$

$$Fe(OH)_{3(S)} + H^+ + e^- \rightarrow Fe(OH)_{2(S)} + H_2O \tag{6}$$

$$Fe^0 + 2H^+ \rightarrow Fe^{2+} + H_2 \tag{7}$$

Both experiments use $FeCl_3$ as the external iron source, which fully explains the effectiveness of $FeCl_3$, although there is no more explanation and exploration on the effect of adding other iron sources. The additional iron source has a profound impact on the benefit of phosphorus recovery, and the price is different. According to mainland China's March quotation, $FeCl_3$ is \$0.26163/kg, while $FeSO_4$ is \$0.055328/kg. Therefore, $FeCl_3$ is relatively more expensive. If $FeSO_4$ can achieve similar results, it is more economical to choose $FeSO_4$ as the external iron source.

pH

The pH of an environment is known to affect the ion concentration. The experimental results of Cao *et al.* (2019) and Wu *et al.* (2020) both show a significant correlation with the pH, which directly affects the efficient recovery of P. Both have designed related pH control experiments, as shown in Tables 1 and 2. The pH experiment of Cao *et al.* (2019) shows that, with decreasing pH, the concentrations of Fe^{2+} and PO_4^{3-} in the solution increase because the solubility of iron and phosphorus compounds increases as the pH decreases.

Similar to the results of Cao *et al.* (2019), Fe^{2+} and PO_4^{3-} are released into the supernatant more efficiently under lower pH conditions in the controlled pH experiments of Wu *et al.* (2020). Moreover, as the concentration of added FW increases, the release rates of Fe^{2+} and PO_4^{3-} also increase to different degrees. Under controlled pH conditions, the Fe^{2+} and PO_4^{3-} release rates of the R3-pH3 batch and the R3-pH4 batch are almost the same, which are the highest among all batches. However, compared with the experimental batch that controls the pH, no additional reagents are added, and only FW co-fermentation is used to freely control the pH of the reactor to produce better results. The concentrations of Fe^{2+} and PO_4^{3-} in the R3-none batch are the highest among all the experimental batches. The experimental data also show that, in the R0-none batch, the concentrations of Fe^{2+} and PO_4^{3-} are the lowest among all batches, and as the fermentation progresses the concentrations of Fe^{2+} and PO_4^{3-} are the lowest among all batches and the concentrations of Fe^{2+} and PO_4^{3-} in the supernatant are negligible. This result also shows that joint fermentation using FW is more important than the control of pH. There is no need to deliberately control the pH, i.e., there is no need to add additional reagents, and there is no secondary pollution, thus reducing cost, manpower, and material resources. Compared with the experiment of Cao *et al.* (2019), this is also the greatest advantage of the experiment of Wu *et al.* (2020).

Furthermore, vivianite is mainly formed in the anaerobic fermentation process, and through the action of DMRB, Fe^{3+} is reduced to Fe^{2+} to form vivianite. Cao *et al.* (2019) effectively reduced the pH of the solution by adding ferric chloride, creating favorable conditions for the survival of reducing microorganisms. However, instead of an external iron source, Wu *et al.* (2020) used volatile fatty acids (VFAs) produced by co-fermentation to reduce the pH of the anaerobic fermentation environment, thus creating conditions conducive to the survival of reducing microorganisms. Experiments have demonstrated that, in WAS, the sludge with added $FeCl_3$ and controlled pH3 (CAO *et al.*, 2019) has a relatively high abundance of Clostridiaceae (40.25%),which belongs to the order Clostridium (42.33%), and the Clostridium family is mainly composed of typical iron-reducing bacteria, namely *Clostridium beckinii* and *metalloalkaliophilus* (WEBER; ACHENBACH; COATES, 2006). These functional bacteria can use organic substrates as carbon sources and electron donors to reduce Fe^{3+}. Therefore, under acidic conditions, abundant Clostridia in the $FeCl_3$-pH3 reactor can greatly accelerate Fe^{3+} reduction, resulting in a high concentration of Fe^{2+}. Although Wu *et al.* (2020) did not discuss the dominant species of bacteria, the VFAs produced by co-fermentation also create an acidic environment to promote the growth of dominant bacteria.

Compared with the experiment of Cao *et al.* (2019), another advantage the experiment of Wu *et al.* (2020) is that co-fermentation also produces a large amount of VFAs. These are important intermediate products in the anaerobic digestion process. Methanogens (such as Methanomonsharveyi) (ROTARU *et al.*, 2014) mainly use VFAs to form methane. Methane is an energy source with a high calorific value.

From the analysis of the above two experiments, the advantage of the co-fermentation experiment of Wu *et al.* (2020) is more obvious. For the time being, regardless of the phosphorus recovery rate and the purity of the crystallized vivianite, the experiment of Wu *et al.* (2020) simultaneously solves the problems associated with FW and WAS, i.e., there is no need for additional acidifiers and no occurrence of secondary pollution. Moreover, the intermediate product VFAs can be further used to produce methane, recycled as an energy source, which fits well with the idea of resource recycling.

Disadvantages of Fe source and pH optimization and co-fermentation

Microbial discomfort in engineering applications

In contrast to the experiment of Wu *et al.* (2020), that of Cao *et al.* (2019) seems to have a technological mismatch for enhanced biological phosphorus removal (EBPR) in large-scale WWTPs. These WWTPs generally use anaerobic digestion. Most of this process uses phosphorus-accumulating organisms (PAOs) to accumulate and release phosphorus. Neutral or slightly alkaline pH conditions are suitable for this kind of bacteria, which is why most WWTPs remain neutral. Overly acidic conditions dissolve PAOs. In the experiment of Cao *et al.* (2019), the release of PO_4^{3-} and Fe^{2+} is the highest in the $FeCl_3$-pH3 fermentation reactor.

Table 1 – Experimental batches with pH ratio of Wu *et al.* (2020).

Reactors	pH uncontrolled	pH 3.0	pH 4.0	pH 5.0
WAS	R0-none	R0-pH 3	R0-pH 4	R0-pH 5
WAS + 10%FW	R1-none	R1-pH 3	R1-pH 4	R1-pH 5
WAS + 20%FW	R2-none	R2-pH 3	R2-pH 4	R2-pH 5
WAS + 30%FW	R3-none	R3-pH 3	R3-pH 4	R3-pH 5

WAS: waste-activated sludge; FW: food waste.
Source: analysis of Wu *et al.* (2020) data regrouping and tabulation.

Table 2 – Experimental batches with pH ratio of Cao *et al.* (2019).

Fe source	pH 3.0	pH 5.0	pH 10.0	pH 12.0	NC
ND	ND-pH 3	ND-pH 3	ND-pH 3	ND-pH 3	ND-pH 3
ZVI	ZVI-pH 3	ZVI-pH 3	ZVI-pH 3	ZVI-pH 3	ZVI-pH 3
$FeCl_3$	$FeCl_3$-pH 3	$FeCl_3$-pH 3	$FeCl_3$-pH 3	$FeCl_3$-pH 3	$FeCl_3$-pH 3

Source: analysis of Cao *et al.* (2019) data regrouping and tabulation.

However, under such pH conditions, PAOs lose their activity, and thus there is no way to release phosphorus and subsequently absorb phosphorus. In addition, the dominant bacteria in the experiment is the Clostridium family, which is composed of typical iron-reducing bacteria. Under acidic conditions, it has a great positive effect on accelerating Fe^{3+} reduction. Although acidic conditions are conducive to the reduction of Fe^{3+} and the release of PO_4^{3-}, because PAOs are moderately alkaline bacteria, there is always an opposing relationship between the two bacterial species in practice. Moreover, to control the pH, it is necessary to add reagents, which may cause secondary pollution, which should be avoided.

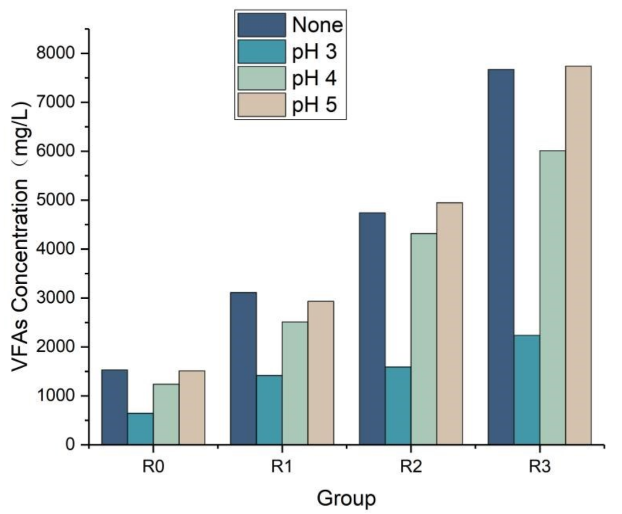
Incompleteness of experimental results

To better carry out reasonable resource allocation in actual engineering applications, and to recycle useful materials as much as possible, unnecessary resource consumption and waste should be reduced. Therefore, it is necessary to clarify the optimal ratio of the experiment to make recommendations for subsequent product processing and recovery.

As shown in Figure 2, analysis of the experimental data of Wu *et al*. (2020) shows that the addition of FW has a positive correlation with the degree of influence of Fe^{2+} and PO_4^{3-}. The greater the addition of FW, the higher the concentrations of Fe^{2+} and PO_4^{3-}. In addition, for the R3-none batch, the dissolved concentrations of Fe^{2+} and PO_4^{3-} also show a rising trend, which means that, for the result of co-fermentation, WAS + 30% FW may not be the most suitable fermentation ratio. Under this condition, the release of Fe^{2+} and PO_4^{3-} is already very high (accounting for 82.88% of total Fe^{2+} and 88.49% of TP). Therefore, a higher FW ratio may achieve better ion concentration release. Unfortunately, the authors did not provide further experimental data. If a higher FW ratio can achieve higher ion release results, then all results will change, and the purity of vivianite will become higher.

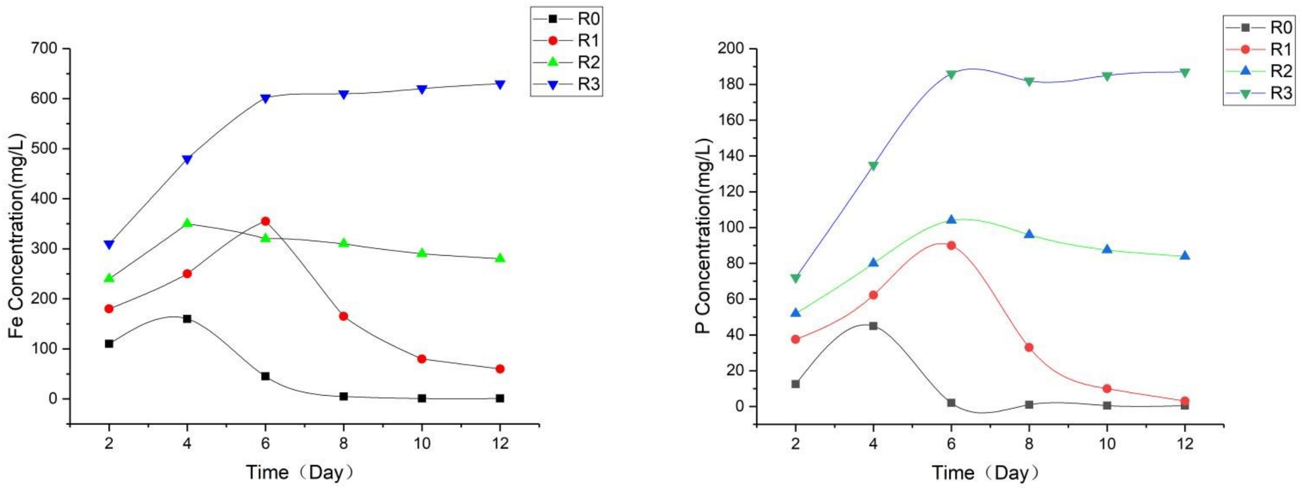
Similarly, by analyzing the experimental results of Wu *et al*. (2020), as shown in Figure 3, the amount of VFAs produced also shows a rising trend regardless of whether the pH is controlled. Therefore, although the amount of VFAs reaches the maximum value in the reaction system under the conditions of R3-none and R3-pH5, whether this is the best ratio remains to be confirmed. Studies have shown that high concentrations of VFAs reduce the pH of the reaction system, and because low pH conditions affect the activity of methane bacteria, the production of methane is inhibited. This has an adverse effect on the final recovered products of the co-fermentation system.

Wu *et al*. (2020) did not analyze and discuss the product, and it was impossible to determine the method they used to treat the product. The method used to treat the final product is an important indicator of cost and is inevitably considered to optimize the engineering plan. Moreover, small differences in the experiment produce huge economic differences in large-scale engineering applications, and thus a complete analysis of the experiment is necessary.



VFAs: volatile fatty acids.
Source: according to the data given by the author Wu *et al.* (2020), after analysis.
R0: WAS; R1: WAS + 10%FW; R2: WAS + 20%FW; R3: WAS + 30%FW.

Figure 3 – Amount of volatile fatty acids generated under different waste-activated sludge (WAS) + food waste (FW) ratios.



Source: according to the data given by the author Wu *et al.* (2020), after analysis.
R0: WAS; R1: WAS + 10%FW; R2: WAS + 20%FW; R3: WAS + 30%FW.

Figure 2 – Fe and P release for different waste-activated sludge (WAS) + food waste (FW) batches.

Discussion of optimization for engineering utilization

Improvement of engineering operation procedures

In both the experiments of Cao *et al.* (2019) and Wu *et al.* (2020), enrichment of Fe^{2+} and PO_4^{3-} into the supernatant is followed by recrystallization, which significantly improves the purity of vivianite. Removal of biological phosphorus traditionally passes through the anaerobic stage of release and then the aerobic stage of phosphorus accumulation to finally obtain phosphorus-rich surplus sludge. There are two ways to use the Cao *et al.* (2019) experiment in engineering. The first is to re-collect the surplus sludge rich in phosphorus and then perform the Cao *et al.* (2019) experiment to finally obtain vivianite. However, this method is too cumbersome to operate. The second method is to change the process flow of the treatment plant. The final result of the traditional process is the removal of P, whereas the final result of the Cao *et al.* (2019) experiment is to obtain a high concentration of PO_4^{3-}, so that the phosphorus can be absorbed through the aerobic stage while removing BOD and then released through the anaerobic stage. Finally, Fe is added to the phosphorus-rich wastewater and the Fe/P molar ratio is controlled for recrystallization. The advantage of this is that the sludge produced contains a small amount of phosphorus. In addition, because this method recovers nearly 82.60% of TP, the phosphorus content in the water after recrystallization is very low, which does not affect the secondary use of water. However, the operability of this improved method needs to be verified by experiments.

Control of the Fe/P molar ratio

In the Wu *et al.* (2020) co-fermentation experiment, the initial Fe/P molar ratio needs to be kept at 1.5. This is the theoretical ratio of vivianite. For all large-scale treatment plants, it is unrealistic to ensure precise control of this ratio, and thus excessive $FeCl_3$ and other flocculants need to be added. However, this increases the cost, and if this addition is excessive the effluent can easily contain a large amount of Fe. In fact, it is unnecessary to deliberately adjust the Fe/P molar ratio before co-fermentation. After co-fermentation, the supernatant is extracted, an appropriate external iron source is selected as the adding reagent, the pH is controlled, and then precipitation occurs. In this way, excessive addition of Fe can be avoided as far as possible, $FeSO_4$ can be chosen as the additional reagent to adjust the pH to 7, and then precipitation is performed. Therefore, it is possible to avoid waste of resources and a large amount of enrichment caused by excessive addition of Fe. In general, the two experiments have high reference value. The high purity of vivianite and high efficiency of phosphorus recovery have triggered further studies on vivianite. Solving the contradiction between using bacteria in WWTPs and ensuring a high PO_4^{3-} release rate is also worthy of further discussion.

Comprehensively increasing the amount of Fe in wastewater treatment plants

Advantages of increasing the amount of Fe

Wilfert *et al.* (2018) analyzed vivianite in the digested sludge of several comprehensive municipal WWTPs in Europe. They verified that these different WWTPs all use Fe to remove phosphate and that phosphorus can be recovered as vivianite using different Fe/P ratios. The data obtained by Wilfert *et al.* (2018) using X-ray diffraction, conventional scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX), environmental SEM-EDX, and Mossbauer spectroscopy indicate that, in digested sludge with the highest iron content, 70–90% of all P are combined in the form of vivianite. Wilfert *et al.* (2018) hypothesized that the iron content affects the recovery of phosphate, and, to verify this hypothesis, controlled increase of iron dosage was realized to determine the effect of iron dosage on the production of vivianite. Prot *et al.* (2020) doubled the iron consumption of the Nieuwveer WWTP, and the results confirmed their hypothesis that the iron content in the sludge is directly related to the content of vivianite.

The advantage of the Prot *et al.* (2020) experiment is that, by increasing the amount of iron in a comprehensive manner, the proportion of phosphorus as vivianite in the digested sludge can be increased from 20 to 50%. Notably, in this experiment, the concentration of H_2S in the biogas is reduced from 26 to 8 ppm mainly because, in the solution, S^{2-} preferentially combines with Fe^{2+} to form FeS precipitates, which is important in reducing H_2S emission. The added iron does not have any adverse effects on the removal of nitrogen, the production of biogas, the removal of chemical oxygen demand, and the dewaterability of sludge, as well as cost.

Advantages of $FeSO_4$

$FeSO_4$ is added in the experiment of Prot *et al.* (2020), which is different from the experiments of Cao *et al.* (2019) and Wu *et al.* (2020). Fe^{2+} can be directly complexed with PO_4^{3-} to form vivianite, without the need for complex biological and chemical reactions to reduce Fe^{3+} to Fe^{2+}. Prot *et al.* (2020) found that external Fe added in the experiment is combined during the formation of vivianite. This is of great significance for studying the formation of vivianite.

As mentioned above, if $FeCl_3$ is replaced by $FeSO_4$ in the experiments of Cao *et al.* (2019) and Wu *et al.* (2020), then there is no need to consider the Fe/P molar ratio in advance. Therefore, Fe can be added after the supernatant is separated, and there is no need to reduce Fe^{3+}. Because external iron is all used to form vivianite, only the pH needs to be controlled for recrystallization. In this way, the amount of added Fe can be effectively controlled, and resource waste can be avoided. Moreover, vivianite can be used to more thoroughly recover phosphorus in the supernatant. Because $FeSO_4$ is cheaper than $FeCl_3$, using $FeSO_4$ as the iron source reduces the production cost.

Disadvantage analysis

The shortcoming of the experiments is the purity of vivianite. Although Prot *et al.* (2020) did not specifically highlight it, we can speculate this from the experimental results. There are many metal ions in sewage that have adverse effects on vivianite formation and thus the purity and recovery of vivianite. The Mossbauer spectroscopy results show that different types of vivianite are formed in the Nieuwveer WWTP. The oxidation of vivianite and the replacement of Fe by non-magnetic cations (e.g., Mg^{2+} and Ca^{2+}) change the structure of vivianite, thereby affecting the magnetic properties, recovery, and purity of vivianite. Wilfert *et al.* (2018) determined that the structure of this impure crystal is similar to that of vivianite. Moreover, by adding more Fe to the Nieuwveer WWTP than before, the proportion of P in the digested sludge can be increased from 20 to 50% for vivianite formation. Nevertheless, such results are still far from the experimental results of Cao *et al.* (2019) and Wu *et al.* (2020).

The experiment of Prot *et al.* (2020) was carried out in a WWTP using the AB method, while the experiment of Cao *et al.* (2019) was performed in a treatment plant using the A_2O method. The biggest difference between the two methods is the way in which phosphorus is removed. The main phosphorus removal stage of the AB method is in stage A, which is mainly based on biological flocculation and adsorption, and the amount of sludge produced is relatively large (approximately 80%). In the Prot *et al.* (2020) experiment, the Fe source is added in stage A, and the produced vivianite is deposited in the sludge. The purity of vivianite formed as a biological complex in stage A is not high.

The A_2O method requires anaerobic fermentation. This process is the opposite of the AB method. In the AB method, PO_4^{3-} is removed through adsorption, flocculation, and sedimentation in the sludge, whereas in the A_2O method, phosphorus is released in the anaerobic digestion stage. This difference affects the subsequent recovery method and the purity of vivianite. In particular, the Prot *et al.* (2020) experiment is not suitable for separating the supernatant and then precipitating vivianite, which is also the most fundamental reason affecting the purity of vivianite. The complexity of various components in the sludge hinders the purity of vivianite crystals.

Although the efficiency of phosphorus recovery is much lower with the Prot *et al.* (2020) experiment than with the Cao *et al.* (2019) and Wu *et al.* (2020) experiments, it is still higher than with the struvite recovery method (30–40%) commonly used internationally. In addition, the authors pointed out that stimulating the formation of vivianite combined with magnetic recovery from sludge is expected to recover 50–60% of phosphorus in the effluent of the Nieuwveer sewage treatment plant and 70–80% of blue iron ore in digested sludge.

The most important point is that Prot *et al.* (2020) carried out operational experiments in large-scale sewage treatment for the first time, and the effect is remarkable, which is a very suitable method for all sewage treatment plants with anaerobic digestion capacity.

PRACTICAL APPLICATIONS OF PHOSPHORUS RECOVERY FROM VIVIANITE

Although phosphorus recovered as vivianite has been studied for a long time, there is still a lack of systematic recommendations on how to proceed. In general, based on the above experimental analysis, there are two mainstream methods that can be adopted:

In situ vivianite formation

The first method entails the induction of in situ vivianite formation (in the sludge) by supplying an external source of iron for subsequent phosphorus removal operations. At present, $FeCl_3$ and $FeSO_4$ are the most widely used iron sources, and choosing different iron sources inevitably leads to different results. $FeCl_3$ reduces the pH of the solution and increases the concentration of released PO_4^{3-}, although it affects the activity of alkaline bacteria (P-accumulating bacteria). Because Fe reduction requires the participation of metal-reducing bacteria, choosing the right bacteria is essential for effective reduction. The final product is sludge flocs rich in vivianite crystals. The sludge after the reaction can control the quality of the effluent and reduce the generation of H_2S gas. The main application is the Prot *et al.* (2020) experiment in sewage treatment plants using the AB method. Through the addition of an external Fe source, PO_4^{3-} in the sludge is co-precipitated to form vivianite, which greatly reduces the P content in the sewage. However, owing to the various physical and chemical changes and uncertain physical and chemical components in the sludge, precipitation cannot be controlled. Therefore, the purity of vivianite produced by this method is low, and Prot *et al.* (2020) did not provide corresponding data. In addition, vivianite is difficult to separate from sludge. In this regard, to obtain high-purity vivianite and highly efficient phosphorus recovery, we can only further optimize the method of vivianite recycling and the supply of additional iron sources.

Recrystallization

The second method involves the induction of large-scale phosphorus release in the sludge, followed by the extraction of the supernatant to synthesize and recrystallize vivianite. The main applications are discussed before. By controlling the pH, phosphorus can be efficiently released into the supernatant. An external iron source is then used for complexation, and the pH is adjusted to recrystallize vivianite. The advantage of this method is that the purity of the formed vivianite is relatively high. For example, the experimental results of Cao *et al.* (2019) show that approximately 82.60% of TP is recovered as vivianite (93.67%). This result is currently the highest purity reported for vivianite formation. This is mainly because the process of first releasing and then recrystallizing no longer uses digested sludge as the substrate, which eliminates the need for complex biochemical reactions in the sludge and avoids other physical and chemical effects to form vivianite, and thus the purity of vivianite is high. However, the disadvantage of this method is that it is not easy to induce the release of phosphorus in wastewater treatment plants using the A_2O method. As already mentioned, the Cao *et al.* (2019) method requires low pH conditions to ensure efficient phosphorus release, and these conditions are not possible in practice. Inevitably, the pH affects the P-accumulating bacteria in the anaerobic fermentation stage of the treatment plant and thus phosphorus release. From this point of view, phosphorus release cannot reach the theoretical maximum release. A feasible solution, mentioned before, is to enrich PO_4^{3-} first, and, after separating the supernatant, to adjust the appropriate Fe/P molar ratio to 1.5 and the pH to 7. $FeSO_4$ is then added for recrystallization. This can avoid inappropriate cost increases from quantitative uncertainties in practical applications.

CONCLUSION

From an analysis of existing research on vivianite, phosphorus recovery from vivianite has broader application prospects than previous methods in terms of economic value, operation method, and phosphorus recovery rate. The premise of the two methods described can be used as the focus of research on phosphorus recovery. For different systems, different vivianite formation methods and recycling methods are used. For example, external iron sources can be used to induce the in situ synthesis of vivianite in septic tank systems and wastewater treatment plants using the AB method. When a concentrated or pure vivianite stream is obtained, vivianite can easily be dissolved under alkaline conditions using KOH. Under these conditions, phosphate and potassium dissolve while Fe and heavy metals precipitate. For WWTPs that adopt the A_2O method and are equipped with anaerobic reactors, supernatant separation and then recrystallization can be used to obtain high-purity vivianite crystals. However, both these methods currently have operational problems that require further exploration. Optimizing the phosphorus recovery method based on vivianite formation and striving to achieve the best combination of environmental and economic benefits will be the focus of our future research.

AUTHOR'S CONTRIBUTIONS

Tengshu, C.: Supervision. Xingfu, S.: Writing – Original Draft.

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