Phosphorus recovery as struvite: Recent concerns for Use of seed, Alternative Mg source, Nitrogen conservation and Fertilizer potential

SAMPRITI KATAKI¹, HELEN WEST², MICHELE CLARKE³, DC BARUAH¹*

¹Energy Conservation Laboratory, Department of Energy, Tezpur University, Assam, India
²School of Biosciences, University of Nottingham, Sutton Bonington Campus, Leicestershire, LE12 5RD, UK
³School of Geography, University of Nottingham, University Park, Nottingham NG7 2RD, UK

Correspondence: DC Baruah, tel. +91 9435508563, fax +91 3712 267005,
E-mail: baruah@tezu.ernet.in (DC Baruah)

Abstract

Finite availability of phosphorus (P) resources makes recovery of this non-substitutable plant nutrient from alternative waste sources an increasingly attractive option of renewed interest. In this context, feasibility of struvite (MgNH₄PO₄·6H₂O) recovery, an alternative P fertilizer is already demonstrated at laboratory scale from range of waste streams of farm, municipal and industrial origin, with reasonably high orthophosphate recovery efficiency (~90%). However, apart from a few commercial extraction units using municipal sludge and urine, large scale struvite recovery is not widely adopted for many of these sources. Moreover, need of some research interventions that are restricting its profitable recovery are also highlighted by earlier studies. To increase recovery efficiency
from identified potential sources in terms of cost and energy input, research focuses on some new aspects of the process such as prospects of alternative recyclable magnesium sources, different seed materials and their related issues, which are analyzed in this review. Prospects of nitrogen conservation through struvite recovery and fertilizer value of struvite considering its properties, comparative performance with conventional fertilizer and interaction with soil and plant growth are also critically reviewed.

Keywords: Struvite, Phosphorus, Recovery, Magnesium, Seed, Nitrogen, Fertilizer

1. Introduction

Global increase in population indicates the need for adequate food production, which can in turn be met through intensification of agricultural sector, with arable land being finite. The role of fertilizer is indispensible for securing escalated agricultural production where phosphorus (P) is one of the non substitutable fertilizers. P being reactive, its association with other elements makes its availability to plants restricted in soil. Therefore, its external supply becomes almost essential.

Presently the only source of commercial P fertilizer is natural phosphate rock spread in handful of countries. China, USA, Morocco and Russia are contributing about 75% of world total P production (Heckenmüller et al., 2014). Consumption of P fertilizer is seen somewhat stabilized in the developed countries, but its demand in the developing world is seen increasing (Heffer and Prud’homme, 2010). The actual extent of commercially viable global phosphate reserve remains a subject of substantial uncertainty in the recent years (Vaccari, 2009; Schröder et al., 2010). However, exhaustion of global reserves of rock phosphate or a peak P is expected to occur considering increasing demand for P fertilizer and finite non renewable natural reserve of rock phosphate (Cordell and White, 2011;
‘Peak phosphorus’ as analogous to ‘peak oil’, means the point of time when maximum production or extraction rate of phosphorus is reached after which rate of production declines. There could be ambivalence among researchers about the timing of peak phosphorus; however, there is no dispute about its occurrence. This is due to decreasing global P stock associated with ever increasing population and subsequent growth of food demand. Therefore, need of the moment is to investigate opportunities for its sustainable management, considering cost-effective, energy efficient and environmentally compatible means of P recycling.

P conservation methods identify recycling of P from viable P sources as an option, which tries to convert P from a source into a product with enhanced nutrient values. Struvite or ammonium magnesium phosphate (AMP) hexahydrate (MgNH₄PO₄·6H₂O) recovery is one of the available methods of P recovery (de Bashan & Bashan, 2004). Equi-molar concentrations (1:1:1) of magnesium (Mg), phosphorous (P), and ammonium (NH₄⁺) with alkaline pH and appropriate mixing are required to precipitate struvite (Rahaman et al., 2008). Struvite, being a slow release fertilizer, can contribute to crop productivity enhancement. Besides its prospect as fertilizer, recovery of struvite has some additional advantages. Such recovery is environmentally useful since the waste becomes suitable for safe disposal after extraction of excess nutrients (Gell et al., 2011). Woods et al. (1999) demonstrated that P recovery from sewage sludge resulted in reduction of sludge volume up to 49% when calcium phosphate recovery was used following conventional biological treatment. Reduction in sludge volume minimizes the operating cost of waste treatment unit. Struvite recovery from municipal waste sludge at global scale is expected to reduce about 1.6% of worldwide phosphate rock mining (Shu et al., 2006). Thus, integration of a such recovery process along with waste management system would help in cost efficient relocation.
of excess nutrients (Burns and Moody, 2002) by closing the P loop in soil–crop–animal–human–soil cycle (Shu et al., 2006).

Importance of developing a slow release N and P fertilizer to meet the projected global crop production is also justified by previous study (Tilman et al., 2002). Previously struvite precipitation was seen in wastewater treatment plant as a problematic spontaneous deposition due to prevailing favourable conditions of struvite formation. Until 2006, majority of the research works focussed on the mitigation strategies of struvite precipitation, as the system efficiency of wastewater treatment plant is reduced due to clogging of conduits by struvite crystals (Doyle and Parsons, 2002). Several control strategies including addition of Fe/Al salt, phosphate fixation with sludge, uses of chemical inhibitors and ultrasonic technology have been attempted with varying degree of success. The difficulties in P recovery from Fe/Al salt and environmental issues of safe disposal of sludge are faced while adopting the above mitigation strategies besides increase in sludge volume (Ohlinger et al., 1998; Wu et al., 2005). In absence of an effective mitigation strategy, designed recovery of struvite has been attempted after increased understanding of the process conditions of struvite formation (Moerman et al., 2012). The associated benefits as mentioned earlier also motivated to adopt ‘struvite production’ as a resource recovery option.

The bio-geochemical P cycle deposits significant amount of P in some easily accessible and abundant natural sources. Recycling of P from such natural source seems to be a potential option to restrict P outflow from the P sedimentary cycle. A range of waste streams of natural origin contains excessive P, which requires reduction before safe disposal. Feasibility of struvite recovery from about twenty sources of farm, municipal and industrial origin has been established at laboratory scale. The precipitation process is simple in majority of the cases. However, modification of process is required due to inherent heterogeneity of some typical sources. Depending upon the characteristics of the
source, pre-treatments such as anaerobic digestion (Beal et al., 1999), acid base leaching (Zhang et al., 2010), chelating agent treatment (Zhang et al., 2010), microwave treatment (Lo et al., 2011) and enhanced biological phosphorus removal (Pastor et al., 2008) are required in order to nullify the effect of non-participating ions such as calcium (Ca) and iron (Fe). In general, to ensure the required molar ratio for struvite precipitation, addition of Mg is required for effective struvite recovery in all Mg deficient sources. Moreover, supplementation of P (and/or NH₄⁺ salt) is also required for sources with inadequate P (and/or inadequate NH₄⁺) which is generally seen for industrial waste sources. Municipal waste water is the mostly used struvite recovery source and farm wastes (cattle, swine, poultry manure, urine) represent the most accessible and abundant stock. However, these sources often need pre-treatments due to presence of limiting interfering ions (Zhang et al., 2010; Shen et al., 2011). On the other hand, addition of P salt (NaH₂PO₄/KH₂PO₄/H₃PO₄) or NH₄⁺ salt (NH₄Cl) becomes necessary for many sources of industrial origin (wastewater from dye, fertilizer, textile, food, tanning, coking, beverage industry), to balance their low inherent nutrient contents (Kabdasli et al., 2000; Chimenos et al., 2003; Folleto et al., 2013; Kumar et al., 2013).

Previous studies have shown feasibility of struvite production at laboratory scale successfully, though full scale installations are limited. At present, municipal wastewater sludge and human urine are the two sources used for commercial struvite recovery, though at a very limited scale. However, recovery of struvite exhibits some difficulties mainly due to heterogeneous characteristics of source. Further, requirements of additional chemical inputs and low recovery efficiency make the process uneconomical. Therefore, in recent times, there are increasing concerns towards the techno-economical aspects of the recovery process to increase process efficiency and cost reduction. Significant progress has been made on three aspects of the recovery processes viz., (a) modification of struvite precipitation mechanism.
for improvement of reaction conditions, (b) investigation on additional benefits of struvite recovery process for its further promotion and (c) prospects of struvite as alternative sources of crop nutrients in view with the regulatory limits of fertilizer. Based on these aspects, this review highlights the development in researches on (a) modification of struvite recovery mechanism for improvement of crystallization with incorporation of alternative Mg sources and seed material, (b) struvite precipitation as a method of nitrogen preservation and (c) assessment of fertilizer value of struvite on a range of crops, considering struvite properties, composition, soil and plant interaction and comparative performance with chemical fertilizer. Attempt is made to analyse the practical relevance and significance of these aspects to help making informed decisions about future directions for struvite research and development.

2. Modification of struvite precipitation mechanism for efficiency enhancement

a) Alternative magnesium sources for struvite recovery

Concept of intentional struvite precipitation has been conceived from the occurrence of spontaneous struvite accumulation in anaerobic digestion units of wastewater treatment plant as mentioned earlier. Struvite incrustation creates nuisance by reducing system efficiency and increasing operational cost (Jaffer, 2002). In such systems, regions of high turbulent flow such as valves, joints of pipe, aeration assemblies are the most prone locations of struvite formation, when concentrations of Mg\(^{2+}\), NH\(_4^+\) and PO\(_4^{3-}\) are favourable and pH and mixing energy are appropriate (Bhuiyan, 2007). Availability of nutrients is enhanced after digestion, (Wu et al., 2005; Masse et al., 2007) due to mineralization of organic bound nutrients (Lukehurst et al., 2010; Seadi et al., 2012) which increases the potential of struvite formation (Bhuiyan et al., 2007). Thus, anaerobically digested source becomes suitable for struvite recovery (Doyle et al., 2002; Pastor et al. 2008; Wang et al., 2013). In anaerobic
digestion of municipal sludge, there remains sufficient mineralized Mg and P
(orthophosphate) released from sludge that react with NH$_4^+$ released from degradation of
nitrogenous material to precipitate struvite spontaneously.

However, in practice, for intentional struvite production, most of the potential struvite
recovery sources need input of chemical in the form of alkali source for pH adjustment, Mg
source and other participating ion (NH$_4^+$ and PO$_4^{3-}$) to reach desired molar ratio (Mg : PO$_4^{3-}$ :
NH$_4^+$) to induce struvite precipitation. Supply of Mg is essentially required to make the
precipitation effective, due to lack of adequate Mg in majority of the potential struvite
sources compared to PO$_4^{3-}$ and NH$_4^+$. Thus, indispensible Mg consumption makes the
precipitation often expensive (Quintana et al., 2004).

The most common Mg sources used in struvite studies are salts of Mg, such as MgCl$_2$,
MgSO$_4$ and MgO. Commercially available struvite recovery technologies *viz.* Phosnix (used
in Japan), Pearl Ostara (used in North America, UK), Phospaq, (used in Netherlands),
Seaborne (used in Germany), AirPrex (used in Germany, Netherlands) and Multiform (used
in America) also employ use of these pure-chemicals. These chemicals are also extensively
used in laboratory feasibility studies of struvite production, mainly due to high reactivity, Mg
content and purity. However, it has been reported that cost of high-grade Mg compounds
contribute up to 75% of overall production costs, limiting large-scale use economically
nonviable (Dockhorn, 2009). Therefore, high input cost of such Mg sources has prompted to
search for alternative Mg compounds (Quintana et al., 2004). Alternative Mg sources used in
struvite recovery are listed in Table 1, along with their Mg concentration, effect on recovery
process and type of source where these are used to precipitate struvite. These renewable Mg
sources include sea water, bittern, magnesite (MgCO$_3$) or by-products of magnesite and Mg
saturated supporting materials (Bentonite, Stevensite and Sepiolite) (Maqueda et al., 1994;
Quintana et al., 2004; Gunay et al., 2008; Huang et al., 2010b; Etter et al., 2011). Mg availability, solubility and reactivity of the Mg sources play a significant role on the feasibility of their uses (Romero-Güiza et al., 2015).

(Table 1. Alternative Magnesium sources used in struvite recovery)

In seawater, Mg is the second most abundant cation (Mg content ~1300 mg l\(^{-1}\)) that enters from weathering of Mg-rich minerals (Shin and Lee, 1997; Kumashiro et al., 2001). Bittern (Mg content 9220-32000 mg l\(^{-1}\)) is the commercial source of Mg, it is the solution remains after crystallization of sodium chloride from brines and seawater. Total PO\(_4^{3-}\) recovery of 95 and 99% were reported from coke manufacturing waste water, using sea water and bittern, respectively (Shin and Lee, 1997), which are comparable with the recoveries made using conventional Mg salts. However, due to presence of insoluble Mg in bittern and seawater, the process needs high Mg dose (Mg : PO\(_4^{3-}\) >1.5:1) for efficient P recovery (Matsumiya et al., 2000; Kumashiro et al., 2001; Quintana et al., 2004). Though their uses are yet to be shown at commercial scale, these two can serve as prospective and economic Mg sources in regions neighboring sea (Shin and Lee, 1997; Matsumiya et al., 2000; Li and Zhao, 2002; Lee et al., 2003; Etter et al., 2011; Crutchik and Garrido, 2011). Seawater and bittern have also been shown effective for struvite precipitation in swine wastewater, coke wastewater, urine, landfill leachate and municipal wastewater as shown in Table 1.

Magnesite (MgCO\(_3\)) is a natural mineral generated as a by-product during MgO production which is 94% MgCO\(_3\) by mass. Solubility of magnesite is low in water requiring high dose for struvite precipitation. Acid dissolution and thermal-decomposition (calcination) have been suggested as effective measure to increase solubility of Mg (Gunay et al., 2008; Huang et al., 2010b). Addition of acid dissolves about 99% Mg of magnesite...
into soluble form and thereby 50% increase in struvite formation as compared to untreated magnesite has been achieved (Gunay et al. 2008). The market prices of such magnesite reckoned per unit of Mg have also been estimated as equivalent to about one-tenth of pure MgCl$_2$ (Huang et al., 2010b). Use of acid dissolved magnesite in struvite production cuts down the overall production cost. However, it leads to higher alkali consumption so as to achieve required alkaline condition neutralizing the acid used for magnesite decomposition. Therefore, overall benefit from cost reduction is somewhat curtailed (Huang et al., 2010b). Thermally decomposed magnesite produces magnesia (MgO) with higher solubility and reactivity which yield similar recovery of PO$_4^{3-}$ and NH$_4^+$ (99.7% and 90.2%, respectively) (Huang et al., 2010b). Magnesia preparation methods (calcinations temperature and time) influence the recovery performance (Huang et al., 2010b). In case of thermal decomposition of magnesite, above certain optimum temperature and time (700°C and 1.5 hours in case of rare earth wastewater), struvite production reaction rate slows down because of increase in surface area of magnesia (Huang et al., 2010b). Recovery is further influenced by reaction condition of magnesite (reaction time, mixing energy, dose of magnesia) (Quintana et al., 2008, Huang et al., 2010b). There is increase in recovery up to certain reaction time and magnesite dose (6 hours and 52 g l$^{-1}$ as reported for rare earth wastewater), above which no significant increase in struvite recovery is found (Huang et al., 2010b). Struvite production using raw magnesite reduces process cost up to 18% (Gunay et al., 2008), with further reduction up to 34% when thermally decomposed magnesite is used as Mg source compared to MgCl$_2$ (Huang et al., 2010b).

Uses of thermal decomposition or pyrolysis product of struvite viz. MgHPO$_4$ and Mg$_2$P$_2$O$_7$ have been reported as recycled Mg sources for struvite production (Zhang et al., 2009; Huang et al., 2009; Yu et al., 2012). Primarily pyrogenation of struvite as Mg source has been reported to use for NH$_4^+$ stripping in the form of struvite from NH$_4^+$ rich waste such
as industrial effluents, with simultaneous recovery of P. For pyrolysis of struvite, two
direct pyrolysis and NaOH assisted pyrogenation of struvite are reported to
generate required Mg source (Türker and Çelen, 2007; He et al., 2007; Zhang et al., 2009; Yu
et al., 2012). Struvite pyrolysis under alkali condition produces MgNaPO$_4$ as per reaction
shown in Eq. (1) (Huang et al., 2011b). When MgNaPO$_4$ is used in a medium containing
NH$_4^+$, it is converted to more stable struvite by replacing Na$^+$ with NH$_4^+$. It has been reported
that the stability of struvite analogues generally declines with the reduction in the size of the
univalent ion (Banks et al., 1975). Therefore, MgNaPO$_4$ is converted to more stable struvite
by taking NH$_4^+$ ions from source as the size of NH$_4^+$ is larger than that of Na. It is also noted
that saving of processing cost up to 48% has been estimated using struvite pyrolysate (He et
al., 2007; Huang et al., 2009).

$$\text{MgNH}_4\text{PO}_4\cdot6\text{H}_2\text{O} + \text{NaOH} \rightarrow \text{MgNaPO}_4(s) + \text{NH}_3(g) + 7\text{H}_2\text{O}_4(g)$$  (1)

The optimum conditions for struvite recovery by struvite pyrolysate vary with
respect to recovery-source. For landfill leachate, up to 96% NH$_4^+$ removal has been
reported under optimum conditions (OH$^-$: NH$_4^+$ = 1:1, temperature=90°C and time=2
hours) (He et al., 2007). Again, up to 87% of NH$_4^+$ recovery has been reported for yeast
industry anaerobic effluent with corresponding optimum conditions (OH$^-$: NH$_4^+$ = 1.5:1,
temperature = 110°C, time = 3 hours and pH = 9) (Uysal and Demir, 2013). However, in
case of repeated use of struvite pyrolysate, the NH$_4^+$ removal efficiency decreases in the
subsequent recycling cycles (He et al., 2007; Huang et al., 2011b). This is because of
accumulation of inactive Mg$_3$P$_2$O$_7$ and Mg$_3$(PO$_4$)$_2$ in recycled pyrolysate (Sugiyama et al.,
2005; Yu et al., 2012). Acidolysis can increase the re-usability of struvite pyrolysate for
NH$_4^+$ removal which removes NH$_4^+$ part of struvite and transforming it into MgHPO$_4$,
which can be further used for NH$_4^+$ recovery (Zhang et al., 2004; Yu et al., 2012). A
combined technology is suggested to use bittern as Mg source and internal recycling of chlorination product of the recovered struvite to remove ammonia from swine wastewater (Huang et al., 2015). Chlorination decomposition products of struvite are Mg\(^{2+}\) and HPO\(_4^{2-}\), which keep levels of the Mg and PO\(_4^{3-}\) same in solution. This is why the process remains efficient in removing excess NH\(_4^+\) or PO\(_4^{3-}\) from solution for multiple cycles. This process has been reported to be 37% more cost effective compared to struvite precipitation using pure chemicals.

While adding Mg source, it is to be noted that, there might be addition of other non-participating ion that may hinder the precipitation process. Table 2 gives the composition of various Mg sources (wood ash, magnesite, seawater, bittern, magnesia and by-product of MgO production (decomposed magnesite)) as reported in literature. Presence of Na, SO\(_4^{2-}\) in these Mg sources may increase induction time (Kabdasli et al., 2006). Moreover, Ca, K, Al present in the Mg source may co-precipitate in product as hydroxides, phosphates and other salt reducing struvite purity (Kozik et al., 2013). Addition of bittern may add chloride (by 1.0 %), sulfate (by 1.7%), potassium (by 2.6%) and sodium (by 13%) in the struvite source (Etter et al., 2011). Ca and Na ions are prevalent in seawater (~400 mg l\(^{-1}\)), which could interfere in recovery process, by promoting formation of phosphates. Magnesite also contains non desirable inhibiting ions such as Ca (1.5 mass%) and Fe (0.8 mass%) (Huang et al., 2010b). High concentration of heavy metal exceeding fertilizer regulatory limit is reported in struvite produced using wood ash as Mg source (Sakthivel et al., 2011). This may limit prospects of wood ash as Mg source. However, heavy metal content can be reduced by a controlled wood ash production process (Sakthivel et al., 2011).

(Table 2. Composition of alternative Mg sources used for struvite production)
From the above discussion, it is seen that, in struvite production high grade Mg can be replaced by by-products of industrial process or other Mg rich renewable sources with a similar NH$_4^+$ or PO$_4^{3-}$ recovery efficiency. Nevertheless, optimum utilization would require strategies for reactivity enhancement and removal for other non-participating impurity ions (Ca, Fe, SO$_4^{2-}$ etc.) from Mg source which have potential to hinder the recovery process.

b) Use of seed in struvite crystallization

A crystallization process is divided into two phases’ viz. nucleation and growth. Nucleation is characterized by arrangement of ions in a characteristic pattern of a crystalline solid, forming foundation sites for deposition of crystallizing particles which then grow into detectable crystals (Ohlinger et al., 1999). Nucleation controls induction time, which is the duration between establishment of super-saturation in crystallizing solution and growth of detectable crystals (Ohlinger et al., 1999). In crystallization, seed material acts as template on which further accumulation of crystallizing material takes place. Seed controls nucleation by providing surface area and thus reduce induction period for crystal development. Large surface area to promote nucleation, inertness to crystallizing liquor and isomorphism with precipitating crystal are the desirable characteristics of seed material (Ali, 2005).

Table 3 shows various seeds reported in struvite recovery along with their specifications and effect on crystallization process. Among the reported seed materials in struvite recovery, struvite fines are the most widely investigated seed (Regy et al., 2002; Ali., 2005; Kim et al., 2006; Rahaman et al., 2008; Liu et al., 2010, Mehta et al., 2013; Yu et al., 2013). Earlier investigations reported insignificant effect of seed on struvite crystallization (Regy et al., 2002; Rahaman et al., 2008). Under no-seed conditions, the largest struvite crystal with least fine formation was obtained compared to seeded
condition with coarse sand, fine sand, struvite and elutriated struvite (Regy et al., 2002). This might be due to greater surface area for new crystal development provided by the newly formed crystal nuclei than the seed crystals (Regy et al., 2002). However, there are some reports that describe enhancement of recovery using struvite seeds. Use of struvite seed could enhance the recovery by 5% and crystallization rate up to 21% compared to un-seeded crystallization (Zhang et al., 2009, Yu et al., 2013). An isomorphic crystal plane of struvite seed promotes adhesion and integration of growing molecules and clusters of struvite without need of nucleation, which makes the process energetically favourable. The shape of newly crystallized struvite remains similar to parent struvite seeds as seed allows crystallizing molecules to inherit characteristics of seed (Ali, 2005; Mehta et al., 2013). Increased surface area of struvite fines help in higher crystal accumulation resulting in enhanced P recovery efficiency. Further, isomorphic crystal of seed struvite intensifies crystallization, minimizing induction time (Liu et al., 2011). Induction time was reduced by 75 minutes using struvite seed compared to un-seeded condition in struvite recovery from fertilizer wastewater (Liu et al., 2011).

Some alternative seeds used in struvite recovery are sand, stainless steel mesh, pumice stone and borosilicate glass with high surface area (Regy et al, 2002; Ali, 2005; Le Corre et al., 2007; Pakdil and Filibeli, 2008). Compared to struvite seed, lower crystallization rates and higher induction time are reported for non struvite seed (Ali, 2005). Use of non-isomorphic non struvite seed changes the type of nucleation from homogeneous to heterogeneous (Ohlinger et al., 1999). Newly precipitating struvite nuclei cannot integrate upon non-isomorphic seed to grow into bigger crystal and as a result the unstable clusters of struvite nuclei break down or re dissolve which increases the induction time (Ali, 2005).
Table 3. Different seeds used in struvite recovery and their effects on recovery

Surface roughness, dosing of the seed, grain size and super-saturation of crystallizing solution directly influence the effectiveness of a seed, under similar process conditions (Ohlinger et al., 1999). Deposition of crystal is directly proportional to relative surface roughness of seed and stainless steel having the maximum roughness was found to be most affective among constructional material followed by polyvinyl chloride and acrylic plastic (Ohlinger et al., 1999). Surface roughness might help creation of local turbulence or increase surface area providing nucleation sites for crystal development (Ohlinger et al., 1999). Increasing the dose and grain size of struvite seed increase ammonium and phosphate removal through struvite formation (Huang et al., 2010a). In saponification wastewater generated from processing of rare-earth elements, maximum ~3% increase in ammonium removal efficiency was achieved through formation of struvite when struvite seed size was increased from a range of 0.05–0.098 mm to 0.098–0.150 mm. Again, ammonium removal efficiency was enhanced by ~3% when the struvite seed dose was increased from 15 g l^{-1} to 60 g l^{-1} (Huang et al., 2010a). The findings reported by Liu et al., 2011 showed that, at a seed dosing of 0.42 g l^{-1}, the induction time was less by 49 minutes in a solution with higher super-saturation compared to a solution with lower super-saturation.

From the above discussion it is seen that, seeding has effect on induction time and recovery efficiency of struvite crystallization. However, process needs optimization with respect to seed dose and size. The process of struvite crystallization through use of seed material is energy and cost intensive process as amounts of seed requirement is often high to make crystallization effective. Energy is needed to keep the seeds suspended in crystallizing solution (Battistoni et al., 2005). Most of the reported findings of seed use in
struvite production are based on synthetic waste (Table 3). Therefore, further investigation is required to investigate efficacy of seed material with varying parameter (such as pumice stone, stainless steel mesh and borosilicate glass) in real waste source.

3. Struvite precipitation as a method of nitrogen conservation

Precipitation of struvite helps in realizing some additional benefits as described in the introduction part, which promotes for adoption of the process at larger scale. Improving compost quality through conservation of nitrogen by struvite precipitation is such a beneficial process, as nitrogen in compost is otherwise susceptible to emission loss. Decline in nitrogen (N) content of compost through gaseous emissions during composting process is a major concern compromising fertilizer value of compost and posing environmental risk from ammonia and gaseous N emission. Depending upon initial N content, temperature and pH (Martins and Dewes, 1992), N loss during manure composting can range from 19-42%. Further, more than 92% of the loss is in the form of ammonia volatilization (Eghball et al., 1997). Control measures (adsorption, scrubbing) require adoption of additional facilities and thus increases the process cost. Struvite recovery has been promoted as a method of N conservation in compost which increases overall efficiency of the composting process (Jeong and Kim, 2001; Xian-yuan et al., 2010; Fukumoto, 2011; Li et al., 2011; Wang et al., 2013). It is reported that, concentration of ammoniacal N increases gradually and stabilizes when struvite precipitation is applied in composting process (Jeong and Kim, 2001).

In composting of food waste, formation of volatile fatty acid creates acidic conditions initially, hindering the further composting process as the microbial growth is inhibited (Xian-yuan et al., 2010; Wang et al., 2013). Alkaline materials such as lime, fly ash) are used to negate the problem. However, rise in pH enhances loss of ammonia (Wang
et al., 2013). Ammonia loss was reported up to remains about 22% of initial N in food compost (Jeong and Kim, 2001). However, this can be reduced to 4.8-5% by using struvite precipitation (Jeong and Kim, 2001; Wang et al., 2013). For precipitation of struvite in food waste compost, Mg and P sources are required to be supplemented from outside. With increase in Mg and P, ammonia emission decreases, with simultaneous increase in struvite production (Jeong and Hwang, 2005). However, high concentrations of Mg and P might create salination causing reduction in microbial activity. This leads to immature compost formation and usability of compost is compromised (Jeong and Kim, 2001; Jeong and Hwang, 2005; Ren et al., 2010). For conserving compost value through struvite formation, an optimum P and Mg dose equivalent to 20% of initial N is suggested (Jeong and Hwang, 2005). Up to 84% decrease in ammonia emission in poultry manure compost is achieved by struvite precipitation depending upon the Mg and P doses (Zhang and Lau, 2007).

Struvite precipitation can be used in combination with nitratation as a measure of N conservation in compost (Fukumoto et al., 2011). Nitratation is the conversion of nitrite to nitrate by the action of nitrite oxidizing bacteria (NOB). During composting, limited inherent growth of NOB after establishment of thermophilic phase accumulates nitrite, inducing N₂O emission. External supply of NOB from mature compost can enhance the nitratation process. In swine manure compost, struvite precipitation conserves 51% of compost N, which rises up to 60% when struvite precipitation is combined with nitratation by supply of NOB (Fukumoto et al., 2011).

From the above discussion it is seen that struvite crystallization can be successfully applied to food waste composting process to improve agronomic value. However, struvite crystallization process has not been demonstrated for any other compost apart from food
waste compost. Care has to be taken for controlling salination that may arise from nutrient supplementation ($\text{PO}_4^{3-}/\text{Mg}$) to induce struvite formation.

4. Application of struvite as soil fertilizer

a) Struvite fertilizer properties

Use of struvite as plant fertilizer was first suggested by Murray in 1857 (cited by Bridger, 1962). Struvite as fertilizer is simple to produce, pure, easy to handle, as it is concentrated, granular, non-sludgy and non-odorous (Bouropoulos and Koutsoukos, 2000). Apart from field crop, struvite has been used as a fertilizer for potted plants, orchards, and ornamental plants. As fertilizer, the N, $\text{P}_2\text{O}_5$, $\text{K}_2\text{O}$ and Mg content of pure struvite are 5.7:29:0:16.4 respectively (Westerman, 2009). The P content of struvite generally remains in the range of 11-26% (Johnston & Richards, 2003) depending upon source and method of production, of which 1-2% is water soluble and rest is acid soluble (Bridger et al., 1962). Struvite was, perhaps, first commercially manufactured under the trade name MagAmp, a slow release fertilizer, using a patented manufacturing process by WR Grace & Co., US (Peng et al., 1979). It was manufactured by adding MgO or Mg(OH)$_2$ to mono-ammonium phosphate. However, its high cost of production made its application limited to high value crops (Peng et al., 1979).

The most advantageous nature of struvite fertilizer is its slow nutrient releasing rate. Struvite is sparingly soluble in water with a solubility of 0.02g/100 ml of water at 0°C, rendering its slow assimilation into soil solution (Li and Zhao, 2002; Negrea et al., 2010). Nitrification *i.e.* biological oxidation of ammonium fraction, a key step of soil nitrogen cycle, releases nitrate ensuring a prolonged and assured nutrient supply for a longer duration. This allows direct and higher application dose of struvite exceeding those of conventional fertilizers without causing any harm to plant health (Li and Zhao, 2002;
However, sometimes the limited availability of N because of low N/P ratio of struvite makes N insufficient for optimal plant growth (Miso, 2009, Gell et al., 2011), as in agriculture, the required amount of N is far higher than the P required. When the struvite application dose is increased to fulfil plant N requirement, it results in higher soil pH compared to other P fertilizer, which might affect nutrient availability and uptake (Rahman et al., 2011). Gell et al., 2011 indicated possibility of Mg accumulation in soil from long term struvite application, by showing change of Ca:Mg ratio from 4:1 to 2:1 over a short term field trial. In general, Ca:Mg in soil varies within the range of 0.5:1 to 20:1, not to affect the crop yields (Schulte and Kelling, 2004). When Mg concentration in soil becomes much higher than Ca, it might affect hydraulic conductivity and aggregate stability and as a result crop yield is affected (Zhang and Norton, 2002). Mg has high hydration energy which results in clay swelling and subsequently soil porosity and aggregation are affected (Zhang and Norton, 2002). Unbalanced Ca:Mg ratio is a matter of concern as the Ca uptake by plants is compromised resulting a Ca deficiency in plants (Stevens et al., 2005). Therefore, struvite in combination with other fertilizers is recommended for optimal use. Struvite is used by fertilizer companies as additive or as a substitute raw material in standard fertilizer production technology (Li and Zhao, 2002; Rafie et al., 2013). The commercial struvite recovery technology of UK (Ostara Nutrient Recovery Technology) uses additional salts of ammonium and potassium to formulate a balanced NPK fertiliser suitable for agricultural use (Scope Newsletter, 2013). The cost of such commercial product largely depends upon processing (drying, storage, creation of a blended product) and transportation (Westerman, 2009).

The fertilizing effect of struvite varies with soil type due to differences in solubility and sorption properties in soils. Struvite is most effective in soil of moderate or low pH but its efficacy is limited in soils with marginal fertility and high pH. Solubility of struvite is
improved under acidic conditions, increasing fertilizer efficiency. Acidic conditions result in enhanced P adsorption to soil and consequently its dissolution and availability (Bowden et al., 1980). Struvite solubility is minimum (0.040 milli-molar) within the pH range of 8.2-8.8 (Le Corre et al., 2009), which can rise up to 1-10 mM at pH <5 (Borgerding, 1972; Abbona et al., 1982). In acidic and neutral soil solution, struvite solubility remains in the range of 65–100%, which is similar to that of conventional P fertilizer (triple superphosphate) (Cabeza et al., 2011). This implies that, under acid and neutral soil conditions, struvite would have similar fertilization effect as that of chemical fertilizer. It is to be noted that, in alkaline calcareous soil, where use of rock phosphate is not suitable because of its low solubility, struvite is found to be more soluble, making it a recommended P fertilizer (Massey et al., 2007). Struvite application is also reported to be advantageous in soils and crops with high Mg and P demand. Its application enhances P uptake, as the Mg present in it, has a synergistic effect on P absorption (Gonzalez-Ponce et al., 2009). Compared to common phosphate minerals (viz. fluorapatite, variscite), struvite forward dissolution rates are significantly higher (Roncal-Herrero and Oelkers, 2011). Relatively higher dissolution is facilitated by the presence of comparatively weak H bonds (Huminicki and Hawthorne, 2002) that binds regular tetrahedral $\text{PO}_4^{3-}$, distorted octahedral $\text{Mg}_6\text{H}_2\text{O}$ and $\text{NH}_4^+$ to form white orthorhombic struvite crystals (Forrest et al., 2008).

In struvite treated soil, N leaching losses are remarkably different compared to chemical fertilizer treated soil, though significant difference is not seen in case of P leaching (Rahamann et al., 2011). Again, N leaching loss is insignificant in struvite treated soil (loss is ~1.99% of the total N supplied in the form of struvite), which was reported to be higher for conventional chemical fertilizer (loss is ~ 7.14% of the total N supplied in the form of fused super phosphate+urea) (Rahamann et al., 2011). This causes N deficiency after certain period of time in case of chemical fertilizer because of immediate ammonium
release and uptake by plants. However, there is not significant variation in P leaching from struvite and chemical fertilizer (fused super phosphate+urea) treated soil, as both are sparingly water soluble and P gets bind to soil particles (Rahaman et al., 2011). Slow release from struvite ensures steady nutrient supply for plants improving fertilizer efficiency. Struvite is recommended for containerized pot. In such pots, considerable amount of irrigation water is drained. Therefore, a slow release fertilizer is recommended (Antonini et al., 2012). For this reason, struvite has been used commercially for potted plants and also for turf, tree seedlings, ornamentals, vegetables, flower boards and other value added crops (Li and Zhao, 2003).

Crushing strength is a quality parameter which predicts handling and storage properties of struvite fertilizer. To facilitate manufacturing, harvesting, transportation and application in the field, struvite pellet with high crushing strength is required. Because, for field application, increased durability with reduced loss of fine materials are desirable (Forrst et al., 2008). The average size of commercial struvite crystal is 2-3.3 mm depending upon reactor conditions viz. upflow velocity, pH, and supersaturation ratio (Forrest et al., 2008). As agricultural fertilizer, low dissolution with steady release is expected, avoiding over application or crop burning, so that, single high-dose application becomes sufficient. Smaller pellets with larger surface area to volume ratio give faster degree of dissolution which slows down with increase in size (Bridger et al., 1962; Bhuiyan et al., 2008; Fattah et al., 2012). However, it is difficult to maintain enough crushing strength for small pellets. Crushing strength increases with the increase in pellet size up to 2.36 mm, beyond which it decreases which can be attributed to low density in larger pellets (Fattah, 2010). To maintain optimum crushing strength for pellets bigger than a particular size, coating of pellet is suggested for hardening (Fattah, 2010). When tested on rye grass under green house condition, it is found that struvite particle size has a direct
influence on nutrient release rate up to certain period of plant growth (Nelson, 2000). N release rate is higher for smaller particles of struvite compared to coarser ones up to 3-6 weeks of plant growth (Nelson, 2000). However, influence of granule size becomes insignificant after certain stage of plant growth, as release rate is accelerated once soil is depleted with plant growth. This however, is a typical characteristic of a slow release fertilizer.

Quality standard of struvite can be described in terms of its composition and purity which is primarily influenced by source, processing and Mg addition (Antonini et al., 2012). Multi-component raw materials like sewage sludge usually contain a number of heavy metals (Cd, Cu, Cr, Ni, Pb, Zn etc.) and organic pollutants. Therefore, their residual content in struvite should be estimated before recommending application. There is a lack of information on residual impurity in struvite derived from a range of sources (Wollmann and Moller, 2015). Table 4 summarizes concentration of some impurity elements in struvite recovered from different sources viz. municipal sludge, urine, landfill leachate and anaerobically digested dairy manure. Municipal sludge derived struvite shows presence of impurity such as Cd, Co, As, Ni, Pb, Hg etc. (Forrest et al., 2008; Benisch et al., 2010). However, the impurity content is reported to be below the regulatory limit for fertilizer usage in countries like Germany and Turkey (Uysal et al., 2010; Latifian et al., 2012; Antonini et al., 2012). Heavy metal in municipal water derived struvite is found to be significantly lower than that of commercial phosphates (Forrest et al., 2008; Latifian et al., 2012). Impurity level within permissible limit indicates possible increase in marketability of struvite. Struvite recovered from anaerobically digested manure reported to be pure in terms of heavy metal content compared to municipal sludge, urine and landfill leachate derived struvite (Table 4). Pathogenic content of struvite from black water and human
urine is found to be below regulatory limit of Dutch fertilizer regulations (Gell et al., 2011).

(Table 4 Composition of struvite recovered from various sources)

b) Struvite fertilizer effect on crop growth

There have been many reports evaluating the effect of struvite as fertilizer on variety of crops. The fertilizer effect of struvite as studied on 20 plant varieties has been presented in Table 5 on some aspects viz. type of plant tested, struvite recovery source, type of experiment, soil type, effect of struvite application on plant and its comparative effect with chemical fertilizer. It is evident from previous studies that, there is no significant difference between P in struvite and P in other phosphate fertilizer. Most of the studies reported comparable effect of struvite with chemical fertilizer (Ghosh et al., 1996; Johnston and Richards., 2003; Li and Zhao., 2003; Plaza et al., 2007; Massey et al., 2009; Perez et al., 2009; Liu et al., 2011; Gell et al., 2011; Dalecha et al., 2012).

In ryegrass, Zea mays L. and red clover, urine derived struvite resulted in similar crop yields and phosphate uptake to that resulted by commercial phosphate fertilizer (Simons, 2008; Antonini et al., 2012). Again, struvite has been reported to yield better results in comparison with some conventional fertilizers such as ammonium phosphate, diammonium phosphate and single superphosphate (Barak and Stafford., 2006; Gonzalez-Ponce et al., 2009; Yetilmezsoy et al., 2013). When compared with single superphosphate, urine derived struvite was found to be more effective in lettuce yield with enhanced P uptake (Gonzalez-Ponce et al., 2009). Higher yield due to struvite application was probably attributed to higher Mg content and the synergistic effect of Mg on P uptake. It has been reported that, P concentration is higher in plants grown with struvite than in plants grown with other P fertilizers (Li and Zhao., 2003; Gonzalez-Ponce and Garcia-
Lopez, 2007). While comparing the effect of struvite with phosphate rock, mono ammonium phosphate and calcium superphosphate on perennial ryegrass, P accumulation has been found to be highest in struvite treated ryegrass (Gonzalez-Ponce & Garcia-Lopez, 2007). The P and Mg levels in soil as well as in crop (*Zea mays* and *Brassica oleracea*) were found to be higher in landfill leachate derived struvite treatment compared to chemical P fertilizer, although the effect was not significant in terms of chlorophyll content, and plant moisture (Prater, 2014). Improvement of P fertilizer efficiency by over 55% with Mg application equivalent to 80 kg ha$^{-1}$ was reported by Rasul et al., 2011. At this recommended rate, no significant difference between the application of struvite and single super phosphate on maize height, leaf area, and dry matter were found.

However, there are also some studies which reported lower yield in struvite treated plants because of lower availability of nutrients compared to chemical fertilizer (Ganrot et al., 2007; Ackerman et al., 2013). Therefore, supplementation of chemical fertilizer with struvite has been recommended for better results (Ackerman et al., 2013). Further, chemical P fertilizer treated crop resulted better yield compared to struvite, which was attributed to potassium deficiency as reflected in crops (Hammond and White, 2005). Nonetheless, out of the 19 studies (Table 5), 14 studies reported superior or comparable effect of struvite fertilizer over the chemical fertilizer on crop growth.

(Table 5 Effect of struvite as fertilizer on various plants)

It is seen from the above discussion that, there is a wide variation in fertilizing effect of struvite on crop growth. Such variation ranges from no significant impact to significant effect on uptake of P and Mg and biomass yield. However, the findings are subjected to various factors such as soil type, plant type and climate. It is also reported that, extraction of Phosphate rock fertilizer is still economical than production of struvite
(Forrest et al., 2008). However, in view of the associated benefits of struvite recovery process (cost savings from sludge volume reduction and prerequisite for chemical treatment; conservation of limited P resources and the safe disposal of waste), struvite recovery could be an attractive and feasible alternative in future.

5. Future prospects

There are future scopes for struvite process improvements addressing the issues of appropriate chemical input and corresponding cost dynamics. Optimum utilization of Mg source would require strategies for reactivity enhancement and removal of other non-participating impurity ions (Ca, Fe, SO$_4^{2-}$ etc.) which otherwise hinder the recovery process. Again, to establish profound effect of seed on struvite precipitation, further investigation is required considering real waste source. Investigation on potential application of struvite on a range of crops corresponding to different climatic and edaphic factors would enhance struvite market development. Further, quality standard of struvite specific to different recovery sources is also expected to bring positive impact on struvite market. Strategy for struvite market development should focus on a holistic approach considering pricing, purity, size, storage, transportation and distribution in view with the legal framework of contaminants and eco-toxicity. This will help to develop an added value P rich product that can be used as a supplement to prevailing nutrient supply system. The overall impacts of such technological successes would be profound on global food security.

6. Conclusions

In the present study, different aspects of struvite recovery processes are critically analyzed with special references to (i) input of alternative Mg sources and (ii) seed aided
crystallization. The efficacy of the process for nitrogen conservation as well as struvite use as alternative fertilizer are also adequately highlighted using the available literature. Study shows process efficiency and cost affectivity can be assured by replacing high grade Mg input with low grade Mg rich by-products. Impurity free Mg sources with significant soluble Mg content improve struvite quality and enhance its acceptability as fertilizer. Further, addition of seed at optimum size and dosing enhances struvite crystallization. Struvite recovery can be successfully integrated to composting process to improve agronomic value of compost. However, compost quality should be checked against salination that could arise due to nutrient supplementation (PO$_4^{3-}$/Mg) to induce struvite formation. Previous research reported variation in fertilizing effect of struvite ranging from non significant effect to significant effect on plant P and Mg uptake and biomass yield. The findings are subjected to factors related to soil type, plant type and climate. Nevertheless, considering the associated benefits of struvite recovery process (viz. conservation of limited P resources, safe disposal of nutrient laden waste and cost savings from problematic spontaneous occurrence), struvite recovery appears to be an attractive and feasible pathway provided uncertain aspects are addressed through appropriate research and development.

**Acknowledgements**

This work was supported by the following grant awards: UKIERI-UGC 086 Optimising Phosphate Recovery from Community Bioenergy Systems: Low Cost Sustainable Fertiliser Production for Rural Communities; UK Engineering and Physical Sciences Research Council – India Department of Science and Technology J000361/1 Rural Hybrid Energy Enterprise Systems; and UK Engineering and Physical Sciences Research Council EP/K00394/1 Global Engagements in Research.
1  References:

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   environmental impact assessment of different urine-derived struvite fertilizers as

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<table>
<thead>
<tr>
<th>S.No.</th>
<th>Mg source</th>
<th>Source of struvite</th>
<th>Mg content</th>
<th>Mg:P</th>
<th>pH</th>
<th>Phosphate Recovery (%)</th>
<th>Key findings</th>
<th>Cost</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Bittern</td>
<td>Coke manufacturing wastewater</td>
<td>31390 mg l⁻¹</td>
<td>1:1</td>
<td>10.5</td>
<td>99</td>
<td>Similar recovery efficiency as MgCl₄</td>
<td>NR</td>
<td>Shin and Lee, 1997</td>
</tr>
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<td></td>
<td></td>
<td>Landfill leachate</td>
<td>9220-24900 mg l⁻¹</td>
<td>1:1</td>
<td>11</td>
<td>NR</td>
<td>Comparable struvite precipitation efficiency with MgCl₂ &amp; MgSO₄</td>
<td>NR</td>
<td>Li &amp; Zhao, 2002</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Biologically treated swine wastewater</td>
<td>32000 mg l⁻¹</td>
<td>1.3:1</td>
<td>9.6</td>
<td>76</td>
<td>Bittern is more effective in P recovery than NH₄⁺ recovery</td>
<td>NR</td>
<td>Lee et al., 2003</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Urine</td>
<td>27500</td>
<td>1:1:1</td>
<td>NR</td>
<td>98</td>
<td>More cost effective in coastal areas</td>
<td>0.23 USD/kg struvite</td>
<td>Etter et al., 2011</td>
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<tr>
<td>2</td>
<td>Sea water</td>
<td>Wastewater from coke manufacturing process</td>
<td>1136 mg l⁻¹</td>
<td>1:1</td>
<td>10.5</td>
<td>95</td>
<td>Same P recovery efficiency as MgCl₂</td>
<td>NR</td>
<td>Shin &amp; Lee, 1997</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Side-stream of water treatment plant</td>
<td>1250 mg l⁻¹</td>
<td>1.6:1 &amp; 2.2:1</td>
<td>7.6-8.4</td>
<td>70</td>
<td>Higher Mg: PO₄³⁻ (&gt;1.5:1) necessary for more than 70% P recovery</td>
<td>NR</td>
<td>Matsumiya et al., 2000</td>
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<td></td>
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<td>Municipal waste water stream from water treatment plant</td>
<td>1250 mg l⁻¹</td>
<td>1.6-2.4</td>
<td>8.4-76</td>
<td>Higher Mg: PO₄³⁻ (&gt;1.5:1) necessary for stabilized and easy P recovery</td>
<td>0.55 USD/kg struvite</td>
<td>Kumashiro et al., 2001</td>
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<tr>
<td></td>
<td></td>
<td>Biologically treated swine wastewater</td>
<td>1200 mg l⁻¹</td>
<td>1.36:1</td>
<td>10</td>
<td>81</td>
<td>Similar recovery efficiency as MgCl₂ (75%)</td>
<td>NR</td>
<td>Lee et al., 2003</td>
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<td>3</td>
<td>Thermally decomposed magnesite (MgO)</td>
<td>Filtrate of wastewater sludge</td>
<td>676.7 g kg⁻¹</td>
<td>2.5:1</td>
<td>8.5-8.8</td>
<td>90</td>
<td>Need higher Mg: PO₄³⁻ molar ratio for effective recovery</td>
<td>NR</td>
<td>Quintana et al., 2004</td>
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<td>4</td>
<td>Brucite</td>
<td>Rare—earth wastewater</td>
<td>650 g kg⁻¹</td>
<td>1:1</td>
<td>8.5-9.5</td>
<td>97</td>
<td>Brucite can be used as liquid, solid Mg source, Reuse of brucite is possible</td>
<td>NR</td>
<td>Huang et al., 2011a</td>
</tr>
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<td>5</td>
<td>Magnesite</td>
<td>Landfill leachate</td>
<td>300 g kg⁻¹</td>
<td>NR</td>
<td>8.6</td>
<td>NR</td>
<td>Acid dissolution of magnesite increase struvite recovery by 50%</td>
<td>18% cost reduction than using MgCl₂</td>
<td>Gunay et al., 2008</td>
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<td>Rare—earth wastewater</td>
<td>940 g kg⁻¹</td>
<td>1.1:1</td>
<td>5-9.2</td>
<td>Up to 99.7</td>
<td>Thermal decomposed magnesite is cost effective than acid dissolved magnesite</td>
<td>34% cost reduction than using MgCl₂</td>
<td>Huang et al., 2010</td>
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<td>Urine</td>
<td>244 g kg⁻¹</td>
<td>1:1:1</td>
<td>NR</td>
<td>90</td>
<td>Cheaper than bittern and MgSO₄</td>
<td>12 USD/kg struvite</td>
<td>Etter et al., 2011</td>
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<td>6</td>
<td>Struvite pyrolysate</td>
<td>Piggery wastewater</td>
<td>530 g kg⁻¹</td>
<td>2.5:1</td>
<td>8-8.5</td>
<td>96</td>
<td>Similar effects on recovery as with Mg salt</td>
<td>81% cost reduction than using MgCl₂</td>
<td>Huang et al., 2011b</td>
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<td>Wood ash</td>
<td>Urine</td>
<td>34 g kg⁻¹</td>
<td>2.7:1</td>
<td>8.8</td>
<td>99</td>
<td>Presence of impurity such as calcite, heavy metal in product</td>
<td>0.016-0.05 USD/kg struvite</td>
<td>Sakthivel et al., 2011</td>
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<tr>
<td>8</td>
<td>Synthetic nanofiltration brine from seawater</td>
<td>Synthetic wastewater, Real wastewater</td>
<td>146mmol l⁻¹</td>
<td>1:1</td>
<td>8</td>
<td>99.5</td>
<td>Effective as Mg source but pH, organic matter influence purity of product</td>
<td>NR</td>
<td>Zewuhn et al., 2011</td>
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<td>9</td>
<td>Desalinated Reject Water</td>
<td>Synthetic centrate</td>
<td>1555-2795 mg l⁻¹</td>
<td>2:1 &amp; 8:1</td>
<td>8.8-5</td>
<td>Up to 55</td>
<td>Presence of other ions (Ca, Na) in reject water reduces recovery efficiency</td>
<td>NR</td>
<td>Fattah et al., 2013</td>
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<td>10</td>
<td>Mg(II) solution from seawater</td>
<td>Supernatant of a municipal-sludge</td>
<td>8000 mg l⁻¹</td>
<td>1:1</td>
<td>7.57, 8.13</td>
<td>90</td>
<td>Higher dose of Mg: PO₄³⁻ (&gt;1:1) has no effect on recovery</td>
<td>25% cost reduction than using Mg chemical</td>
<td>Lahav et al., 2013</td>
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*NR Not Reported
Table 2 Composition of alternative Mg sources used for struvite production

<table>
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<tr>
<th>Composition</th>
<th>Wood ash, ppm</th>
<th>Bittern, ppm</th>
<th>By-product of MgO production, ppm</th>
<th>Magnesite, ppm</th>
<th>Magnesia (MgO), ppm</th>
<th>Seawater, ppm</th>
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<tr>
<td>Mg</td>
<td>34200</td>
<td>9220-44000</td>
<td>67670(^1)</td>
<td>94000(^3)</td>
<td>898000-634000(^1)</td>
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<td>Ca</td>
<td>27400</td>
<td>10-650</td>
<td>95800(^4)</td>
<td>10000-15000(^3)</td>
<td>15000-87000(^3)</td>
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<td>Al(_2)O(_3)</td>
<td>10800(^5)</td>
<td>3700</td>
<td>2600</td>
<td>7000-38000</td>
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<td>Fe(_2)O(_3)</td>
<td>6090(^2)</td>
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<td>3000-8000</td>
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<td>Cl(^-)</td>
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<td>Br</td>
<td>5300</td>
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</tbody>
</table>

Reference: Sakthivel et al., 2011; Li and Zhao, 2002; Etter et al., 2011; Huang et al., 2014; Quintana et al., 2008; Gunay et al., 2008; Huang et al., 2010b; Romero Guiza et al., 2015; Li and Zhao, 2002

\(^1\) as MgO; \(^2\) as MgCO\(_3\); \(^3\) as CaO; \(^4\) as Al\(^{3+}\); \(^5\) as Fe; \(^6\) as SO\(_4\)\(^2-\)
Table 3 Different seed material used in struvite precipitation and their effects on recovery

<table>
<thead>
<tr>
<th>S. No</th>
<th>Seed used</th>
<th>Source of Struvite</th>
<th>Seed Size (µm)</th>
<th>Effects on struvite production</th>
<th>Reference</th>
</tr>
</thead>
</table>
| 1     | Struvite        | Synthetic liquor                    | 1000           | • Production of struvite fine as product  
• Seeding is insignificant (process appeared "self-seeding") | Regy et al., 2002          |
|       | Syn. liquor and | Sludge from wastewater plant        | 45-63          | • Crystals have similar shape with seed (no phase transformation during growth)               | Ali, 2005                  |
|       | Landfill leachate|                                     | 75-150         | • Effectiveness of seed requires consideration of pH (pH 9 being optimum)                    | Kim et al., 2006           |
|       | Synthetic liquor| NR                                  | 250-500        | • No enhancement of P recovery and reduction in induction time                               | Rahaman et al., 2008       |
|       | Coking wastewater|NR                                   | 200-300        | • Increase in recovery by approximately 5% (at pH 9.5)  
• No effect of overdosing of seed on recovery (pH 9.5) | Zhang et al., 2009          |
|       | Synthetic wastes| NR                                  | 30-50          | • Reduced induction time up to 75 minutes depending upon super-saturation                     | Liu et al., 2011           |
|       | Fertilizer wastewater| NR                               | 1000 um hole   | • No significant increase in crystallization  
• Reduction in struvite fine particle  | Le Corre et al., 2007      |
| 2     | Coarse sand     | Synthetic liquor                    | 200-300        | • No fixation of struvite on sand surface                                                    | Regy et al., 2002          |
| 3     | Fine sand       | Synthetic liquor                    | 150-200        | • Strong primary nucleation and formation of fine                                              | Regy et al., 2002          |
| 4     | Borosilicate    | Synthetic liquor                    | 45-63          | • Slower reaction rate compared to struvite seed                                              | Ali, 2005                  |
| 5     | Sand grain/Quartz particle| Sludge liquor in wastewater plant | 210-350        | • Recovery of 80% of P onto seed bed                                                           | Battistoni et al., 2000    |
|       | Synthetic liquor| 45-63                               |                | • Slower reaction rate compared to struvite seed                                               | Ali, 2005                  |
| 6     | Phosphate rock  | Dairy effluent                      | NR             | • No effect mentioned on crystal                                                              | Massey et al., 2007        |
| 7     | Stainless steel mesh| Synthetic liquor                  | 1000 um hole   | • No significant increase in crystallization  
• Reduction in struvite fine particle  | Le Corre et al., 2007      |
| 8     | Pumice stone    | Synthetic liquor                    | NR             | • No effect of seed dosing on recovery  
• Co precipitation of Ca & silica on seed                                                        | Pakdil and Filibeli, 2008  |
Table 4 Composition of struvite recovered from various sources

<table>
<thead>
<tr>
<th>Elements</th>
<th>Sources</th>
<th>Municipal Wastewater derived struvite, ppm</th>
<th>Landfill Leachate derived struvite ppm</th>
<th>Anaerobically digested cattle manure and fish waste derived struvite, ppm</th>
<th>Human Urine derived struvite, ppm</th>
<th>Yeast industry anaerobic effluent, derived struvite, ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>N</td>
<td></td>
<td>29000-57500</td>
<td>-</td>
<td>51128</td>
<td>29000</td>
<td>35000</td>
</tr>
<tr>
<td>P</td>
<td></td>
<td>91000-128000</td>
<td>-</td>
<td>123684</td>
<td>71000-126000</td>
<td>108000</td>
</tr>
<tr>
<td>Mg</td>
<td></td>
<td>99000</td>
<td>-</td>
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<td>79700</td>
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<td>K</td>
<td></td>
<td>100-7000</td>
<td>-</td>
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<td>2000-15000</td>
<td>12100</td>
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<tr>
<td>Ca</td>
<td></td>
<td>2000-8400</td>
<td>-</td>
<td>14</td>
<td>16000</td>
<td>21800</td>
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<tr>
<td>Na</td>
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<td>-</td>
<td>-</td>
<td></td>
<td>8980</td>
<td>11100</td>
</tr>
<tr>
<td>S</td>
<td></td>
<td>-</td>
<td>-</td>
<td></td>
<td>1350</td>
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</tr>
<tr>
<td>Fe</td>
<td></td>
<td>300-2018</td>
<td>346</td>
<td>114</td>
<td>14-1050</td>
<td>300</td>
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<tr>
<td>Al</td>
<td></td>
<td>100-1161</td>
<td>269-312</td>
<td>316</td>
<td>11-558</td>
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<tr>
<td>Mn</td>
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<td>113-236</td>
<td>32-33</td>
<td>16</td>
<td>0.1-92.3</td>
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<td>B</td>
<td></td>
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<td>505-507</td>
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<tr>
<td>Cd,</td>
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<td>0.01-0.7</td>
<td>0.02-0.2</td>
<td>BDL</td>
<td>0.2</td>
<td>&lt;1</td>
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<tr>
<td>Cu</td>
<td></td>
<td>0.9-80</td>
<td>5.7-6.6</td>
<td>20</td>
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<tr>
<td>Co</td>
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<td>0.1</td>
<td>0.4-2.5</td>
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<td>0.3-1.7</td>
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<td>Zn</td>
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<td>3.3-100</td>
<td>4.1-16.2</td>
<td>98</td>
<td>7-142</td>
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<td>As</td>
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<td>0.3-1</td>
<td>0.8-2.8</td>
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<td>Ni</td>
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<td>0.3-9.4</td>
<td>2.5-2.9</td>
<td>BDL</td>
<td>0.8-2.3</td>
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<tr>
<td>Ag</td>
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<td>0.9-6.3</td>
<td>&lt;25</td>
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<td>2-6</td>
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<tr>
<td>Cr</td>
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<td>1.8-11</td>
<td>4.9-5.3</td>
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<td>&lt;10</td>
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<td>Ur</td>
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<td>-</td>
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<td>-</td>
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<td>Li</td>
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<td>0.4</td>
<td>-</td>
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<td>1-2.1</td>
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</tr>
<tr>
<td>Hg</td>
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<td>0.01</td>
<td>-</td>
<td></td>
<td>4.2</td>
<td>&lt;1.5</td>
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<tr>
<td>Sn</td>
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<td>9.1</td>
<td>-</td>
<td></td>
<td>1.4</td>
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</table>

References: Britton et al., 2005; Fattah et al., 2008; Forrest et al., 2008; Benisch et al., 2010; Prater, 2014; Estevez et al., 2014; Antonini, 2012; Uysal et al., 2014

BDL: Below detection limit
<table>
<thead>
<tr>
<th>S No</th>
<th>Crop/plant</th>
<th>Struvite source</th>
<th>Type of Experiment</th>
<th>Chemical fertilizer used</th>
<th>Soil type/Growing media</th>
<th>Effect of struvite on crop/plant</th>
<th>Remark</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Gram (Cicer arietinum L.)</td>
<td>Synthetic water</td>
<td>Pot</td>
<td>Single superphosphate, Di ammonium phosphate, Ammonium polyphosphate</td>
<td>Typical acid</td>
<td>Variation of P uptake with level of P application</td>
<td>Superior or equally effective as chemical fertilizer</td>
<td>Ghosh et al., 1996</td>
</tr>
<tr>
<td>2</td>
<td>Chinese flowering cabbage (Brassica parachinensis)</td>
<td>Municipal landfill leachate</td>
<td>Pot</td>
<td>Ammonium nitrate+ Calcium phosphate</td>
<td>Sandy clay (Red Earth) (pH 6.2)</td>
<td>Similar vegetable growth and more Mg, P uptake compared to chemical fertilizer</td>
<td>Comparable effect with chemical fertilizer</td>
<td>Li and Zhao, 2003</td>
</tr>
<tr>
<td>3</td>
<td>Water convolvulus (Ipomea aquatica, I. reptans)</td>
<td>Municipal landfill leachate</td>
<td>Pot</td>
<td>_</td>
<td>Sandy clay (Red Earth) (pH 6.2)</td>
<td>No significant difference in growth and no burning effect with increase in struvite dose</td>
<td>Higher dose of struvite does not affect plant</td>
<td>Li and Zhao, 2003</td>
</tr>
<tr>
<td>4</td>
<td>Water spinach (Ipomoea aquatica)</td>
<td>Municipal landfill leachate</td>
<td>Pot</td>
<td>Ammonium nitrate+ Calcium phosphate</td>
<td>Sandy clay (Red Earth) (pH 6.2)</td>
<td>Similar vegetable growth and more Mg, P uptake compared to chemical fertilizer</td>
<td>Comparable effect with chemical fertilizer</td>
<td>Li and Zhao, 2003</td>
</tr>
<tr>
<td>5</td>
<td>Chinese chard (Brassica rapavar. chinensis)</td>
<td>Municipal landfill leachate</td>
<td>Pot</td>
<td>Ammonium nitrate+ Calcium phosphate</td>
<td>Sandy clay (Red Earth) (pH 6.2)</td>
<td>Similar vegetable growth and more Mg, P uptake compared to chemical fertilizer</td>
<td>Comparable effect with chemical fertilizer</td>
<td>Li and Zhao, 2003</td>
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<tr>
<td>6</td>
<td>Maize</td>
<td>NR</td>
<td>Greenhouse Pot</td>
<td>Diammonium phosphate</td>
<td>NR</td>
<td>P uptake is efficiency for struvite is 117% and residual P availability is 178%</td>
<td>Higher efficiency compared to chemical fertilizer</td>
<td>Barak and Stafford, 2006</td>
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<td></td>
<td></td>
<td>Equally effective with chemical fertilizer</td>
<td>Liu et al., 2011</td>
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<td></td>
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<td></td>
<td>Superphosphate &amp; Urea</td>
<td>Sandy loam</td>
<td>Similar plant height, higher biomass, less N₂O emission as with chemical fertilizer</td>
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<td></td>
<td>Field</td>
<td>Triple superphosphate (Andosol)</td>
<td>No significant difference in dry yield compared to chemical fertilizer</td>
<td>Similar effect with chemical fertilizer, P in struvite is not limiting for plant</td>
<td>Gell et al., 2011</td>
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<td>Field</td>
<td>Triple superphosphate (Andosol)</td>
<td>No significant difference in dry yield compared chemical fertilizer</td>
<td>Similar effect with chemical fertilizer, P is not limiting</td>
<td>Gell et al., 2011</td>
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<td></td>
<td>Small plot</td>
<td>Diammonium phosphate</td>
<td>Similar leaf diameter and height with chemical fertilizer</td>
<td>Comparable to chemical fertilizer</td>
<td>Dalecha et al., 2012</td>
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<td>Field</td>
<td>Triple superphosphate</td>
<td>Plant P uptake is higher than chemical fertilizer by 4-21% depending upon application rate</td>
<td>Nutrient availability is similar to chemical fertilizer</td>
<td>Thompson, 2013</td>
</tr>
<tr>
<td>Plant Type</td>
<td>Waste/Manure Type</td>
<td>Growth Conditions</td>
<td>Fertilizer/Amendment</td>
<td>Note</td>
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<tr>
<td>Wheat (Triticum aestivum L.)</td>
<td>Urine</td>
<td>Climate chamber Pot</td>
<td>NPK mixture (14-4-21)</td>
<td>Lower dry weight (by 50%) than chemical fertilizer</td>
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<tr>
<td></td>
<td>Dairy wastewater</td>
<td>Greenhouse Pot</td>
<td>Triple superphosphate, Rock phosphate</td>
<td>Low availability of nutrients (N) than chemical fertilizer</td>
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<tr>
<td></td>
<td>Greenhouse Pot</td>
<td>Fine-loamy over sandy or sandy-skeletal, mixed, mesic Aridic Argiustoll</td>
<td>Increase in total P uptake in basic soil</td>
<td>Similar effect with chemical fertilizer</td>
<td></td>
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<tr>
<td>Perennial Ryegrass (Lolium Perenne)</td>
<td>Municipal sewage sludge</td>
<td>Glasshouse Pot</td>
<td>Monocalcium phosphate</td>
<td>Increase in total P uptake in basic soil</td>
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<tr>
<td></td>
<td>Synthetic liquor and municipal sewage sludge</td>
<td>Glasshouse Pot</td>
<td>sandy loam and sandy clay loam</td>
<td>Similar dry matter yield and P uptake as with chemical fertilizer</td>
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<tr>
<td></td>
<td>Poultry manure</td>
<td>Greenhouse pot</td>
<td>Sand</td>
<td>Similar effect on crop yield as with chemical fertilizer</td>
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<td>White lupin (Lupinus albus L.)</td>
<td>Wastewater</td>
<td>Greenhouse Pot</td>
<td>Calcium superphosphate</td>
<td>Similar effect with chemical fertilizer</td>
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<td>Municipal sewage sludge</td>
<td>Field</td>
<td>Single superphosphate</td>
<td>Similar effect with chemical fertilizer</td>
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<tr>
<td>Oil seed rape</td>
<td>Municipal sewage sludge</td>
<td>Triple superphosphate, Rock phosphate</td>
<td>P-deficient loamy sand</td>
<td>Increase in weight and rate of increase is dependent upon type of plant, soil media</td>
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<td>Purslane (Portulaca oleracea)</td>
<td>Poultry manure</td>
<td>Greenhouse pot</td>
<td>Sand</td>
<td>Increase in weight and rate of increase is dependent upon type of plant, soil media</td>
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<tr>
<td>Garden cress (Lepidum sativum)</td>
<td>Poultry manure</td>
<td>Greenhouse pot</td>
<td>Sand</td>
<td>Increase in weight and rate of increase is dependent upon type of plant, soil media</td>
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<tr>
<td>Winter barley</td>
<td>Municipal sewage sludge</td>
<td>Field</td>
<td>Triple superphosphate, Rock phosphate</td>
<td>Similar P uptake and grain yield compared to chemical fertilizer/rock phosphate</td>
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<tr>
<td>Lettuce (Lactuca sativa L.)</td>
<td>Anaerobicallly digested</td>
<td>Greenhouse pot</td>
<td>Single superphosphate</td>
<td>More efficient than chemical fertilizer in increasing yield &amp;</td>
<td></td>
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<tr>
<td></td>
<td></td>
<td>P-deficient loamy sand</td>
<td></td>
<td>Comparable to chemical fertilizers or</td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>

Ganrot et al., 2007
Massey et al., 2009
Plaza et al., 2007
Johnston and Richards, 2003
Yetilmezsoy and Zengin, 2009
Gonzalez and Garcia, 2008
Perez et al., 2009
Yetilmezsoy and Zengin, 2009
Perez et al., 2009
Gonzalez et al., 2009
<table>
<thead>
<tr>
<th>No.</th>
<th>Plant</th>
<th>Sludge/Manure Source</th>
<th>fertilizer</th>
<th>Soil</th>
<th>P uptake Comments</th>
<th>Notes</th>
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<tbody>
<tr>
<td>15</td>
<td>Garden rocket (<em>Eruca sativa</em>)</td>
<td>Anaerobic Sludge of poultry manure</td>
<td>Greenhouse pot</td>
<td>Ammonium nitrate+ Potassium dihydrogen orthophosphate</td>
<td>Garden soil (pH 5.5-6)</td>
<td>More gain in plant wet, dry weight and height compared to chemical fertilizer</td>
</tr>
<tr>
<td>16</td>
<td>Dill (<em>Anethum graveolens</em>)</td>
<td>Anaerobic Sludge of poultry manure</td>
<td>Greenhouse pot</td>
<td>–</td>
<td>Garden soil (pH 5.5-6)</td>
<td>Increase in dry weight by 191% compared to no fertilizer</td>
</tr>
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<td>17</td>
<td>Fennel (<em>Foeniculum vulgare</em>)</td>
<td>Anaerobic Sludge of poultry manure</td>
<td>Greenhouse pot</td>
<td>–</td>
<td>Garden soil (pH 5.5-6)</td>
<td>Increase in dry weight by 208% compared to no fertilizer</td>
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<td>18</td>
<td>Parsley (<em>Petroselinum crispum</em>)</td>
<td>Anaerobic Sludge of poultry manure</td>
<td>Greenhouse pot</td>
<td>–</td>
<td>Garden soil (pH 5.5-6)</td>
<td>Increase in dry weight by 379% compared to no fertilizer</td>
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<td>19</td>
<td>Canola</td>
<td>Swine manure</td>
<td>Pot</td>
<td>Monoammonium phosphate, polymer-coated monoammonium phosphate</td>
<td>Sandy loam</td>
<td>Similar P uptake but lower biomass yield/unit of P uptake compared to chemical fertilizer because of lower solubility at basic soil</td>
</tr>
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<td>20</td>
<td>Tomato</td>
<td>Yeast industry wastewater</td>
<td>Pot</td>
<td>Potassium phosphate, ammonium nitrate</td>
<td>Light alkali nutrient poor soil (pH 8.4)</td>
<td>Higher N, P and Mg uptake of plant for double/triple and quadruple dose of struvite compared to NPK treatment</td>
</tr>
</tbody>
</table>

NR: Not Reported