

Recovery of struvite for organic production: Mineral-based magnesium supplementation and pH elevation

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ABSTRACT

Phosphate in wastewater can be recovered in the form of struvite crystals for use as slow-release fertilizer. Currently, struvite recovery often requires supplementing magnesium ions and raising pH with chemicals, making the recovered struvite unfavorable for organic production. In an effort for cleaner production, this study developed a versatile approach employing two mineral products in variable combinations for optimal supplementation of magnesium and elevation of pH. Magnesite, a mineral of MgCO_3 , was ground and calcined without use of any catalysts. The magnesite calcined under the optimum conditions (800 °C for 30 min) can be dissolved in near-neutral filtrate of sludge digestate to supplement magnesium and raise pH for effective struvite formation. The OMRI-listed Epsom salts ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$), mineral-based water-soluble commercial products, can be used to supplement magnesium without changing pH of alkaline wastewater. Six-hour batch operation of an air-lift crystallizer removed 85.7% and 94.7% of phosphate in hydrolyzed human urine when magnesium was amended to $1.2 \times$ molar concentration of phosphate with calcined magnesite and an OMRI-listed Epsom salt, respectively. More than 98% of phosphate was removed from filtrate of sludge digestate in 3-h batch operation using calcined magnesite to raise pH to 8.5 and the Epsom salt for further magnesium supplementation. Struvite accounted for 85.7%, 90.5%, and 81.5% of the crystals recovered from urine with calcined magnesite, urine with Epsom salt, and filtrate with both mineral products, respectively. The material and energy costs of this green process were estimated to be \$0.16/kg struvite from urine with calcined magnesite, \$1.37/kg struvite from urine with Epsom salt, and \$0.94/kg struvite from filtrate with both mineral products. This study proved the technical and economic feasibility of chemical-free magnesium supplementation and pH elevation, making the recovered struvite potentially certifiable for organic production.

1. Introduction

Recovery of struvite ($\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$) from phosphate-rich wastewater such as source-separated human urine and anaerobic digestate has gained growing interest in research and commercial applications (Desmidt et al., 2015; Krishnamoorthy et al., 2021; Vasa and Chacko, 2021; Zhu et al., 2023). Fresh human urine has high concentrations of urea, which is quickly hydrolyzed to ammonia in the presence of urease (Krishnamoorthy et al., 2020; Tao et al., 2019). Urea hydrolysis can raise urine pH to around 9, thus reaching the optimum pH level for struvite precipitation (Krishnamoorthy et al., 2020; Tao et al., 2019). Nevertheless, hydrolyzed human urine has a lower magnesium concentration relative to ammonium and phosphate, demanding supplementation of Mg^{2+} for struvite precipitation (Tao et al., 2016).

Commonly, Mg^{2+} is supplemented with soluble salts such as MgCl_2 and MgSO_4 , which often account for 75% or more of the operating cost for struvite recovery (Alemayehu et al., 2020; Min and Park, 2021; Orner et al., 2022; Yetilmezsoy et al., 2017). Although seawater and desalination brine have been used to reduce the cost for Mg^{2+} supplementation, they are locally available only and may increase wastewater ionic strength and concentrations of interfering ions that in turn hinder struvite precipitation (Bradford-Hartke et al., 2021). Similarly, anaerobic digestate is deficient in Mg^{2+} relative to phosphate and has lower pH values unfavorable for struvite precipitation (Table A1). Cheaper $\text{Mg}(\text{OH})_2$ and MgO can be used to supplement Mg^{2+} and raise pH (Hao et al., 2022), but the dosages to reach the optimum pH of 8.5–9.5 and optimum $\text{Mg}^{2+} : \text{PO}_4^{3-}$ ratio of greater than 1.2 are often different, and their solubilities are relatively low (Guan et al., 2023; Bradford-Hartke

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et al., 2021; Min and Park, 2021; Tansel et al., 2018; Tao et al., 2016). It has been a challenge to find cost-effective sources of Mg^{2+} and alkali for struvite recovery from the near-neutral digestate. Additionally, magnesium and alkali supplements should be derived from natural or organic sources so that the recovered struvite has the potential to be listed as materials suitable for certified organic production.

Organic production systems rely on organic fertilizers such as animal manure, compost, poultry droppings, bone/blood meal, and biosolids, while use of chemically synthesized fertilizers is not allowed (Løes et al., 2017; Bünnemann et al., 2024). Commonly, all such organic fertilizers have limited availability, low nutrient rating, and inconsistent nutrient content and rely on soil microbes for nutrient mineralization, leading to crop yields from organic farming being 25% lower than conventional farming (Bünnemann et al., 2024; Seufert et al., 2012). Therefore, high-grade natural fertilizers are highly needed to increase the productivity of organic production systems. Natural fertilizer is “a substance composed only of natural organic and/or natural inorganic fertilizer materials and natural fillers” (AAPFCO, 2019). When struvite crystals are recovered from wastewater without use of chemicals, the recovered crystals are natural fertilizers and expected to be accepted for certified organic production.

In the European Union, ‘recovered struvite and precipitated phosphate salts’ have been approved for use in organic production by their inclusion in annex II of Regulation 2021/1165 (European Commission, 2023). According to the U.S. National Organic Program standards, however, struvite recovered from wastewater is considered a synthetic fertilizer, thus being prohibited in certified organic production (USEPA, 2023). Most organic regulations do not allow chemical processing or use of synthetic compounds in the manufacturing processes, but physical and mechanical processing is allowed (Løes and Adler, 2019). Therefore, natural minerals after physical or mechanical processing offer a prospect to recover struvite from wastewater for organic production.

Minerals such as brucite ($\text{Mg}(\text{OH})_2 \cdot 6\text{H}_2\text{O}$) and serpentine ($\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$) have been explored for magnesium supplementation and pH elevation. However, acid dissolution of brucite (Huang et al., 2011) is not suitable to produce struvite for organic production. The recovery efficiency by addition of milled serpentine decreased with increasing PO_4^{3-} concentration greater than 7 mM (Li et al., 2022), making it unsuitable for struvite recovery from wastewater having a high phosphate concentration. The pilot tests by Li et al. (2022) with filtered black water at the high dosage of 13.7 g $\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4/\text{g}$ $\text{P}_{\text{removed}}$ recovered crystals containing only 70% struvite because Si released from serpentine acted as seeds for secondary struvite nucleation. When the mineral magnesite is calcined, MgCO_3 is converted to MgO as in Eq. (1). Calcined magnesite has a higher solubility in water than ground magnesite (Krähenbühl et al., 2016; Yu et al., 2017), thus being able to simultaneously supplement magnesium and raise pH as shown in Eq. (2). Using calcined magnesite for struvite recovery costs less than using brine and chemicals such as MgO , MgCl_2 , and MgSO_4 (Al-Mallahi et al., 2020; Etter et al., 2011; Huang et al., 2010; Yu et al., 2017). Compared with milled serpentine, a smaller dosage of calcined magnesite is needed due to its high magnesium content, thus minimizing the residuals left in wastewater.



Mineral-derived water-soluble magnesium salts, for instance, the OMRI-listed Magriculture® Epsom salt made of the mineral epsomite following good manufacturing practices, can be directly added to supplement magnesium. Nevertheless, chemical-free pH elevation is still required for most wastewater streams to effectively precipitate struvite for organic production. Moreover, addition of an epsomite product alone to supplement magnesium increases salinity, which may decrease the effectiveness of struvite formation (Tao et al., 2016). When only calcined magnesite is dosed to reach a $\text{Mg}^{2+}:\text{PO}_4^{3-}$ ratio greater than

1.2, however, pH may fall outside the optimum range of 8.5–9.5. Vice versa, $\text{Mg}^{2+}:\text{PO}_4^{3-}$ ratio may still be smaller than 1.2 when calcined magnesite is dosed to reach the optimum pH range.

This study for the first time explored the combined use of calcined magnesite and an OMRI-listed water-soluble mineral as an inclusive approach to recovering struvite from various wastewaters for organic production. It evaluated the efficacy of struvite recovery from alkaline hydrolyzed urine with addition of either calcined magnesite or OMRI-listed Epsom salt as well as from near-neutral filtrate of sludge digestate with addition of both calcined magnesite and the Epsom salt. To the best of our knowledge, there are no studies using an OMRI-listed water-soluble epsomite product alone or a combination of calcined magnesite and mineral salt to produce struvite. The process parameters for light-burnt magnesite were optimized for the first time for struvite recovery from hydrolyzed human urine. The prospect for upscaling this green process is also discussed.

2. Materials and methods

2.1. Calcination of magnesite

Ground magnesite was obtained from Premier Magnesia’s manufacturing plant in Gabbs, Nevada. Particle size distribution in the accompanying Certificate of Analysis was 98.8% < 0.044 mm, 1.0% at 0.044–0.074 mm, and 0.2% at 0.074–0.149 mm. Calcination of the ground magnesite was performed in triplicate using a Thermo Scientific Thermolyne large-chamber muffle furnace at six temperatures: 500, 600, 700, 800, 900, and 1000 °C in the light-burnt range for producing reactive materials. When the furnace temperature reached a target set on its digital controller, 6 porcelain dishes with ground magnesite (2 g each in a thin layer) were moved in for calcination for 5, 10, 15, 30, 60, and 120 min, respectively. These temperatures and durations were selected based on previous studies on calcination of magnesite (Al-Mallahi et al., 2020; Huang et al., 2010; Krähenbühl et al., 2016; Yu et al., 2017). In general, light-burnt MgO (at 700–1000 °C) has the highest reactivity and greatest specific surface area compared with hard-burnt MgO (1000–1500 °C) and dead-burnt periclase (1400–2000 °C) (Nobre et al., 2020). At the end of a calcination duration, the dish was transferred to a desiccator to cool down to room temperature, and product weight was measured. Fourier transform infrared spectroscopy (FTIR) was performed with a PerkinElmer spectrometer to confirm the molecular composition of the calcined samples and ground magnesite. Transmittance spectra were acquired in the wavenumber range of 4000–550 $1/\text{cm}$ at 16 scans per sample. X-ray powder diffraction (XRD) measurements were carried out to confirm the efficacy of calcination, using a Bruker D2 Phaser Diffractometer with $\text{Cu K}\alpha$ radiation (1.54060 Å) as incident beam from 10° to 70° by step size of 0.02° (2 θ) with 0.5 s intervals. Surface morphology and elemental composition of the samples were determined by scanning electron microscopy (SEM) - energy dispersive X-ray spectroscopy (EDS) using a JEOL JSM – IT100LA microscope as described by Tao et al. (2024).

2.2. Preparation and characterization of wastewater

Two types of phosphate-rich wastewater were used for phosphate removal and recovery tests, alkaline hydrolyzed human urine and near-neutral sludge digestate. Waterless male urine was collected in clean urinals and stored at room temperature in 20-L capped wastewater sampling containers for natural urea hydrolysis. Total ammonia nitrogen (TAN) concentration, pH, and electrical conductivity were determined periodically to track the progress of urea hydrolysis (Tao et al., 2019). Conductivity, pH, and TAN concentration were measured with portable meters as described by Tao et al. (2024). When TAN concentration, pH, and conductivity were stabilized after 2–4 weeks of storage, precipitates greater than 38 μm were removed by screening the hydrolyzed urine through a #400 sieve prior to further use for struvite

recovery experiments. The concentrations of PO_4^{3-} , Mg^{2+} and Ca^{2+} were measured with an AquaMate UV-visible spectrophotometer as described by Tao et al. (2019). Table 1 presents the characteristics of the fresh and hydrolyzed urine samples. After hydrolysis, the urine pH values from 9.09 to 9.47 were close to the optimum pH range of 8.5–9.5 for efficient struvite recovery (Guan et al., 2023; Tao et al., 2016; Yetilmezsoy et al., 2017; Zamora et al., 2017).

The supernatant and filtrate of anaerobic sludge digestate were sampled from a thickener and filter press, respectively, at the Water Resource Recovery Facility, Watertown, New York. The filtrate separated from anaerobic co-digester influent (sewage sludge and chicken manure) was collected from the belt press at Opequon Water Reclamation Facility, Winchester, Virginia. The supernatant and filtrate were characterized in the same methods as for urine (Table 1).

2.3. Jar tests on phosphate removal to optimize the calcination process

To determine the optimum calcination conditions, batch experiments for phosphate removal from hydrolyzed human urine were carried out in triplicate at room temperature. Each 250-mL beaker was added 100 mL of hydrolyzed urine and magnetically stirred at 230 rpm. While stirring, ground magnesite, calcined magnesite, or Epsom salt was added to reach an initial $\text{Mg}^{2+}:\text{PO}_4^{3-}$ molar ratio of 1.2. A molar ratio close to 1.2 has been recommended by various studies as optimal for struvite recovery (Bradford-Hartke et al., 2021; Tao et al., 2019; Yetilmezsoy et al., 2017). A total of 49 jar tests with ground magnesite, Epsom salt, and magnesite calcined at 600 °C for 120 min (CM1), 700 °C for 60 min (CM2), 800 °C for 30 min (CM3), 900 °C for 15 min (CM4), and 1000 °C for 10 min (CM5) lasted for 30, 60, 120, 180, 240, 300, and 360 min. The calcination duration for each temperature was selected to be the minimum time for stabilized weight loss in the calcination experiments as described in Section 2.1. The Epsom salt was Magri-culture® agricultural-grade magnesium sulfate heptahydrate (Giles Chemical, Waynesville, North Carolina), which is an OMRI-listed product in the crop fertilizers and soil amendments class for certified organic production (OMRI, 2023). The urine sampled at the end of each batch was centrifuged at 10,000×g for 10 min for determination of PO_4^{3-} concentration. Conductivity and pH of urine were monitored throughout the experiments.

2.4. Developing dosing curves of calcined magnesite for elevation of wastewater pH

To recover struvite from near-neutral anaerobic digestate, calcined magnesite can be supplemented to reach the optimum pH values for struvite precipitation, i.e., around 8.5 (Guan et al., 2023; Zamora et al., 2017), which increases Mg^{2+} concentration as well. Each sample (0.1 L) was transferred to a 200-mL beaker and stirred for 30–60 min at 130 rpm to purge CO_2 for pH increase. CM3 was then added gradually to develop dosing curves for elevation of pH in supernatant and filtrate of sludge digestate and filtrate of co-digester influent.

2.5. Struvite recovery from hydrolyzed urine with single-source magnesium amendment

To assess the performance of struvite recovery employing mineral-based magnesium supplementation, a functional prototype of air-lift

crystallizer (Fig. 1) was operated in a batch mode. The air-lift crystallizer was assembled with tri-clamp stainless steel spools and fittings. For each batch run, 3.2 L of hydrolyzed urine was added to the crystallizer. Compressed air introduced at the sparger lifts the mixture of urine, air, and fine crystals up through the riser. The fluid mixture overflows at the top of the riser into the downcomer. The riser and downcomer have similar cross-sectional areas. Air pressure at 162 kPa and flow rate at 1497 mL/min were maintained using a pressure regulator and a rotameter respectively, providing a velocity gradient of 1568 1/s in the riser. 2.9 ± 0.2 g of CM3 or 18.1 ± 2.8 g of Epsom salt were added to each batch to reach an initial $\text{Mg}^{2+}:\text{PO}_4^{3-}$ molar ratio of 1.2. Conductivity and pH were measured in situ initially and every hour. Urine samples were taken hourly after adding magnesium, centrifuged at 10,000×g for 10 min, and determined for PO_4^{3-} concentration. After 6 h of batch operation, crystals were collected on the 38- μm sieve, washed with tap water,

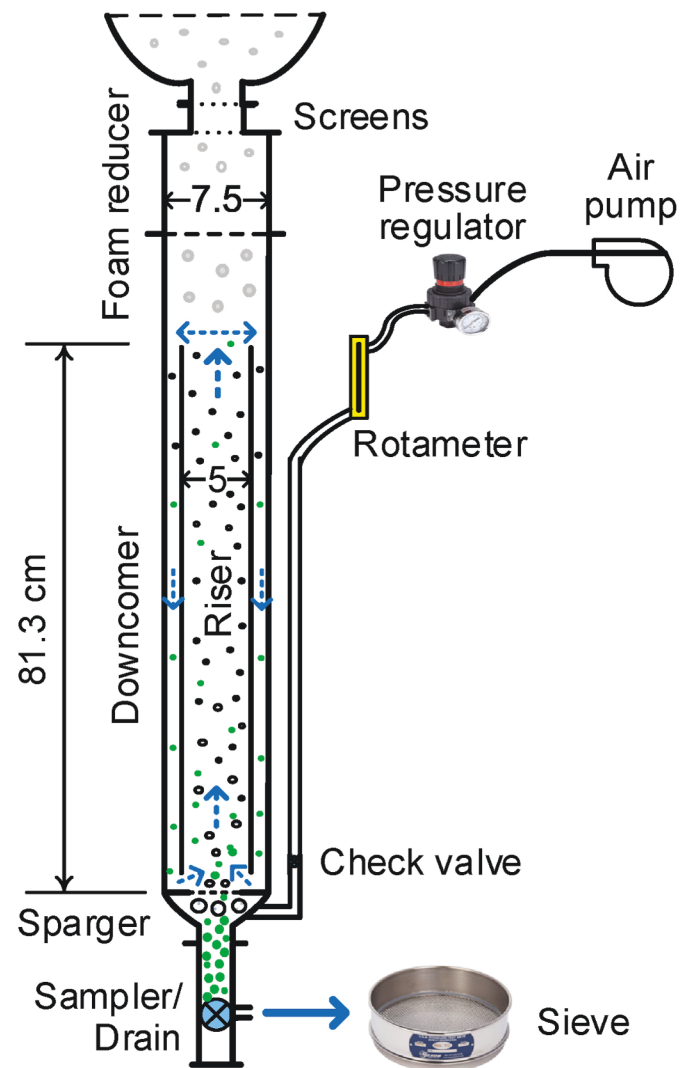


Fig. 1. Schematic of air-lift crystallizer.

Table 1
Characteristics of male urine and filtrate of anaerobic sludge digestate.

Type of wastewater	pH	Conductivity, mS/cm	Alkalinity, mg/L as CaCO_3	Total ammonia-N, mg/L	$\text{PO}_4^{3-}\text{-P}$, mg/L	Mg^{2+} , mg/L	Ca^{2+} , mg/L
Fresh urine	5.84	21.6	n/a	567	1027	76.2	5.9
Hydrolyzed urine	9.25	58.0	31000	11147	601	0.85	4.4
Filtrate of digestate	7.61	4.66	2655	754	4.03	26.0	21.7
Filtrate of co-digester influent	7.63	5.00	2590	588	41.2	27.2	20.8

dried at room temperature, and weighed. A sample of the final sieved urine was centrifuged for determination of PO_4^{3-} , Mg^{2+} , and TAN concentrations. The air-dried crystals were further oven dried at 45 °C for 24 h and characterized by SEM-EDS for surface morphology and elemental composition, FTIR for molecular composition, and XRD for determination of crystal phases. The high-purity struvite crystals precipitated from synthetic wastewater (Huchzermeier and Tao, 2012) were used as a reference for FTIR analysis. The XRD diffractogram for reference struvite was obtained from the American Mineralogist Crystal Structure Database (RRUFF ID R050540.1). Each dried crystal sample (0.1 g) was digested in 0.01 L of 5 N H_2SO_4 at 150 °C for 60 min. The acid extracts were filtered through 0.22- μm membrane filters and examined for PO_4^{3-} , Mg^{2+} , and TAN concentrations. Struvite recovery efficiency and struvite content in the recovered crystals were calculated using Eqs. (3) and (4).

$$\lambda = 100 \times Y_a / Y_t \quad (3)$$

$$\eta = 100 \times \text{Min}(\text{Mg}, \text{N}, \text{P}) / M \quad (4)$$

where λ = struvite recovery efficiency (%); Y_a = specific yield of crystals having a particle size larger than 38 μm (g/L); Y_t = theoretical yield of struvite (g/L) based on the decrease of phosphate concentration in urine; η = struvite content in crystals (%); Mg, N, and P = Mg^{2+} , TAN, and PO_4^{3-} concentrations in the acid extracts (mM); and M = struvite molar concentration in the acid extracts assuming the extracted crystals had 100% struvite (mM).

2.6. Struvite recovery from filtrate of anaerobic digestate with two mineral products

To evaluate the efficacy of using both mineral products to supplement Mg^{2+} and raise pH of near-neutral, P-rich sludge digestate, 3.25 L of the filtrate was filtered through the 38- μm sieve and transferred to the air-lift crystallizer. Since the filtrate collected from the local Facility was low in PO_4^{3-} concentration (Table 1), lab-grade Na_2HPO_4 was added to reach the average PO_4^{3-} concentration (5.7 mM) of anaerobic sludge digestate used for struvite recovery (Table A1). The amount of calcined magnesite needed to increase pH to above 8.5 was estimated from the dosing curve developed as described in Section 2.4. The dosage of Epsom salt for further magnesium supplementation was estimated stoichiometrically in Eq. (5) since 1) dissolution of 1 mol of calcined magnesite produces 1 mol of Mg^{2+} ; 2) dissolution of 1 mol of Epsom salt ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$) produces 1 mol of Mg^{2+} ; and 3) Mg^{2+} and PO_4^{3-} react in a molar ratio of 1 in the struvite precipitation process although a molar ratio of 1.2 or greater is often recommended for real wastewater having interfering ions.

$$ES = \theta \times C_p - CM \quad (5)$$

where ES = dosage of Epsom salt for further Mg supplementation after addition of calcined magnesite, mM; θ = the minimum Mg^{2+} : PO_4^{3-} molar ratio for struvite recovery = 1.1 or greater depending on the presence of ions that interfere with struvite formation; C_p = wastewater PO_4^{3-} concentration, mM; and CM = dosage of calcined magnesite to reach pH 8.5, mM.

After running the crystallizer for 30 min to purge CO_2 , CM3 (374 mg each) was added to supplement Mg and increase pH to 8.5. Epsom salt (2.389 g each) was then added to reach a total Mg^{2+} : PO_4^{3-} ratio of 1.2. Conductivity and pH were continuously monitored and filtrate samples were taken hourly to measure PO_4^{3-} , Mg^{2+} , and Ca^{2+} concentrations. After 3 h of crystallization upon addition of Epsom salt, the filtrate-crystal mixture was sieved and characterized as described in Section 2.5. The above batch test was conducted in 4 replicates.

3. Results and discussion

3.1. Effects of temperature and duration on surface properties of calcined magnesite

The weight loss of magnesite upon calcination (Fig. 2) reached up to 49.4% of the initial weight of magnesite, which was slightly lower than the theoretical weight loss (52.2%) when pure MgCO_3 is fully converted to MgO as shown in Eq. (1) and very close to the value in the product certificate (49.16%). As Fig. 2 shows, 500 °C was not high enough to satisfactorily calcine magnesite within 120 min. CM2-CM5 achieved more than 49% weight loss with less weight loss in CM1.

Fig. 3a and b and Fig. A1 present SEM micrographs, EDS spectra, and elemental compositions of the ground and calcined magnesite samples. The SEM micrographs revealed rugged surfaces of ground magnesite while the surfaces of calcined magnesite were smooth with cracks. The EDS analysis showed that the ground magnesite sample had atomic percentages of Mg, C, and O very close to the theoretical atomic composition of pure MgCO_3 (Mg = 20%, C = 20%, and O = 60%). All the calcined magnesite samples had almost the same O percentages and a little lower Mg percentage than the theoretical atomic percentages of pure MgO (Mg = 50 and O = 50). Among all the calcined magnesite samples, CM3 had the highest Mg percentage and lowest residual C percentage, indicating the optimum calcination conditions of 800 °C for 30 min. At lower SEM magnifications, both the calcined and ground magnesite particles were quadrangular in varying sizes (Fig. A2). Similar shapes of calcined magnesite have been reported by Ngulube et al. (2018).

The FTIR transmittance bands of calcined and ground magnesite are presented in Fig. 3c. The spectral peaks of ground magnesite at 1430, 880, and 747 $1/\text{cm}$ represent typical magnesium carbonate asymmetric stretching ν_3 , asymmetric bending ν_2 , and symmetric bending ν_4 , respectively (Kim et al., 2021; Wang et al., 2019). These peaks either decreased at 1430 and 880 $1/\text{cm}$ or disappeared at 747 $1/\text{cm}$ as calcination temperature increased, indicating the removal of CO_3^{2-} during calcination and production of MgO (Yu et al., 2017). The spectra of all the calcined magnesite samples showed a trend of developing peaks below 700 $1/\text{cm}$ while such peaks were absent in the ground magnesite spectrum, indicating the presence of MgO (Nga et al., 2020). The XRD diffractograms (Fig. 3d) revealed the high purity of ground magnesite as MgCO_3 and CM3 as MgO when compared to magnesite (RRUFF ID R050676.1) and periclase (AMCSD ID 0000501) diffractograms in the

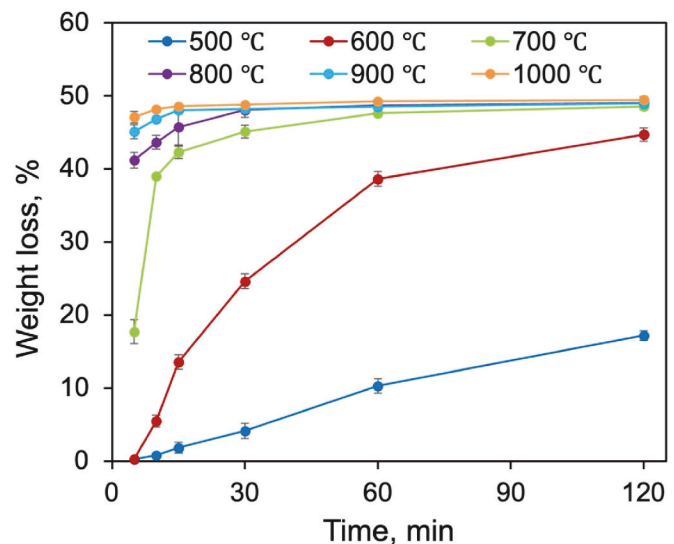


Fig. 2. Weight loss of magnesite in response to calcination temperature and duration. Error bar = Standard deviation of triplicates.

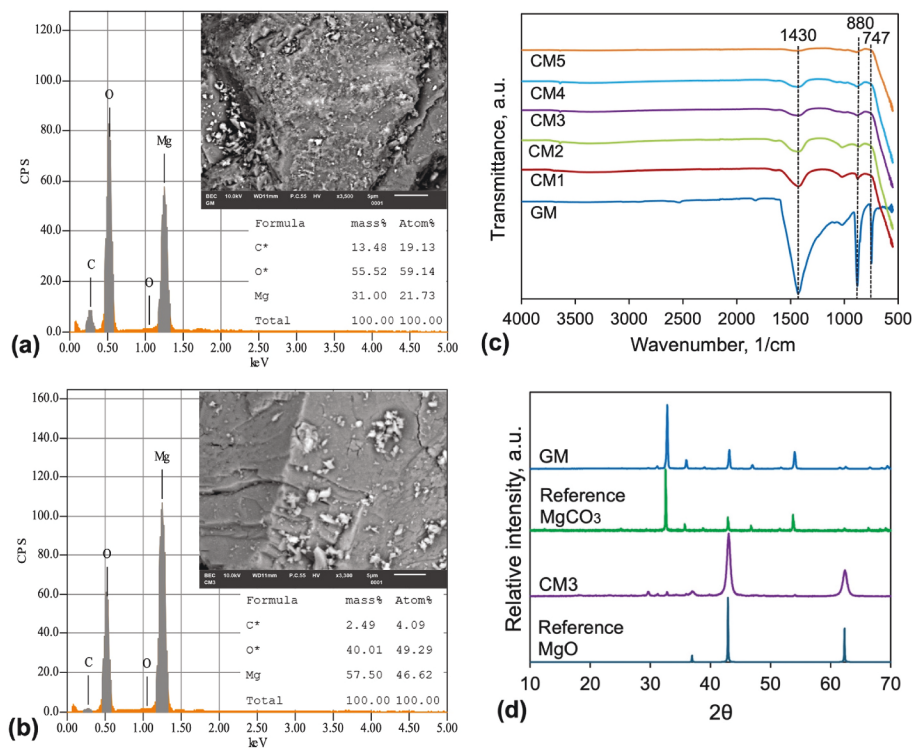


Fig. 3. Characterization of (a) ground magnesite by SEM micrograph (5-μm scale bar) and EDS spectrum; (b) CM3 by SEM and EDS; (c) ground magnesite (GM) and magnesite calcined at 600 °C (CM1), 700 °C (CM2), 800 °C (CM3), 900 °C (CM4), and 1000 °C (CM5) by FTIR spectra; and (d) GM and CM3 along with references by XRD diffractograms..

American Mineralogist Crystal Structure Database. The diffraction patterns of MgCO₃ were absent in the CM3 sample, indicating the conversion of MgCO₃ to MgO.

3.2. Effects of calcination temperature and duration on phosphate removal

As shown in Fig. 4, supplementing urine with ground magnesite resulted in a very low phosphate removal efficiency (7.1%). Supplementing urine with Epsom salt attained immediate phosphate removal,

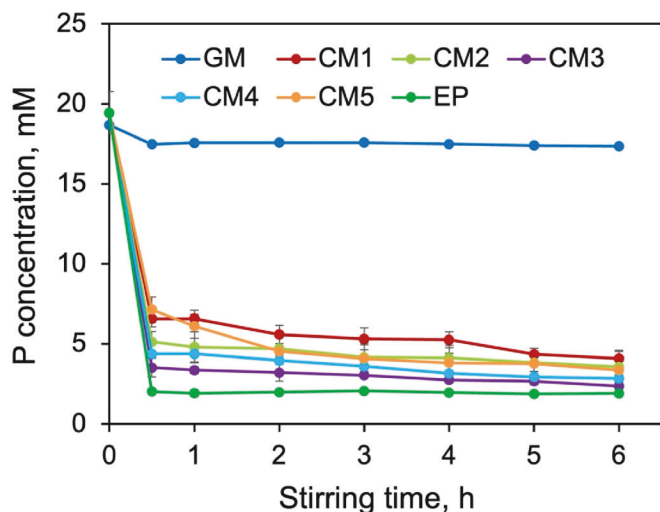


Fig. 4. PO₄³⁻-P concentration over stirring time in jar tests with different magnesium sources. EP = Epsom salt; the other legend items are the same as given in Fig. 3. Each dot = average of 3 replicates; error bar = standard deviation.

reaching the highest phosphate removal efficiency of 89.8%. Among the urine samples supplemented with magnesite calcined under the selected conditions, CM3 resulted in the greatest phosphate removal efficiency of 87.8%. Besides the greater solubility of MgO than MgCO₃, the cracks on the surfaces of the calcined magnesite (Fig. 3) could have promoted its reactive behavior in comparison to uncalcined magnesite (Drnek et al., 2018). The specific surface area and pore volume of calcined magnesite decrease considerably from light-burnt (700–1000 °C) to hard burnt (1000–1500 °C) calcination temperature and residence time (Nobre et al., 2020), resulting in the greatest hydration activity of CM3 that was calcined at a lower temperature. During the 6 h of crystallization in the jar tests with hydrolyzed urine, there were little changes in pH and the final pH 8.93–9.06 (Fig. A3) were suitable for struvite precipitation. Conductivity decreased over time as ions were precipitated (Fig. A4a), suggesting the appropriate dosage of calcined magnesite.

The highest phosphate removal efficiency in the present study exceeded the efficiency (75%) observed by Al-Mallahi et al. (2020) in liquid digestate with magnesite calcined at 900 °C for 0.25 h, close to the efficiency (88.2%) obtained by Yu et al. (2017) in acidic electroplating wastewater with magnesite calcined at 700 °C for 2.0 h, and was lower than the efficiencies (97.8–99.7%) reported by Huang et al. (2010) for rare-earth element separation wastewater with magnesite calcined at 700 °C for 1.5 h. Moreover, Yu et al. (2017) found that a longer holding time is needed for phosphate removal when supplementing magnesite calcined at a lower temperature in the range of 600–1200 °C for 0.5–3 h. Therefore, the optimum calcination conditions might be between 700 °C for 1.5 and 900 °C for 0.25 h, depending on particle size of ground magnesite. The best calcination conditions for a specific source of ground magnesite shall be determined by further finetuning in this narrowed temperature-residence time range. Based on the highest phosphate removal from urine in the jar tests, CM3 was chosen for the struvite recovery tests in the crystallizer.

3.3. Mineral-based struvite recovery in alkaline hydrolyzed urine

Fig. 5a shows that phosphate concentration in urine with addition of CM3 or OMRI-listed Epsom salt decreased steeply in the first hour and slightly in the following hours, confirming fast dissolution of CM3. Although dissolution of calcined magnesite generates OH^- ions as shown in Eq. (2), urine pH changed little and remained within the optimum range of 8.5–9.5 for struvite precipitation due to the high alkalinity of the hydrolyzed urine (Table 1) and release of H^+ ions from struvite formation reaction. Like phosphate removal in the jar tests, conductivity of hydrolyzed urine in the crystallizer decreased over time (Fig. A4b). The efficiency to remove PO_4^{3-} from urine with addition of CM3 ($85.7 \pm 1.6\%$) was similar to or higher than those from other wastewaters with addition of calcined magnesite (Al-Mallahi et al., 2020; Huang et al., 2010), commercial light-calcined magnesite (Wei et al., 2019), acid dissolved magnesite (Yu et al., 2017), and electrochemically dissolved magnesite (Hao et al., 2022; Li et al., 2021). The greater PO_4^{3-} removal efficiencies when dosing Epsom salt ($94.7 \pm 2.1\%$) could be attributed to the greater purity of the Epsom salt. The actual dosages were $1.84 \text{ g/g } P_{\text{removed}}$ of calcined magnesite and $10.1 \text{ g/g } P_{\text{removed}}$ of Epsom salt.

The struvite recovery efficiencies were slightly lower when dosing calcined magnesite ($82.7 \pm 2.0\%$) than those when dosing Epsom salt ($88.8 \pm 6.0\%$). Compared with the reductions in magnesium ($18.9 \pm 2.0 \text{ mM}$) and phosphate ($18.0 \pm 2.5 \text{ mM}$) in urine with addition of Epsom salt, the greater Mg^{2+} reduction ($23.9 \pm 1.9 \text{ mM}$) and lower phosphate removal ($15.9 \pm 0.9 \text{ mM}$) in urine with addition of calcined magnesite indicated the formation of non-phosphate magnesium precipitates, possibly MgCO_3 due to competitive effects of carbonate with phosphate (Guan et al., 2023; Wei et al., 2019) and Nesquehonite ($\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$) at the high urine pH and alkalinity levels (Al-Mallahi et al., 2020). The much greater reduction of TAN than PO_4^{3-} and Mg^{2+} in urine with addition of calcined magnesite ($59.8 \pm 3.9 \text{ mM}$) and Epsom salt ($62.0 \pm 4.4 \text{ mM}$) could be attributed to the volatilization of free ammonia at the top of the crystallizer. Similar observations have been made in previous studies (Tao et al., 2019; Zamora et al., 2017).

Based on the lowest molar concentration of struvite ions in acid extracts of the recovered crystals, struvite accounted for $85.7 \pm 0.4\%$ and

$90.5 \pm 1.2\%$ of the crystals harvested from urine with addition of calcined magnesite and Epsom salt, respectively. The phosphorus and magnesium contents were close to the theoretical values of pure struvite, but ammonia content was lower (Table A2), indicating formation of impure precipitates. The measured Mg: P molar ratios were close to 1 while the Mg: N and P: N ratios were slightly higher than 1 in the acid extracts (Table A2). Such disparity in molar ratios was also reported by Zamora et al. (2017). The greater Mg and P contents than N in the harvested crystals, especially when calcined magnesite was added, were attributed possibly to undissolved MgO and formation of other precipitates such as calcium phosphates and magnesium phosphates (Tansel et al., 2018).

The crystals obtained from urine dosed with calcined magnesite (Fig. 5c) and Epsom salt (Fig. 5d) had the typical orthorhombic crystalline structure (Bradford-Hartke et al., 2021; Liao et al., 2020; Wei et al., 2019). The transmittance peaks and bands in the FTIR spectra of the recovered crystals were identical to those of the reference struvite (Fig. 5b). The peaks at 566, 750, 982, and 1432 $1/\text{cm}$ were attributed to asymmetric bending ν_4 of PO_4^{3-} , hydrogen bonding between $\text{H}_2\text{O}-\text{H}_2\text{O}$, asymmetric stretch ν_3 of PO_4^{3-} , and asymmetric bending ν_4 of NH_4^+ , respectively (Kirinovic et al., 2017; Liao et al., 2020; Rabinovich et al., 2021; Yu et al., 2017). The bands between 1500 and 1800 $1/\text{cm}$ were due to water ν_2 (H–O–H) deformation and N–H bending vibration in the ammonium group (Kirinovic et al., 2017; Rabinovich et al., 2021). The band around 2330 $1/\text{cm}$ could be attributed to $\text{H}_2\text{O}-\text{PO}_4^{3-}-\text{H}$ bonding (Kirinovic et al., 2017). The broad band around 2890 $1/\text{cm}$ was associated with the OH and NH stretching vibration (Liao et al., 2020). The XRD diffraction patterns of the struvite samples obtained from urine (Fig. 5e) were similar to those of reference struvite (RRUFF ID R050540.1), confirming the high purity.

3.4. Versatile dosing of two mineral products to raise pH and supplement magnesium

One advantage of air-lift crystallizers is that air sparging purges CO_2 out of high-alkalinity wastewater such as anaerobic digestate, thus raising pH (Tao et al., 2016). Stirring wastewater samples at room temperature in shallow beakers increased pH by 0.17 in the supernatant

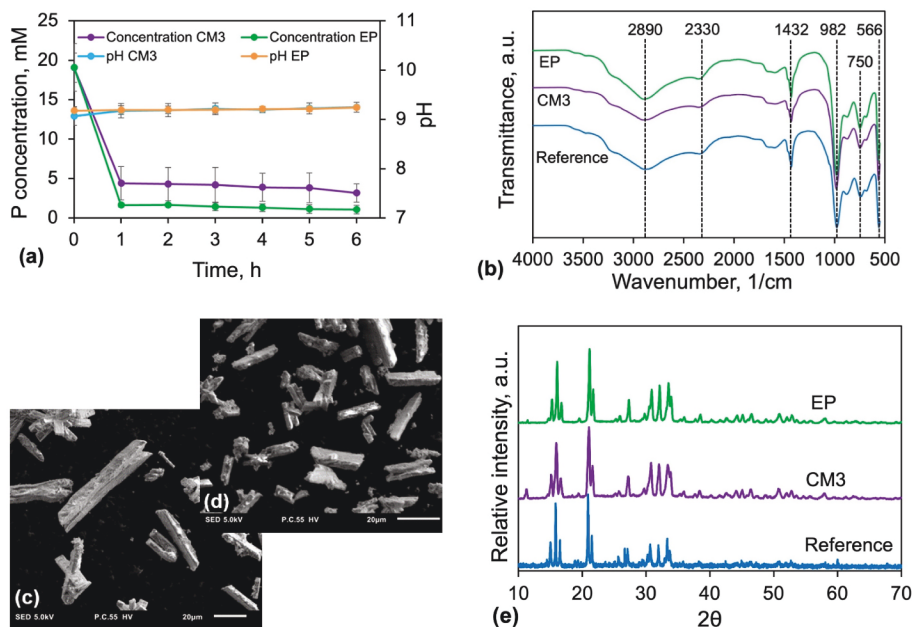


Fig. 5. Variations of PO_4^{3-} -P concentration and pH of urine inside crystallizer over time after dosing calcined magnesite (CM3) and Epsom salt (EP) (a); FTIR spectra of struvite crystals harvested from urine dosed with CM3 and EP in comparison to reference struvite (b); SEM micrographs (20-μm scale bar) of crystals harvested from urine dosed with CM3 (c) and EP (d); and XRD diffractograms of struvite crystals (e). Each dot = average of 3 replicates; error bar = standard deviation.

of sludge digestate and 0.31 in the filtrate of sludge digestate upon 0.5 h of stirring (Fig. 6a) as well as 0.51 in the filtrate of co-digester influent upon 1.0 h of stirring (Fig. 6b). It is hence noted that CO₂ purging is a mandatory step before adding an alkali to correctly develop dosing curves for such struvite reactors as air-lift crystallizers. The dosage of calcined magnesite to reach pH 8.5 was in the range of 213–230 mg/L for sludge digestate (Fig. 6), corresponding to 5.29–5.71 mM of Mg²⁺ increases (CM). Therefore, further magnesium supplementation at 1.13–1.55 mM (ES) to sludge digestate having an average PO₄³⁻ concentration (C_p) of 5.70 mM (Table A1) was still required for effective struvite recovery at the minimum initial Mg²⁺: PO₄³⁻ ratio of 1.2 based on Eq. (5). A recent review paper (Zhu et al., 2023) showed even higher PO₄³⁻ concentrations in the wastewaters for phosphate recovery at commercial scale in the European Union, approximately 6.96 mM on average. This greater average phosphate concentration indicates that more than one half of these struvite recovery systems would need to dose both calcined magnesite and Epsom salt and less than half of the systems that have phosphate concentrations below 4.41–4.76 mM would need to dose just calcined magnesite.

As shown in Fig. 7a, filtrate pH increased by 0.60 upon 0.5 h of air sparging, reached 8.5 at 1.0 h after adding calcined magnesite twice at a total dosage of 2.85 mM or 115 mg/L, and stayed between 8.6 and 8.9 after dosing 735 mg/L of Epsom salt at 1.5 h. This dosage of calcined magnesite was smaller than that shown in the dosing curve in Fig. 6a because pH increased more by air sparging in the crystallizer (Fig. 7a) than in the stirred beakers (Fig. 6a). It was possibly due to the vigorous air bubbling in the riser of the crystallizer that purged more CO₂ out of the filtrate and resulted in a pH of 8.9 at the end of batch operation.

As pH was increased by air sparging, phosphate concentration decreased by 47.5%, likely due to precipitation of struvite and CaH₂PO₄·2H₂O (brushite) based on the relative decreases in Mg²⁺, PO₄³⁻, and Ca²⁺ molar concentrations (Table A3). Calcium phosphates may precipitate at pH above 8 (Tansel et al., 2018; Tao et al., 2016). When pH was higher after adding calcined magnesite, phosphate concentration continued to decrease quickly due to precipitation of struvite plus Ca₅(OH)(PO₄)₃ (hydroxyapatite) (Zhu et al., 2023; Desmidt et al., 2015; Tao et al., 2016). Phosphate concentration stabilized at 0.11–0.17 mM 1 h after adding Epsom salt and magnesium concentration stabilized at 2.05–2.12 mM, indicating overdosing of Epsom salt that resulted in formation of likely Mg₃(PO₄)₂·8H₂O (bobierrite) in addition to struvite based on the relative decreases in Mg²⁺, PO₄³⁻, and Ca²⁺ molar concentrations (Table A3). The overdosing of Epsom salt was ascribed to the unexpected precipitation of calcium and magnesium phosphates. The average PO₄³⁻ removal efficiency of 98.5% was much higher than those reported by earlier pilot-scale and full-scale studies (Bouzas et al., 2019; Desmidt et al., 2015; Vasa and Chacko, 2021). The actual dosages were 0.662 g/g P_{removed} of calcined magnesite plus 4.23 g/g P_{removed} of Epsom salt. It is noteworthy that these dissolution and precipitation processes and the pH effects could be further elucidated by chemical equilibrium

modeling using the Visual MINTEQ software as demonstrated by Lee et al. (2023), if the speciation of the struvite ions and interfering ions such as Ca, Fe and K in wastewater was determined.

The average struvite recovery efficiency of 41.2 ± 7.6% in filtrate was lower than that with hydrolyzed urine (82.7–88.8%), which could be attributed to 1) the shorter hydraulic residence time for crystal growth in the batch tests with filtrate (3 h) than urine (6 h); and 2) the lower phosphate concentration in the filtrate (5.7 mM) than the hydrolyzed urine (19.4 mM). When CM3 and Epsom salt were added, precipitates would form at a lower concentration in the filtrate than hydrolyzed urine, resulting in less efficient macroscale flocculation through both differential settling and velocity gradient. In particular, the strong shear stress associated with air lifting of fine crystal-air-water mixture inside the riser may hinder formation of crystals greater than the opening size (38 μm) of the sieve used to collect crystals. Rather, granular fertilizers may be produced in the future by mechanical granulation of gravity-settled struvite powder instead of longtime crystal growth inside crystallizers.

The harvested crystals were assayed to be 81.5 ± 4.0% struvite, which was higher than or comparable to previous pilot-scale studies (Crutchik et al., 2017; Le et al., 2021; Li et al., 2022). Because of co-precipitation of struvite with calcium phosphates and magnesium phosphates, the harvested crystals contained 12.8% P, which was slightly greater than 12.6% in pure struvite. Overall, the harvested crystals had a high phosphate (P₂O₅) content with a fertilizer grade of 5-29-0 plus 8% of secondary nutrient Mg. The SEM micrograph (Fig. 7b) confirmed the dominance of orthorhombic crystalline struvite (Bradford-Hartke et al., 2021; Wei et al., 2019) with fewer smaller hexagonal crystals (possibly hydroxyapatite) and monoclinic crystals (possibly brushite and bobierrite). The elemental mapping of harvested crystals using SEM-EDS also depicted the presence of calcium in addition to magnesium although no other metals were detected (Fig. A5). The FTIR spectra (Fig. 7c) and XRD diffractograms (Fig. 7d) of the recovered crystals were similar to those obtained from urine (Fig. 5b–e) and reference struvite, confirming its high purity.

3.5. Prospects of mineral-based recovery of struvite for organic production

Magnesite and epsomite are naturally occurring minerals. Magnesite reserves are estimated at more than 13 Gt that are mainly found in China, North Korea, Russia, and Slovakia (Drnek et al., 2018). Magnesite is the major source of MgO production (Li et al., 2021) at different calcination temperatures for different uses (Nobre et al., 2020). Cheaper calcined magnesite locally available as reported by Etter et al. (2011) may be directly used upon confirmation of reactivity. Otherwise, magnesite can be custom calcined at the optimum temperature for struvite recovery. Epsomite is widespread in the Earth's crust and is mainly found in walls of caves and mines, outcrops of magnesian rocks,

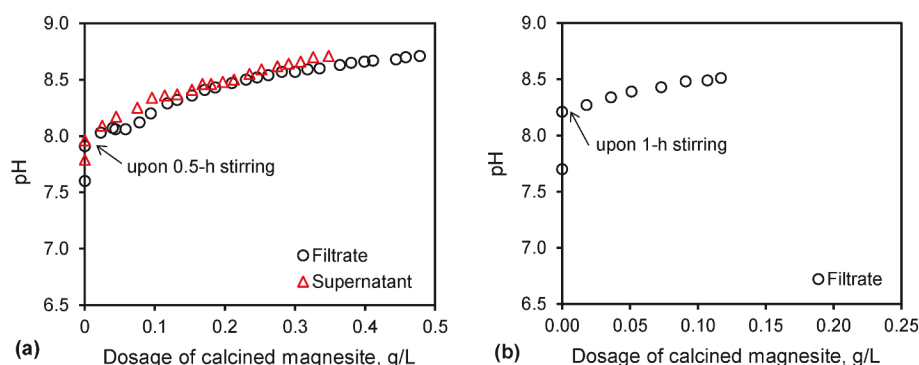


Fig. 6. Dosing curves of calcined magnesite (CM3) to raise pH of (a) filtrate and supernatant of sludge digestate; and (b) filtrate separated from co-digestion influent of sludge and chicken manure.

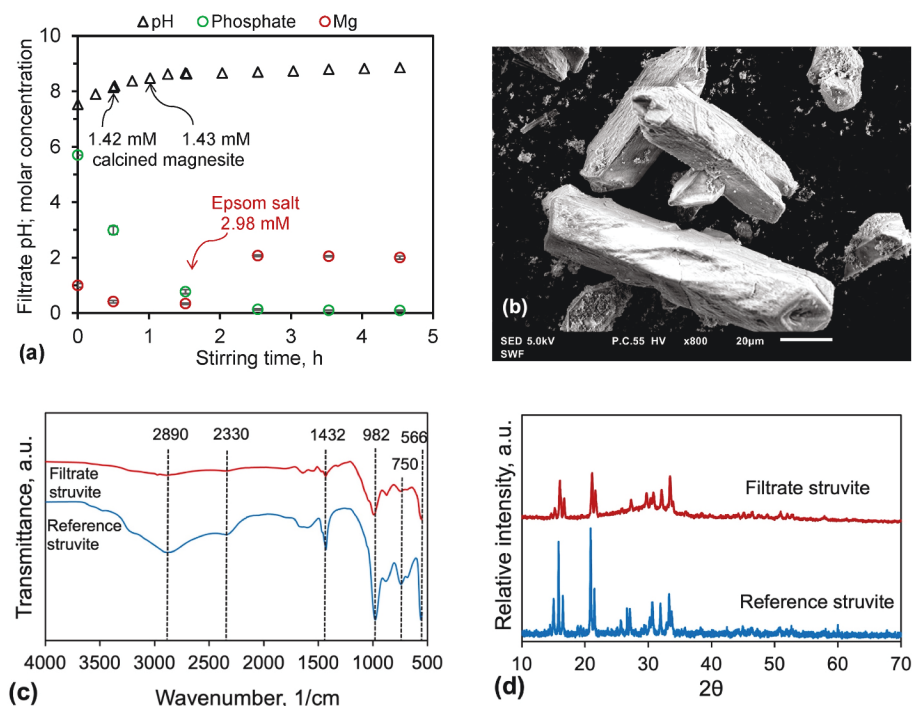


Fig. 7. Variations of filtrate pH and concentrations of PO_4^{3-} and Mg^{2+} overtime inside the crystallizer (a); SEM micrograph (20- μm scale bar) of crystals harvested from filtrate (b); FTIR spectra of harvested crystals (c); and XRD diffractograms of harvested crystals (d). Each dot = average of 4 replicates; error bar = standard deviation.

and as evaporite in saline lakes and mineral springs (Giordani et al., 2022). The OMRI Products List (OMRI, 2023) includes 11 Epsom salt products allowed under the U.S. National Organic Program to be used as crop fertilizers and soil amendments, livestock feed ingredients, and livestock health care.

Table 2 presents cost estimation for mineral-based struvite recovery from hydrolyzed urine and filtrate of sludge digestate at pilot scale (6 m^3/d). To minimize calcium phosphates in the crystals recovered from sludge digestate, it is suggested to separate calcium phosphate precipitates by purging filtrate of sludge digestate for 1.0 h and idling for 1.0 h, then discharging supernatant to a crystallizer to recover struvite. Upon collection of crystals formed during urea hydrolysis (Krishnamoorthy et al., 2020), hydrolyzed urine can be directly applied for struvite recovery. High-purity struvite powder will be recovered from hydrolyzed urine and Ca-depleted sludge digestate liquor in a 500-L air-lift crystallizer operated cyclically from 1.0-h circulation to 1.0-h settling and decanting. The settled struvite powder can be quickly pressed into granular fertilizers (Krishnamoorthy et al., 2021). A slightly smaller $\text{Mg}^{2+}:\text{PO}_4^{3-}$ ratio, 1.1, is proposed to minimize magnesium phosphate content in the recovered crystals. The cost to pump influent for minutes per cycle is negligible. Energy cost is based on the electricity price of \$0.07/kWh (Tao et al., 2024; Orner et al., 2022).

The total material and energy costs to recover struvite from urine with calcined magnesite is estimated to be much lower than previously reported at \$0.47–0.93/kg struvite when chemicals such as MgCl_2 , MgSO_4 , and NaOH were used (Etter et al., 2011; Tao et al., 2019) and close to \$0.12–0.15/kg struvite when calcined magnesite was proposed (Etter et al., 2011; Krähenbühl et al., 2016). However, the cost to use Epsom salt for recovering struvite from urine is higher due to the high retail cost of OMRI-listed Epsom salts. The material and energy costs to recover struvite from filtrate of sludge digestate employing a combination of calcined magnesite and Epsom salt is lower than earlier economic analysis, \$0.93–3.66/kg struvite and \$2.96–13.99/ m^3 for struvite recovery from digestate liquid and landfill leachate using chemicals such as MgCl_2 , MgO and NaOH (Bouzas et al., 2019; Min and Park, 2021; Huang et al., 2014). When magnesite is calcined at 800 °C onsite at

scale, the estimated total costs of ground magnesite plus calcination energy consumption (\$0.28/kg) were much lower than \$7.97–8.60/kg of commercially available MgO as reported by Min and Park (2021) and web searched for wholesale prices. Orner et al. (2022) reported the selling price of chemically recovered struvite at \$0.99/kg. Web search found that the lowest wholesale price of OMRI-listed Epsom salt was 32% higher than general purpose Epsom salt. Our customer discovery in 2023 also found that farm managers and owners were willing to pay 30–40% higher for OMRI-listed fertilizers. Therefore, the mineral-based recovery of natural struvite fertilizer is potentially profitable. Meanwhile, it creates an affordable, reliable local supply of high nutrient grade alternative to organic fertilizers. For a detailed economic analysis, the capital cost and total operating cost (including labor and granulation of struvite powder) should be assessed in comparison with the current chemical-based struvite recovery technologies that mostly run crystallizers at long hydraulic retention times for crystal growth inside the crystallizers.

4. Conclusion

Chemical-free, mineral-based struvite recovery from wastewater produces natural fertilizers suitable for organic production. Light-burnt magnesite and OMRI-listed Epsom salt can be combined at different ratios to simultaneously supplement magnesium and raise pH to their optimum levels for both alkaline and neutral wastewater streams.

When ground magnesite is calcined to light-burnt MgO under the optimum conditions of 800 °C for 30 min, dosing the calcined magnesite at 213–230 mg/L could supplement magnesium ions while raising pH of near-neutral sludge digestate to above 8.5.

Six-h batch operation of an air-lift crystallizer with addition of calcined magnesite and Epsom salt removed 85.7% and 94.7% of PO_4^{3-} in hydrolyzed human urine, respectively. More than 98% of PO_4^{3-} was removed from filtrate of sludge digestate with addition of both calcined magnesite and Epsom salt, producing crystals having a fertilizer N–P–K rating of 5–29–0.

The mineral-based struvite recovery approach removes phosphate

Table 2Cost estimation for mineral-based struvite recovery from 6 m³/d of wastewater.

Parameter	Wastewater and mineral(s) to use			Remarks
	Urine with calcined magnesite (CM3)	Urine with OMRI-listed Epsom salt	Filtrate with calcined magnesite & Epsom salt	
Influent PO ₄ ³⁻	19.1 mM	19.1 mM	5.7 mM	Based on this study
Expected effluent PO ₄ ³⁻	2.7 mM	1.0 mM	0.1 mM	
Calcined magnesite to add	5.080 kg	n/a	0.690 kg	
Magnesite to calcine	10.04 kg	n/a	1.363 kg	Based on this study
Magnesite cost	\$2.56	n/a	\$0.35	\$0.255/kg market price (Indexbox, 2023)
Energy cost for calcination	\$0.27	n/a	\$0.04	377 Wh/kg for light-burnt magnesite in lime kiln (Krähenbühl et al., 2016) and furnace (Al-Mallahi et al., 2020)
Epsom salt to add	n/a	31.05 kg	5.05 kg	9.22 g/g P _{removed} to urine and 4.85 g/g P _{removed} to filtrate
Epsom salt cost	n/a	\$31.98	\$5.20	\$1.03/kg retail price (OMRI-listed Magriculture®)
Compressed air cost	\$0.42	\$0.42	\$0.84	500-W air compressor for each crystallizer (Tao et al., 2019)
Material & energy cost Struvite recovered	\$0.54/m ³ 20.03 kg	\$5.40/m ³ 23.71 kg	\$1.07/m ³ 6.84 kg	83% and 89% of recovery from urine in this study; 83% for filtrate upon optimized mixing
Material & energy costs	\$0.16/kg struvite	\$1.37/kg struvite	\$0.94/kg struvite	

from wastewater at a material and energy cost of \$0.16–1.37/kg struvite, providing organic farms with a local supply of high-grade slow-release fertilizers.

CRedit authorship contribution statement

Aysha Iftikhar: Methodology, Investigation, Formal analysis, Data curation, Writing – original draft. **Wendong Tao:** Supervision, Writing – review & editing, Conceptualization, Formal analysis, Funding acquisition, Resources.

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.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jclepro.2024.142244>.

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