Science of the Total Environment 892 (2023) 164517

Contents lists available at ScienceDirect

Science of the Total Environment

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

Human urine: A novel source of phosphorus for vivianite production

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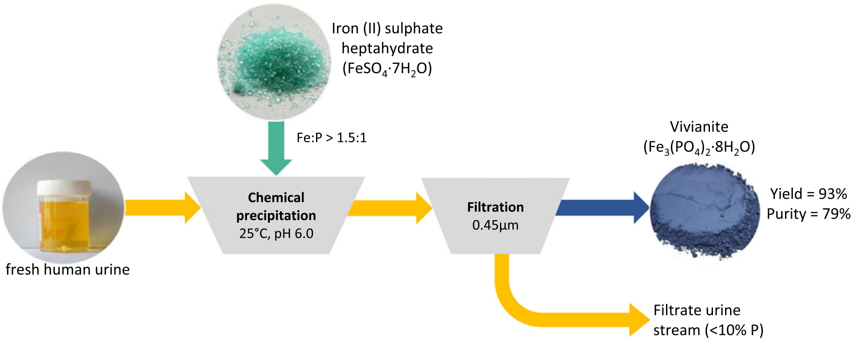
HIGHLIGHTS

- Vivianite produced from fresh human urine
- High yield (93 %) and purity (79 %) at pH 6
- High Fe:P molar ratio prevents formation of other precipitates.
- Organics affects purity of solids.
- Washing solids improves purity by 15.5 %.

GRAPHICAL ABSTRACT



ARTICLE INFO

Editor: Huu Hao Ngo

Keywords:
Decentralized sanitation
Fertilizers
Nutrient recycling
Resource recovery
Stabilization
Wastewater treatment

ABSTRACT

Human urine contributes up to 50 % of the phosphorus load in domestic wastewater. Decentralized sanitation systems that separately collect urine provide an opportunity to recover this phosphorus. In this study, we leveraged the unique and complex chemistry of urine in favor of recovering phosphorus as vivianite. We found that the type of urine affected the yield and purity of vivianite, but the kind of iron salt used, and reaction temperature, did not affect the yield and purity. Ultimately, it was the urine pH that affected the solubility of vivianite and other co-precipitates, with the highest yield (93 ± 2 %) and purity (79 ± 3 %) of vivianite obtained at pH 6.0. Yield and purity of vivianite were both maximized when Fe:P molar ratio was >1.5:1, but <2.2:1. This molar ratio provided sufficient iron to react with all available phosphorus, while exerting a competitive effect that suppressed the precipitation of other precipitates. Vivianite produced from fresh urine was less pure than vivianite produced from synthetic urine, because of the presence of organics in real urine, but washing the solids with deionized water improved the purity by 15.5 % at pH 6.0. Overall, this novel work adds to the growing body of literature on phosphorus recovery as vivianite from wastewater.

1. Introduction

Excess phosphorus (P) in the environment is harmful, as it can cause hypoxia and eutrophication in natural water bodies (Preisner et al., 2020). Domestic wastewater is a major contributor to the global flux of P. Considering that 80 % of wastewater produced globally receives no treatment (Connor et al., 2017), it is unsurprising that eutrophication remains a problem worldwide (Hendriks and Langeveld, 2017), especially in developing countries (Sikosana et al., 2017). This has led to the implementation of stricter effluent standards across the world on discharge of treated wastewater to the environment. However, treatment that only removes P from wastewater is not sufficient and the focus must be shifted to recovering P, as it is a finite resource (Priambodo et al., 2017). The majority of mined P (98 %) is produced via the wet process (Gantner et al., 2014), which is

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http://dx.doi.org/10.1016/j.scitotenv.2023.164517
Received 5 April 2023; Received in revised form 17 May 2023; Accepted 26 May 2023

environmentally unsustainable and results in production of 5 Mt. of phosphogypsum per mt of phosphoric acid, of which 88 % is landfilled and 10 % is disposed of at sea (Tayibi et al., 2009). Nitric acid can be used in wet P mining to prevent precipitation of phosphogypsum and produce a marketable calcium nitrate product. However, nitric acid is significantly more costly than e.g. sulfuric acid, leading to only 10 % of wet P mining globally being conducted with nitric acid (Schrödter et al., 2008). Domestic wastewater contains about 3.7 Mt. of P, which, if recycled, could meet 20 % of current global fertilizer demand (Kok et al., 2018), help meet the growing global demand for fertilizer, and reduce the demands on conventional mining (Jupp et al., 2021).

The two main technological processes available for P recovery from wastewater are chemical precipitation and enhanced biological P removal (EBPR) (Jupp et al., 2021). Chemical precipitation involves addition of a metal salt to wastewater to precipitate metal phosphates, and can recover 85 % or more of the available P (Kemacheevakul et al., 2011). EBPR involves the use of microorganisms to remove P from wastewater and can recover 90 % of the P in wastewater, but P only makes up 2–4 % of the sludge by mass (Liao et al., 2005). The P recovered in the sludge is often not valorized, as the sludge is incinerated because it contains pollutants such as pharmaceutical residues, endocrine disruptors, heavy metals, and pathogens (Jupp et al., 2021).

One P-rich waste stream that has received a great deal of research attention is human urine (Tao et al., 2019). Urine contributes about 50 % of the P in domestic wastewater (Vinnerås and Jönsson, 2002), but only 1 % of the total volume (Larsen and Gujer, 1996). Separating human urine at source using novel no-mix toilets (Gundlach et al., 2021) and urinals (Mufunde and Randall, 2022), has the potential to improve the performance of existing wastewater treatment plants (WWTPs) (Wilsenach and van Loosdrecht, 2006), while providing a path for P recovery that might otherwise be difficult to implement at a WWTP that treats mixed wastewater. The two most common techniques for recovering P from source-separated urine are addition of calcium hydroxide ($Ca(OH)_2$) to fresh urine, which precipitates calcium phosphate (Randall et al., 2016), and the addition of magnesium (Mg) to hydrolyzed urine to produce struvite (Bhuiyan et al., 2008), both of which can then be used as fertilizers (Jupp et al., 2021).

However, there could be a greater value proposition in recovery of the P in urine as vivianite ($Fe(II)_3(PO_4)_3{\cdot}8H_2O$). Vivianite scaling is common in WWTPs that use iron (Fe) for removing P (Prot et al., 2021). Vivianite has been recovered from wastewaters using different technologies, each with their own recovery efficiencies, advantages, and challenges. Chemical precipitation of vivianite from wastewater by Fe^{2+} dosing results in high recovery efficiencies (>80 %), is easy to operate but affects the biological processes in wastewater (Zhang et al., 2021). Vivianite recovery using electrochemical crystallization requires no chemical addition as the Fe^{2+} is produced by a sacrificial anode, achieving recovery efficiencies >80 %. Vivianite is also paramagnetic and can be recovered using magnetic separators once formed (Wijdeveld et al., 2022). In addition, H_2 gas can be produced, which could be used as a potential fuel source, but the energy costs can be high and fluctuate depending on the wastewater conductivity (Martin et al., 2020). Biomineralization is the most environmentally friendly process to recover vivianite from wastewater, but it has recovery efficiencies <60 % and is very sensitive to pH and temperature (Wang et al., 2022). Like struvite and calcium phosphate, this hydrated iron phosphate mineral can be used as a fertilizer (Cabeza et al., 2011). However, it is also in demand in the electronics industry for use in lithium-ion battery production (Rao and Varadaraju, 2015) and in the art industry as a pigment in paint (Rao and Varadaraju, 2015). Vivianite crystals can be sold for \$100–500 kg^{-1} (Alibaba.com, 2022), while as a pigment used in paint it is even more valuable, selling for as much as \$700–800 kg^{-1} (Etsy.com, 2022). Considering that struvite and calcium phosphate can typically only be sold for \$1 kg^{-1} (Alibaba.com, 2022), recovering P as vivianite would likely be significantly more profitable. Income generated from the sale of vivianite could partly fund the cost of treating urine and providing services in decentralized sanitation systems. While studies have investigated P recovery as vivianite from municipal wastewater (Prot et al., 2019; Wilfert et al., 2018), to our knowledge, no previous study has investigated recovery of P as vivianite from human urine.

In freshly excreted human urine, most of the nitrogen present is in the form of urea (Kabdaşlı et al., 2006). However, hydrolysis of urea in the presence of urease-producing bacteria increases the NH_4^+ ion concentration and the pH of the solution, promoting struvite precipitation. If magnesium does not limit the precipitation of struvite, then most of the P in urine is precipitated as struvite (Simha et al., 2022). Urine can be stabilized to prevent urea hydrolysis by addition of a base such as $Ca(OH)_2$ (Randall et al., 2016) or magnesium hydroxide ($Mg(OH)_2$) (Vasiljev et al., 2022) or an organic/inorganic acid (Simha et al., 2023). The increased pH during base stabilization promotes precipitation of phosphorus as calcium phosphate and struvite. There is also evidence that vivianite precipitation is inhibited at low pH values (<5.0) (Wilfert et al., 2018).

The overall aim of this study was therefore to leverage the unique and complex chemistry of human urine in favor of recovering P as vivianite. The specific objectives were to investigate the influence:

1. The type of urine has on the yield and purity of vivianite;
2. The type of iron salt, pH, and dose concentration has on the yield and purity of vivianite;
3. Temperature has on yield and purity of vivianite;
4. Urine composition has on the yield and purity of vivianite;

We then compared the yield and purity of vivianite precipitated from synthetic and real urine under different conditions, by combining empirical experimental data with thermodynamic modelling of urine chemistry. Finally, we investigated methods for improving the purity of vivianite. Ultimately, this study advances the knowledge of chemical precipitation of P from source-segregated wastewater fractions such as human urine. To our knowledge, it is also the first time that vivianite production from human urine has been investigated and the study describes a novel method for P removal from human urine.

2. Materials and methods

2.1. Urine collection and preparation

2.1.1. Synthetic urine preparation

We first used synthetic urine and a one-factor-at-a-time method to evaluate the effect of various parameters on vivianite precipitation. Subsequently, we validated these results with real human urine The synthetic urine recipe was designed to reflect the average composition of real fresh urine. Based on values in Courtney et al. (2021), the synthetic urine contained ions in the following concentrations: 13000 mg L^{-1} urea, 402 mg L^{-1} NH_4^+, 151 mg L^{-1} Ca^{2+}, 61 mg L^{-1} Mg^{2+}, 1995 mg L^{-1} K^+, 350 mg L^{-1} PO_4^{-3}, 2170 mg L^{-1} SO_4^{2-}, and 4430 mg L^{-1} Cl^-.

2.1.2. Real urine collection

Fresh urine was collected anonymously from young to middle-aged men, using a waterless urinal developed by Flanagan and Randall (2018). The collection container was thoroughly washed and rinsed with 1 M HCl between collection cycles. The urine was collected over a working day (<8 h), stored at room temperature (25 °C), and used within 48 h of collection.

2.2. Thermodynamic modelling

Thermodynamic modelling was conducted using the Mixed Solvent Electrolyte (MSE) model in OLI Stream Analyzer (OLI System Inc., 2021), which is not restrained by ionic strength, and can simulate complex aqueous streams over a wide range of conditions using a state-of-the-art thermodynamic framework (Liu and Papangelakis, 2005). The model was used to investigate the effects of type of iron salt used, operating temperature, molar ratio (Fe:P), and pH on precipitation and on the yield and purity of vivianite that could be recovered from urine. The different Fe and P minerals used in the model are given in Table S1. Potential complexation by organic substances is not included in the model. The composition of the synthetic urine used in the experiments was assumed when modelling these factors. When the model outputs were compared against data on real urine, the input ion concentrations were adjusted to mimic those in the real urine.

2.3. Equipment set-up and procedure

Three sets of physical experiments were conducted. The first set was conducted with synthetic urine, to validate the model findings concerning pH and Fe^{2+} dosage, the second set to determine the effects of pH and Fe^{2+} dosage on real fresh urine, and the third set to determine the optimal operating conditions for vivianite recovery from fresh urine. Temperature was not experimentally investigated further as the modelling results showed that temperature did not have a major effect on precipitation.

All three sets of experiments were conducted using 500 mL of urine, which was added to a jacketed crystallizer (GlassChem, Cape Town, South Africa) that was temperature-controlled by water circulation at 25 °C using a chiller (M1907–0156, PolyScience, Illinois, United States). The pH, temperature, and composition of the urine were analyzed before and after dosing the urine with $FeSO_4{\cdot}7H_2O$. A pH probe (HANNA Instrument, Rhodes Island, United States) was used to determine the pH of urine before and after iron dosing, and also during the reaction. Solution pH was controlled by an automated pH controller and logger (GlassChem Instrument, Cape Town, South Africa). A magnetic stirrer (M520, LabCon, California, United States) was set to 150 rpm to keep the solution homogeneous during the experiment. Sodium hydroxide (NaOH, 1 mol L^{-1}) and hydrochloric acid (HCl, 0.5 mol L^{-1}) were used to regulate the pH, at a dosage rate of 51 μL per event. Once the urine solution was dosed with iron salt, the experiments were run for 15 min as this was shown to limit the oxidation of Fe^{2+} in solution (Fig. S2). All experiments were conducted in triplicate.

When the 15-min reaction time was over, the urine was filtered using filter paper (0.45 μm) and a vacuum pump. The mass of the filter paper was weighed and recorded before use. The filtrate was collected separately in an Erlenmeyer flask, and the solids and filter paper were dried in a shelf oven (M275, Scientific, Johannesburg, South Africa) set to 30 °C for 24 h. A temperature of 30 °C was used for drying to ensure that solids did not transform to other compounds at elevated temperatures. Mass of the dried solids and filter paper was recorded using a beam balance (B164A Electronic Scale, 0.0001 g, OPTIKASCIENCE, Rome, Italy). To determine ash content and volatile solids content, the dried solids were weighed and then incinerated at 600 °C for 0.5 h in an oven (LABOFURN, KILN Contractors (PYT), Cape Town, South Africa), and then re-weighed.

2.4. Vivianite purification

During the experiments, we observed that organic compounds and other minerals in urine co-precipitated with vivianite. Therefore, we conducted a further experiment to determine whether the purity of the vivianite obtained could be improved by dissolving impurities and washing away any residual filtrate present in the filtered solids. This purification step was performed, immediately after the solids were precipitated and collected, by washing the solids with 10 mL of solvent using a filter paper (0.45 μm) at 2 mL/min with a vacuum pump (ABF 71/4C-7RQ, 230 V ATB pump, Air Vacuum technologies, Johannesburg, South Africa). The solids were then dried for 24 h in a shelf oven (M275, Scientific, Johannesburg, South Africa) 30 °C. The solvents tested were ethanol (Ethanol Absolute Assay 99.5 %, Sigma-Aldrich, Johannesburg, South Africa) and deionized water. The washing process was conducted three times for each filtered solids sample and for each solvent.

2.5. Analytical methods

The concentration of dissolved substances was determined using colorimetric methods. All liquid samples were analyzed within 30 min of sampling. The solid samples were prepared for analysis by digestion using 12 M HCl, after which the pH of the solution was adjusted to between 2.9 and 3.5 using 1 M NaOH and its composition was analyzed colorimetrically. The concentrations of urea, total iron (Fe^{2+} and Fe^{3+}), NH_4^+, phosphate (PO_4-P), Mg^{2+}, Ca^{2+}, sulfate (SO_4^{2-}), chlorine (Cl^-) and potassium (K^+), where required, were tested automatically with a Gallery™ Discrete Analyzer (ThermoFisher Scientific, Massachusetts). The concentration of Fe^{2+} was determined using the HACH USEPA[1] FerroVer® Method[2] and photometer test reagent set (FerroVer Iron Reagent Powder Pillows, 0.02–3.00 mg L^{-1} Fe, 25 mL). Chemical oxygen demand (COD) of the urine was determined using a Wastewater Treatment Photometer (HI83399–02, HANNA Instrument, Rhodes Island, United States) and COD reagent (H193754, HANNA Instrument, Rhodes Island, United States). The solid samples were characterized using 2-theta X-ray diffraction (XRD), to identify the presence of vivianite. A D8 advanced diffractometer (Bruker, Germany) fitted with a position-sensitive detector (LYNXEYE), and Bragg Brentano geometry was used for the analysis. Power to the cobalt anode was set at 35 kV and 40 mA. A range of 20° to 120° ($d^{-1} = 0.19$ to 0.97 $Å^{-1}$) with a 0.017° step size (0.84 s per step) was used to acquire the diffraction patterns. The ICDD database (PDF4+, released 2020) was used to compare the diffraction patterns against reference data files. To determine the fate of different elements, we analyzed the elemental composition of the precipitated solids and conducted a mass balance. Supplementary Information (Section 1.4) describes the method for determining the purity and the yield of the solids.

3. Results and discussion

3.1. Thermodynamic modelling for identifying conditions for producing vivianite in human urine

3.1.1. Influence of type of urine on the yield and purity of the vivianite

Using acid-stabilized urine achieves the same yields and purities of vivianite as using fresh urine (Fig. 1). This is because there are no other precipitates in the urine or cations to compete for P. In alkalized urine, gypsum ($CaSO_4{\cdot}2H_2O$) is precipitated at pH >1.0 (Fig. S4). This limits the purity of the vivianite to a maximum of 61 % (Fig. 1A). Additionally, at pH >8.0, dosing Fe would not precipitate vivianite as struvite or HAP are preferentially precipitated, depending on the type of base added.

In hydrolyzed urine, 41 % of the P precipitated as HAP and struvite. If the pH of hydrolyzed urine is lowered to between 4.5 and 6.0, then P can be recovered as vivianite. In contrast, the yield of vivianite precipitated from fresh urine is at its highest in a broader pH range (4.5 to 8.4) (Fig. 1A). This difference in pH range and purity is mainly due to the precipitation of co-precipitates in the hydrolyzed urine. During urea hydrolysis, carbonate ions are also formed (Naveed et al., 2020), thus resulting in the precipitation of iron carbonate ($FeCO_3$) when the urine is dosed with Fe (Fig. S4). At pH values >6.0, the precipitation of $FeCO_3$ is favoured over vivianite precipitation. This competition for Fe^{2+} between the carbonate system and phosphate system results in lower yields of vivianite in the hydrolyzed urine streams at pH values (>6.0) (Fig. 1B). The chemical demand for optimizing the yield of vivianite in hydrolyzed urine was 20-fold higher than that in fresh human urine. Therefore, in all subsequent simulations and experiments, we used fresh human urine.

3.1.2. Influence of the type of iron salt, pH, and dose concentration

Three different iron salts were compared, using a fixed dose based on a Fe:P molar ratio of 1.5, to determine how dosage affected the yield and purity of vivianite formed at varying pH values. A Fe:P molar ratio of 1.5 is the stoichiometric ratio of Fe and P required to make one mole of vivianite. At a fixed Fe:P molar ratio, it was observed that the type of iron salt did not affect the yield and purity of vivianite (Fig. S5). Therefore, the preferred choice of iron salt was determined by price and availability. Iron hydroxide ($Fe(OH)_2$) is unstable and tends to oxidize rapidly when exposed to oxygen (Gayer and Wootner, 1957), which limits the amount of Fe^{2+} available to react with the P in urine, and is therefore unsuitable for vivianite

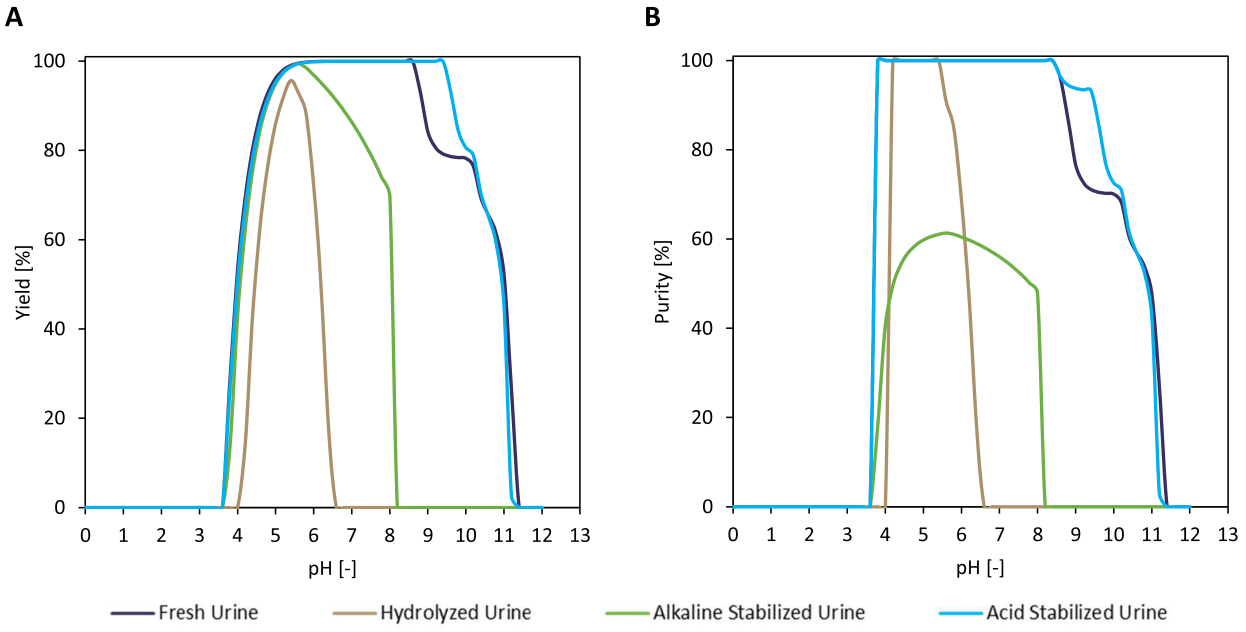

Fig. 1. Simulated purity and yield of vivianite obtained from fresh, hydrolyzed, alkaline stabilized, and acid stabilized urine. Each urine type was dosed with 5250 mg L^{-1} of $FeSO_4·7H_2O$ at 25 °C. The fresh urine (Table S1, U11) had a pH of (6.3). The hydrolyzed urine was completely hydrolyzed and had a pH o 9.1. The acid-stabilized urine was created by adding 7800 mg L^{-1} of citric acid to the fresh urine (U11) and had a pH of 3.9. The alkaline stabilized urine was created by adding 5050 mg L^{-1} of $Ca(OH)_2$ to the fresh urine (U11) and stabilized at a pH of 12.5.

production. Although iron chloride ($FeCl_2·4H_2O$) is commonly used in wastewater treatment plants for flocculation (Medeiros and Molot, 2006), it is more expensive ($1.2–3.54 kg^{-1}; Alibaba.com, 2022) than iron sulfate ($FeSO_4·7H_2O$) ($0.07–0.12 kg^{-1}; Alibaba.com, 2022). Dosing with $FeSO_4·7H_2O$ would add additional sulfate ions to urine, which can be an advantage if urine is applied to soil as a crop fertilizer (Kertesz and Mirleau, 2004).

It was also observed that regardless of iron dose, operation outside the pH range 5.0–8.0 adversely impacted the yield of vivianite (Fig. 2A). In jar-tests on different wastewaters, (Wu et al., 2019) also found that vivianite precipitation is generally possible in the pH range 5.0–8.5, although much lower yields have been reported at the extremes of this range (Liu et al., 2018). Reaction pH directly affects the solubility of compounds present in urine. Studies on industrial wastewater have found that vivianite precipitation is favoured in the low pH range, while co-precipitate precipitation is favoured in the high pH range (Priambodo et al., 2017).

For each iron dose tested in the present study, the yield was maximized between pH 5.5 and 8.5 (Fig. 2A). Within this pH range, the variation in yield depended on the amount of iron salt added. The yield was expected to be maximized when the Fe:P molar ratio achieved by dosing was >1.5:1. It was found that excess Fe^{2+} competed with Ca^{2+} and Mg^{2+} for P, hence preventing precipitation of compounds containing these cations (e.g., hydroxyapatite (HAP), bobierrite and struvite), resulting in higher yield and purity of vivianite. Hydroxyapatite begins to form at pH 6.5 and increases in concentration as the pH increases. The solubility of HAP declines as the pH increases, resulting in Ca^{2+} competing with Fe^{2+} for P. The amount of HAP that formed when the urine was underdosed with iron (Fig. 2B) was significantly greater than that formed when the Fe:P molar ratio was 1.5 (Fig. 2C) or when iron was overdosed (Fig. 2D), in increasing order. Struvite precipitation was only observed when urine was underdosed with iron (Fig. 2B). Excess Fe^{2+} inhibited the precipitation of calcium and magnesium precipitates at pH values below 8.3. In the pH range 5.5–8.5, the highest vivianite yields were achieved when the iron dose was equal to or greater than a Fe:P molar ratio of 1.5. The highest purity was obtained from pH 4.0 (when the solid began to form) to pH 7.0–8.0, depending on the Fe:P molar ratio. This agrees with findings in the literature that the optimal pH range to maximize the yield and purity of vivianite extraction from wastewater is pH 6.0–8.0 (Wu et al., 2019).

The yield depended on the pH and the amount of Fe salt added, which in combination govern the solubility of vivianite. When the pH conditions were fixed, adding excess salt resulted in the highest yield due to higher saturation. This was evident from the yield curves for different pH values (Fig. 3A). The results show that the purity of the vivianite was affected by co-precipitation of other solids in urine, which in turn was affected by pH, with Ca and Mg—P precipitates forming at pH values greater than pH 5.0. When conditions favoured precipitation of vivianite and other solids of Ca and Mg (pH 6.0 to 8.0), the purity was also dependent on the amount of Fe^{2+} added to the urine solution. Excess Fe^{2+} restricted formation of other co-precipitates, resulting in high purity (Fig. 3B).

Generally, operating in a pH range of 4.0 to 5.5 always produced the highest purity of vivianite, but at the expense of reduced yield due to the relatively higher solubility of vivianite in this pH range (Table 1). Yield of vivianite was maximized between pH 6.0 and 8.3, while the purity depended on the Fe:P molar ratio. Higher dosages of Fe^{2+} favoured the precipitation of vivianite over other precipitates of calcium and magnesium within the pH range of 6.0 to 8.3. Within the pH range 4.0 to 8.5, when urine was overdosed with iron (Fig. 2D), vivianite was produced in its purest form as the only solid. Above pH 8.5, $Fe(OH)_2$ began to precipitate, consuming Fe^{2+} and reducing the Fe^{2+} concentration in the solution, thus limiting the amount of Fe^{2+} available to form vivianite.

3.1.3. Influence of temperature on yield and purity of vivianite

The maximum operating temperature was limited to 40 °C, as chemical urea hydrolysis will likely occur beyond this temperature (Randall et al., 2022). It was observed that operating temperature had no effect on the yield of vivianite (Fig. 4A). Previous studies have observed similar trends for vivianite production, in anoxic conditions, in the temperature range 5–90 °C (Al-Borno and Tomson, 1994). In the crystallization of vivianite from sludge using rusty scrap iron, the temperature was found to have limited influence between 15 °C and 45 °C (Chen et al., 2022). However, varying the temperature influenced the type and amount of co-precipitates formed in the urine. Thus, the temperature did affect the purity of the

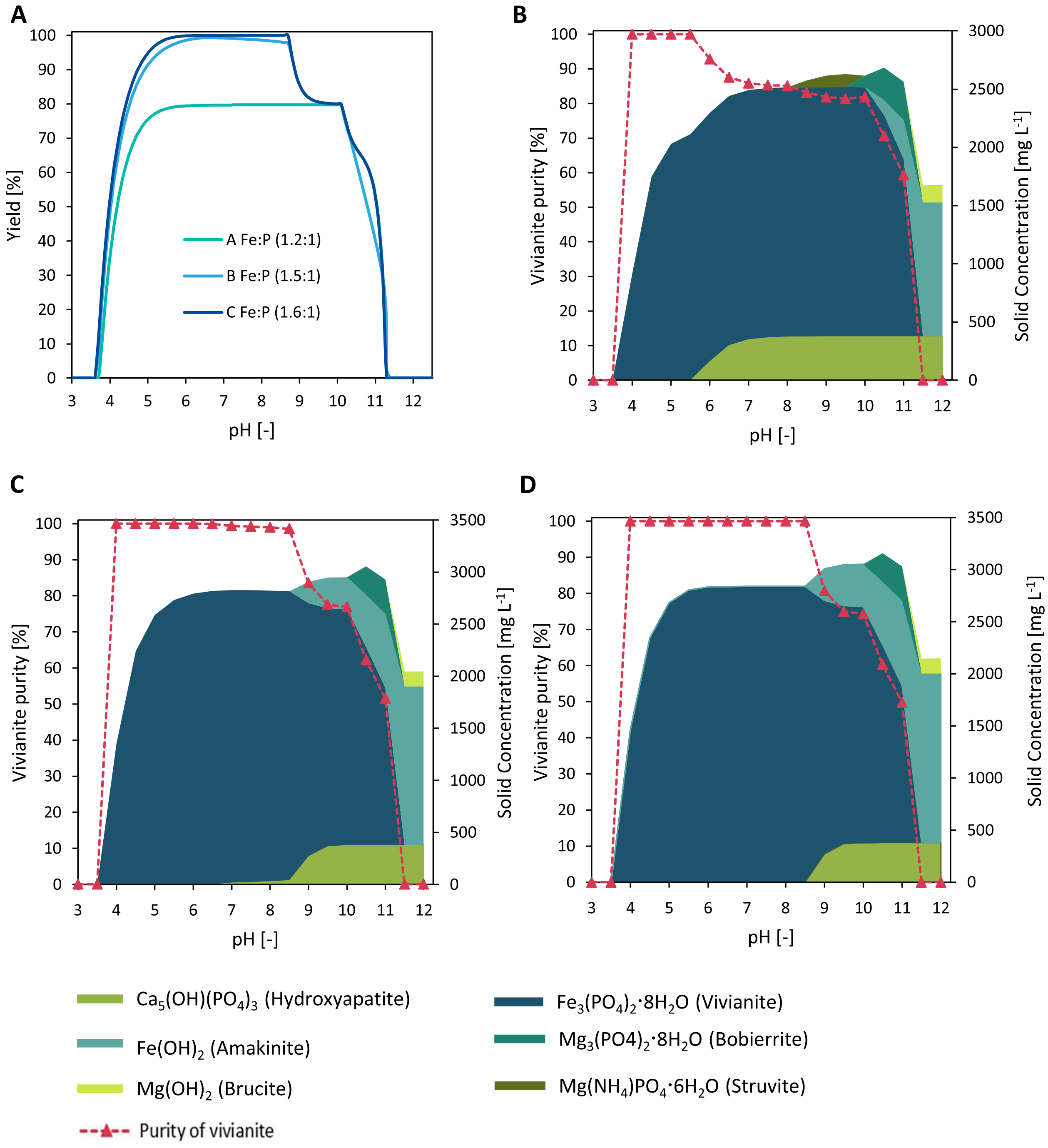

Fig. 2. Thermodynamic modelling results showing the (A) effect at different pH levels of iron sulfate ($FeSO_4$) dose on yield of vivianite, and effect of pH on vivianite purity and solids concentration when $FeSO_4$ was (B) underdosed [Fe:P molar ratio 1.2], (C) dosed in the exact molar ratio [Fe:P molar ratio 1.5], and (D) overdosed [Fe:P molar ratio 1.6].

vivianite depending on the Fe:P molar ratio (Fig. 4B). When the Fe:P molar ratio was <1.5 and the temperature > 30 °C, there was a slight reduction in the purity of the vivianite (Fig. 4B). This is due to the increased formation of Ca and Mg co-precipitates.

At pH values >8.0 the effects of temperature are not dependent on dosage. However, these pH values (>8.0) are outside the ideal operating range to produce vivianite. In this pH region (>8.0), the mass of vivianite precipitated reduced as temperature increased (Fig. 5A). In contrast, the amount of HAP precipitated increased with increased temperature (Fig. 5B). Likewise, the amount of $Fe(OH)_2$ and $Mg(OH)_2$ increased (Fig. 5C and Fig. 5E). Bobierrite, however, only precipitated at temperatures below 30 °C (Fig. 5D).

3.1.4. Influence of urine composition

The amount of $FeSO_4{\cdot}7H_2O$ required to achieve an exact dose will vary depending on urine composition, because the P concentration in urine can differ significantly between individuals as a result of differences in diet and water consumption (Rose et al., 2015). The composition of 10 different fresh urine samples was analyzed to determine an ideal Fe dosage for maximum P recovery as vivianite (compositions given in Table S1). We found that the amount of P in urine was normally distributed (Supplementary Information, Fig. S1), so statistical inference was used to determine a general dosage value for any urine composition. Two dosages were tested: the mean dose and the mean dose plus one standard deviation (Fig. 6) as this resulted in 90 % of the samples achieving a 100 % purity for vivianite.

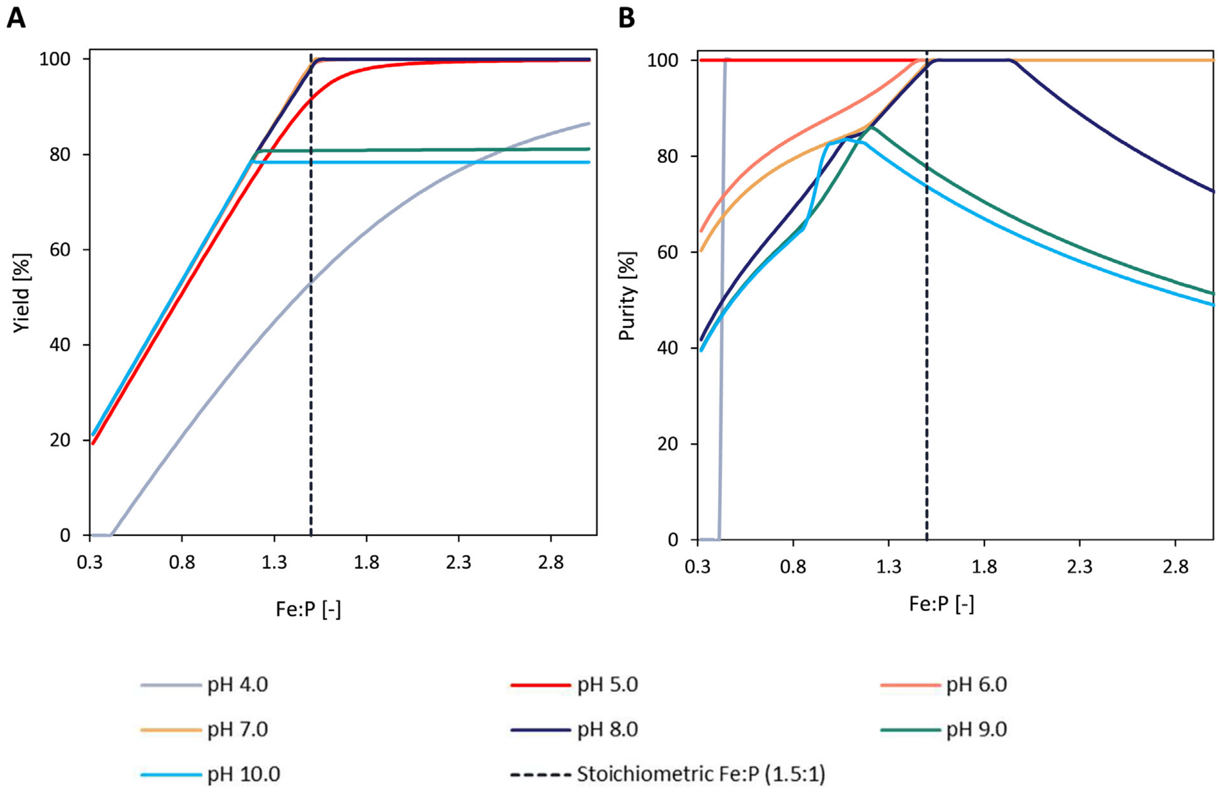

Fig. 3. Thermodynamic modelling results showing the influence of dosage and pH in the yield (A) and purity (B).

On average, yield and purity were 86 % and 94 %, respectively, for the mean iron dose and 98 % and 99 %, respectively for the mean dose plus one standard deviation. The implications of underdosing, adding less than the 1.5:1 Fe:P molar ratio, are that not all P will be recovered as vivianite and that the solid fraction obtained will contain impurities of Ca and Mg co-precipitates. Overdosing results in excess Fe^{2+} being present in the urine after vivianite precipitation because more Fe is added than what is stoichiometrically required.

Provided that the reaction occurs in the optimum pH region of 6.0 to 7.0 and that excess iron is added, then the only factor affecting the amount of vivianite produced will be the calcium concentration in urine, as Ca^{2+} competes for P. Therefore, increasing concentrations of calcium will reduce the yield and purity of the vivianite, but only when the urine is not overdosed with iron. In addition, the reductions in yield and purity will only become significant when the calcium concentration exceeds approximately 500 mg L^{-1} (Supplementary information, Fig. S9). The amount of urine produced per day by an average individual contains 100–250 mg calcium (Foley and Boccuzzi, 2010), which approximates to 50–300 mg Ca L^{-1} based on urine production of 0.8–2 L day^{-1}. Therefore, the effects of calcium on the yield of vivianite are insignificant compared with the influence of P concentration in the urine.

3.2. Model vs. experimental results for vivianite precipitation in urine

The experiments in this study were run in two stages. In the first stage, synthetic urine was used to validate the model by comparing the yield and purity (Fig. 7A and Fig. 5B). In the second stage, real urine was dosed in the ideal operating pH range with the design dosage (based on the average P concentration of 10 urine compositions plus one standard deviation; giving an Fe:P of 2.5:1 for this particular urine composition) and the results were compared with those of the model (Fig. 7C, Fig. 7D). It was found that the yield and purity of vivianite obtained in the synthetic urine experiments accurately matched the results of the thermodynamic modelling (Fig. 7A, 5B). There was a reduction in the purity of vivianite as the pH increased, which was attributed to increased precipitation of co-precipitates such as $Ca_5(OH)(PO_4)_3$, $Mg(NH_4)PO_4{\cdot}6H_2O$, $Mg(OH)_2$, and $Mg_3(PO4)_2{\cdot}8H_2O$. This was verified experimentally by the increased presence of calcium and magnesium in the solid fraction obtained. The nature of the co-precipitates formed

Table 1
Summary of vivianite yield and purity in different urine pH ranges and iron (Fe) salt doses based on thermodynamic modelling results.

pH range/ Dose	Fe:P molar ratio		
	Underdosed (1.2:1)	Exact dose (1.5:1)	Overdosed (1.6:1)
4.0-5.5	Low yield High purity	Mid-range yield High purity	Mid-range yield High purity
5.5-8.0	Mid-range yield Mid-range purity	High yield High purity	High yield High purity
8.0-12.0	Low yield Low purity (multiple co-precipitates)	Low yield Low purity (multiple co-precipitates)	Low yield Low purity (multiple co-precipitates)

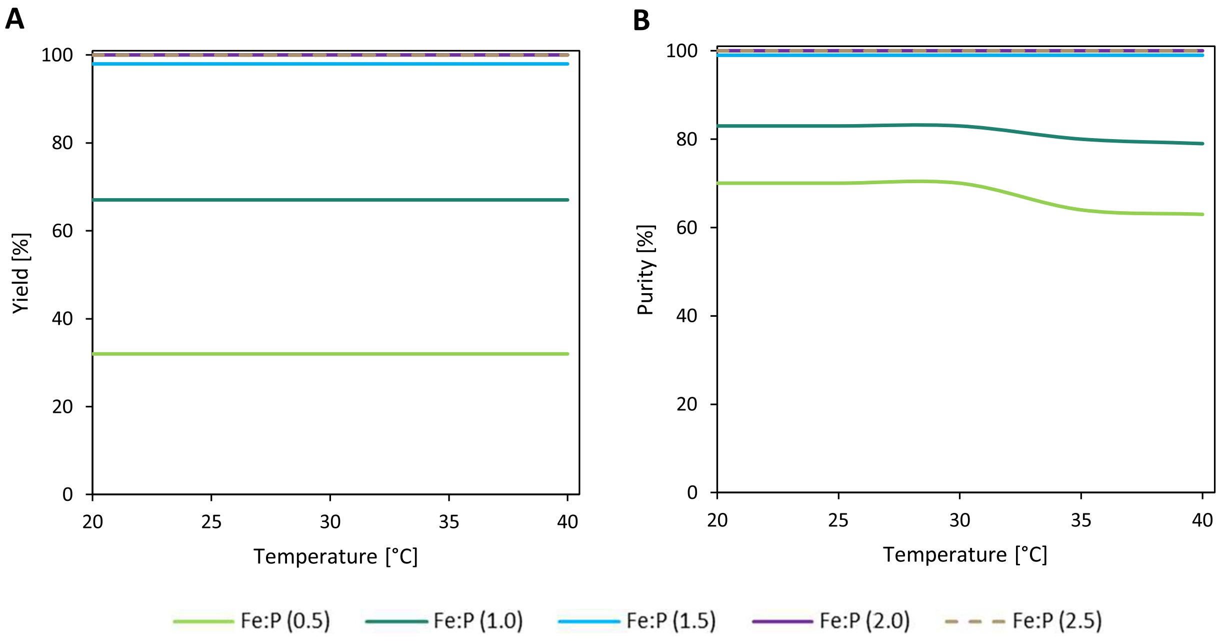

Fig. 4. The effects of operating temperature on the yield (A) and purity (B) of vivianite between 20 and 40 °C at a fixed pH of (7).

was determined using XRD analysis (Supplementary Information, Section 2.4), where the solids formed were matched to sample-solids in an XRD database. Vivianite was identified in the solid fraction formed at pH 6.0, 7.0, 8.0, and 9.0. The XRD scan became noisier as the pH increased, indicating increasing presence of amorphous compounds such as HAP and other calcium phosphate compounds with different Ca:P molar ratios, which are likely to form in the solid fraction (Linder and Little, 1986). The solids at pH 10.0 were determined to be completely amorphous. Additionally, above pH 8, $Fe(OH)_2$ began to precipitate, thus reducing the purity of vivianite (Supplementary Information, Section 2.6). The purity predicted by the model when the urine was significantly overdosed with iron salt (Fig. 7D) tended to decline rapidly above pH 7.0, while an exact iron dose (Fig. 7B) resulted in a more gradual reduction in purity. This was because overdosing the urine with iron exceeded the solubility limit for precipitation of $Fe(OH)_2$, resulting in more $Fe(OH)_2$ forming above pH 7.0. The lower yield of vivianite at pH 4.0 could be due to a disparity in reaction time, as the model predicted a thermodynamically stable state while the experiments were run for 15 min. The purity at pH 9 (Fig. 7B) was also lower, which could be due to oxidation of Fe^{2+} and precipitation of $Fe(OH)_2$.

For real urine, yields and purities were lower than predicted by the model (Fig. 7C and Fig. 7D), and there was no fit between the model data and experimental data. This indicates that the model was unable to predict the yield and purity of vivianite precipitated from real fresh urine. Organic substances can affect the purity of vivianite (Zhang et al., 2020). Carboxyl (COOH) groups present in organic compounds tend to form complexes with divalent metal ions (Karthik and Meenakshi, 2015), which can result in the consumption of Fe^{2+}. Additionally, the complexes formed can grow around the already-formed crystals and mask the growth points (Wei et al., 2019), limiting the yield and purity of vivianite.

The model does not include many common organics found in real urine such as creatinine, creatinine, uric acid, which may have affected the model accuracy. (Chen et al., 2022; Li and Sheng, 2021; Zhang et al., 2020) all found that complexation between iron and organic matter was the main cause in the reduction of P recovery as vivianite. Similarly, Courtney et al. (2021) found that the modelling of air bubbling in urine only matched experimental results when the organic creatinine was added to the model. The experiments showed a similarly increasing yield as pH increased, though at higher pH levels (5.0 to 6.5) than compared to the model predication. The purity of vivianite precipitated from real urine (75 ± 5 %) was significantly lower than that of vivianite precipitated from synthetic urine (95 ± 2 %) or that predicted by the thermodynamic model (100 %). The purity of vivianite obtained from real urine was relatively consistent as the pH varied (Fig. 7D).

3.3. Improving the purity of vivianite

The purity of vivianite recovered from real urine (75 ± 5 %) was found to be lower than synthetic urine (95 %) and it was hypothesized that this was due the presence of organics in real urine. To determine if the impurities in vivianite produced from real urine were organic in nature an incineration experiment was done (see Section 2.5 of the supplementary information).

The solid fractions obtained from synthetic and real urine were weighed before and after incineration to determine the volatile and inorganic solids content. All the organic content would be converted to water and CO_2 whilst the inorganic content would remain (Supplementary information, Section 2.5). The mass loss recorded from the vivianite produced from synthetic urine was 24.7 %. This corresponds within measurement error to the theoretical mass loss that would occur (25 %) when the waters of hydration present in vivianite ($Fe_3(PO_4)_2{\cdot}8H_2O$) are vaporized and the P and Fe are converted to P_2O_5 and Fe_2O_3, respectively, The mass loss recorded from the vivianite produced from real fresh urine was 38.9 %, 37.5 %, and 40.8 % at pH 5.0, 6.0, and 7.0, respectively. The additional mass loss is therefore likely due to the combustion of organics.

The water of hydration in vivianite ($Fe_3(PO_4)_2{\cdot}8H_2O$) makes up 25 % of the mass of the solid (Supplementary Information, Section 2.6). The synthetic solid lost (24.7 ± 0.5 %) of its mass after incineration, indicating high purity. The solid fraction from real urine lost on average 15 % more mass than the synthetic solid (Supplementary Information, Fig. S11), confirming the likely presence of organic matter in the solid precipitate formed from real fresh urine. The consistent mass loss, regardless of pH, was similar to the consistency in the purity of the solid fraction as pH varied (Fig. 7D). Li and Sheng (2021) found that organic matter in synthetic wastewater affected vivianite precipitation, with P recovery as vivianite inhibited by up to 12.1 %. The complex nature of real urine, which has a high organic presence, interferes with vivianite precipitation, affecting the yield and purity.

Washing the impure vivianite solid fraction that formed in real urine using water and ethanol was investigated, to determine its effect on purity.

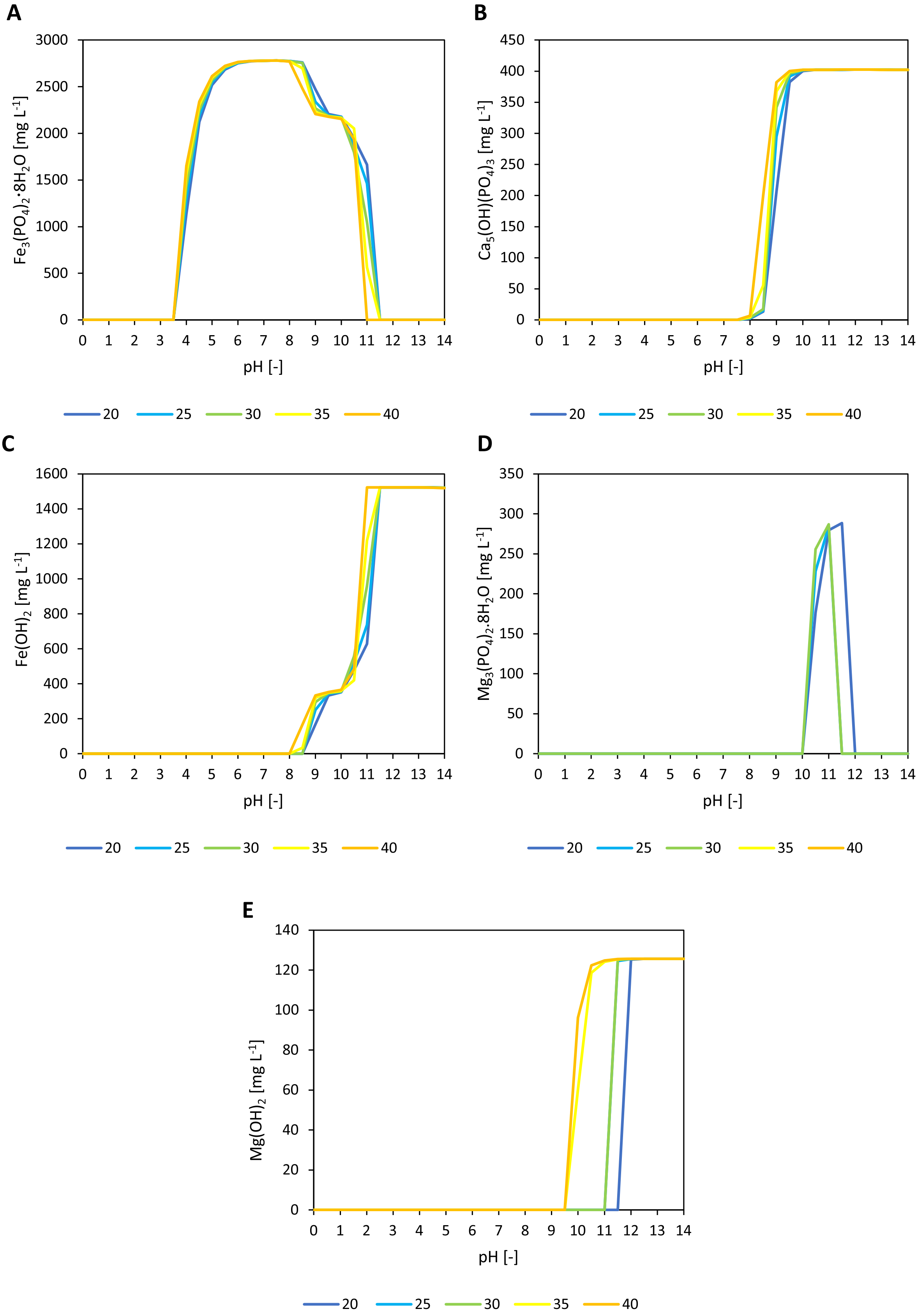

Fig. 5. The effects of temperature on the different co- precipitates formed as pH was varied: (A) vivianite, (B) HAP, (C) $Fe(OH)_2$, (D) $Mg_3(PO_4)_2{\cdot}8H_2O$, and (E) $Mg(OH)_2$. The experiments were dosed with a Fe:P of 1.5:1.

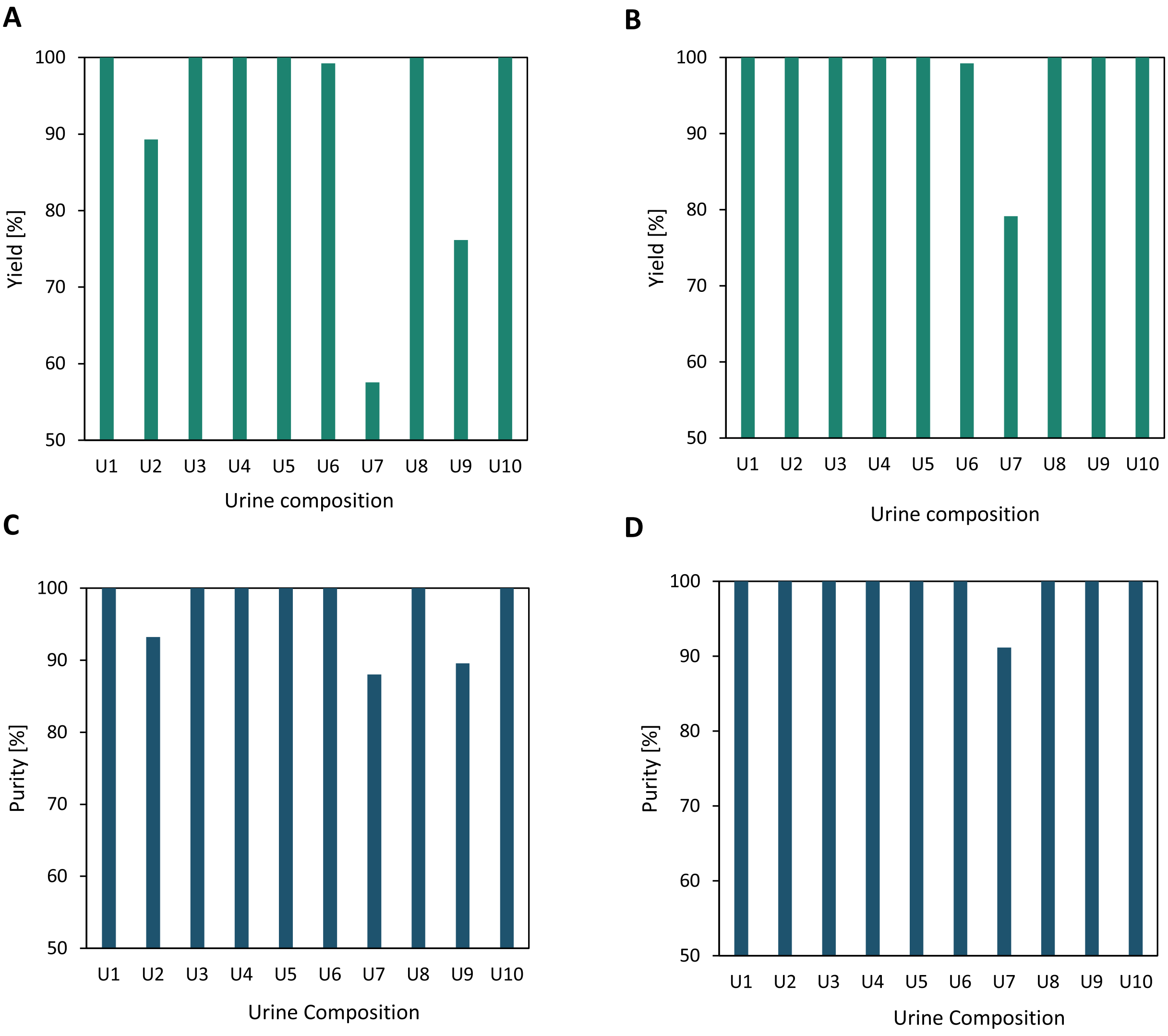

Fig. 6. Thermodynamic modelling results of (A, B) vivianite yield and (C, D) purity of vivianite formed from 10 different urine compositions with (A, C) the mean dose of iron salt required (5735 mg L^{-1}), and (B, D) the mean dose plus one standard deviation (7886 mg L^{-1}). The dose required was calculated based on mean phosphorus concentration in the 10 urine compositions.

Washing the solid was expected to dissolve some organic matter and to flush out free cations/anions left in the filtered solids from the urine. It was found that washing the solids with deionized water and ethanol improved the purity by 15.5 % and 11.7 %, respectively, at a pH of 6.0 (where the highest purities were achieved) (Fig. 8). Washing the solids with water was found to improve the purity more when compared to using ethanol.

Increasing the pH from 6.0 to 6.5 resulted in higher vivianite yield, but with a slight reduction in purity associated with increased precipitation of $Fe(OH)_2$. Additionally, increasing the pH was found to have a significant effect on the oxidation state of iron (Fe^{2+} to Fe^{3+}) (Supplementary Information, Section 2.7). The concentration of aqueous Fe^{2+} decreases with increasing pH between pH 5.0 and 8.0 due to oxidation, since Fe^{2+} exposed to oxygen in the air oxidizes to Fe^{3+} (Morgan and Lahav, 2007). The rate of oxidation will increase as the pH of the solution increases, driven by the increasing concentration of $Fe(OH)_2$, which is more easily oxidized than Fe^{2+} and $FeOH^{+}$ (Morgan and Lahav, 2007). Despite the yield and purity of vivianite obtained from real urine being lower than that of the synthetic urine and the model, the optimal pH value (6.0) was within the pH range determined by the model and synthetic urine experiments to maximize yield and purity. Future work should investigate which specific organics present in human urine are responsible for affecting the purity of vivianite production and alternative methods for removing these.

3.4. Practical considerations and limitations

While this work focused on lab-scale experiments and feasibility of recovering from human urine, the technical requirement and real-world feasibility of such a system are also important. We envision that vivianite will be recovered from novel fertilizer-producing urinals (Flanagan and Randall, 2018), where an Fe solution is dosed directly to the fresh urine as it is collected. Thereafter, the solid-liquid solution could be passed over a magnetic separation system (Prot et al., 2019) to recover the vivianite as a separate solid that is periodically collected from each urinal. The remaining urine solution can then be stabilized to prevent urea hydrolysis (Randall et al., 2016) and concentrated using membrane processes (Courtney and Randall, 2022) or dehydration (Simha et al., 2020). These aspects would have to be investigated in future work to test the feasibility in a non-laboratory setting. This work did not investigate the potential complexation of organic substances with Fe in urine and this should also be investigated further as this would influence the purity of vivianite formed.

4. Conclusions

This work demonstrated that vivianite can be chemically precipitated from fresh human urine through the addition of iron salts, with a maximum

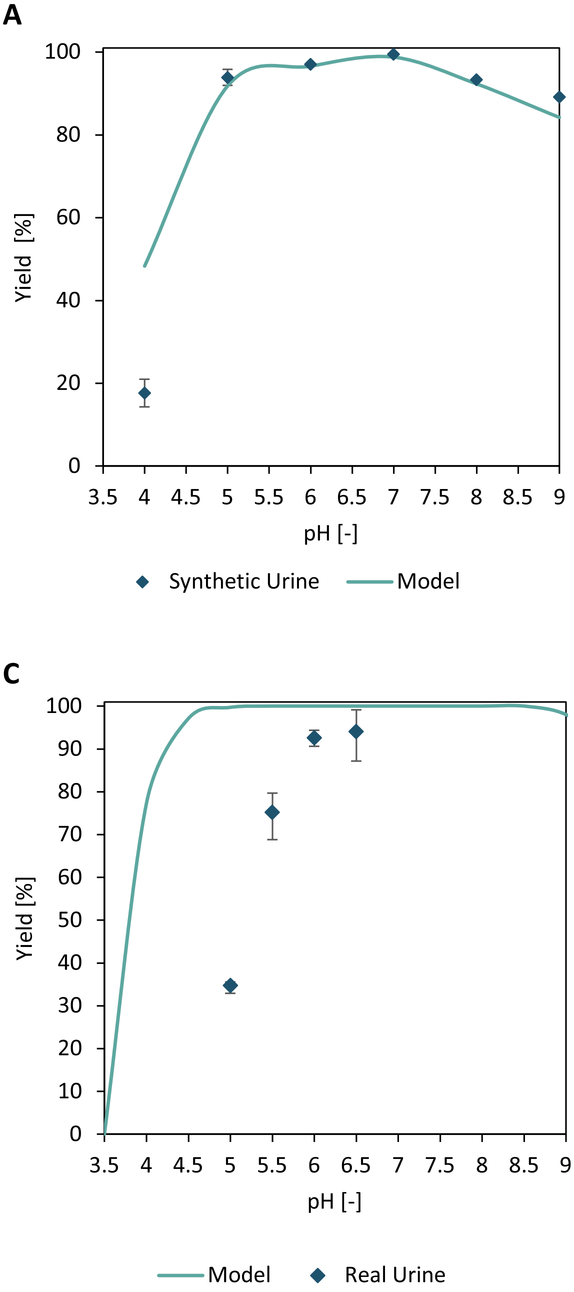

Fig. 7. Comparison of the yield and purity of vivianite predicted by the model and determined experimentally for synthetic and real urine. The thermodynamic modelling and the synthetic urine experiments were run at a Fe:P molar ratio of 1.5:1 (A, B), while the modelling and the real urine experiments were run at a Fe:P molar ratio of 3.1:1 (C, D). All experiments were run at room temperature (25 ± 1 °C). The error bars represent the experimental error for three repeat experiments. Where not visible, the error was low.

yield of 93 ± 2 % and a maximum purity of 79 ± 3 % obtained at an optimal pH of 6.0. Other types of urine such as stabilized ($4 < pH > 10$) or hydrolyzed urine should not be used for vivianite production because of reduced yields and purities.

The type of iron salt used did not affect the yield and purity of the solid fraction obtained, therefore the choice of Fe salt was only influenced by the amount of solid formed and the operating costs. In addition, overdosing the Fe salt can compensate for differences in urine composition. Overdosing also provided sufficient Fe^{2+} to react with all P and had a competitive effect that suppressed the precipitation of other co-precipitates of Ca and Mg.

Solution pH was found to affect the solubility of vivianite and other co-precipitates of Mg and Ca, and the rate of oxidation of Fe^{2+} when exposed to oxygen in the air. A Fe:P molar ratio of between 1.5:1 to 2.2:1 maximized the yield and purity of vivianite extracted from urine. Washing the solids that formed with deionized water improved the vivianite purity from 63.1 % to 78.6 % by mass.

Operating temperature had little to no effect on the yield and purity of vivianite, and only affected the solubility of Ca and Mg precipitates at pH values above 8.0, which is outside the ideal pH range for vivianite recovery from human urine.

Overall, this work provides useful operating conditions for producing vivianite from human urine. Next steps should focus on the practical application of P recovery from human urine as vivianite to ascertain the feasibility in a real-life setting using novel urinals or other non-sewered sanitation systems. In addition, improving the purity of the vivianite should also be investigated, especially if high-value vivianite is to be produced.

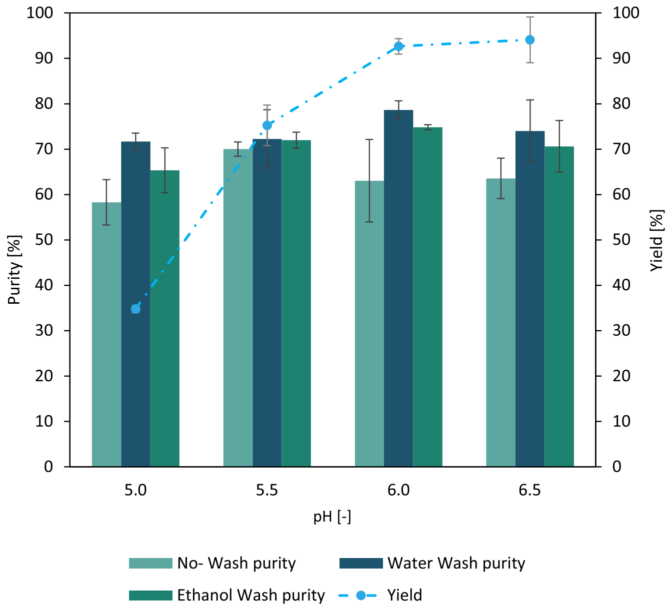

Fig. 8. Effect of washing with ethanol or deionized water on the purity of vivianite in the solid fraction that formed in real urine. The solid fraction was washed three times after filtration, dried, and analyzed.

CRediT authorship contribution statement

CS ran all experiments, conducted the simulations, and wrote the paper. CC co-supervised the work, helped with experimental work and the simulations, and edited the paper. PS conceptualized the study, co-supervised the work and edited the paper. NF interpreted the XRD analysis results and edited the paper. DGR conceptualized the study, secured the funding, and led the study and edited the paper.

Data availability

Data will be made available on request.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Dyllon Randall reports financial support was provided by Water Research Commission. Prithvi Simha reports financial support was provided by Stiftelsen Lantbruksforskning. Prithvi Simha reports financial support was provided by Swedish Research Council Formas. Dyllon Randall reports financial support was provided by August T Larsson Guest Researcher Programme. Chibambila Simbeye reports financial support was provided by Water Research Commission.

Acknowledgements

This work would not have been possible without financial support from the Water Research Commission. We would also like to acknowledge the University of Cape Town for providing the laboratory facilities necessary to complete this work. In addition, we would like to thank Njabulo Thela and Hector Mafungwa at the Water Quality Lab for their technical support, and Rachel Cupido at the Catalysis Institute, University of Cape Town, for the work on XRD analysis of the solids. Prithvi Simha was supported by grants from Stiftelsen Lantbruksforskning for the project "Växtnäringskretslopp till uthållig ölproduktion" (Grant number JTI-20-83-489) and the Swedish Research Council Formas for the project "Urintorkning processoptimering och underliggande processer" (Grant number 2019-00986). Dyllon Randall was supported by funding from the August T Larsson Guest Researcher Programme at the Swedish University of Agricultural Sciences.

Appendix A. Supplementary information

Supplementary information to this article can be found online at https://doi.org/10.1016/j.scitotenv.2023.164517.

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