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Pilot-scale magnetic recovery of vivianite from digested sewage sludge

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ABSTRACT

Phosphorus (P) is an essential resource for food production and chemical industry. Phosphorus use has to become more sustainable and should include phosphorus recycling from secondary sources. About 20% of P ends up in sewage sludge, making this a substantial secondary P source. There is currently a technological gap to recover P from sludge locally at wastewater treatment plants (WWTP) that remove P by dosing iron. Vivianite ($Fe_3(PO_4)_2 \bullet 8(H_2O)$) is the main iron phosphate mineral that forms during anaerobic digestion of sewage sludge, provided that enough iron is present. Vivianite is paramagnetic and can be recovered using a magnetic separator. In this study, we have scaled up vivianite separation from lab-scale to bench- and pilot-scale. Bench-scale tests showed good separation of vivianite from digested sewage sludge and that a pulsation force is crucial for obtaining a concentrate with a high P grade. A pilot-scale magnetic separator (capacity 1.0 m^3/h) was used to recover vivianite from digested sewage sludge at a WWTP. Recirculating and reprocessing sludge allows over 80% vivianite recovery within three passes. A concentrated P-product was produced with a vivianite content of up to 800 mg/g and a P content of 98 mg/g. P recovery is limited by the amount of P bound in vivianite and can be increased by increased iron dosing. With sufficient iron dosing, the vivianite content can be increased, and subsequently more P can be recovered. This would allow compliance with existing German legislation, which requires a P recovery larger than 50%.

1. Introduction

1.1. Incentive for recovery

Phosphorus (P) is an essential resource for food production and chemical industry. The primary source of phosphorus is phosphate rock. About 80% of mined phosphate rock ($Ca_{10}(PO_4)_6(OH)_2$) is used in the fertilizer industry (Van Vuuren et al., 2010). Phosphate rock is a finite resource and reserves are concentrated in a few countries (USGS, 2020). The EU has almost no phosphate rock reserves and depends therefore almost entirely on import from other countries. This means there is a supply risk of phosphorus for the EU. Consequently, this is why the EU added phosphate rock and phosphorus to the list of critical raw materials in 2014 and 2017, respectively (European Commission, 2017, 2014). Hence, phosphorus use has to become more sustainable and should include phosphorus recycling from secondary sources. In 2005, the primary P import of the EU-27 was 1777 kton (van Dijk et al., 2016). Europe's Urban Waste Water Treatment Plants annually remove approximately 370 kton P by immobilization in the sewage sludge (van

Dijk et al., 2016). Therefore, about 20% of imported P ends up in sewage sludge, making this a substantial secondary source of P and one of the largest secondary sources after animal manure (Cordell and White, 2013). In 2015, Switzerland implemented legislation demanding P recovery from sewage sludge by 2026, followed by Germany demanding 50% recovery in 2017 (BAFU, 2015; BMUV, 2017).

1.2. Technological gap for decentralized P recovery at iron-dosing WWTPs

Land application of sewage sludge is the most straightforward and low-cost option to reuse phosphorus. Besides rising concerns about impurities in sludge such as micropollutants, pathogens, and heavy metals, the biggest challenge with direct land application of sewage sludge is the geographic imbalance of P. There are areas, for example in West-Europe, where there is a P surplus due to manure from livestock farming (MacDonald et al., 2011). Transporting sludge to areas with a P-deficit is economically and environmentally unthinkable due to transport costs and emissions. It is, therefore, desirable to recover a more concentrated

phosphorus product.

Towards this end, phosphorus can be recovered in a centralized manner by incineration of the sludge followed by chemical leaching of P from the ash. Phosphorus recovery from sludge incineration ash has an advantage due to economy of scale and high recovery efficiency (Korving et al., 2019). However, these technologies rely on expensive and strongly centralized infrastructure. Compliance with phosphorus recovery legislation alone will not be a sufficient reason to build sludge incinerators. Alternatively, phosphorus can be recovered at the wastewater treatment plant (WWTP) by the separation of P-bearing minerals from the sludge, i.e., struvite (Doyle and Parsons, 2002). P-recovery at the WWTP level has been shown to be environmentally more beneficial than sludge incineration, although less phosphorus can be recovered (STOWA, 2016).

In municipal wastewater treatment, the most favored advanced phosphorus removal technologies are Chemical Phosphorus Removal (CPR) using iron or aluminum salts and Enhanced Biological Phosphorus Removal (EBPR). EBPR plants have the option to recover a small fraction (10–30%) of the P from the sludge as struvite ($MgNH_4PO_4 \bullet 6H_2O$) or calcium phosphate (Egle et al., 2016). For CPR plants, there is currently a technological gap to recover P from the sludge locally at the WWTP.

1.3. Vivianite recovery

The majority of WWTP in Europe utilize CPR (Korving et al., 2019). If iron salts are dosed for CPR, phosphorus precipitates as iron phosphate minerals and is immobilized in the produced sludge. This sludge is then often anaerobically digested for hygienisation and energy recovery via methane production. Iron can also be added in the treatment process as a coagulant to enhance primary sedimentation and thus biogas production or to prevent hydrogen sulfide emissions (Charles et al., 2006; Ge et al., 2013).

Recently, research has shown that vivianite ($Fe_3(PO_4)_2 \bullet 8(H_2O)$) is the main iron phosphate mineral that forms during digestion of sewage sludge and that up to 80–90% of all phosphorus in digested sludge can be present as vivianite, provided that enough iron is present (Wilfert, 2018). Unwanted vivianite scaling and accumulation in WWTPs can result in the blockage of pipes which leads to an increased need for maintenance (Prot et al., 2021). The authors also describe simple mitigation strategies (i.e., design and operational considerations) to prevent vivianite scaling. Vivianite can be used as an iron fertilizer to prevent iron-chlorosis of crops like strawberries, olive trees, lupin, kiwi, grapevines, peach trees, and citrus trees growing on calcareous soils (Caballero et al., 2009; de Santiago et al., 2013; de Santiago and Delgado, 2010; Domenico Rombolà et al., 2003; Eynard et al., 1992; Rosado et al., 2002). Furthermore, vivianite can also be split via an alkaline treatment into a liquid phosphate fertilizer and an iron oxide precipitate (Prot et al., 2019), which potentially can be reused as a raw material to produce iron salts for phosphate binding in sewage treatment plants, thus creating circular use of the dosed iron.

Vivianite recovery receives increasing interest as a novel approach to phosphorus recovery. However, recovery of vivianite from sewage sludge presents a separation challenge as the vivianite particles are typically small, ranging from 10 to 200 μm. Vivianite is paramagnetic, and therefore a magnetic separation approach has been suggested and demonstrated at lab-scale (Prot et al., 2019). In this context, the application of industrial mining separators (i.e., High-Gradient Magnetic Separator), which are designed for extraction of paramagnetic minerals (Wills and Finch, 2016), allows for a clear pathway for upscaling of the vivianite recovery from digested sewage sludge. The SLon Vertically Pulsating High Gradient Magnetic Separator (VPHGMS) is widely used in the mining industry for ore concentration. Among other applications, the SLon separator has been used to concentrate fine particles such as hematite and ilmenite and for desulfurization and dephosphorization of iron ore feeds prior to steelmaking (Xiong et al., 2015).

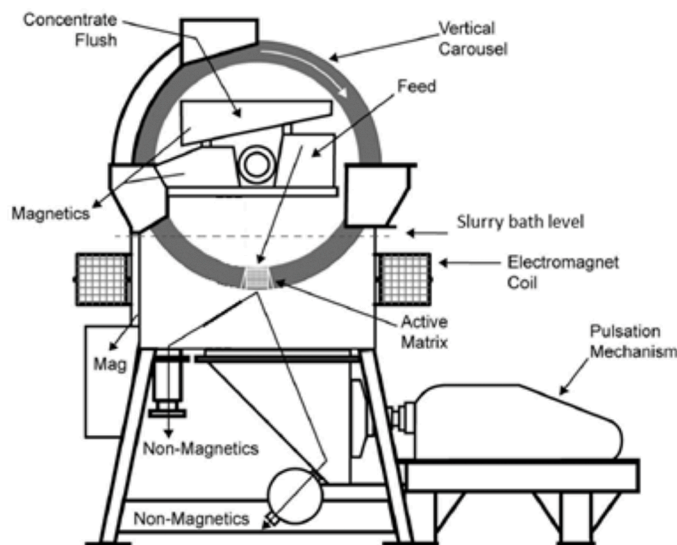In a VPHGMS (Fig. 1), in order to capture paramagnetic particles, a

Fig. 1. SLon VPHGMS. Courtesy of Outotec.

strong magnetic field is applied over a steel rod matrix which creates many points of high field gradient. These rods, in this way, attract paramagnetic particles, and non-magnetic particles are allowed to pass through the separator without being captured. Pulsation is achieved in the separation zone by an actuated diaphragm to assist in separation by agitating the sludge and keeping particles in a loose state. This minimizes the entrapment of particles and maximizes the usable surface area of the steel rods for magnetics collection (Wills and Finch, 2016).

This study evaluates the application of a VPHGMS for the separation of vivianite from digested sewage sludge. Firstly, a bench-scale VPHGMS was used for processing 0.5 L samples in batches to show the feasibility of the separation process. Secondly, a vivianite separation was studied at pilot-scale VPHGMS installation at a WWTP in the Netherlands, able to process 1 m^3/h of sludge continuously. Based on these studies, we evaluate the potential and further development of vivianite recovery by magnetic separation.

2. Materials and methods

2.1. Bench-scale magnetic separator SLon-100

A SLon-100 unit was provided by Outotec for the bench-scale tests. This machine is located in Outotecs R&D center in Frankfurt (Germany). The SLon-100 can process batch samples of 0.5 L, the magnetic field intensity is adjustable up to 1 Tesla, and steel rod matrices with different diameters can be utilized.

A steady flow of tap water of 4 L/h is created over the matrix, and pulsation is achieved with a diaphragm acted on by a motor. A digested sludge sample of approximately 0.5 L is then fed to the top of the machine, and the sludge is carried over the matrix by the water flow. The magnetic particles are retained by the magnetic field on the matrix, while the non-magnetics are carried out at the bottom of the machine.

Table 1
Overview of bench-scale tests with SLon-100.

Matrix rod diameter [mm]	Pulsation [Yes/No]	Magnetic field strength [T]
1	Yes	1.0
1	No	1.0
1	Yes	0.9
2	Yes	1.0
2	No	1.0
2	No	0.5

Table 1 provides an overview of the performed tests using the Slon-100.

2.2. Pilot plant installation

The pilot installation consisted of a SLon-750 VPHGMS and auxiliary equipment, namely a feed tank (1 m^3), tailings (=treated sludge) tank (1 m^3), and Dortmund type settler unit (1 m^3). Feed and tailings tanks were stirred. Worm pumps were used to supply the sludge. It was possible to reprocess tailings by cycling them back to the feed tank. Fig. 2 shows a simplified flow scheme diagram of the installation.

2.3. WWTP Nieuwveer

The pilot study took place at WWTP Nieuwveer, the Netherlands, from 01/09/2018 to 30/06/2019. The WWTP has a size of 375000 population equivalent (p.e.) with an average influent of 75000 m^3/day. At the WWTP Fe(II) is added in the aerated primary treatment for P removal. Sludge from primary and secondary treatment is anaerobically digested for 20 days. The digester receives sludge from other WWTPs, which accounts for about 30% of the total sludge load. During the pilot study, parallel research on the influence of the Fe dosing increase on vivianite formation was performed. The quantity of Fe(II) dosed in the A-stage was doubled for 4 months (Prot et al., 2020). The share of phosphorus present as vivianite in the digested sludge increased from 20 to 50% after increasing the Fe dosing, making more phosphorus available for magnetic separation.

2.4. Pilot plant separation testing and sampling

Digested sludge with a dry matter content of typically 4% was tapped off from the main process before dewatering, sieved, and then fed to the pilot installation. Separation tests were performed to determine the separation performance with varying operational parameters. For each test, the parameters were set, and the magnetic separator was started. The feed was started through the SLon, and necessary adjustments were made to the outflow valves to maintain a steady slurry level in the separator and to achieve stable operation. Once this was achieved, the starting time was noted, and samples were taken every 15 min. On average, tests lasted 30 min to 1 h, with 2 to 4 samples taken for the concentrate and tailings stream. The samples for each stream were then combined to decrease minor variations during the testing time.

2.5. Analytical methods

2.5.1. Microwave digestion and ICP-OES analysis

The dried solid samples were digested in ultrapure HNO$_3$ (69%) in an Ethos Easy digester from Milestone equipped with an SK-15 High-Pressure rotor. The samples were placed in Teflon vessels, to which 10 ml of the HNO$_3$ was added. For digested sludge, 50 mg of sample was used, while for concentrate 30 mg was used. The chosen digestion program heats the acid to 200 °C in 15 min, maintains this temperature for 15 min, followed by a cool-down period of 1 h.

The digested samples are then diluted and analysed with Inductively Coupled Plasma (Perkin Elmer, type Optima 5300 DV) equipped with an Optical Emission Spectroscope (ICP-OES). A Perkin Elmer type ESI-SC-4 DX autosampler was used, and the data was processed with Perkin Elmer WinLab32. A solution of 10 mg/L Yttrium and a 2% HNO$_3$ solution were used as an internal standard solution and rinsing solution, respectively.

2.5.2. Mössbauer spectroscopy

The sample was put in a plastic ring sealed with Kapton foil and epoxy glue and wrapped in aluminum foil to prevent exposure to oxygen and light. The sample mass was adjusted with carbon powder to contain a maximum of 17.5 mg of Fe/cm^2. Transmission ^{57}Fe Mössbauer absorption spectra were acquired at a temperature of 300 K with a conventional constant-acceleration spectrometer using a ^{57}Co (Rh) source. Velocity calibration was performed using an α-Fe foil. The Mössbauer spectra were fitted using the Mosswinn 4.0 program (Klencsár, 1997).

2.5.3. Dry solids

To determine dry solids percentage. Samples were dried in a Petri dish in a fumehood at room temperature to prevent loss of crystalline water from the vivianite structures.

2.6. Measures of separation

2.6.1. Grade

Grade commonly refers to the content of a particular element or
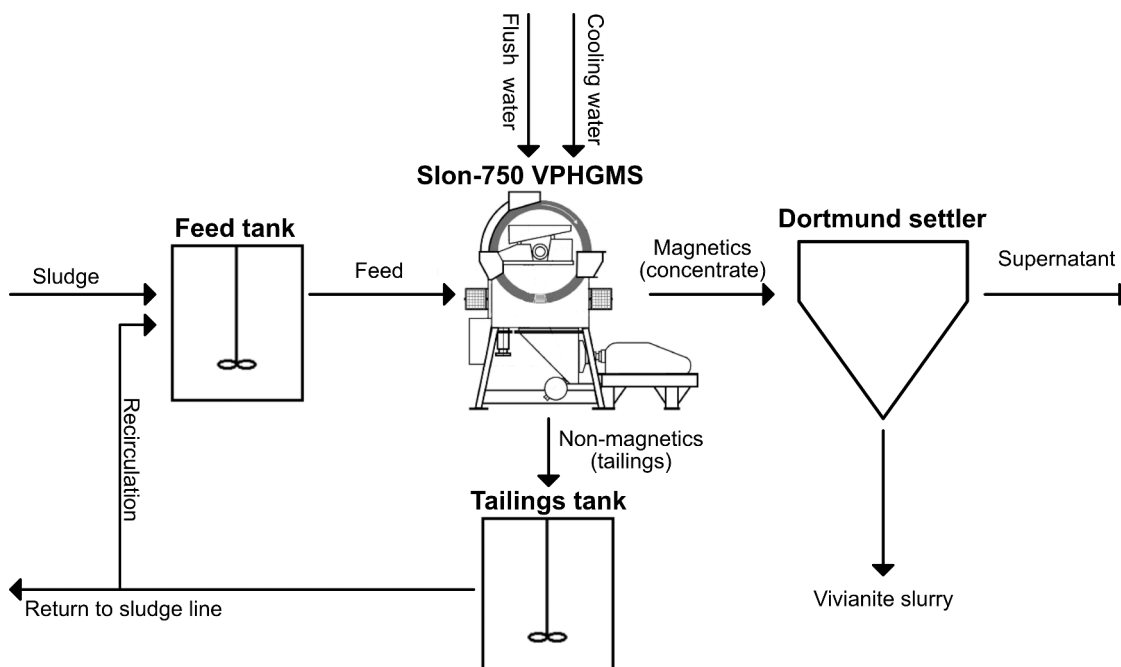

Fig. 2. Simplified flow scheme of pilot installation for vivianite recovery deployed at the WWTP Nieuwveer (The Netherlands).

mineral in any stream, such as the feed and concentrate. The grade will be expressed in the weight ratio unit mg/g.

We adapted a method developed by (Prot et al. 2020) to determine the grade of vivianite in the sludge, which is based on Mössbauer spectroscopy. Mössbauer spectroscopy can detect and speciate iron minerals very accurately and can determine the part of the total iron in the sludge that is bound in vivianite. Using the data from Prot et al. (experiment performed during the same time period at the same location), the molar Fe:P ratio can be correlated to the amount of vivianite in the digested sludge, which is expressed as the percentage of P bound to vivianite. The following equation was derived from the data of Prot et al., (2020).

$$P_{viv} = 0.98 \cdot Fe/P - 0.53 \quad \pm 0.05 \tag{1}$$

where P_{viv} is the fraction of total phosphorus in the sludge that is immobilized in the form of vivianite, and Fe/P is the molar Fe to P ratio.

Another but less accurate approach is to estimate the vivianite grade of the concentrate purely based on the P content of the concentrate. Pure vivianite has a P grade of 12.35%. Therefore dividing the P grade of the concentrate by this value will give an estimate of the vivianite grade of the concentrate. Since vivianite is the only P-bearing magnetic mineral that is likely to be present, this is a reasonable approach, although some sludge and other impurities (potentially containing P) may also be entrained.

2.6.2. Recovery

The recovery is the percentage of the total element or mineral contained in the sludge that is recovered in the concentrate. The calculation requires the mass balance of the separation, as well as the grades of feed and concentrate:

$$R = \frac{c * C}{f * F} \tag{2}$$

where c is the grade (content) of element or mineral in the concentrate, f is the grade of the feed. C is the mass (or flowrate) of concentrate, and F the mass or flow rate of feed.

2.7. Response surface analysis

A wet magnetic separator has several operational parameters which influence the separation efficiency, and their net effect cannot be predicted in advance. Therefore, a response surface analysis was performed to determine the most relevant influences. The parameters and their expected effects on vivianite separation are as follows. Response surface methodology (RSM) is a collection of statistical techniques useful for developing and optimizing processes. Response surface equations model how changes in variables affect a response of interest. For the performed screening experiment in this study, the experimental data are evaluated to fit a statistical model using Minitab® (Version 18.1). The experimental data is fitted by using least-squares regression.

2.7.1. Pulsation frequency

Pulsation agitates the sludge and keeps particles in a loose state, which minimizes entrapment of non-magnetic particles. Pulsation also maximizes the area of the steel rods that are used to trap magnetic particles. However, due to the pulsation drag forces, fine vivianite particles may not stay attached to the rods, which will decrease recovery. The workings of the pulsation mechanism and the effect on fine vivianite particles suggest that there would be an optimum pulsation frequency.

2.7.2. Rod matrix diameter

In the magnetic separator, the applied magnetic field creates many points of high field gradient in the steel rod matrix in order to capture the vivianite particles. Agglomeration of the particles can take place if they are small and/or have a high magnetic susceptibility if the field is intense. This effect can entrap sludge particles as well as bridge the gaps between magnetic poles, reducing the efficiency of separation. A smaller rod diameter results in a higher magnetic field gradient, which can increase this effect. Smaller diameter rods also have a smaller distance between them, which can increase the bridging effect. In general, this results in a higher recovery percentage for small rod diameters but a lower vivianite grade of the product, as more sludge particles are entrapped.

2.7.3. Magnetic field intensity

The magnetic field intensity should be high enough to make sure that a particle that collides with a matrix rod will remain attached to that rod. Any further increase of the field intensity will only retain particles with weaker magnetic properties (less pure) or entrap non-magnetic particles by agglomeration. Another negative effect of high field intensity is that a high field strength can actually decrease the magnetic susceptibility of a particle if this particle shows some degree of magnetic ordering (Svoboda, 1994). The magnetic force on a particle is directly proportional to the magnetic field gradient in the separator, as well as the magnetic susceptibility of the particle. Therefore, the net effect of increased field intensity can actually be a decrease in the magnetic force experienced by the particle. Applying the appropriate magnetic field is therefore crucial for a good separation performance.

The response surface analysis with different operating parameters was done on the 34 pilot-scale separation tests to statistically investigate their effect. A custom response surface design was defined using Minitabversion 18. As continuous factors were chosen molar Fe/P ratio of feed, Matrix rod diameter, Pulsation frequency, Magnetic field intensity, and Feed rate. The following levels were specified as low and high (Table 2).

The response surface results were then analysed by plotting normal plots for 'Vivianite grade', 'Vivianite recovery', 'P Recovery' ,'P Grade' ,'Fe Recovery', and 'Fe Grade'.

A normal probability plot shows the standardized effects relative to a distribution fit line for the case when all the effects would be 0. The standardized effects are t-tests that test the null hypothesis that the effect is 0. Positive effects have an increased response when the setting increases from a low to high value, whereas negative effects would have a decreased response to this. The greater the magnitude of the effect, the further from 0 they are on the x-axis.

3. Results

3.1. Bench-scale tests: good separation of vivianite and pulsation is crucial

Digested sludge from WWTP Nieuwveer was subjected to a bench-scale separation test to evaluate the effect of pulsation, applied magnetic field strength, and matrix rod diameter. Fig. 3 shows the bench-scale results with the Slon-100 machine in terms of recovery and grade of P.

The results show that pulsation frequency has a significant effect on separation. With pulsation, the grade of the vivianite concentrate is significantly higher than without while the recovery decreases. Pulsation agitates the slurry and keeps particles in a loose state, which

Table 2
Low and high values for parameters used in response surface analysis.

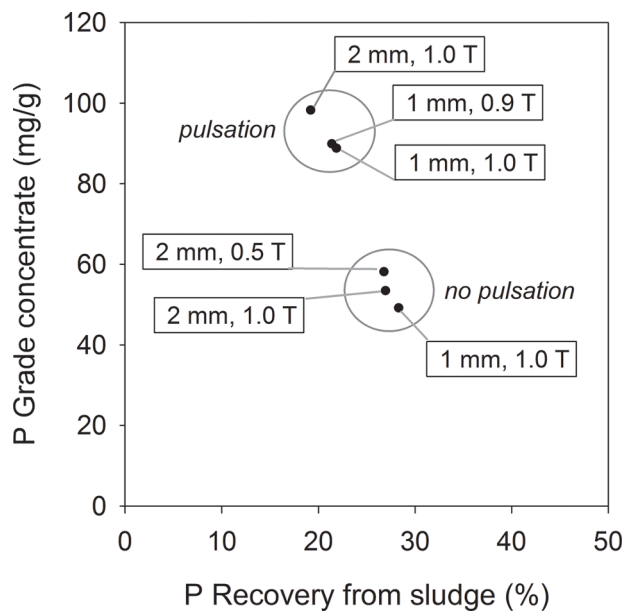| Factor	Name	Low	High
A	Molar Fe/P ratio feed	0.82	1.12
B	Matrix [mm]	1	3
C	Pulsation frequency [rpm]	0	200
D	Magnetic field [T]	0.5	1.0
E	Feed rate [m^3/h]	0.5	1.0

Fig. 3. Impact of pulsation in bench-scale magnetic vivianite separation expressed in phosphorus recovery and quality of recovered material. Labels show matrix rod diameter and magnetic field intensity in the magnetic separator. Pulsation enhances the grade of the recovered concentrate. A bigger rod diameter shows an increase in concentrate P grade and a decrease in P recovery.

Fig. 4. Separation performance of all tests conducted with pilot-scale magnetic separator expressed in phosphorus recovery and quality of recovered material. Difference in steel matrix rod diameter is shown in graph. Δ = 1 mm, $\blacksquare$ = 1.5 mm $\bullet$ = 3 mm. Outliers are marked with a circle. With a larger rod diameter, the P grade of the concentrate increases.

minimizes entrapment of non-magnetic particles. Pulsation also maximizes the area of the magnetized rods that is used to trap magnetic particles. One would expect that pulsation increases the recovery. However, due to the pulsation drag forces, fine vivianite particles will likely not stay attached to the rods, which will decrease the recovery. The workings of the pulsation mechanism and the effect on fine vivianite particles already suggest that there would be an optimum pulsation frequency. Too much pulsation will remove fines, but not enough pulsation will entrap non-magnetic particles. Another smaller effect that can be observed from the bench-scale separation tests is the effect of rod diameter. A bigger rod diameter shows an increase in grade and a decrease in recovery. With a bigger rod diameter, the distance between rods is larger, which will decrease the magnetic field gradient. The larger distance causes less entrapment by fines, and the decrease in field gradient will separate the more susceptible and purer vivianite, which will increase the concentrate grade.

The theoretical maximum phosphorus grade that can be reached is 123.5 mg/g, which is pure vivianite. The bench-scale separation tests showed promising results that vivianite can be recovered from sludge with a relatively high grade and establishes the potential for this technology on a large scale.

3.2. Pilot-scale separation tests show that over 80% of vivianite can be recovered in three passes

Pilot testing was performed over a period of 9 months. The vivianite content of the sludge during the pilot testing varied between 44 and 148 mg/g, which immobilizes 18% to 54% of the phosphorus in the sludge in the form of vivianite, respectively. The variation in the vivianite content is due to the experimental increase and decrease of iron salt dosing during the same period as discussed in Prot et al. 2020. During the operational period, 34 separation tests were performed with different operational parameters and varying vivianite content of the feed sludge. The results of all the separation tests are plotted in Fig. 4.

Table 3 shows additional detailed information for selected results with calculated vivianite recoveries and grades (full results are available in the supporting information).
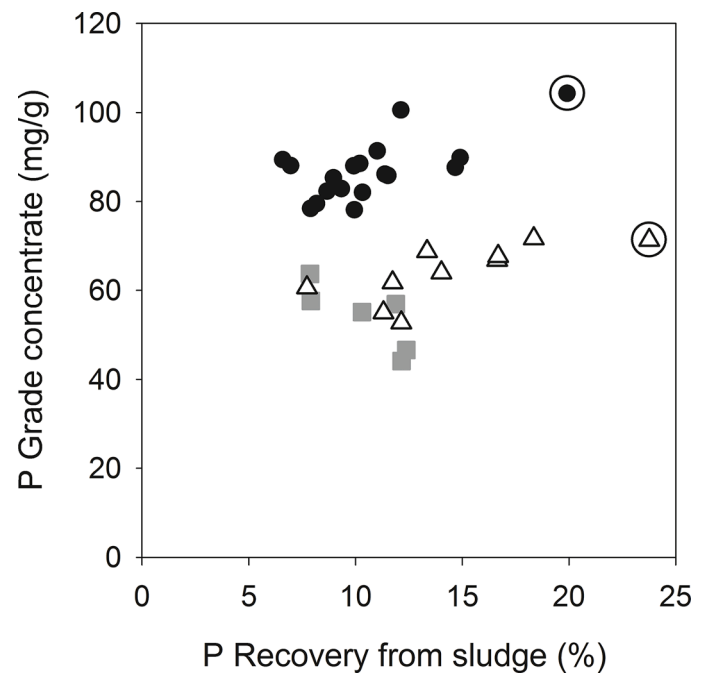
3.3. Recirculation increased the vivianite recovery to over 80%

From separation testing, it was apparent that a 3 mm rod matrix performed better over time. Small diameter rods are more prone to bend and break under the influence of the strong magnetic field. In fact, a 1 mm diameter rod matrix is not recommended for industrial use by the machine supplier due to this reason (personal communication Outotec). Furthermore, a fine rod matrix is prone to blocking by coarse material, which was experienced during pilot testing. Additionally, a high-grade concentrate is desirable due to transport costs of concentrate. This suggests using a big diameter rod matrix. Therefore, a 3 mm rod matrix is the best choice for industrial application of this technology for vivianite recovery. However, a 3 mm rod matrix has a low vivianite recovery. Only about 30% of the vivianite in the sludge is recovered in one pass. To increase the recovery, tests were performed where sludge was processed by the magnetic separator in three separate passes, increasing the recovery with each pass. The results are shown in Table 4.

With enough iron dosing, more than 80% of the P in the sludge can be immobilized in the form of vivianite (Wilfert et al., 2018). If 80% of the vivianite is recovered, the total P recovery from sludge will be over 64%. This recovery potential is higher than that of struvite, which reaches typically only 10–30% of the total P load (Cornel and Schaum, 2009; Egle et al., 2016; Lodder et al., 2011) and complies with existing legislation in Switzerland and Germany where 50% of P recovery from sludge is demanded. Despite its occurrence in WWTPs dosing iron, no vivianite scaling was observed in the magnetic separator unit over several months of operation. This is in line with the findings of Prot et al., 2021 who suggest that occurrence of vivianite scaling after digestion is unlikely (Prot et al., 2021).

3.4. The effect of parameters and their interaction is complex and can be optimized by response surface methodology

As discussed in the materials and methods section, the following operational parameters are expected to influence the separation

Table 3

Selected results of separation performance of pilot installation showing parameters used for maximum recovery, maximum grade, and long-term operation.

	Rod diameter [mm]	Field intensity T	Pulsation [rpm]	P grade [mg/g]	P recovery [%]	Vivianite grade [mg/g]	Vivianite recovery [%]
Max. recovery	1	0.5	100	72	18	580	52
Max. grade	3	1	100	101	12	814	36
Average of long-term operation	3	1	100	91	12	735	31

Table 4

Recirculation test results of 17-1: matrix 3 mm, pulsation 100 rpm, Field 1T, Feed rate 0.5 m^3/h. Vivianite content in the sludge 73 mg/g dry. A total vivianite recovery of 81% from the original feed sludge was achieved in 3 passes.

Pass	Mass yield (%)	Fe recovery from feed (%)	P recovery from feed (%)	Vivianite recovery from feed (%)	Vivianite grade concentrate (mg/g)
1	4	17	11	36	697
2	4	13	9	27	731
3	3	8	6	18	683
Total	11	38	26	81	705

efficiency: pulsation frequency, rod matrix diameter, magnetic field intensity. A response surface analysis was done on the 34 pilot-scale separation tests to statistically investigate the effect of each of the operational parameters.

Normal plots for the standardized effect are given for the vivianite recovery in Fig. 5 and vivianite grade in Fig. 6 below.

The normal plots show that the pulsation frequency has the biggest effect on recovery, followed by the matrix rod diameter. The parameters or combinations thereof that have a significant effect on the vivianite grade of the concentrate, in order of magnitude, are pulsation frequency, combination pulsation frequency and magnetic field, combination pulsation frequency and matrix rod diameter, and the combination of Fe/P ratio and magnetic field. The significance of the combination of pulsation frequency with the other parameters shows that the effect of pulsation is dependent on other parameters, for example, magnetic field, and could be optimized using response surface methodology. An interesting observation from the response surface analysis is the significant negative effect of the combination of Fe/P ratio and magnetic field. This means that if the Fe/P ratio increased and magnetic field strength
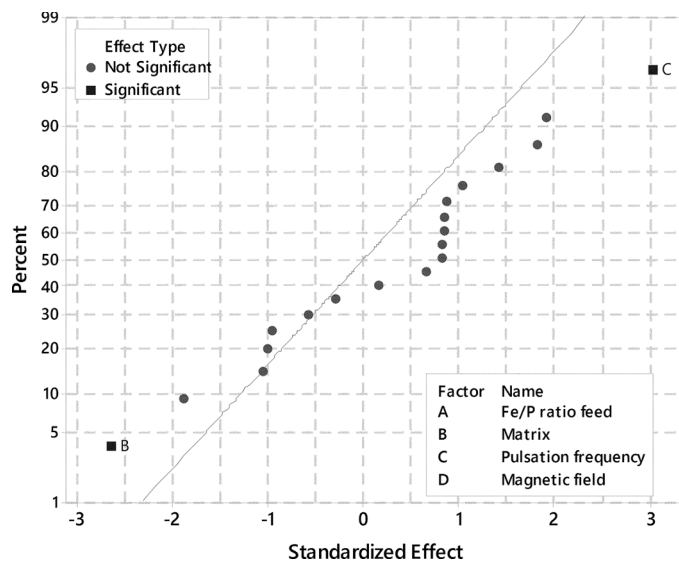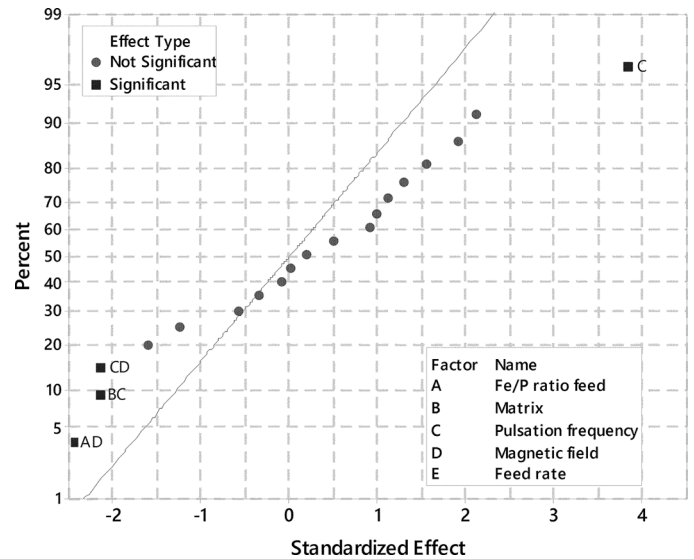

Fig. 6. Normal plot of the standardized effects on vivianite grade of the concentrate($\alpha = 0.95$). The significant effects are Pulsation frequency (C, positive), combination of pulsation frequency with magnetic field intensity (CD), combination of pulsation frequency with matrix rod diameter (BC), and combination of Fe/P ratio of the feed and magnetic field intensity (AD) (negative).

increased, the vivianite grade of the concentrate decreased. The Fe/P ratio is increased by additional iron dosing. The newly formed vivianite from additional dosing could be present as finer particles, which can form flocs that entrap organics, lowering the concentrate vivianite grade. Another explanation that could add to this effect is that other Fe minerals are formed, which are recovered in the magnetic fraction.

3.5. A concentrated phosphorus product was produced by magnetic separation

Mössbauer spectroscopy was performed on a sample of mixed concentrate from the pilot installation. The results showed that the vivianite grade of the concentrate was 710 ± 40 mg/g based on the iron speciation. It is known that iron can be replaced by other divalent ions (like Ca, Mg and Mn) in the vivianite structure, and therefore it is better to speak of vivianite-like structures (Wilfert, 2018). If we assume that the Ca, Mg, and Mn that we measured in the concentrate is in fact replacing iron sites in the vivianite-like structures, then the vivianite grade will be higher as this part of the vivianite is not quantified by Mössbauer spectroscopy. The vivianite content of the concentrate would then be 800 mg/g. 96% of the phosphorus in the concentrate was bound to vivianite in this case. The total carbon content of the concentrate was 10%, the total nitrogen content was 1%. The phosphorus content of the concentrate is 9.8% P, or 22.4% P_2O_5 equivalent. Supported by the mass balance calculations (see SI), no P losses or vivianite accumulation have been observed in the pilot installation. Additionally, XRD and SEM-EDX analyses performed by Prot et al. 2020 on the digested sludge from Nieuwveer during the operation time of this pilot experiments revealed the presence of vivianite, while struvite was absent (Prot et al., 2020). A complete elemental analyses, including heavy metals, were performed

Fig. 5. Normal plot of the standardized effect on vivianite recovery($\alpha = 0.95$). The significant effects are pulsation frequency (C, positive effect), and Matrix rod diameter (B, negative effect).

on the concentrate and reported in the supplemental information. Heavy metal concentrations were in line and somewhat lower than earlier reported for lab-scale magnetic separation tests (Prot et al., 2019).

4. Discussion

The pilot tests were performed with a SLon-750 VPHGMS and were operated with feed flow rates of either 0.5 or 1 m³/h of digested sludge that was tapped of before the final dewatering of the sewage sludge. Sewage sludge presents a very different matrix when compared to iron ore slurries that are typically treated in this type of separator. The treated digested sludge's viscosity was comparable to these sludges (see SI) but had a significantly lower dry matter content (ca. 4% dry matter for digested sludge compared to 20–40% dry matter for iron ore slurries) (Xiong et al., 2015). For this sewage treatment plant (raw sewage inflow of 75000 m³/day) the total digested sludge production is roughly 16 m³/h. Upscaling of the pilot system requires an increase in the ring diameter and/or the width of the ring. VPHGMS equipment is commercially available in capacities ranging from 10 to 1000 m³/h iron ore slurry input and is, therefore, more than large enough to treat the full capacity of this or even significantly larger sewage treatment plants, also if recirculation is needed to maximize the recovery efficiency. A full-scale ViviMag installation for Nieuwveer WWTP would have to treat 16 m³/h of digested sludge. An industrial scale Slon-1000 has a nominal throughput of 10–20 m³/h and it requires 3.3 kW of electrical power (Gruening et al., 2020). Hence, the power consumption is approximately 0.5–1 kWh/m³ sludge treated, assuming three passes to obtained the desired efficiency. This is comparable to the energy consumption of a sludge dewatering centrifuge, which is 1.0–1.6 kWh/m³ (DWA, 2013).

An important aspect in a full-scale application is the potential effect of the magnetic separation on the dewaterability of the digested sludge. A lower dewaterability would imply higher sludge disposal volumes and associated disposal costs. Therefore, preliminary dewaterability tests were performed both in lab-scale experiments and at pilot-scale using a decanter centrifuge. The results are reported in the supplemental information and show that there was a small negative effect on the dewaterability of the treated sludge. This effect will be compensated by the reduction in sludge volume that needs to be dewatered through the removal of vivianite from the sludge. Further optimization of the selection of the poly-electrolyte used for flocculation may further improve the dewatering.

This study shows that commercially available VPHGMS-equipment can be used to "mine" this vivianite from the digested sewage sludge. Typically, sewage treatment plants remove 90% of all phosphorus from the sewage influent and concentrate it in the surplus sludge, which is often digested in the larger sewage treatment plants to produce biogas. If enough iron is dosed either in the main water line and/or in the sludge digester, then 80–90% of the phosphorus in the sewage sludge is present as vivianite (Wilfert 2018). The current study shows that a magnetic separation approach can recover 80% of this vivianite. Overall, this means that 60–64% of the phosphorus in the sewage influent can be recovered as vivianite while recovering most of the dosed iron as well. Such an approach (called ViviMag) makes phosphorus recovery possible for sewage plants that employ chemical phosphorus removal, where currently this is not possible. The ViviMag approach would also have higher recovery efficiencies compared to struvite recovery approaches that are currently being implemented in sewage treatment plants applying enhanced biological phosphorus removal and typically show a recovery potential of 10–40% of the influent phosphorus (Korving et al., 2019). The market potential for this technology is enormous as the majority of WWTPs in Europe utilize CPR with iron salt addition either as a main phosphorus removal strategy, or to support the EBPR technology (Korving et al., 2019).

Future work should focus on further optimizing the magnetic separation to improve recovery efficiencies and purity of the magnetic concentrate, and suggestions were made for the main parameters to focus on. Also, additional purification steps (for instance, a washing approach) can improve the purity of the recovered vivianite. Further research on alkaline splitting the vivianite into an iron phase and phosphate phase would make it possible to create circular use of iron salts for phosphorus recovery at a WWTP (Prot et al., 2019).

5. Conclusions

- Vivianite recovery is emerging as a promising approach for phosphorus recovery from sewage treatment plants employing iron salts for phosphorus removal. The small particle size of vivianite particles and the complex sludge matrix make an efficient separation challenging.
- Magnetic separation equipment commonly used in the mining industry was able to extract the paramagnetic vivianite efficiently from digested sludge, thus truly introducing a concept of "urban mining".
- With this approach a recovery efficiency from digested sludge of 80% was achieved, making it possible to recover over 60% of the influent phosphorus load.
- The recovered magnetic concentrate has a purity of up to 800 mg vivianite per gram (98 mg P/g) with low concentrations of heavy metals.
- The effect of the operational parameters on the separation performance is complex and was optimized by using response surface methodology.

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.

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.watres.2022.118131.

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