



Review

Formation of struvite from agricultural wastewaters and its reuse on farmlands: Status and hindrances to closing the nutrient loop

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ABSTRACT

To meet the needs of a fast growing global population, agriculture and livestock production have been intensified, resulting in environmental pollution, climate change, and soil health declining. Closing the nutrient circular loop is one of the most important sustainability factors that affect these issues. Apart from being a serious environmental issue, the discharge of N and P via agricultural wastewater is also a major factor that disturbs nutrient cycling in agriculture. In this study, the performance, in terms of recovery, of N and P (individually, as well as simultaneously) from agricultural wastewaters via struvite has been comparatively summarized. Details on the hindrances to nutrient recovery through struvite formation from agricultural effluents, along with strategies to overcome these hindrances, are provided. In addition, various strategies for recovery performance intensification and operational cost reduction are comprehensively discussed. This work will provide scientists and engineers with a better idea on how to solve the bottlenecks of this technique and integrate it successfully into their treatment systems, which will ultimately help close the nutrient loop in agriculture.

1. Introduction

The manifestations of rapid population growth, urbanization, improved standards of living, and concurrent intensification of socioeconomic activities on overall environmental health are well recognized and acknowledged (Cordell et al., 2009; Clarke, 2013). Global cereal production has doubled in the past 40 years, mainly from the increased yields resulting from greater inputs of fertilizer, water, pesticides, and so on. This has increased the global per capita food supply and alleviate hunger in poverty-stricken areas (Alexandratos and Bruinsma, 2012). During this process, however, the increase in nitrogenous fertilizer application and exhaustion of the limited reserves of rock phosphate have been quite considerable. At present, the annual fertilizer consumption of rock phosphate is reported to be over one million tons, while the use of N fertilizer could be three times as much (Rahman et al., 2011). Moreover, it is estimated that within 100 years, mined P rocks will be completely exhausted (Cordell and White, 2014”).

Global cycling of these nutrients has been altered, owing to their widespread use in intensive agriculture, in ways that can contribute to severe environmental issues. Predominantly, nutrients can escape from

farm fields to the surrounding soils, air, and waterways, when applied in excess of the plants' needs (Deng et al., 2006). Hence, the notion of a closed-loop nutrient cycle provides a simple, persuasive, and elegant approach for realizing efficient natural resource management-improved human well-being, and long-term food security (Maurer et al., 2006). The closing of the nutrient loop includes a wide range of ongoing efforts to make sure that nutrients are applied at times and places that align with the requirements of the plants. It also includes efforts to recover nutrients in usable forms from waste effluents and recycle them into cropping systems (Yorgey, 2014). The logic is that by recovering nutrients from waste effluents, a more “closed” system for sustainable agricultural development can be created.

For the recovery of nutrients (N and P), several techniques have been developed in the last five decades, including biological uptake, physical adsorption, and chemical precipitation (Tran et al., 2014; Güiza et al., 2015). Living organisms, such as microbes and plants, can be used to recover N and P as essential elements through uptake mechanisms. However, this process is highly dependent on the growth of these living organisms, which is often influenced by seasonal fluctuations (Cai et al., 2013; Pérez et al., 2015). For adsorption processes, N and P compounds in wastewater can be adsorbed onto the surface of

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adsorbents that are made of porous materials with a large surface area. This technique is often the last step in the wastewater treatment process and is suitable for waters with low pollutant contents. Compared to biological uptake and physical adsorption processes discussed above, chemical precipitation might be more effective, due to its high recovery efficiency. Therefore, it would be more economical to use this method for agricultural wastewaters with high contents of N and P.

Struvite formation is one promising option that can be used to sustain the nutrient loop in agriculture, as it simultaneously recovers N and P from waste effluents. Furthermore, the precipitated struvite ($\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$) is in the form of stable orthorhombic crystals and can potentially be used as a slow-release fertilizer. Compared with traditional chemical fertilizers, struvite can equal crop production, but has fewer negative effects in runoffs into downstream water bodies (Liu et al., 2011; Dalecha et al., 2012). However, the use of struvite as a fertilizer still represents a challenge because of poor market development, high operating costs and lower crystal sizes. The potential of struvite for nutrient recovery from various wastewaters has been studied extensively, and some review papers have been published accordingly. However, those review papers did not specifically target agricultural wastewater (Kumar and Pal, 2015; Darwish et al., 2016; Katakai et al., 2016a, 2016b). Theoretically, this technology can be used to close the nutrient loop in agriculture, however, its efficiency will vary with type of agriculture wastewater because of the variability in the physical and chemical characteristics of different wastewaters. Therefore, the literature lacks a comprehensive review specifically targeting the status of, and hindrances to, nutrient recovery from agricultural effluents via struvite formation. Moreover, agriculture is a low-profit industry, hence technology developed to close the nutrient loop should be economical (Ravallion et al., 2007). Furthermore, information about the specific characteristics of agricultural wastewaters and ways to improve struvite formation efficiency and reduce costs is needed but not well reported.

In this review, the variability in the chemical composition of various agricultural wastewaters is compiled to assess their suitability for maximum nutrient recovery via struvite. Then, the performance in terms of recovery of N and P, individually as well as simultaneously, from agricultural wastewaters is comparatively summarized. Moreover, a detailed discussion on the hindrances to nutrient recovery from agricultural effluents through struvite formation is presented, as well as on the strategies to overcome those hindrances. The potential of struvite as a fertilizer for improving the growth and production of different crops is addressed. Most importantly, various strategies extracted from the latest publications on recovery performance intensification and operational cost reductions are comprehensively discussed. This will enable scientists and engineers to have a better idea on how to solve the bottlenecks of this technique and to integrate it successfully into their treatment systems, which ultimately will help in maintaining the nutrient loop in agriculture.

2. Sources and characterization of agricultural wastewater

Agricultural wastewater is generated from a variety of farm activities, including animal feeding operations and the processing of agricultural products. Sources of agricultural wastewaters include, but are not limited to, animal breeding discharge, agricultural food processing wastewater, leachate from the composting of biomass or manure, digested effluents, slaughterhouse wastewaters, horse washing waters, barnyard and feedlot runoff, and egg washing and processing effluent. Additionally, runoff from cropland results in sedimentation and fertilizer and pesticide discharges in water streams (Table 1). Discharge of agriculture-based wastewaters not only results in water pollution but also leads to the loss of essential nutrients (N and P). Therefore, recovery of these nutrients from such wastewaters could be a suitable option for closing the nutrient loop. However, some wastewaters, such as agricultural field runoff, effluents from the beverage and brewery

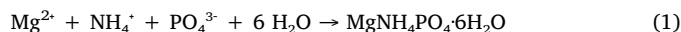
industries, and horse washing waters, are not suitable for recovery because of their very low nutrient contents.

Livestock breeding effluent, from dairy, beef, swine, and poultry operations, as well as the anaerobic digestates of manure, are optimal for recovery, as they are rich in nutrients (Table 2). The chemical composition of agricultural wastes (manures) and effluents varies among daily operations and seasonally within the same operation (Bernet and Béline, 2009). Generally, multiple factors, including animal feed, animal age, local climate, bedding material, manure collection, storage, and handling are responsible for the variability in the chemical composition of agricultural wastes.

3. Struvite and its recovery performance from agricultural wastewaters

3.1. Struvite formation

Struvite is a crystalline compound, formed with equal molar concentrations of magnesium, ammonium, and phosphate, combined with six water molecules ($\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$), as depicted in Equation (1).



Its molecular weight is $245.43 \text{ g mol}^{-1}$, and its solubility varies from sparingly soluble to readily soluble in alkaline and acidic conditions, respectively (Chirmuley, 1994). Its solubility value in water is 0.018 g mL^{-1} at 25°C , while the solubility value increases from 0.033 g mL^{-1} to 0.178 g mL^{-1} at 25°C as the concentration of HCl in solution increases from 0.001 M to 0.01 M (Le Corre et al., 2009). The crystallization process occurs across a wide range of alkaline conditions. Struvite might be described as a soft mineral due to its low specific gravity (1.7 g cm^{-3}) and orthorhombic structure (Lee et al., 2009). It can occur as an elongated structure, a tight aggregate of fine crystals, star-like particles, or coarse crystals in white, yellowish or brownish-white colors (Rahman et al., 2011; Kozik et al., 2011; Hutnik et al., 2013; Matynia et al., 2013). The size of struvite crystals can vary from $15 \mu\text{m}$ to 3.5 mm in length depending upon the production conditions (Adnan et al., 2003; Zhang et al., 2009). The chemical composition of struvite contains around 13%, 6% and 10% of P, N and Mg, respectively Ueno and Fujii (2001).

The development of struvite crystals takes place in two phases: crystal birth or nucleation, and crystal growth. Factors such as the initial crystal state of the compound, liquid-solid equilibrium thermodynamics, mass transfer between the liquid and solid phases, and reaction kinetics (Jones, 2002; Ohlinger et al., 1999) control the process of struvite formation. Nucleation begins with the formation of a crystal embryo from the combination of ions in solution (Mullin, 1992). Depending upon the supersaturation level, one of several mechanisms (homogenous primary nucleation, heterogeneous primary nucleation, surface secondary nucleation, etc.) could allow struvite to nucleate.

Homogenous primary nucleation requires the highest degree of supersaturation as nuclei apparition takes place in a supersaturated solution. Heterogeneous primary nucleation requires a lower degree of supersaturation, and nucleation takes place on a foreign surface, such as dust particles or parts of the crystallizer. Surface secondary nucleation (true nucleation) requires suspended particles of the same species as the solid being crystallized. The new surface nuclei are then detached either by particle shock or fluid shear forces (Regy et al., 2002).

After nucleation, struvite crystal growth begins, and the crystal embryos grow into noticeable crystals. Mass transfer and surface transfer or agitation methods control the growth rate of struvite crystals. The transport of solutes from a solution to the crystal surface by diffusion, convection, or a combination of the two are referred to as mass transfer, while the incorporation of materials into the crystal lattice through surface integration mechanisms is called surface transfer or agitation. Various physiological parameters like solution pH,

Table 1
Main agricultural wastewaters and their sources.

Wastewater	Sources	Reference
Agriculture food industry wastewater	Brewery, beverage, vegetable oil, milk/dairy product, starch, daily dishes	[S1]
Leaching from composting process	Effluent from biomass or manures composting	[S2]
Discharge from livestock breeding operations	Scrapped earthen and concrete lot, lagoon effluent, slurry (liquid) from dairy, swine, beef farms	[S3]
Poultry and poultry industry wastewater	Broiler and turkey litter, egg washing and processing	[S4]
Slaughterhouse wastewater	Effluent from dairy, beef, swine and poultry slaughtering	[S5]
Fertilizer industry	Effluent from fertilizer production and processing industry	[S6]
Run-off wastewater	Runoff due to heavy rain, over fertilization and pesticides	[S7]
Digestate effluents	Digestate obtained from anaerobic digestion of manures	[S8]

The references in this Table are provided in the [E-supplementary material](#).

Table 2
Chemical characteristics of agricultural wastewaters.

Effluent	pH	SS	VS	TN/NH4	TP/PO4	Ca	Mg	K	COD	BOD	Reference
Raw SW	7.7	45	–	-/730	-/110	53	16	301	3532	–	[S9]
Raw SW	7.9	–	–	1036/845	159/31	–	–	–	5139	–	[S10]
AD SW	8.2	916	–	3141/-	80/61	–	5.6	–	–	–	[S11]
AD SW	7.6	–	–	-/789	72/-	120	48	–	–	–	[S12]
Raw SW	7.8	–	–	-/426	-/103	64	13	293	4105	–	[S13]
Raw SW	7.7	10770	450	1035/-	64/-	196	39	1506	4085	–	[S14]
Raw SW	7.9	4160	–	-/845	-/31	–	–	–	5139	–	[S15]
AD SW	8.2	–	–	2350/1775	612/221	–	–	–	–	–	[S16]
AD SW	7.4	25400	16100	-/2110	-/53	163	45	1760	–	–	[S17]
AD SW	8.4	–	–	-/4342	-/87.8	418	120	2641	14880	–	[S18]
Raw SW	7.7	–	–	378/-	105/-	39	21	342	2756	–	[S19]
Raw SW	7.0	8.80	–	-/535	187/89.5	253	131	–	7094	–	[S20]
Raw SW	7.5	–	–	-/406	-/128	58	28	–	3298	–	[S21]
Raw SW	7.6	–	–	-/695	-/125	75	21	386	3950	–	[S22]
Raw SW	8.5	1487	–	3034/-	190/-	–	–	–	–	–	[S23]
Raw SW	7.8	–	–	1212/985	182/161	135	6.7	–	2388	1035	[S24]
Hog manure	6.6	9300	4715	–	336/202	217	174	–	–	–	[S25]
DW	6.0	938	–	-/70	-/45	348	156	–	890	216	[S26]
Cow urine	7.4	–	–	8200/-	390/-	–	2310	4200	–	–	[S27]
ADW	8.3	–	–	-/709	-/51	–	–	150	742	–	[S28]
ADW	8.3	60300	38500	1150/1060	460/450	570	150	–	–	–	[S29]
ADPW	7.9	39000	26910	6173/3907	209/60	441	10	5380	44208	–	[S30]
ADPW	8.6	16300	9356	5838/4612	287/163	78.6	5.3	3111	14516	–	[S31]
FIW	–	–	–	–	4450	440	306	46	–	–	[S6]
BYW	7.7	1460	–	-/529	-/10.8	259	36	827	5432	–	[S32]

The references in this Table are provided in the [E-supplementary material](#).

*SW = swine wastewater, ADSW = anaerobically digested swine wastewater, DW = dairy wastewater, ADW = anaerobically digested dairy wastewater, ADPW = anaerobically digested poultry wastewater, FIW = fertilizer industry wastewater, BYW = Bakery yeast wastewater.

supersaturation, mixing, and foreign ion concentrations (Le Corre et al., 2007; Zhang et al., 2009) influence these mechanisms.

3.2. Recovery performance

Successful recovery of nutrients (P or N) from agricultural wastewaters via struvite has been advocated mostly at the laboratory and pilot scales (Table 3). Previously conducted studies have focused on either P or N, or the simultaneous recovery of both P and N. However, variations in recovery efficiency have been found, which may be attributed to the changes in the chemical composition of wastewaters, which in turn relies upon the aforementioned factors (Section 2) (Bernet and Béline, 2009). Furthermore, the operating parameters like solution pH and supersaturation, Mg, ammonium, and phosphate concentrations, mixing energy applied, the presence of foreign ions, and reaction time, additionally can also affect nutrient recovery through the struvite precipitation process (Zhang et al., 2009; Kim et al., 2016). The reported P recovery ranged from 31% for hog manure (Ackerman et al., 2015) to 99.5% for swine wastewater (Ye et al., 2016). Higher P recovery was due to a higher saturation index, whereas very low recovery was presumably due to higher solid contents and low pH (Ye et al., 2016; Ackerman et al., 2015).

Struvite precipitation also has been deliberated as a valid

alternative for the removal and recovery of high ammonium concentrations, especially from agricultural-strength wastewaters i.e., agricultural-based wastewaters that are rich in nutrients, especially N and P (Yu et al., 2013). With aeration as a means to correct pH, struvite precipitation has been found to be a valid method for the recovery of phosphorus from digestate (> 80%; Battistoni et al., 2001), whereas efficient ammonia removal through struvite precipitation is challenging using aeration for pH correction, even after the addition of Mg and P salts reported by Siciliano and Rosa (2014). They observed that the maximum ammonia removal from anaerobically digested calf manure was around 45% when aeration was used to correct the pH, while this value was about 75% when the pH was altered using chemicals instead of aeration. The sequence of reagent addition had a mild to strong impact on ammonium removal from wastewaters, as reported by Santinelli et al. (2013). They concluded that the premixing of MgO with phosphoric acid before application profoundly affected ammonium removal (79–83%) during the struvite precipitation process, compared to the addition of MgO followed by phosphoric acid supplementation (47–72%).

To maximize the recovery of N, it is essential to provide additional phosphate salts for the simultaneous recovery of nutrients. A summary of studies conducted for the recovery of both phosphate and ammonium from agricultural wastewaters is given in Table 3. The recoveries of

Table 3
Nutrient recovery performance of struvite from various agricultural wastewaters.

Wastewater Type	Scale	P recovery %	N recovery %	pH	Reference
Swine wastewater	LS	92	81	–	[S10]
Swine wastewater	LS	96.4	97.3	9.5	[S11]
Swine wastewater	PS	99.5	–	9.0	[S12]
Swine wastewater	PS	99	> 92	9.0	[S13]
Swine wastewater	LS	> 90	> 90	8.0	[S14]
Swine wastewater	LS	–	81	9.0	[S15]
Swine wastewater	LS	94	83	9.0	[S16]
Swine wastewater	LS	–	72	8.2	[S17]
Swine wastewater	PS	–	85	9.0	[S18]
Swine wastewater	LS	97	91	9.0	[S19]
Swine wastewater	LS	91	85	10	[S20]
Swine wastewater	PS	98	93	9.0	[S21]
Swine wastewater	PS	> 90	–	9.0	[S22]
Swine wastewater	LS	93	87	10	[S33]
Swine wastewater	FS	93	31	8.5	[S34]
Swine wastewater	LS	67	80	8.4	[S23]
Swine wastewater	LS	93	65	8.2	[S24]
Anaerobic digestate	LS	96	–	9.0	[S28]
Calf manure digestate	LS	–	> 90	9.0	[S29]
Anaerobic digestate	LS	> 90	–	8.5	[S30]
Dairy wastewater	LS	93	89	9.2	[S26]
Dairy manure	LS	69	–	7.2	[S35]
Dairy wastewater	LS	≤ 95	–	9.0	[S36]
Poultry manure	LS	–	85	9.0	[S37]
Poultry manure	LS	–	97	9.0	[S31]
Baker's industry effluent	PS	97	92	8.5	[S32]
Yeast industry wastewater	LS	–	87	9.0	[S38]
Yeast industry wastewater	LS	83	81	9.5	[S39]
Beverage wastewater	LS	97	–	9.5	[S40]
Potato industry wastewater	LS	89	–	8.6	[S41]
Beverage wastewater	LS	–	98	9.0	[S42]
Sugar industry wastewater	LS	–	97	9.5	[S43]

The references in this Table are provided in the [E-supplementary material](#).

*LS = lab scale; PS = pilot scale.

phosphate and ammonium from anaerobically digested swine wastewater were 97.7% and 11.3%, respectively, following the addition of magnesium only during struvite precipitation; however, with supplementation of both phosphate and magnesium, the ammonium recovery increased to 85.7% (Kwon et al., 2017). Likewise, the ammonium and phosphate recoveries from swine wastewater were 19% and 95%, respectively, with the application of magnesium alone, whereas both were 90% when supplemented with both magnesium and phosphate salts (Kim et al., 2016). Therefore, it seems that most of the previous studies were conducted using swine wastewater because it contained sufficient amounts of both N and P. It was also concluded that for the recovery of both ammonia and phosphate, both magnesium and phosphate salts have to be supplemented. However, supplementation with magnesium and phosphate salts is costly, whereas recycling of recovered product was found to be economical. In the following chapters, the recycling of struvite as an economically feasible strategy for the simultaneous recovery of N and P will be discussed. In addition, some methods for the decomposition and recycling of struvite will be introduced.

4. Commercial development of struvite products

Struvite was used as a fertilizer for the first time in 1957, as suggested by Mauravin (Bridger et al., 1962). On the commercial scale, W.R. Grace & Co., in the US, first manufactured struvite with the trade name Mag-Amp (Peng et al., 1979). However, the high manufacturing costs using MgO or Mg(OH)₂, with monoammonium phosphate, limited

its commercial development (Peng et al., 1979). Other factors, such as transportation, storage, composition, and purity of struvite were also responsible for the compound's poor commercial-scale development.

Storage and transportation require struvite pellets with high crushing strength (Forrest et al., 2008). Crushing strength increases with size, up to 2.36 mm, after which the crushing strength starts to decrease. Therefore, moderately dense struvite pellets sized up to 2.36 mm are best for easy storage and transportation. Depending upon the reactor conditions, such as pH, supersaturation ratio, and upflow velocity, the average commercial struvite crystal size is 2.0–3.3 mm. The addition of a coating can increase the crushing strength of larger struvite pellets (Fattah et al., 2015).

In addition, the composition and purity of struvite are important for commercial development because these are key parameters for fertilizers. Regarding struvite composition, it is often determined by the source from which it is precipitated, the process used, and the type and amount of chemicals used (Antonini et al., 2012). Because of its compositional variation, struvite may contain between 11 and 26% P, of which only 1–2% is water-soluble, with the remainder acid-soluble (Johnston and Richards, 2003).

Furthermore, the efficacy of struvite as a fertilizer depends on the solubility and sorption characteristics of the soil to which it is applied. The solubility of struvite is influenced by the soil pH, with struvite more effective in acidic soils with moderate to low pH (Cabeza et al., 2011). Its efficiency is nominal in high pH soils. This specificity of struvite for acidic soils may also be a reason for its limited commercial development.

Struvite precipitation has been successfully implemented at large scales and in commercially established processes including AIRPREX, Berliner Wasserbetriebe (Germany, DE), ANPHOS, Colsen (the Netherlands, NL), CAFR, NALVA (Germany, DE), NuReSys, Akwadok (Belgium, BE), Nutritec, Sustec (the Netherlands, NL), Pearl, Ostara (Canada, CA), Phosnix, Unitika (Japan, JP), PHOSPAQ, Paques (the Netherlands, NL) and PRISA, Aachen University in Germany (Montag et al., 2007; Abma et al., 2010; Desmidt et al., 2012). Furthermore, four installations in Gelderland (the Netherlands, NL) are involved in the production of K-struvite (KMgPO₄·6H₂O) from calf manure (Graeser et al., 2008). These commercially available processes are recovering struvite with crystal or pellet sizes ranging from 0.5 to 5 mm by employing fluidized bed reactors and continuously stirred tank reactors.

5. Hindrances to struvite recovery from agricultural wastes

Struvite precipitation is often reported as a suitable technology for nutrient recovery from high-strength wastewaters, such as agricultural wastewaters. However, a few failure stories also have been shared, without the causes for the failures being disclosed. Herein, we summarized most of the reported hindrances to struvite recovery from agricultural wastewaters, including contents of suspended solids, calcium, phosphorus, heavy metals, and pathogens. Other factors, such as pH maintenance, molar ratio, and release of phosphorus, are important from an economic point of view.

5.1. Suspended solids

Suspended solid content significantly influences the recovery efficiency of struvite. The solids in wastewater have both positive and negative impacts on struvite crystal growth. On one hand, they might enhance struvite precipitation and crystal growth by providing an initial embryo for nucleation, whereas on the other hand, they might hinder growth and reduce the growth rate by blocking active growth sites (Le Corre et al., 2005). Higher amounts of suspended solids not only affect recovery efficiency but also influence crystal morphology and size (Shih and Yan, 2016). Struvite crystals were found to be needle-like when formed in lower solid contents yet were aggregated and increased in size as the suspended solids content increased (Tarragó

et al., 2018). Furthermore, suspended solids not only favor nucleation, but also provide nuclei for heterogeneous nucleation, thereby increasing crystal growth (Liu et al., 2013). Suspended solids enhance the bond linkage between crystals, thus favoring crystal aggregation and growth.

However, there is a discrepancy in the results and a debate among researchers regarding the effect of suspended solids on the struvite precipitation process. The process of struvite precipitation was reported to slow down because of higher suspended solid contents in liquid dairy manure and digested cattle manure (Qureshi et al., 2008; Shen et al., 2011). A concentration of suspended solids above 1000 mg L^{-1} was found to hinder the precipitation of struvite (Schuiling and Andrade, 1999). The recovery of phosphate was reduced by 50% when recovered from a manure solution containing 100% manure in comparison to a 10% manure solution, as reported by Tarragó et al. (2018). Moreover, Ping et al. (2016) showed that phosphate removal efficiency, average pellet diameter, and struvite purity decreased significantly, with an increase in suspended solid contents. Likewise, Zeng and Li (2006) recovered nutrients in the form of struvite from anaerobically digested manure and found a significant decline in recovery due to higher contents of suspended solids. Considering the high content of solids in digestate obtained from anaerobic digestion of manures, normally containing $15\text{--}90 \text{ g L}^{-1}$ total solids, some sort of pretreatment for minimizing the suspended solid content might be needed (Xia et al., 2012).

5.2. Calcium interference

In addition to variable contents of phosphorus, nitrogen, and magnesium (constituents of struvite), agricultural wastes also contain various ions, such as calcium, zinc, and copper ions, carbonate (CO_3^{2-}), and sulfate (SO_4^{2-}) (Table 4). These non-struvite constituents can affect the reaction time, recovery efficiency, crystal morphology, and purity during struvite precipitation (Acelas et al., 2015). Among these ions, calcium is often present in the highest concentration, especially in manures and agricultural effluents. Calcium, combined with low magnesium and ammonium concentrations, can significantly affect the crystal growth and characteristics, according to Le Corre et al. (2005). Calcium adversely affects struvite quality by competing with magnesium and producing unexpected precipitates, such as $\text{Ca}_5(\text{PO}_4)_3\text{OH}$, $\text{Ca}_3(\text{PO}_4)_2$, $\text{Ca}_8(\text{HPO}_4)_2(\text{PO}_4)_4 \cdot 5\text{H}_2\text{O}$, and CaHPO_4 (Zhang et al., 2010; Huchzermeier and Tao, 2012). The formation of these unwanted precipitates makes handling, separation, and application troublesome (Bauer et al., 2007). Generally, negligible hindrance to struvite precipitation occurs at a Ca: Mg molar ratio of 0.2 and noticeable hindrance to struvite formation is found at molar ratios of 0.5–1.0, whereas struvite formation is restricted at Ca:Mg molar ratios of 0.75–1.0 or

higher (Moerman et al., 2009; Huchzermeier and Tao, 2012). Moreover, a negative linear correlation was observed between the weight of struvite in the precipitate and the initial Ca:Mg ratio in the wastewater (Yan and Shih, 2016).

Intensive interference from calcium in the formation of struvite and in the removal efficiency of phosphorus from pilot- and full-scale agricultural industry wastewater was reported by Moerman et al. (2009). Similarly, Hao et al. (2013) also found that struvite purity was affected by calcium. To date, most research has been undertaken to assess the impact of calcium on phosphorus recovery efficiency, without any consideration regarding struvite purity, therefore, the exact ratio of ionic species which would adversely affect struvite quality is unknown.

5.3. Heavy metals and pathogens

Agricultural wastewaters also can contain harmful substances, such as heavy metals and pathogens (Yang et al., 2017). For example, livestock effluents often contain high contents of metals, such as Zn, Cu, Cd, and As (Table 5), which can accumulate through land application, thereby affecting soil fertility and product quality (Shi et al., 2011). However, the contents of heavy metals vary among wastewater types and even within the same type of wastewater, which may be due to the type of feed, size of the farm, and age and health of the animals. Animal feeds are the main source of these toxic metals because of the addition of higher amounts of salts in the diet, not only as essential nutrients but also to improve feed conversion efficiency and animal health (Bolan et al., 2004).

Heavy metals can be incorporated into the crystal lattice or adsorbed to the surface of the struvite. Substitution for both magnesium and ammonium ions within the struvite molecule is also reported in the literature (Ronteltap et al., 2007). The contents of zinc decreased from 5.56 to 1.40 mg L^{-1} during struvite precipitation due to settling and recovery of Zn-containing solids with the precipitated struvite (Suzuki et al., 2007). Similarly, Rouff (2012) reported that chromium may be adsorbed or coprecipitated during the struvite process, ultimately reducing the struvite crystal quality.

5.4. Lack of soluble phosphorus

A low fraction of soluble reactive P in the total P (TP) makes recovering struvite difficult, as most of the P in manures and their anaerobic digestates is in a particulate form. The majority of the P in the anaerobic digestates of manures was reported to exist as suspended calcium phosphates, including $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$, CaHPO_4 , and $\text{Ca}_4\text{H}(\text{PO}_4)_3 \cdot 3\text{H}_2\text{O}$ thereby hindering struvite recovery (Zhang et al., 2010). Hence, prior to P recovery from agricultural wastes, it is essential to

Table 4
Effect of different foreign ions on struvite precipitation.

Foreign ion	Concentration	Effect on struvite	Reference
Ca	Mg: Ca = 2:1 & 1:2	Formation of amorphous Ca phosphate	[S44]
Ca	$40\text{--}160 \text{ mg L}^{-1}$	Decrease in struvite purity and calcium phosphate	[S45]
Ca	$10\text{--}59 \text{ mg L}^{-1}$	37% reduction in struvite precipitation	[S46]
Ca	$0.01\text{--}0.20 \text{ mass\%}$	Formation of tubular crystal with 46% reduction in size	[S47]
Ca	$128\text{--}361 \text{ mg L}^{-1}$	Decreased struvite purity at Ca: P > 0.5:1	[S48]
Ca	$30\text{--}60 \text{ mg L}^{-1}$	Smaller size struvite particles formation	[S49]
Na	$(1.0\text{--}35) \times 10^8 \text{ mg L}^{-1}$	Na cause slight increase in induction time	[S50]
CO3-2	$(12\text{--}30) \times 10^7 \text{ mg L}^{-1}$	Marginal increase in induction time	[S50]
CO3-2	$3309\text{--}6567 \text{ mg L}^{-1}$	Increases struvite formation by removing Ca as CaCO_3	[S48]
SO4-2	$(12\text{--}72) \times 10^8 \text{ mg L}^{-1}$	Increase in induction time	[S50]
NO3-1	$0.044\text{--}0.89 \text{ mass\%}$	29% reduction in crystal size	[S50]
Cu	$0.2\text{--}0.5 \text{ mg kg}^{-1}$	Formation of tubular crystal	[S50]
Zn	$2.05 \times 10^{-5} \text{ mass\%}$	Reduction in struvite purity	[S51]
K	0.025 mass\%	Reduction struvite purity	[S51]

The references in this Table are provided in the E-supplementary material.

Table 5
Heavy metal contents of various agricultural wastewaters (mg/L).

WW	Zn	Cu	Fe	Pb	Cd	Cr	Ni	Reference
SW	1.06	0.174	–	0.012	0.0007	0.014	0.005	[S12]
SW	89.8	15.3	–	< 1.4	< 0.5	6.5	3.2	[S18]
SW	17.2	7.8	36	41	6.0	152	87	[S52]
DW	177.7	42.4	–	16.7	1.64	–	–	[S53]
DW	1.59	0.21	–	0.24	0.007	0.03	–	[S28]
Cow urine	–	0.15	–	0.0004	0.0001	0.0002	0.96	[S27]
PM	15.5	3.40	110	0.30	< 0.025	0.30	0.30	[S30]
FIW	2.2	0.25	8.9	–	–	–	–	[S6]
DM	169	49	–	13.9	0.97	52	55	[S54]
GM	159	50	–	14.6	0.88	6.42	19	[S54]
CM	365	185	–	17.3	0.93	33.7	45	[S54]
DW	34.9	10.7	–	–	–	0.5	1.2	[S55]
PD	2743	1158	–	21.5	–	61	73	[S56]
PD	2300	1200	–	< 5	0.4	< 10	20	[S57]
PD	550	210	–	< 5	0.4	< 10	9	[S58]

The references in this Table are provided in the [E-supplementary material](#).

WW = wastewater, SW = swine wastewater, DW = dairy wastewater, PM = poultry manure, PIW = fertilizer industry wastewater, GM = goat manure, PD = pig digestate.

understand the speciation dynamics of P and its distribution between the soluble and particulate forms (Petzet and Cornel, 2011). To maximize P recovery, the P needs to be mobilized into an available form using appropriate pretreatments.

5.5. Imbalance of N, Mg, and P

Molar ratios of the main components of struvite, such as phosphorus, ammonium, and magnesium, have a significant effect on its crystallization (Pastor et al., 2008). Theoretically, the Mg:N:P molar ratio of 1:1:1 is a basic requirement for struvite precipitation, but in practical applications, the situation is somewhat different (Zhang et al., 2009). Agricultural wastewaters normally have P and Mg concentrations that are relatively low compared to the ammonium-N concentration. Critical examination of the previous findings regarding the chemical composition of various agricultural wastewaters (Table 2) illustrated that swine wastewater is rich in ammonium and phosphate contents while its magnesium content is very low. Cow urine has higher contents of ammonium and magnesium but has a lower phosphate content. Likewise, poultry wastewater contains a very high content of ammonium compared to that of phosphate, with nominal magnesium content.

In wastewater with a low magnesium content, supplementation of Mg is required to maximize the recovery of ammonium and phosphate (Liu et al., 2011). The removal efficiency of ammonium also has been shown to improve with increased phosphate concentration, rather than with increased Mg concentration (Zhou and Wu, 2012). Siciliano et al. (2013) and Li et al. (2012) obtained results contradictory to these findings, which may be due to differences in the chemical composition of the wastewater or experimental conditions. Increases in phosphate content also resulted in higher ammonium removal but overdosing of Mg is preferable because overdosing of phosphate leads to its accumulation in the effluent, thus increasing the cost of treatment (Zhou and Wu, 2012). Therefore, an imbalance of N, P, and Mg in agricultural wastewater is also a hindrance from the viewpoint of the economic feasibility of the struvite precipitation, owing to the cost incurred through the supplementation of Mg and P salts in order to maintain an equimolar ratio.

5.6. Costly pH adjustment

The distribution of nitrogen, phosphorus, and magnesium in solution is pH controlled (Fig. 1). The activities of the component ions of struvite should increase and struvite solubility decrease to enhance struvite precipitation, as pH varies. Therefore, the pH must be

maintained within a certain range to maximize the struvite formation efficiency and purity. Commonly, bases, including calcium hydroxide ($\text{Ca}(\text{OH})_2$), magnesium hydroxide ($\text{Mg}(\text{OH})_2$), and sodium hydroxide (NaOH), were used to elevate the pH to a level suitable for struvite precipitation. $\text{Ca}(\text{OH})_2$ is the preferred base from a cost perspective, however, its addition in the precipitation process leads to the formation of amorphous calcium phosphate. The use of NaOH is not economical, but is suitable from an engineering point of view because it is easy to handle compared to $\text{Ca}(\text{OH})_2$ and $\text{Mg}(\text{OH})_2$ (Carballa et al., 2009). Furthermore, the dissolution rates of $\text{Ca}(\text{OH})_2$ and $\text{Mg}(\text{OH})_2$ are low, so their use may induce high local pH conditions, thus hampering crystal formation and rendering less control over the precipitation process (Carballa et al., 2009).

6. Strategies for performance intensification and operational cost reductions

It has become a critical challenge, from both a sustainability and economical viewpoint, to close nutrient cycles and migrate to more effective and sustainable resource management strategies (Scholz and Wellmer, 2013). Struvite precipitation can facilitate nutrient cycling from agricultural wastewaters and close the nutrient loop. However, this technique could be optimized, from both the recovery performance and operational cost reduction perspectives. Therefore, some strategies for minimizing the hindrances mentioned in Section 5 are discussed.

6.1. Suspended solids removal

Suspended solids reduction would not only aid struvite recovery but would also permit better handling and storage of manure. Mechanical processes, including screw press separators, belt filters, centrifugal decanters, and screening, are commonly employed for the on-site separation of suspended solids from the digester effluent (Kunz et al., 2005; Fuchs and Drogg, 2013). Two-stage pebble and sand filtration systems were developed for solid-liquid separation of anaerobically digested dairy manure, attaining suspended solids of 5.5 g L^{-1} and 793 mg L^{-1} (on an average basis) after pebble and sand filtration, respectively (Xia et al., 2012). Likewise, Rishel and Ebeling (2006) employed alum and polymer as coagulant/flocculent aids for the reduction of suspended solids; 99% of the suspended solids were removed, with final solids contents of $4\text{--}20 \text{ mg L}^{-1}$. The removal of suspended solids, facilitated by these methods, aims to make further treatment easier. From the limited literature information on this topic, their applicability to the removal of suspended solids during struvite precipitation is unclear. Therefore, these methods should be explored for their efficiency

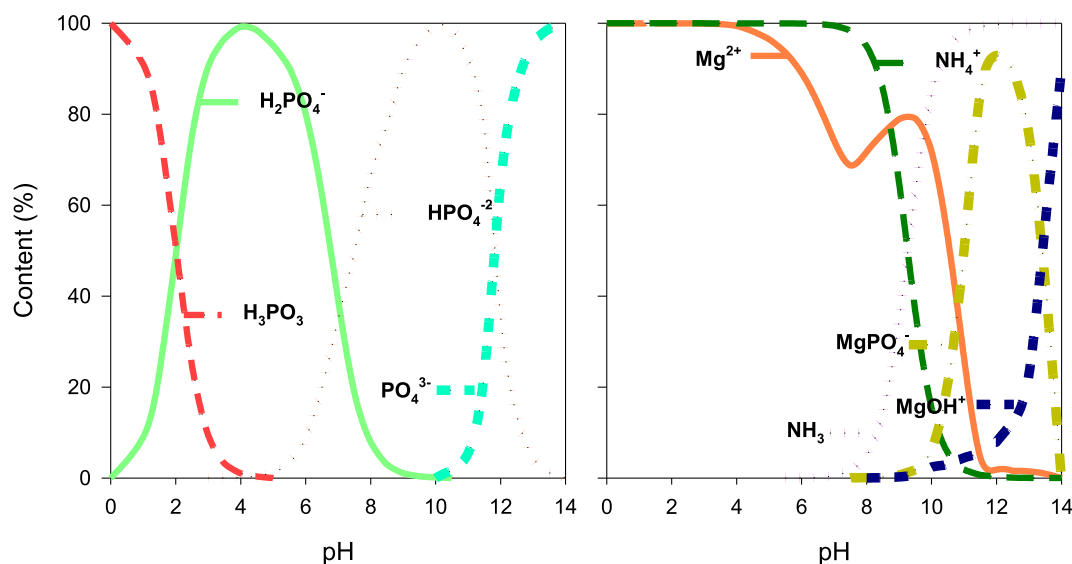


Fig. 1. pH dependence of phosphorus, nitrogen and magnesium at 25 °C (S88).

during struvite formation, and likewise, measures for faster and more economically feasible filtration of different agricultural wastewaters for suitable struvite recovery must also be explored.

6.2. Decrease the calcium interference

Acidification of anaerobically digested dairy manure, followed by supplementation with a chelating agent, such as EDTA or oxalic acid, was found to reduce the hindrance by calcium. The chelating agent complexes with the calcium, allowing phosphorus to react with magnesium and ammonium, thereby improving struvite purity (Zhang et al., 2010; Shen et al., 2011). The stability constant of the calcium-EDTA complex is two orders of magnitude higher than that of the Mg-EDTA complex; after binding with all of the available calcium, the chelating agent will bind with magnesium (Zhang et al., 2010). Moreover, the calcium content declined to 46–76% after calcium carbonate formation at pH values between 9 and 10 (Huchzermeier and Tao, 2012). Therefore, calcium carbonate precipitation might be another feasible technique to reduce calcium interference and retain phosphate for struvite precipitation in manure digestates.

Increasing the magnesium concentration is another way to reduce the hindrance to struvite precipitation imposed by calcium. This is because the increasing magnesium content causes Mg to react with phosphate rather than calcium, thereby reducing the interference due to Ca (Jaffer et al., 2002). Likewise, it was reported that calcium re-dissolution may occur when the thermodynamic energy difference between struvite and calcium phosphate formation is high enough (Lee et al., 2013). This could be used to improve the struvite precipitation process and reduce Ca interruption. However, this phenomenon has been explored very little.

6.3. Control the levels of heavy metals and the influence of pathogens

The worth of struvite technology not only lays in its capacity for nutrient removal but also in its ability to produce quality slow-release fertilizer. However, if high contents of heavy metals and/or pathogens are coprecipitated during this process, it will influence its beneficial use. A method of sulfide precipitation using sodium sulfide (Na_2S) was proposed by Franz (2008) in order to reduce the contents of heavy metals, thereby improving the quality of struvite. Franz further suggested a method of sorption via the utilization of cation exchange resins to minimize the heavy metal content. Moreover, low-cost agriculture-based adsorbents (sugarcane bagasse, rice husk, sawdust, coconut husk,

oil palm shell, neem bark) have been employed in heavy metal removal from wastewater (Hegazi, 2013). However, during these adsorption processes, the contents of P, N, and Mg may also be removed simultaneously, which is not desirable for struvite formation.

Raising the pH during struvite precipitation from wastewater may enhance the coprecipitation of heavy metals and thus decrease the quality of struvite (Matynia et al., 2013). pH values below 7 are less prone to heavy metal adsorption and coprecipitation, although these pH values are not appropriate for nutrient recovery via struvite, owing to the decrease in supersaturation (Bountas and Koutsoukos, 2014). This conflict might be minimized by using the continuous crystallizer operation mode under constant supersaturation (Kofina and Koutsoukos, 2005).

Interference by pathogens during the struvite formation process may not be significant if struvite is precipitated at alkaline pH. This is because some pathogens are negatively charged at alkaline pH, as is struvite, so owing to electrostatic repulsion, they will not be able to adsorb onto struvite particles (Michen and Graule, 2010). Furthermore, inactivation of pathogens can also be accomplished by drying struvite in sunlight or at elevated temperatures (40–50 °C) with low humidity (Decrey et al., 2011).

6.4. Solubilize the particulate P

Solubilization of phosphorus is necessary prior to nutrient recovery from agricultural manures through struvite, as phosphorus commonly exists in the particulate form in the materials mentioned in Section 5.4. The P in manure usually exists in inorganic or organic forms. Inorganic P may be present in the form of Ca, Mg, or Fe phosphates, whereas organic P is found in various organic compounds, such as nucleic acids. Acidification, using hydrochloric or sulfuric acid, enhances struvite formation for P recovery by releasing P into the solution. Most of the P becomes soluble, irrespective of the acid type (Zhang et al., 2015). The acid treatment causes protonation of the phosphate ions bound to Ca or Mg, which lowers their ionic product below their solubility product and leads to precipitation as struvite. Oliveira et al. (2016) reported that 100% of the phosphorus found in cattle manures was extracted by nitric acid treatment after two hours at a pH of 4.5. Szogi et al. (2008) demonstrated that 60–80% of organically bound P can be released via acid treatment, whereas lowering the pH of anaerobically digested dairy manure to 3.8 increased the availability of P by 500% (Zhang et al., 2010). Shen et al. (2011) reported that 43–100% of the total P in dairy manure became available by decreasing the pH to 4.5 using acid

treatment methods.

Microwave irradiation is a thermochemical treatment that can enhance the solubilization of organically and inorganically bound P in manure, thereby improving recovery through struvite precipitation (Jin et al., 2009). Microwave irradiation has been proposed as a possible pretreatment to release particulate P, with the extent of release dependent on the form of P in the manure (Pan et al., 2006; Qureshi et al., 2008). The microwave operating temperature and heating duration control the degree of P solubilization. Pan et al. (2006) reported that, with heating at 170 °C for 5 min, about 80% of the total P was released from dairy manure.

Pretreatment with microwave heating was further modified by the integration of chemical microwave digestion with acids, bases, or oxidants (Pan et al., 2006; Qureshi et al., 2008). Jin et al. (2009) verified that successful recovery of P from dairy manure through struvite precipitation can be achieved by integrating microwave treatment with NaOH or HCl. Microwave heating for 5 min, along with microwave-enhanced oxidation using H₂O₂, caused the amount of phosphate recovered to increase from 21% to 86% in dairy manure (Qureshi et al., 2008). The quantity of soluble P in dairy manure was amplified noticeably with organic acids (acetic, oxalic, and citric acids) and microwave-enhanced advanced oxidation (Zhang et al., 2015). Nearly 84% of the total P from dairy manure was solubilized via a microwave-enhanced advanced oxidation process at a pilot plant (Srinivasan et al., 2016).

6.5. Supplement with cheap external nutrients

The majority of struvite sources, such as agricultural wastewaters, lack an adequate quantity of Mg. Hence, a supply of Mg is required to enable the precipitation process. In some instances, such as when using poultry wastewater, both P and Mg have to be supplemented to maximize nutrient recovery through struvite precipitation. Thus, the indispensable consumption of Mg, or both Mg and P, often makes the precipitation costlier (Quintana et al., 2008). The use of alternate sources of both Mg and P would make this process more cost-effective. Currently, the most common salts used to supply Mg during struvite precipitation include MgCl₂, MgSO₄, and MgO.

Instead of using pure Mg reagents, several low-cost sources of Mg (Table 6) can be used effectively as alternatives in NH₄⁺-N and PO₄³⁻-P recovery (Zhang et al., 2009; Liu et al., 2013). The feasibility of these

Table 6
Alternate sources of magnesium.

Alternative source	Wastewater	Mg (g L ⁻¹)	Reference
Brine	SSU	2.374	[S59]
Brine	TW	1.25	[S60]
Sea water	MWW	1.25	[S61]
Sea water	BTW	1.20	[S62]
Sea water	SSU	27.15	[S63]
Sea water	BTW	32.0	[S62]
Sea water	AND	69.0	[S29]
Sea water	LL	48.5	[S64]
Seawater bittern	LL	9.22	[S65]
Seawater bittern	BTW	32.0	[S62]
Seawater bittern	LL	9.20–24.9	[S65]
Natural Magnesite	LL	98% as Mg CO ₃	[S66]
Natural Magnesite	Urine	244	[S63]
Natural Brucite	REW	65% as MgO	[S67]
Natural Brucite	LL	300	[S66]
Technical-grade MgO	IWW	84–86%	[S68]
Mg(II) from seawater	SSW	8.0	[S69]

The references in this Table are provided in the [E-supplementary material](#).

SSU = source separated urine, TW = treated wastewater, MWW = municipal wastewater, BTW = biological treated wastewater, AD = anaerobic digestate, LL = landfill leachate, REW = rare earth wastewater, IWW = industrial wastewater, SSW = sewage sludge wastewater.

alternatives (seawater bittern, low-grade MgO, nanofiltration brine, etc.), however, depends upon the quality, abundance, and pretreatment required. MgO is one of the cheapest sources of Mg and has been efficiently applied in the struvite formation process with different wastewaters (Li et al., 2012). Application of MgO has a dual function, because it is used as an Mg source and its alkalinity makes it suitable for adjusting the solution pH (Lee et al., 2003). The sole drawback of using MgO is its low solubility, which ultimately lengthens the reaction time. Magnesite (MgCO₃) and brucite (Mg(OH)₂) are good options in locations where they are abundant (Gunay et al., 2008). Their low solubility, although an issue, can be addressed by dissolution in acid or with a higher application dose.

The use of phosphorus salts to maintain the balance between Mg, P, and N, which is required for struvite to precipitate, is also a major contributor to the cost of this process (Siciliano et al., 2013). Until now, only a few studies have been conducted to search for alternative sources of P, despite the scarcity and high cost of P salts. Waste phosphoric acid was employed as an alternative source of P for nutrient recovery and found that its efficiency was similar to that achieved with pure chemicals (Huang et al., 2014). Likewise, Siciliano and De Rosa (2014) used bonemeal waste (a by-product of meat waste) as a low-cost P source for nutrient recovery from the anaerobic digestate of calf manure through struvite. They concluded that the recovery efficiency was more than 90% and was accompanied by a 50% reduction in the cost of the process.

6.6. Adjust the pH cheaply

Adjustment of the pH is of prime importance for struvite precipitation, but the cost incurred is extremely high. Carbon dioxide (CO₂) purging could prove effective in raising the pH for struvite precipitation (Fattah et al., 2015) because as the CO₂ is liberated from the solution, the carbonate speciation changes, causing the pH to increase. CO₂ stripping is inexpensive, relatively simple, and beneficial, but increasing the pH via this technique is possible only when the solution is significantly supersaturated, which is the case in animal manures and their anaerobic digestates (Liu et al., 2014). However, the combined use of CO₂ stripping and a strong base is advocated in some instances (Carballa et al., 2009).

Another low-cost source, furnace slag, has been found to be an effective alternative to increase the pH of liquid manures. The hydrolysis of the contained metal (Ca, Si, Fe, Al, Mn, etc.) oxides generates OH⁻, which ultimately leads to an increase in pH. Wen et al. (2013) used furnace slag for struvite recovery from anaerobically digested dairy manure and found it effective in increasing the pH. Furthermore, they found no appreciable increase in the heavy metal content with its application; furnace slag contains heavy metals that could be precipitated with the struvite.

7. Use of struvite as an alternative fertilizer in the soil

7.1. Interactions with plants

Struvite can be effectively used as a fertilizer for field crops as well as for potted, orchard, and ornamental plants. Struvite is utilized commercially for tree seedlings, vegetables, potted plants, ornamentals, turf, and other value-added crops (Li and Zhao, 2003). It is recommended for use in pots because a substantial amount of irrigation water is drained from the pots, which causes a steady-state release of nutrients from the slow-release struvite fertilizer (Antonini et al., 2012). Struvite is also the best option for crops that require low solubility fertilizers. The presence of Mg also makes struvite an efficient fertilizer for grasses as Mg is an essential element of chlorophyll.

Many studies have evaluated the effect of struvite fertilizer application on the growth of different crops (Table 7). Struvite fertilizer has been shown to be as effective as other chemical fertilizers in improving

Table 7
Effect of struvite fertilizer on growth and yield of different crops.

Crop	Study	Soil	St. S	CF	Findings	Reference
Corn, oat	Pot	Acidic, alkaline	DW	MAP	Higher yield and P uptake than chemical fertilizer in acidic soil while statistically similar was found in alkaline soil	[S70]
Maize, Sorghum	Pot	Acidic loamy sand	AD	TSP	Higher crop yield, growth and P uptake with struvite than chemical fertilizer	[S71]
Maize	Field	Silt loam	IW	TSP	Plant P uptake is higher than chemical fertilizer by 4–21% depending upon application rate	[S72]
Maize, Rye	Pot	P deficient	HU	AN and P fertilizer	Higher yield and P uptake was obtained with struvite than chemical fertilizers	[S73]
Maize	Pot	Sandy loam	SW	SP & urea	Similar plant height, higher biomass, less N ₂ O emission as with chemical fertilizer	[S23]
Maize	Pot	Sandy loam	HU	TSP	No significant difference in dry yield compared chemical fertilizer	[S74]
Maize	Pot	Quartz sand	HU	NPK	Lower dry weight (by 50%) than chemical fertilizer	[S75]
Lettuce	Pot	Sandy soil	SW	Complex fertilizer	Struvite as effective as complex fertilizers regarding growth and biomass yield	[S15]
Lettuce	Pot	Loamy sand	AD	SSP	More efficient than chemical fertilizer in increasing yield & P uptake	[S76]
Wheat	Pot	Loamy	DW	TSP, RP	Increase in total P uptake in basic soil	[S77]
Wheat	Field	Sandy loam	HU	TSP	No significant difference in dry yield compared to chemical fertilizer	[S74]
Ryegrass	Pot	Sandy	PM	–	76 and 60% more fresh and dry weight compared to in control and faster growth	[S38]
Ryegrass	Pot	Loam	AD	SSP	Similar increase in dry matter, P uptake compared to chemical fertilizer	[S78]
Chinese cabbage	Pot	Sandy loam	IW	Compound	Struvite as effective as complex fertilizers regarding growth and biomass yield	[S77]
Chinese cabbage	Pot	Sandy clay	LL	AN and CaP	Similar vegetable growth and more Mg, P uptake compared to chemical fertilizer	[S79]
Chinese chard	Pot	–	–	DAP	P uptake efficiency for struvite is 117% and residual P availability is 178%	[S80]
Chinese chard	Pot	Sandy clay	LL	AN and CaP	Similar vegetable growth and more Mg, P uptake compared to chemical fertilizer	[S79]
Canola	Pot	Sandy loam	SW	MAP	Similar P uptake but lower biomass yield/unit of P uptake compared to chemical fertilizer	[S25]
Water convolvulus	Pot	Sandy clay	LL	–	No significant difference in growth and no burning effect with increase in struvite dose	[S79]
Water spinach	Pot	Sandy clay	LL	AN and CaP	Similar vegetable growth and more Mg, P uptake compared to chemical fertilizer	[S79]
Rape seed	Field	Loam	AD	TSP, RP	Higher P uptake and grain yield compared to synthetic fertilizer/rock phosphate	[S81]
Winter barley	Field	Loam	AD	TSP, RP	Similar P uptake and grain yield compared to chemical fertilizer/rock phosphate	[S81]
Garden rocket	Pot	Garden soil	AD	AN and KH ₂ PO ₄	More gain in plant wet, dry weight and height compared to chemical fertilizer	[S82]
Dill	Pot	Garden soil	AD	–	Increase in dry weight by 191% compared to no fertilizer	[S82]
Fennel	Pot	Garden soil	AD	–	208% increase in yield compared to no fertilizer	[S82]
Parsley	Pot	Garden soil	AD	–	379% more dry weight by compared to no fertilizer	[S82]
Purslane	Pot	Sandy	PM	–	150% and 207% increase in fresh and dry weight than control with faster growth	[S37]
Garden cress	Pot	Sandy	PM	–	28 and 115% increase in fresh and dry weight by compared to control with faster growth	[S37]
Tomato	Pot	Alkali	IW	Potassium P, AN	Increased nutrient uptake with increase in dose of struvite compared to NPK treatment	[S32]
Corn, Soybean	Field	Silty	IW	TSP	Grain yield and P uptake with struvite was higher than with chemical fertilizer	[S72]

The references in this Table are provided in the [E-supplementary material](#).

SW = swine wastewater, HU = human urine, LL = landfill leachate, AD = anaerobic digestate, PM = poultry manure, IW = industrial wastewater, DW = dairy wastewater, MAP = monoammonium phosphate, SP = super phosphate, AN = Ammonium nitrate, DAP = Diammonium phosphate, SSP = Single super phosphate, TSP = Triple super phosphate, CaP = Calcium phosphate, RP = rock phosphate, St. S = Struvite source, CF = Chemical fertilizer.

the growth and development of different crops (Gell et al., 2011). Ponce et al. (2009) reported that, for lettuce, the yield and P uptake obtained with the application of urine-derived struvite was greater than that with the application of single superphosphate (SSP). They concluded that the better results from the use of struvite could be attributed to the higher Mg contents and the synergistic effect on P uptake. Rasul et al. (2011) made a comparison between the application of Mg at 80 kg ha⁻¹ and struvite for maize crop and found that the plant height, leaf area, and dry matter yield were similar between the struvite and chemical fertilizer treatments.

However, some researchers have reported contradictory results, i.e., a lower crop yield with struvite fertilizer than with chemical fertilizers (Ganrot et al., 2007). However, doses of struvite that exceed those of conventional chemical fertilizers can be applied without any negative effect on plant health (Rafie et al., 2013). To date, struvite fertilizer has been found effective for crops (corn, wheat, barley, oats, etc.), vegetables (cabbage, tomato, lettuce, spinach, etc.) and grasses, however, most of these studies were conducted in pots and in greenhouse environments. Therefore, the use of struvite fertilizer on various crops under different climatic and field conditions should be investigated to help improve the struvite fertilizer market.

7.2. Interactions with soil

Generally, acidic soils are found to be more suitable for struvite application because they improve its solubility, which in turn results in enhanced P absorption and dissolution in the soil and increased

fertilizer efficiency. Struvite is sparingly soluble in water (0.02 g cL⁻¹ of water at 0 °C), leading to its slow assimilation into the soil (Negrea et al., 2010). In acidic soil, the low pH improves the solubility of struvite (in the range of 65–100%), so that it is as effective as chemical fertilizers (Cabeza et al., 2011). A high concentration of calcium phosphate makes calcareous soils less suitable for the application of rock phosphate as fertilizer because calcium phosphate decreases the solubility of rock phosphate significantly. Therefore, in calcareous soils, struvite would perform comparatively better than rock phosphate (Lindsay, 1979). This might be due to the presence of Mg, which has a synergistic effect on the dissolution of P in soil solutions (Ponce et al., 2009).

Mg accumulation in soil might occur with prolonged application of struvite, as reported by Gell et al. (2011), who observed a change in the Ca:Mg ratio from 4:1 to 2:1 in a field trial. Generally, variations in the Ca:Mg ratios of soil do not affect plant growth and yield (Schulte and Kelling, 2004). When Mg concentrations become much higher than those of Ca, however, crop yield may be affected due to disturbance to the soil porosity, aggregate stability, and hydraulic conductivity (Zhang and Norton, 2002). Therefore, it is recommended that struvite should be used in conjunction with other chemical fertilizers, rather than alone for long periods.

7.3. Interactions with the environment

Soil and water pollution can result from the excessive land application of manure and the discharge of nutrients into water bodies

(Cordell et al., 2009). Conversely, the dominant sources of gaseous emissions (NO, N₂O) are the excessive application of nitrogenous fertilizers (Aguilera et al., 2013). The contribution of agriculture to global carbon dioxide emissions is 1%, whereas its contributions to CH₄ and N₂O emissions are 39% and 60%, respectively. Worldwide, fertilization with urea and other chemical fertilizers leads to the loss of nutrients (N and P) through volatilization, leaching, runoff, or adsorption to the soil. The application of struvite fertilizer could help minimize nutrient losses because it is a slow-release fertilizer (Li and Zhao, 2003; Negrea et al., 2010). Struvite fertilizer is, therefore, less prone to losses through leaching, volatilization, or runoff. Rahman et al. (2011) reported that N leaching losses were considerably less in struvite-treated soils than in soils receiving chemical fertilizers (approx. 1.99% in struvite-treated soils versus 7.14% in chemical-treated soils). However, no significant difference in P leaching was seen between the soils, as both fertilizers are sparingly soluble in water and the P adsorbed to soil surfaces.

Struvite can also reduce gas emissions, as observed in the application of chemical nitrogenous fertilizers. Reduction in nitrous oxide emissions by the use of struvite could be attributed to the fact that, after application to the soil, plants take up most of the N (Lee et al., 2009). Liu et al. (2011) observed that emissions of nitrous oxide were six times less for struvite than for chemical fertilizer. Previously, higher nitrous oxide emissions were also reported for nitrogenous fertilizers, whereas nitrous oxide emissions were lower for slow-release fertilizers such as struvite (Chu et al., 2007). The interaction of struvite with the environment should be investigated further to explore its potential in reducing gas emissions from the soil and improving water quality.

8. Economic evaluation

The introduction of struvite as a fertilizer would be a profitable investment for the agriculture sector. To fertilize a 2.6 ha area of arable land by applying P at 40 kg ha⁻¹ (as P₂O₅) annually, production of one kg of struvite per day is sufficient (Zheng et al., 2004). Shu et al. (2006) predicted that an increase of nine tons in dry grain yield could be attained if 100 m³ of wastewater could generate 1 kg of struvite via recovery. Furthermore, the application of struvite as a fertilizer reduces the need for rock phosphate and closes the nutrient loop, thus creating a more sustainable environment. Struvite crystallization is always reported to be economical and profitable compared with chemical precipitation and biological removal of N and P (Shu et al., 2006). This method produces savings from a reduction in the quantities of chemicals used for precipitation and the amount of sludge that must be disposed. However, the high operational cost is still the bottleneck of this technology.

Various types of wastewaters have P and Mg concentrations that are relatively low compared to the ammonium-N concentration. The cost of struvite crystallization will be higher for these cases because of the P and Mg salts required to attain the appropriate molar ratio of Mg:N:P for struvite to precipitate. The economics of the struvite process is also influenced by the initial concentration of phosphate in the wastewater. As the content of phosphate-P increases from 50 to 800 mg L⁻¹, the cost of struvite is predicted to drop from 2800 to 520 € t⁻¹ (Dockhorn, 2009). In most pilot- and large-scale applications, struvite formation is economical for P recovery from wastewaters with higher contents of P because only Mg salts are required for successful treatment (Pastor et al., 2008). However, the same applications would be more expensive for NH₄-N recovery from NH₄-N-rich, P-deficient wastewater, such as poultry wastewater, because of the required supplementation with both Mg and P salts (Li et al., 2012). The cost of different chemicals used for struvite precipitation and the cost reductions by utilizing alternatives are given in Table 8. The prices of P salts are a limiting factor in the economic feasibility of struvite precipitation (Siciliano et al., 2013). Therefore, the recovery of all NH₄-N present in the wastewater would not be the target of the struvite precipitation process, especially when applied as a pretreatment, to avoid consumption of significant

Table 8

Cost reduction by alternate sources of Mg and P.

Alternate chemical	Cost	Pure chemical	Cost	Reduction %	Reference
Seawater	0.50	MgSO ₄ ·7H ₂ O	2.79	25	[S70]
Magnesite	0.95	MgCl ₂ ·6H ₂ O	1.17	18	[S67]
Magnesite	1.04	MgSO ₄ ·7H ₂ O	3.21	67	[S83]
Low cost MgO	0.04	MgCl ₂ ·6H ₂ O	0.08	50	[S84]

The references in this Table are provided in the E-supplementary material.

quantities of Mg and P reagents.

To minimize the cost of supplementation with external nutrients, struvite can be reused effectively to reproduce Mg and P compounds, which can then be applied as sources of Mg and P for the recovery of NH₄-N. For the recycling of struvite, four techniques have been studied: (i) pyrogenation (heating under alkali conditions), (ii) distillation with alkaline addition, (iii) ultrasound stripping, and (iv) electrolysis (Yu et al., 2013; Huang et al., 2016). The cost reduction via recycling using these techniques is given in Table 9. A ~95% reduction in the cost of nutrient recovery could be attained by the adoption of pyrogenation as a recycling technique (Türker and Celen, 2007), whereas a 79% cost reduction is possible using an ultrasound stripping technique (Huang et al., 2016).

As an effective slow-release fertilizer, struvite proves to be an efficient alternative to conventional fertilizers because of its resource-saving, labor-saving, and eco-friendly characteristics. However, its application is still confined primarily to ornamental and horticultural agriculture, owing to the high cost of struvite relative to that of conventional fertilizers. Therefore, promotion of the struvite market will lead to its large-scale production, which will lower the cost, making it an attractive fertilizer for major crops.

9. Conclusions

Struvite crystallization is an effective and eco-friendly technique that converts nutrients from wastewater into a valuable resource. Various factors, including the suspended solids, and calcium, phosphorus and heavy metals concentrations, hinder the closure of nutrient cycles in the agriculture sector by struvite precipitation. Application of low-cost sources of Mg and P can improve the economics of this method. Likewise, the adoption of pH-increasing strategies, such as air stripping along with base (NaOH) application, can further reduce costs. The most effective and economical method is to reproduce Mg and P compounds by recycling struvite, using techniques like pyrogenation, ultrasound stripping, and electrolysis. The effect of struvite fertilizers on nutrient uptake and crop yields has been reported; nevertheless contradictory results exist. Although struvite has good potential for nutrient recovery from various agricultural wastewaters, future research on its utilization as a fertilizer, especially for major crops under various field conditions, is still needed.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jenvman.2018.09.030>.

Table 9
Cost reduction by recycling of struvite (\$).

WW	Recycling technique	Cost with recycling	Cost without recycling	Reduction %	Reference
LL	Pyrogenation technique	2.52/ton	4.50/ton	44	[S85]
AD	Distillation with caustic addition	0.36/kg NH ₄	7.70/kg NH ₄	95	[S86]
SW	Chlorination decomposition	6.09/m ³	9.21/m ³	34	[S87]
SW	Pyrogenation technique	4.90/m ³	10.3/m ³	49	[S24]
LL	Ultrasound stripping	2.76/kg NH ₄	13.3/kg NH ₄	79	[S13]
SW	Decomposition with air stripping	4.54/kg NH ₄	9.83/kg NH ₄	54	[S19]
LL	Chlorination decomposition	2.58/kg NH ₄	4.10/kg NH ₄	37	[S21]

The references in this Table are provided in the E-supplementary material.

Note: SW = swine wastewater, LL = landfill leachate, AD = anaerobic digestate of molasses based industrial wastewater, The references in this Table are provided in the E-supplementary material.

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