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

3 SAMPRITI KATAKI¹, HELEN WEST², MICHÈLE CLARKE³, DC BARUAH^{1*}

4 ¹*Energy Conservation Laboratory, Department of Energy, Tezpur University, Assam, India*

5 ²*School of Biosciences, University of Nottingham, Sutton Bonington Campus, Leicestershire,*
6 *LE12 5RD, UK*

7 ³*School of Geography, University of Nottingham, University Park, Nottingham NG7 2RD,*
8 *UK*

9 *Correspondence: DC Baruah, tel. +91 9435508563, fax +91 3712 267005,*

10 *E-mail: baruahd@tezu.ernet.in (DC Baruah)*

11

12 **Abstract**

13 Finite availability of phosphorus (P) resources makes recovery of this non-
14 substitutable plant nutrient from alternative waste sources an increasingly attractive option
15 of renewed interest. In this context, feasibility of struvite ($\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$) recovery, an
16 alternative P fertilizer is already demonstrated at laboratory scale from range of waste
17 streams of farm, municipal and industrial origin, with reasonably high orthophosphate
18 recovery efficiency (~90%). However, apart from a few commercial extraction units using
19 municipal sludge and urine, large scale struvite recovery is not widely adopted for many of
20 these sources. Moreover, need of some research interventions that are restricting its
21 profitable recovery are also highlighted by earlier studies. To increase recovery efficiency

1 from identified potential sources in terms of cost and energy input, research focuses on
2 some new aspects of the process such as prospects of alternative recyclable magnesium
3 sources, different seed materials and their related issues, which are analyzed in this review.
4 Prospects of nitrogen conservation through struvite recovery and fertilizer value of struvite
5 considering its properties, comparative performance with conventional fertilizer and
6 interaction with soil and plant growth are also critically reviewed.

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

8 **1. Introduction**

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

15 Presently the only source of commercial P fertilizer is natural phosphate rock spread
16 in handful of countries. China, USA, Morocco and Russia are contributing about 75% of
17 world total P production (Heckenmüller et al., 2014). Consumption of P fertilizer is seen
18 somewhat stabilized in the developed countries, but its demand in the developing world is
19 seen increasing (Heffer and Prud'homme, 2010). The actual extent of commercially viable
20 global phosphate reserve remains a subject of substantial uncertainty in the recent years
21 (Vaccari, 2009; Schröder et al., 2010). However, exhaustion of global reserves of rock
22 phosphate or a peak P is expected to occur considering increasing demand for P fertilizer and
23 finite non renewable natural reserve of rock phosphate (Cordell and White, 2011;

1 Heckenmuller et al., 2014). ‘Peak phosphorus’ as analogous to ‘peak oil’, means the point of
2 time when maximum production or extraction rate of phosphorus is reached after which rate
3 of production declines. There could be ambivalence among researchers about the timing of
4 peak phosphorus; however, there is no dispute about its occurrence. This is due to
5 decreasing global P stock associated with ever increasing population and subsequent growth
6 of food demand. Therefore, need of the moment is to investigate opportunities for its
7 sustainable management, considering cost-effective, energy efficient and environmentally
8 compatible means of P recycling.

9 P conservation methods identify recycling of P from viable P sources as an option,
10 which tries to convert P from a source into a product with enhanced nutrient values. Struvite
11 or ammonium magnesium phosphate (AMP) hexahydrate ($\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$) recovery is one
12 of the available methods of P recovery (de Bashan & Bashan, 2004). Equi-molar
13 concentrations (1:1:1) of magnesium (Mg), phosphorous (P), and ammonium (NH_4^+) with
14 alkaline pH and appropriate mixing are required to precipitate struvite (Rahaman et al.,
15 2008). Struvite, being a slow release fertilizer, can contribute to crop productivity
16 enhancement. Besides its prospect as fertilizer, recovery of struvite has some additional
17 advantages. Such recovery is environmentally useful since the waste becomes suitable for
18 safe disposal after extraction of excess nutrients (Gell et al., 2011). Woods et al. (1999)
19 demonstrated that P recovery from sewage sludge resulted in reduction of sludge volume up
20 to 49% when calcium phosphate recovery was used following conventional biological
21 treatment. Reduction in sludge volume minimizes the operating cost of waste treatment unit.
22 Struvite recovery from municipal waste sludge at global scale is expected to reduce about
23 1.6% of worldwide phosphate rock mining (Shu et al., 2006). Thus, integration of a such
24 recovery process along with waste management system would help in cost efficient relocation

1 of excess nutrients (Burns and Moody, 2002) by closing the P loop in soil–crop–animal–
2 human–soil cycle (Shu et al., 2006).

3 Importance of developing a slow release N and P fertilizer to meet the projected
4 global crop production is also justified by previous study (Tilman et al., 2002). Previously
5 struvite precipitation was seen in wastewater treatment plant as a problematic spontaneous
6 deposition due to prevailing favourable conditions of struvite formation. Until 2006, majority
7 of the research works focussed on the mitigation strategies of struvite precipitation, as the
8 system efficiency of wastewater treatment plant is reduced due to clogging of conduits by
9 struvite crystals (Doyle and Parsons, 2002). Several control strategies including addition of
10 Fe/Al salt, phosphate fixation with sludge, uses of chemical inhibitors and ultrasonic
11 technology have been attempted with varying degree of success. The difficulties in P
12 recovery from Fe/Al salt and environmental issues of safe disposal of sludge are faced while
13 adopting the above mitigation strategies besides increase in sludge volume (Ohlinger et al.,
14 1998; Wu et al., 2005). In absence of an effective mitigation strategy, designed recovery of
15 struvite has been attempted after increased understanding of the process conditions of struvite
16 formation (Moerman et al., 2012). The associated benefits as mentioned earlier also
17 motivated to adopt ‘struvite production’ as a resource recovery option.

18 The bio-geochemical P cycle deposits significant amount of P in some easily
19 accessible and abundant natural sources. Recycling of P from such natural source seems to
20 be a potential option to restrict P outflow from the P sedimentary cycle. A range of waste
21 streams of natural origin contains excessive P, which requires reduction before safe
22 disposal. Feasibility of struvite recovery from about twenty sources of farm, municipal and
23 industrial origin has been established at laboratory scale. The precipitation process is
24 simple in majority of the cases. However, modification of process is required due to
25 inherent heterogeneity of some typical sources. Depending upon the characteristics of the

1 source, pre-treatments such as anaerobic digestion (Beal et al., 1999), acid base leaching
2 (Zhang et al., 2010), chelating agent treatment (Zhang et al., 2010), microwave treatment
3 (Lo et al., 2011) and enhanced biological phosphorus removal (Pastor et al., 2008) are
4 required in order to nullify the effect of non-participating ions such as calcium (Ca) and
5 iron (Fe). In general, to ensure the required molar ratio for struvite precipitation, addition
6 of Mg is required for effective struvite recovery in all Mg deficient sources. Moreover,
7 supplementation of P (and/or NH_4^+ salt) is also required for sources with inadequate P
8 (and/or inadequate NH_4^+) which is generally seen for industrial waste sources. Municipal
9 waste water is the mostly used struvite recovery source and farm wastes (cattle, swine,
10 poultry manure, urine) represent the most accessible and abundant stock. However, these
11 sources often need pre-treatments due to presence of limiting interfering ions (Zhang et al.,
12 2010; Shen et al., 2011). On the other hand, addition of P salt ($\text{NaH}_2\text{PO}_4/\text{KH}_2\text{PO}_4/\text{H}_3\text{PO}_4$) or
13 NH_4^+ salt (NH_4Cl) becomes necessary for many sources of industrial origin (wastewater
14 from dye, fertilizer, textile, food, tanning, coking, beverage industry), to balance their low
15 inherent nutrient contents (Kabdasli et al., 2000; Chimenos et al., 2003; Folleto et al.,
16 2013; Kumar et al., 2013).

17 Previous studies have shown feasibility of struvite production at laboratory scale
18 successfully, though full scale installations are limited. At present, municipal wastewater
19 sludge and human urine are the two sources used for commercial struvite recovery, though at
20 a very limited scale. However, recovery of struvite exhibits some difficulties mainly due to
21 heterogeneous characteristics of source. Further, requirements of additional chemical inputs
22 and low recovery efficiency make the process uneconomical. Therefore, in recent times, there
23 are increasing concerns towards the techno-economical aspects of the recovery process to
24 increase process efficiency and cost reduction. Significant progress has been made on three
25 aspects of the recovery processes *viz.*, (a) modification of struvite precipitation mechanism

1 for improvement of reaction conditions, (b) investigation on additional benefits of struvite
2 recovery process for its further promotion and (c) prospects of struvite as alternative sources
3 of crop nutrients in view with the regulatory limits of fertilizer. Based on these aspects, this
4 review highlights the development in researches on (a) modification of struvite recovery
5 mechanism for improvement of crystallization with incorporation of alternative Mg sources
6 and seed material, (b) struvite precipitation as a method of nitrogen preservation and (c)
7 assessment of fertilizer value of struvite on a range of crops, considering struvite properties,
8 composition, soil and plant interaction and comparative performance with chemical fertilizer.
9 Attempt is made to analyse the practical relevance and significance of these aspects to help
10 making informed decisions about future directions for struvite research and development.

11 **2. Modification of struvite precipitation mechanism for efficiency** 12 **enhancement**

13 **a) Alternative magnesium sources for struvite recovery**

14 Concept of intentional struvite precipitation has been conceived from the occurrence
15 of spontaneous struvite accumulation in anaerobic digestion units of wastewater treatment
16 plant as mentioned earlier. Struvite incrustation creates nuisance by reducing system
17 efficiency and increasing operational cost (Jaffer, 2002). In such systems, regions of high
18 turbulent flow such as valves, joints of pipe, aeration assemblies are the most prone locations
19 of struvite formation, when concentrations of Mg^{2+} , NH_4^+ and PO_4^{3-} are favourable and pH
20 and mixing energy are appropriate (Bhuiyan, 2007). Availability of nutrients is enhanced
21 after digestion, (Wu et al., 2005; Masse et al., 2007) due to mineralization of organic bound
22 nutrients (Lukehurst et al., 2010; Seadi et al., 2012) which increases the potential of struvite
23 formation (Bhuiyan et al., 2007). Thus, anaerobically digested source becomes suitable for
24 struvite recovery (Doyle et al., 2002; Pastor et al. 2008; Wang et al., 2013). In anaerobic

1 digestion of municipal sludge, there remains sufficient mineralized Mg and P
2 (orthophosphate) released from sludge that react with NH_4^+ released from degradation of
3 nitrogenous material to precipitate struvite spontaneously.

4 However, in practice, for intentional struvite production, most of the potential struvite
5 recovery sources need input of chemical in the form of alkali source for pH adjustment, Mg
6 source and other participating ion (NH_4^+ and PO_4^{3-}) to reach desired molar ratio (Mg : PO_4^{3-} :
7 NH_4^+) to induce struvite precipitation. Supply of Mg is essentially required to make the
8 precipitation effective, due to lack of adequate Mg in majority of the potential struvite
9 sources compared to PO_4^{3-} and NH_4^+ . Thus, indispensable Mg consumption makes the
10 precipitation often expensive (Quintana et al., 2004).

11 The most common Mg sources used in struvite studies are salts of Mg, such as MgCl_2 ,
12 MgSO_4 and MgO. Commercially available struvite recovery technologies *viz.* Phosnix (used
13 in Japan), Pearl Ostara (used in North America, UK), Phospaq, (used in Netherlands),
14 Seaborne (used in Germany), AirPrex (used in Germany, Netherlands) and Multiform (used
15 in America) also employ use of these pure-chemicals. These chemicals are also extensively
16 used in laboratory feasibility studies of struvite production, mainly due to high reactivity, Mg
17 content and purity. However, it has been reported that cost of high-grade Mg compounds
18 contribute up to 75% of overall production costs, limiting large-scale use economically
19 nonviable (Dockhorn, 2009). Therefore, high input cost of such Mg sources has prompted to
20 search for alternative Mg compounds (Quintana et al., 2004). Alternative Mg sources used in
21 struvite recovery are listed in Table 1, along with their Mg concentration, effect on recovery
22 process and type of source where these are used to precipitate struvite. These renewable Mg
23 sources include sea water, bittern, magnesite (MgCO_3) or by-products of magnesite and Mg
24 saturated supporting materials (Bentonite, Stevensite and Sepiolite) (Maqueda et al., 1994;

1 Quintana et al., 2004; Gunay et al., 2008; Huang et al., 2010b; Etter et al., 2011). Mg
2 availability, solubility and reactivity of the Mg sources play a significant role on the
3 feasibility of their uses (Romero-Güiza et al., 2015).

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

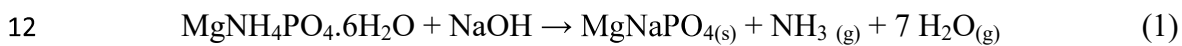
5 In seawater, Mg is the second most abundant cation (Mg content $\sim 1300 \text{ mg l}^{-1}$) that
6 enters from weathering of Mg-rich minerals (Shin and Lee, 1997; Kumashiro et al., 2001).
7 Bittern (Mg content $9220\text{-}32000 \text{ mg l}^{-1}$) is the commercial source of Mg, it is the solution
8 remains after crystallization of sodium chloride from brines and seawater. Total PO_4^{3-}
9 recovery of 95 and 99% were reported from coke manufacturing waste water, using sea
10 water and bittern, respectively (Shin and Lee, 1997), which are comparable with the
11 recoveries made using conventional Mg salts. However, due to presence of insoluble Mg in
12 bittern and seawater, the process needs high Mg dose ($\text{Mg} : \text{PO}_4^{3-} > 1.5:1$) for efficient P
13 recovery (Matsumiya et al., 2000; Kumashiro et al., 2001; Quintana et al., 2004). Though
14 their uses are yet to be shown at commercial scale, these two can serve as prospective and
15 economic Mg sources in regions neighboring sea (Shin and Lee, 1997; Matsumiya et al.,
16 2000; Li and Zhao, 2002; Lee et al., 2003; Etter et al., 2011; Crutchik and Garrido, 2011).
17 Seawater and bittern have also been shown effective for struvite precipitation in swine
18 wastewater, coke wastewater, urine, landfill leachate and municipal wastewater as shown
19 in Table 1.

20 Magnesite (MgCO_3) is a natural mineral generated as a by-product during MgO
21 production which is 94% MgCO_3 by mass. Solubility of magnesite is low in water
22 requiring high dose for struvite precipitation. Acid dissolution and thermal-decomposition
23 (calcination) have been suggested as effective measure to increase solubility of Mg (Gunay
24 et al., 2008; Huang et al., 2010b). Addition of acid dissolves about 99% Mg of magnesite

1 into soluble form and thereby 50% increase in struvite formation as compared to untreated
2 magnesite has been achieved (Gunay et al. 2008). The market prices of such magnesite
3 reckoned per unit of Mg have also been estimated as equivalent to about one-tenth of pure
4 $MgCl_2$ (Huang et al., 2010b). Use of acid dissolved magnesite in struvite production cuts
5 down the overall production cost. However, it leads to higher alkali consumption so as to
6 achieve required alkaline condition neutralizing the acid used for magnesite
7 decomposition. Therefore, overall benefit from cost reduction is somewhat curtailed
8 (Huang et al., 2010b). Thermally decomposed magnesite produces magnesia (MgO) with
9 higher solubility and reactivity which yield similar recovery of PO_4^{3-} and NH_4^+ (99.7% and
10 90.2%, respectively) (Huang et al., 2010b). Magnesia preparation methods (calcinations
11 temperature and time) influence the recovery performance (Huang et al., 2010b). In case of
12 thermal decomposition of magnesite, above certain optimum temperature and time (700°C
13 and 1.5 hours in case of rare earth wastewater), struvite production reaction rate slows
14 down because of increase in surface area of magnesia (Huang et al., 2010b). Recovery is
15 further influenced by reaction condition of magnesite (reaction time, mixing energy, dose
16 of magnesia) (Quintana et al., 2008, Huang et al., 2010b). There is increase in recovery up
17 to certain reaction time and magnesite dose (6 hours and 52 g l⁻¹ as reported for rare earth
18 wastewater), above which no significant increase in struvite recovery is found (Huang et
19 al., 2010b). Struvite production using raw magnesite reduces process cost up to 18%
20 (Gunay et al., 2008), with further reduction up to 34% when thermally decomposed
21 magnesite is used as Mg source compared to $MgCl_2$ (Huang et al., 2010b).

22 Uses of thermal decomposition or pyrolysis product of struvite *viz.* $MgHPO_4$ and
23 $Mg_2P_2O_7$ have been reported as recycled Mg sources for struvite production (Zhang et al.,
24 2009; Huang et al., 2009; Yu et al., 2012). Primarily pyrogenation of struvite as Mg source
25 has been reported to use for NH_4^+ stripping in the form of struvite from NH_4^+ rich waste such

1 as industrial effluents, with simultaneous recovery of P. For pyrolysis of struvite, two
2 approaches *viz.* direct pyrolysis and NaOH assisted pyrogenation of struvite are reported to
3 generate required Mg source (Türker and Çelen, 2007; He et al., 2007; Zhang et al., 2009; Yu
4 et al., 2012). Struvite pyrolysis under alkali condition produces MgNaPO₄ as per reaction
5 shown in Eq. (1) (Huang et al., 2011b). When MgNaPO₄ is used in a medium containing
6 NH₄⁺, it is converted to more stable struvite by replacing Na⁺ with NH₄⁺. It has been reported
7 that the stability of struvite analogues generally declines with the reduction in the size of the
8 univalent ion (Banks et al., 1975). Therefore, MgNaPO₄ is converted to more stable struvite
9 by taking NH₄⁺ ions from source as the size of NH₄⁺ is larger than that of Na. It is also noted
10 that saving of processing cost up to 48% has been estimated using struvite pyrolysate (He et
11 al., 2007; Huang et al., 2009).



13 The optimum conditions for struvite recovery by struvite pyrolysate vary with
14 respect to recovery-source. For landfill leachate, up to 96% NH₄⁺ removal has been
15 reported under optimum conditions (OH⁻: NH₄⁺ = 1:1, temperature=90⁰C and time=2
16 hours) (He et al., 2007). Again, up to 87% of NH₄⁺ recovery has been reported for yeast
17 industry anaerobic effluent with corresponding optimum conditions (OH⁻: NH₄⁺ = 1.5:1,
18 temperature = 110⁰C, time = 3 hours and pH = 9) (Uysal and Demir, 2013). However, in
19 case of repeated use of struvite pyrolysate, the NH₄⁺ removal efficiency decreases in the
20 subsequent recycling cycles (He et al., 2007; Huang et al., 2011b). This is because of
21 accumulation of inactive Mg₂P₂O₇ and Mg₃(PO₄)₂ in recycled pyrolysate (Sugiyama et al.,
22 2005; Yu et al., 2012). Acidolysis can increase the re-usability of struvite pyrolysate for
23 NH₄⁺ removal which removes NH₄⁺ part of struvite and transforming it into MgHPO₄,
24 which can be further used for NH₄⁺ recovery (Zhang et al., 2004; Yu et al., 2012). A

1 combined technology is suggested to use bittern as Mg source and internal recycling of
2 chlorination product of the recovered struvite to remove ammonia from swine wastewater
3 (Huang et al., 2015). Chlorination decomposition products of struvite are Mg^{2+} and HPO_4^{2-} ,
4 which keep levels of the Mg and PO_4^{3-} same in solution. This is why the process remains
5 efficient in removing excess NH_4^+ or PO_4^{3-} from solution for multiple cycles. This process
6 has been reported to be 37% more cost effective compared to struvite precipitation using
7 pure chemicals.

8 While adding Mg source, it is to be noted that, there might be addition of other non-
9 participating ion that may hinder the precipitation process. Table 2 gives the composition
10 of various Mg sources (wood ash, magnesite, seawater, bittern, magnesia and by-product
11 of MgO production (decomposed magnesite)) as reported in literature. Presence of Na,
12 SO_4^{2-} in these Mg sources may increase induction time (Kabdasli et al., 2006). Moreover,
13 Ca, K, Al present in the Mg source may co-precipitate in product as hydroxides,
14 phosphates and other salt reducing struvite purity (Kozik et al., 2013). Addition of bittern
15 may add chloride (by 1.0 %), sulfate (by 1.7%), potassium (by 2.6%) and sodium (by 13%)
16 in the struvite source (Etter et al., 2011). Ca and Na ions are prevalent in seawater (~400
17 $mg\ l^{-1}$), which could interfere in recovery process, by promoting formation of phosphates.
18 Magnesite also contains non desirable inhibiting ions such as Ca (1.5 mass%) and Fe (0.8
19 mass%) (Huang et al., 2010b). High concentration of heavy metal exceeding fertilizer
20 regulatory limit is reported in struvite produced using wood ash as Mg source (Sakthivel et
21 al., 2011). This may limit prospects of wood ash as Mg source. However, heavy metal
22 content can be reduced by a controlled wood ash production process (Sakthivel et al.,
23 2011).

24 (**Table 2.** Composition of alternative Mg sources used for struvite production)

1 From the above discussion, it is seen that, in struvite production high grade Mg can
2 be replaced by by-products of industrial process or other Mg rich renewable sources with a
3 similar NH_4^+ or PO_4^{3-} recovery efficiency. Nevertheless, optimum utilization would require
4 strategies for reactivity enhancement and removal for other non-participating impurity ions
5 (Ca, Fe, SO_4^{2-} etc.) from Mg source which have potential to hinder the recovery process.

6 **b) Use of seed in struvite crystallization**

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

18 Table 3 shows various seeds reported in struvite recovery along with their
19 specifications and effect on crystallization process. Among the reported seed materials in
20 struvite recovery, struvite fines are the most widely investigated seed (Regy et al., 2002;
21 Ali., 2005; Kim et al., 2006; Rahaman et al., 2008; Liu et al., 2010, Mehta et al., 2013; Yu
22 et al., 2013). Earlier investigations reported insignificant effect of seed on struvite
23 crystallization (Regy et al., 2002; Rahaman et al., 2008). Under no-seed conditions, the
24 largest struvite crystal with least fine formation was obtained compared to seeded

1 condition with coarse sand, fine sand, struvite and elutriated struvite (Regy et al., 2002).
2 This might be due to greater surface area for new crystal development provided by the
3 newly formed crystal nuclei than the seed crystals (Regy et al., 2002). However, there are
4 some reports that describe enhancement of recovery using struvite seeds. Use of struvite
5 seed could enhance the recovery by 5% and crystallization rate up to 21% compared to un-
6 seeded crystallization (Zhang et al., 2009, Yu et al., 2013). An isomorphic crystal plane of
7 struvite seed promotes adhesion and integration of growing molecules and clusters of
8 struvite without need of nucleation, which makes the process energetically favourable. The
9 shape of newly crystallized struvite remains similar to parent struvite seeds as seed allows
10 crystallizing molecules to inherit characteristics of seed (Ali, 2005; Mehta et al., 2013).
11 Increased surface area of struvite fines help in higher crystal accumulation resulting in
12 enhanced P recovery efficiency. Further, isomorphic crystal of seed struvite intensifies
13 crystallization, minimizing induction time (Liu et al., 2011). Induction time was reduced
14 by 75 minutes using struvite seed compared to un-seeded condition in struvite recovery
15 from fertilizer wastewater (Liu et al., 2011).

16 Some alternative seeds used in struvite recovery are sand, stainless steel mesh,
17 pumice stone and borosilicate glass with high surface area (Regy et al, 2002; Ali, 2005; Le
18 Corre et al., 2007; Pakdil and Filibeli, 2008). Compared to struvite seed, lower
19 crystallization rates and higher induction time are reported for non struvite seed (Ali,
20 2005). Use of non-isomorphic non struvite seed changes the type of nucleation from
21 homogeneous to heterogeneous (Ohlinger et al., 1999). Newly precipitating struvite nuclei
22 cannot integrate upon non-isomorphic seed to grow into bigger crystal and as a result the
23 unstable clusters of struvite nuclei break down or re dissolve which increases the induction
24 time (Ali, 2005).

1 **(Table 3. Different seeds used in struvite recovery and their effects on recovery)**

2 Surface roughness, dosing of the seed, grain size and super-saturation of
3 crystallizing solution directly influence the effectiveness of a seed, under similar process
4 conditions (Ohlinger et al., 1999). Deposition of crystal is directly proportional to relative
5 surface roughness of seed and stainless steel having the maximum roughness was found to
6 be most affective among constructional material followed by polyvinyl chloride and
7 acrylic plastic (Ohlinger et al., 1999). Surface roughness might help creation of local
8 turbulence or increase surface area providing nucleation sites for crystal development
9 (Ohlinger et al., 1999). Increasing the dose and grain size of struvite seed increase
10 ammonium and phosphate removal through struvite formation (Huang et al., 2010a). In
11 saponification wastewater generated from processing of rare-earth elements, maximum
12 ~3% increase in ammonium removal efficiency was achieved through formation of struvite
13 when struvite seed size was increased from a range of 0.05–0.098 mm to 0.098–0.150 mm.
14 Again, ammonium removal efficiency was enhanced by ~3% when the struvite seed dose
15 was increased from 15 g l⁻¹ to 60 g l⁻¹ (Huang et al., 2010a). The findings reported by Liu et
16 al., 2011 showed that, at a seed dosing of 0.42 g l⁻¹, the induction time was less by 49
17 minutes in a solution with higher super-saturation compared to a solution with lower super-
18 saturation.

19 From the above discussion it is seen that, seeding has effect on induction time and
20 recovery efficiency of struvite crystallization. However, process needs optimization with
21 respect to seed dose and size. The process of struvite crystallization through use of seed
22 material is energy and cost intensive process as amounts of seed requirement is often high
23 to make crystallization effective. Energy is needed to keep the seeds suspended in
24 crystallizing solution (Battistoni et al., 2005). Most of the reported findings of seed use in

1 struvite production are based on synthetic waste (Table 3). Therefore, further investigation
2 is required to investigate efficacy of seed material with varying parameter (such as pumice
3 stone, stainless steel mesh and borosilicate glass) in real waste source.

4 **3. Struvite precipitation as a method of nitrogen conservation**

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

21 In composting of food waste, formation of volatile fatty acid creates acidic
22 conditions initially, hindering the further composting process as the microbial growth is
23 inhibited (Xian-yuan et al., 2010; Wang et al., 2013). Alkaline materials such as lime, fly
24 ash) are used to negate the problem. However, rise in pH enhances loss of ammonia (Wang

1 et al., 2013). Ammonia loss was reported up to remains about 22% of initial N in food
2 compost (Jeong and Kim, 2001). However, this can be reduced to 4.8-5% by using struvite
3 precipitation (Jeong and Kim, 2001; Wang et al., 2013). For precipitation of struvite in
4 food waste compost, Mg and P sources are required to be supplemented from outside. With
5 increase in Mg and P, ammonia emission decreases, with simultaneous increase in struvite
6 production (Jeong and Hwang, 2005). However, high concentrations of Mg and P might
7 create salination causing reduction in microbial activity. This leads to immature compost
8 formation and usability of compost is compromised (Jeong and Kim, 2001; Jeong and
9 Hwang, 2005; Ren et al., 2010). For conserving compost value through struvite formation,
10 an optimum P and Mg dose equivalent to 20% of initial N is suggested (Jeong and Hwang,
11 2005). Up to 84% decrease in ammonia emission in poultry manure compost is achieved
12 by struvite precipitation depending upon the Mg and P doses (Zhang and Lau, 2007).

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

21 From the above discussion it is seen that struvite crystallization can be successfully
22 applied to food waste composting process to improve agronomic value. However, struvite
23 crystallization process has not been demonstrated for any other compost apart from food

1 waste compost. Care has to be taken for controlling salination that may arise from nutrient
2 supplementation ($\text{PO}_4^{3-}/\text{Mg}$) to induce struvite formation.

3 **4. Application of struvite as soil fertilizer**

4 **a) Struvite fertilizer properties**

5 Use of struvite as plant fertilizer was first suggested by Murray in 1857 (cited by
6 Bridger, 1962). Struvite as fertilizer is simple to produce, pure, easy to handle, as it is
7 concentrated, granular, non-sludgy and non-odorous (Bouropoulos and Koutsoukos.,
8 2000). Apart from field crop, struvite has been used as a fertilizer for potted plants,
9 orchards, and ornamental plants. As fertilizer, the N, P_2O_5 , K_2O and Mg content of pure
10 struvite are 5.7:29:0:16.4 respectively (Westerman, 2009). The P content of struvite
11 generally remains in the range of 11-26% (Johnston & Richards, 2003) depending upon
12 source and method of production, of which 1-2% is water soluble and rest is acid soluble
13 (Bridger et al., 1962). Struvite was, perhaps, first commercially manufactured under the
14 trade name *MagAmp*, a slow release fertilizer, using a patented manufacturing process by
15 WR Grace & Co., US (Peng et al., 1979). It was manufactured by adding MgO or
16 $\text{Mg}(\text{OH})_2$ to mono-ammonium phosphate. However, its high cost of production made its
17 application limited to high value crops (Peng et al., 1979).

18 The most advantageous nature of struvite fertilizer is its slow nutrient releasing
19 rate. Struvite is sparingly soluble in water with a solubility of 0.02g/100 ml of water at
20 0°C , rendering its slow assimilation into soil solution (Li and Zhao, 2002; Negrea et al.,
21 2010). Nitrification *i.e.* biological oxidation of ammonium fraction, a key step of soil
22 nitrogen cycle, releases nitrate ensuring a prolonged and assured nutrient supply for a
23 longer duration. This allows direct and higher application dose of struvite exceeding those
24 of conventional fertilizers without causing any harm to plant health (Li and Zhao, 2002;

1 Rafie et al., 2013). However, sometimes the limited availability of N because of low
2 N/P₂O₅ ratio of struvite makes N insufficient for optimal plant growth (Miso, 2009, Gell et
3 al., 2011), as in agriculture, the required amount of N is far higher than the P required.
4 When the struvite application dose is increased to fulfil plant N requirement, it results in
5 higher soil pH compared to other P fertilizer, which might affect nutrient availability and
6 uptake (Rahman et al., 2011). Gell et al., 2011 indicated possibility of Mg accumulation in
7 soil from long term struvite application, by showing change of Ca:Mg ratio from 4:1 to 2:1
8 over a short term field trial. In general, Ca:Mg in soil varies within the range of 0.5:1 to
9 20:1, not to affect the crop yields (Schulte and Kelling, 2004). When Mg concentration in
10 soil becomes much higher than Ca, it might affect hydraulic conductivity and aggregate
11 stability and as a result crop yield is affected (Zhang and Norton, 2002). Mg has high
12 hydration energy which results in clay swelling and subsequently soil porosity and
13 aggregation are affected (Zhang and Norton, 2002). Unbalanced Ca:Mg ratio is a matter of
14 concern as the Ca uptake by plants is compromised resulting a Ca deficiency in plants
15 (Stevens et al., 2005). Therefore, struvite in combination with other fertilizers is
16 recommended for optimal use. Struvite is used by fertilizer companies as additive or as a
17 substitute raw material in standard fertilizer production technology (Li and Zhao, 2002;
18 Rafie et al., 2013). The commercial struvite recovery technology of UK (Ostara Nutrient
19 Recovery Technology) uses additional salts of ammonium and potassium to formulate a
20 balanced NPK fertiliser suitable for agricultural use (Scope Newsletter, 2013). The cost of
21 such commercial product largely depends upon processing (drying, storage, creation of a
22 blended product) and transportation (Westerman, 2009).

23 The fertilizing effect of struvite varies with soil type due to differences in solubility
24 and sorption properties in soils. Struvite is most effective in soil of moderate or low pH but
25 its efficacy is limited in soils with marginal fertility and high pH. Solubility of struvite is

1 improved under acidic conditions, increasing fertilizer efficiency. Acidic conditions result
2 in enhanced P adsorption to soil and consequently its dissolution and availability (Bowden
3 et al., 1980). Struvite solubility is minimum (0.040 milli-molar) within the pH range of
4 8.2-8.8 (Le Corre et al., 2009), which can rise up to 1-10 mM at pH <5 (Borgerding, 1972;
5 Abbona et al., 1982). In acidic and neutral soil solution, struvite solubility remains in the
6 range of 65–100%, which is similar to that of conventional P fertilizer (triple
7 superphosphate) (Cabeza et al., 2011). This implies that, under acid and neutral soil
8 conditions, struvite would have similar fertilization effect as that of chemical fertilizer. It is
9 to be noted that, in alkaline calcareous soil, where use of rock phosphate is not suitable
10 because of its low solubility, struvite is found to be more soluble, making it a
11 recommended P fertilizer (Massey et al., 2007). Struvite application is also reported to be
12 advantageous in soils and crops with high Mg and P demand. Its application enhances P
13 uptake, as the Mg present in it, has a synergistic effect on P absorption (Gonzalez-Ponce et
14 al., 2009). Compared to common phosphate minerals (*viz.* fluorapatite, variscite), struvite
15 forward dissolution rates are significantly higher (Roncal-Herrero and Oelkers, 2011).
16 Relatively higher dissolution is facilitated by the presence of comparatively weak H bonds
17 (Huminicki and Hawthorne, 2002) that binds regular tetrahedral PO_4^{3-} , distorted octahedral
18 $\text{Mg} \cdot 6\text{H}_2\text{O}$ and NH_4^+ to form white orthorhombic struvite crystals (Forrest et al., 2008).

19 In struvite treated soil, N leaching losses are remarkably different compared to
20 chemical fertilizer treated soil, though significant difference is not seen in case of P
21 leaching (Rahamann et al., 2011). Again, N leaching loss is insignificant in struvite treated
22 soil (loss is ~1.99% of the total N supplied in the form of struvite), which was reported to
23 be higher for conventional chemical fertilizer (loss is ~ 7.14% of the total N supplied in the
24 form of fused super phosphate+urea) (Rahamann et al., 2011). This causes N deficiency
25 after certain period of time in case of chemical fertilizer because of immediate ammonium

1 release and uptake by plants. However, there is not significant variation in P leaching from
2 struvite and chemical fertilizer (fused super phosphate+urea) treated soil, as both are
3 sparingly water soluble and P gets bind to soil particles (Rahaman et al., 2011). Slow
4 release from struvite ensures steady nutrient supply for plants improving fertilizer
5 efficiency. Struvite is recommended for containerized pot. In such pots, considerable
6 amount of irrigation water is drained. Therefore, a slow release fertilizer is recommended
7 (Antonini et al., 2012). For this reason, struvite has been used commercially for potted
8 plants and also for turf, tree seedlings, ornamentals, vegetables, flower boards and other
9 value added crops (Li and Zhao, 2003).

10 Crushing strength is a quality parameter which predicts handling and storage
11 properties of struvite fertilizer. To facilitate manufacturing, harvesting, transportation and
12 application in the field, struvite pellet with high crushing strength is required. Because, for
13 field application, increased durability with reduced loss of fine materials are desirable
14 (Forrst et al., 2008). The average size of commercial struvite crystal is 2-3.3 mm
15 depending upon reactor conditions viz. upflow velocity, pH, and supersaturaion ratio
16 (Forrest et al., 2008). As agricultural fertilizer, low dissolution with steady release is
17 expected, avoiding over application or crop burning, so that, single high-dose application
18 becomes sufficient. Smaller pellets with larger surface area to volume ratio give faster
19 degree of dissolution which slows down with increase in size (Bridger et al., 1962;
20 Bhuiyan et al., 2008; Fattah et al., 2012). However, it is difficult to maintain enough
21 crushing strength for small pellets. Crushing strength increases with the increase in pellet
22 size up to 2.36 mm, beyond which it decreases which can be attributed to low density in
23 larger pellets (Fattah, 2010). To maintain optimum crushing strength for pellets bigger than
24 a particular size, coating of pellet is suggested for hardening (Fattah, 2010). When tested
25 on rye grass under green house condition, it is found that struvite particle size has a direct

1 influence on nutrient release rate up to certain period of plant growth (Nelson, 2000). N
2 release rate is higher for smaller particles of struvite compared to coarser ones up to 3-6
3 weeks of plant growth (Nelson, 2000). However, influence of granule size becomes
4 insignificant after certain stage of plant growth, as release rate is accelerated once soil is
5 depleted with plant growth. This however, is a typical characteristic of a slow release
6 fertilizer.

7 Quality standard of struvite can be described in terms of its composition and purity
8 which is primarily influenced by source, processing and Mg addition (Antonini et al.,
9 2012). Multi-component raw materials like sewage sludge usually contain a number of
10 heavy metals (Cd, Cu, Cr, Ni, Pb, Zn *etc.*) and organic pollutants. Therefore, their residual
11 content in struvite should be estimated before recommending application. There is a lack of
12 information on residual impurity in struvite derived from a range of sources (Wollmann
13 and Moller, 2015). Table 4 summarizes concentration of some impurity elements in
14 struvite recovered from different sources *viz.* municipal sludge, urine, landfill leachate and
15 anaerobically digested dairy manure. Municipal sludge derived struvite shows presence of
16 impurity such as Cd, Co, As, Ni, Pb, Hg *etc.* (Forrest et al., 2008; Benisch et al., 2010).
17 However, the impurity content is reported to be below the regulatory limit for fertilizer
18 usage in countries like Germany and Turkey (Uysal et al., 2010; Latifian et al., 2012;
19 Antonini et al., 2012). Heavy metal in municipal water derived struvite is found to be
20 significantly lower than that of commercial phosphates (Forrest et al., 2008; Latifian et al.,
21 2012). Impurity level within permissible limit indicates possible increase in marketability
22 of struvite. Struvite recovered from anaerobically digested manure reported to be pure in
23 terms of heavy metal content compared to municipal sludge, urine and landfill leachate
24 derived struvite (Table 4). Pathogenic content of struvite from black water and human

1 urine is found to be below regulatory limit of Dutch fertilizer regulations (Gell et al.,
2 2011).

3 (**Table 4** Composition of struvite recovered from various sources)

4 **b) Struvite fertilizer effect on crop growth**

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

14 In ryegrass, *Zea mays* L. and red clover, urine derived struvite resulted in similar
15 crop yields and phosphate uptake to that resulted by commercial phosphate fertilizer
16 (Simons, 2008; Antonini et al., 2012). Again, struvite has been reported to yield better
17 results in comparison with some conventional fertilizers such as ammonium phosphate,
18 diammonium phosphate and single superphosphate (Barak and Stafford., 2006; Gonzalez-
19 Ponce et al., 2009; Yetilmezsoy et al., 2013). When compared with single superphosphate,
20 urine derived struvite was found to be more effective in lettuce yield with enhanced P
21 uptake (Gonzalez-Ponce et al., 2009). Higher yield due to struvite application was
22 probably attributed to higher Mg content and the synergistic effect of Mg on P uptake. It
23 has been reported that, P concentration is higher in plants grown with struvite than in
24 plants grown with other P fertilizers (Li and Zhao., 2003; Gonzalez-Ponce and Garcia-

1 Lopez, 2007). While comparing the effect of struvite with phosphate rock, mono
2 ammonium phosphate and calcium superphosphate on perennial ryegrass, P accumulation
3 has been found to be highest in struvite treated ryegrass (Gonzalez-Ponce & Garcia-Lopez,
4 2007). The P and Mg levels in soil as well as in crop (*Zea mays* and *Brassica oleracea*)
5 were found to be higher in landfill leachate derived struvite treatment compared to
6 chemical P fertilizer, although the effect was not significant in terms of chlorophyll
7 content, and plant moisture (Prater, 2014). Improvement of P fertilizer efficiency by over
8 55% with Mg application equivalent to 80 kg ha⁻¹ was reported by Rasul et al., 2011. At
9 this recommended rate, no significant difference between the application of struvite and
10 single super phosphate on maize height, leaf area, and dry matter were found.

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

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

20 It is seen from the above discussion that, there is a wide variation in fertilizing
21 effect of struvite on crop growth. Such variation ranges from no significant impact to
22 significant effect on uptake of P and Mg and biomass yield. However, the findings are
23 subjected to various factors such as soil type, plant type and climate. It is also reported
24 that, extraction of Phosphate rock fertilizer is still economical than production of struvite

1 (Forrest et al., 2008). However, in view of the associated benefits of struvite recovery
2 process (cost savings from sludge volume reduction and prerequisite for chemical
3 treatment; conservation of limited P resources and the safe disposal of waste), struvite
4 recovery could to be an attractive and feasible alternative in future.

5 **5. Future prospects**

6 There are future scopes for struvite process improvements addressing the issues of
7 appropriate chemical input and corresponding cost dynamics. Optimum utilization of Mg
8 source would require strategies for reactivity enhancement and removal of other non-
9 participating impurity ions (Ca, Fe, SO_4^{2-} etc.) which otherwise hinder the recovery
10 process. Again, to establish profound effect of seed on struvite precipitation, further
11 investigation is required considering real waste source. Investigation on potential
12 application of struvite on a range of crops corresponding to different climatic and edaphic
13 factors would enhance struvite market development. Further, quality standard of struvite
14 specific to different recovery sources is also expected to bring positive impact on struvite
15 market. Strategy for struvite market development should focus on a holistic approach
16 considering pricing, purity, size, storage, transportation and distribution in view with the
17 legal framework of contaminants and eco-toxicity. This will help to develop an added
18 value P rich product that can be used as a supplement to prevailing nutrient supply system.
19 The overall impacts of such technological successes would be profound on global food
20 security.

21 **6. Conclusions**

22 In the present study, different aspects of struvite recovery processes are critically
23 analyzed with special references to (i) input of alternative Mg sources and (ii) seed aided

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

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9

Table 1_mg sources

Table 1 Alternative Mg sources used in struvite recovery

S.No.	Mg source	Source of struvite	Mg content	Mg:P	pH	Phosphate Recovery (%)	Key findings	Cost	Reference
1	Bittern	Coke manufacturing wastewater	31390 mg l ⁻¹	1:1	10.5	99	Similar recovery efficiency as MgCl ₂	NR	Shin and Lee, 1997
		Landfill leachate	9220-24900 mg l ⁻¹	1:1	11	NR	Comparable struvite precipitation efficiency with MgCl ₂ & MgSO ₄	NR	Li & Zhao, 2002
2	Sea water	Biologically treated swine wastewater	32000 mg l ⁻¹	1.3:1	9.6	76	Bittern is more effective in P recovery than NH ₄ ⁺ recovery	NR	Lee et al., 2003
		Urine	27500	1.1:1	NR	98	More cost effective in coastal areas	0.23 USD/kg struvite	Etter et al., 2011
		Wastewater from coke manufacturing process	1136 mg l ⁻¹	1:1	10.5	95	Same P recovery efficiency as MgCl ₂	NR	Shin & Lee, 1997
		Side-stream of water treatment plant	1250 mg l ⁻¹	1.6:1 & 2.2:1	7.6-8.4	70	Higher Mg:PO ₄ ³⁻ (>1.5:1) necessary for more than 70% P recovery	NR	Matsumiya et al., 2000
3	Thermally decomposed magnesite (MgO)	Municipal Waste water stream from water treatment plant	1250 mg l ⁻¹	1.6-2.4	8.4-76	Higher Mg: PO ₄ ³⁻ (>1.5:1) necessary for stabilized and easy P recovery	0.55 USD/kg struvite	Kumashiro et al., 2001	
		Biologically treated swine wastewater	1200 mg l ⁻¹	1.36:1	10	81	Similar recovery efficiency as MgCl ₂ (75%)	NR	Lee et al., 2003
3	Thermally decomposed magnesite (MgO)	Filtrate of wastewater sludge	676.7 g kg ⁻¹	2.5:1	8.5-8.8	90	Need higher Mg: PO ₄ ³⁻ molar ratio for effective recovery	NR	Quintana et al., 2004
4	Brucite	Rare –earth wastewater	650 g kg ⁻¹	1:1	8.5-9.5	97	Brucite can be used as liquid, solid Mg source, Reuse of brucite is possible	NR	Huang et al., 2011a
5	Magnesite	Landfill leachate	300 g kg ⁻¹	NR	8.6	NR	Acid dissolution of magnesite increase struvite recovery by 50%	18% cost reduction than using MgCl ₂	Gunay et al., 2008
		Rare –earth wastewater	940g kg ⁻¹	1.1:1	5-9.2	Up to 99.7	Thermal decomposed magnesite is cost effective than acid dissolved magnesite	34% cost reduction than using MgCl ₂	Huang et al., 2010
6	Struvite pyrolysate	Urine	244 g kg ⁻¹	1:1:1	NR	90	Cheaper than bittern and MgSO ₄	12 USD/kg struvite	Etter et al., 2011
		Piggery wastewater	530 g kg ⁻¹	2.5:1	8-8.5	96	Similar effects on recovery as with Mg salt	81% cost reduction than using MgCl ₂	Huang et al., 2011b
7	Wood ash	Urine	34 g kg ⁻¹	2.7:1	8.8	99	Presence of impurity such as calcite, heavy metal in product	0.016-0.05 USD/kg struvite	Sakthivel et al., 2011
8	Synthetic nanofiltration brine from seawater	Synthetic wastewater, Real wastewater	146mmol l ⁻¹	1:1	8	99.5	Effective as Mg source but pH, organic matter influence purity of product	NR	Zewulh et al., 2012
9	Desalinated Reject Water	Synthetic centrate	1555-2795 mg ⁻¹	2:1 & 8:1	8-8.5	Up to 55	Presence of other ions (Ca, Na) in reject water reduces recovery efficiency	NR	Fattah et al., 2013
10	Mg(II) solution from seawater	Supernatant of a municipal-sludge	8000 mg ⁻¹	1:1	7.57, 8.13	90	Higher dose of Mg: PO ₄ ³⁻ (>1:1) has no effect on recovery	25% cost reduction than using Mg chemical	Lahav et al., 2013

*NR Not Reported

Table 2 Composition of alternative Mg sources used for struvite production

	Wood ash, ppm	Bittern, ppm	By-product of MgO production, ppm	Magnesite, ppm	Magnesia (MgO), ppm	Seawater, ppm
Mg	34200	9220-44000	676700 ¹	940000 ²	898000-634000 ¹	1010
Ca	27400	10-650	95800 ³	10000-15000 ³	15000-87000 ³	950
Al ₂ O ₃	10800 ⁴		3700	2000		
Fe ₂ O ₃	6090 ⁵		26300	3000-8000	24000	
SO ₃	12300 ⁶	3300-60000 ⁶	39500		38000	
SiO ₂			26000	7000-38000	32000	
K	74600	1900-12300				207
Mn	19300					
Na	5160	3200-78100				9658
Zn	2670					
Cr	1290					
Cu	1050					
Pd	590					
Ni	49					
Cd	28					
Cl ⁻		17400-202000				
Br ⁻		5300				
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 MgCO₃; ³ as CaO; ⁴ as Al³⁺; ⁵ as Fe; ⁶ as SO₄²⁻

Table 3 Different seed material used in struvite precipitation and their effects on recovery

S. No	Seed used	Source of Struvite	Seed Size (μm)	Effects on struvite production	Reference
1	Struvite	Synthetic liquor	1000	<ul style="list-style-type: none"> • Production of struvite fine as product • Seeding is insignificant (process appeared “self-seeding”) 	Regy et al., 2002
		Synthetic liquor and Sludge from wastewater plant	45-63	<ul style="list-style-type: none"> • Crystals have similar shape with seed (no phase transformation during growth) 	Ali, 2005
		Landfill leachate	75-150	<ul style="list-style-type: none"> • Effectiveness of seed requires consideration of pH (pH 9 being optimum) 	Kim et al., 2006
		Synthetic liquor	NR	<ul style="list-style-type: none"> • Enhancement of crystallization by 19% at low P concentration • Increased crystal size, settle ability 	Liu et al., 2008
		Synthetic liquor	250-500	<ul style="list-style-type: none"> • No enhancement of P recovery and reduction in induction time 	Rahaman et al., 2008
		Coking wastewater	NR	<ul style="list-style-type: none"> • 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 wastewaters	NR	<ul style="list-style-type: none"> • Reduction in induction time upto 75 minute depending upon super-saturation 	Liu et al., 2011
		Synthetic liquor	30-50	<ul style="list-style-type: none"> • Similar shape of struvite with seed 	Mehta et al., 2013
	Fertilizer wastewater	NR	<ul style="list-style-type: none"> • Increase in rate of crystallization (by 21%) and size of crystal (from 1.72 nm to 2.08 nm) 	Yu et al., 2013	
2	Coarse sand	Synthetic liquor	200-300	<ul style="list-style-type: none"> • No fixation of struvite on sand surface 	Regy et al., 2002
3	Fine sand	Synthetic liquor	150-200	<ul style="list-style-type: none"> • Strong primary nucleation and formation of fine 	Regy et al., 2002
4	Borosilicate glass	Synthetic liquor	45-63	<ul style="list-style-type: none"> • Slower reaction rate compared to struvite seed 	Ali, 2005
5	Sand grain/Quartz particle	Sludge liquor in wastewater plant	210-350	<ul style="list-style-type: none"> • Recovery of 80% of P onto seed bed 	Battistoni et al., 2000
		Synthetic liquor	45-63	<ul style="list-style-type: none"> • Slower reaction rate compared to struvite seed 	Ali, 2005
6	Phosphate rock	Dairy effluent	NR	<ul style="list-style-type: none"> • No effect mentioned on crystal 	Massey et al., 2007
7	Stainless steel mesh	Synthetic liquor	1000 μm hole	<ul style="list-style-type: none"> • No significant increase in crystallization • Reduction in struvite fine particle 	Le Corre et al., 2007
8	Pumice stone	Synthetic liquor	NR	<ul style="list-style-type: none"> • 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

Elements	Sources				
	Municipal Wastewater derived struvite, ppm	Landfill Leachate derived struvite ppm	Anaerobically digested cattle manure and fish waste derived struvite, ppm	Human Urine derived struvite, ppm	Yeast industry anaerobic effluent, derived struvite, ppm
N	29000-57500	-	51128	29000	35000
P	91000-128000	-	123684	71000-126000	108000
Mg	99000	-	-	-	79700
K	100-7000	-	-	2000-15000	12100
Ca	2000-8400	-	14	16000	21800
Na	-	-	-	8980	11100
S	-	-	-	1350	-
Fe	300-2018	346	114	14-1050	300
Al	100-1161	269-312	316	11-558	-
Mn	113-236	32-33	16	0.1-92.3	-
B	-	505-507	-	-	-
Cd,	0.01-0.7	0.02-0.2	BDL	0.2	<1
Cu	0.9-80	5.7-6.6	20	-	102
Co	0.1	0.4-2.5	-	0.3-1.7	-
Zn	3.3-100	4.1-16.2	98	7-142	<2
As	0.3-1	0.8-2.8	-	15	-
Ni	0.3-9.4	2.5-2.9	BDL	0.8-2.3	<10
Ag	-	0.2-0.6	BDL	-	-
Pb	0.6-5	0.06-2.1	BDL	0.9-6.3	<25
Se	-	2-6	-	-	-
Cr	1.8-11	4.9-5.3	BDL	0.2	<10
Ur	0.05	-	-	-	-
Li	0.4	-	-	1-2.1	-
Hg	0.01	-	-	4.2	<1.5
Sn	9.1	-	-	1.4	-
Cl	-	-	-	-	1500
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 5 Effect of struvite as fertilizer on various plants

S No	Crop/plant	Struvite source	Type of Experiment	Chemical fertilizer used	Soil type/Growing media	Effect of struvite on crop/plant	Remark	Reference
1	Gram (<i>Cicer arietinum L.</i>)	Synthetic water	Pot	Single superphosphate, Di ammonium phosphate, Ammonium polyphosphate	Typical acid	Variation of P uptake with level of P application	Superior or equally effective as chemical fertilizer	Ghosh et al., 1996
2	Chinese flowering cabbage (<i>Brassica parachinensis</i>)	Municipal landfill leachate	Pot	Ammonium nitrate+ Calcium phosphate	Sandy clay (Red Earth) (pH 6.2)	Similar vegetable growth and more Mg, P uptake compared to chemical fertilizer	Comparable effect with chemical fertilizer	Li and Zhao, 2003
3	Water convolvulus (<i>Ipomea aquatica, I. reptans</i>)	Municipal landfill leachate	Pot	-	Sandy clay (Red Earth) (pH 6.2)	No significant difference in growth and no burning effect with increase in struvite dose	Higher dose of struvite does not affect plant	Li and Zhao, 2003
4	Water spinach (<i>Ipomea aquatica</i>)	Municipal landfill leachate	Pot	Ammonium nitrate+ Calcium phosphate	Sandy clay (Red Earth), (pH 6.2)	Similar vegetable growth and more Mg, P uptake compared to chemical fertilizer	Comparable effect with chemical fertilizer	Li and Zhao, 2003
5	Chinese chard (<i>Brassica rapavar. chinensis</i>)	Municipal landfill leachate	Pot	Ammonium nitrate+ Calcium phosphate	Sandy clay (Red Earth) (pH 6.2)	Similar vegetable growth and more Mg, P uptake compared to chemical fertilizer	Comparable effect with chemical fertilizer	Li and Zhao, 2003
6	Maize	NR	Greenhouse Pot	Diammonium phosphate	NR	P uptake is efficiency for struvite is 117% and residual P availability is 178%	Higher efficiency compared to chemical fertilizer	Barak and Stafford, 2006
		Swine wastewater	Pot	Superphosphate & Urea	Sandy loam	Similar plant height, higher biomass, less N ₂ O emission as with chemical fertilizer	Equally effective with chemical fertilizer	Liu et al., 2011
		Urine	Field	Triple superphosphate	Sandy loam (Andosol)	No significant difference in dry yield compared to chemical fertilizer	Similar effect with chemical fertilizer, P in struvite is not limiting for plant	Gell et al., 2011
		Black water	Field	Triple superphosphate	Sandy loam (Andosol)	No significant difference in dry yield compared chemical fertilizer	Similar effect with chemical fertilizer, P is not limiting	Gell et al., 2011
		Urine	Small plot	Diammonium phosphate	NR	Similar leaf diameter and height with chemical fertilizer	Comparable to chemical fertilizer	Dalecha et al., 2012
		Corn fibre processing wastewater	Field	Triple superphosphate	Silt loam, loam, silt clay	Plant P uptake is higher than chemical fertilizer by 4-21% depending upon application rate	Nutrient availability is similar to chemical fertilizer	Thompson, 2013

7	Wheat (<i>Triticum aestivum</i> L.)	Urine	Climate chamber	NPK mixture (14-4-21)	Quartz sand	Lower dry weight (by 50%) than chemical fertilizer	Low availability of nutrients (N) than chemical fertilizer	Ganrot et al., 2007
		Dairy wastewater	Greenhouse pot	Triple superphosphate, Rock phosphate	Fine-loamy over sandy or sandy-skeletal, mixed, mesic Aridic Argiustoll	Increase in total P uptake in basic soil	Similar effect with chemical fertilizer	Massey et al., 2009
8	Perennial Ryegrass (<i>Lolium Perenne</i>)	Municipal sewage sludge	Greenhouse Pot	Single superphosphate	P-deficient loamy sand	Similar increase in dry matter, P uptake compared to chemical fertilizer	Comparable to chemical fertilizer	Plaza et al., 2007
		Synthetic liquor and municipal sewage sludge	Glasshouse Pot	Monocalcium phosphate	sandy loam and sandy clay loam	Similar dry matter yield and P uptake as with chemical fertilizer	Similar effect on crop yield as with chemical fertilizer	Johnston and Richards, 2003
		Poultry manure	Greenhouse pot	–	Sand	Increase in fresh and dry weight by 76% compared to 60% in control, faster growth than with control	Increase in weight and rate of increase is dependent upon type of plant, soil media	Yetilmezsoy and Zengin, 2009
9	White lupin (<i>Lupinus albus</i> L.)	Wastewater	Greenhouse pot	Calcium superphosphate	NR	Equal P uptake and higher Mg uptake compared to P fertilizer	Similar effect with chemical fertilizer	Gonzalez and Garcia, 2008
10	Oil seed rape	Municipal sewage sludge	Field	Triple superphosphate, Rock phosphate	P deficient loam	Higher P uptake and grain yield compared to synthetic fertilizer/rock phosphate	Comparable P availability with synthetic fertilizer	Perez et al., 2009
11	Purslane (<i>Portulaca oleracea</i>)	Poultry manure	Greenhouse pot	–	Sand	Increase in fresh and dry weight by 150% compared to 207% in control, faster growth than with control	Increase in weight and rate of increase is dependent upon type of plant, soil media	Yetilmezsoy and Zengin, 2009
12	Garden cress (<i>Lepidium sativum</i>)	Poultry manure	Greenhouse pot	–	Sand	Increase in fresh and dry weight by 28% compared to 115% in control, faster growth than with control	Increase in weight and rate of increase is dependent upon type of plant, soil media	Yetilmezsoy and Zengin, 2009
13	Winter barley	Municipal sewage sludge	Field	Triple superphosphate, Rock phosphate	P deficient loam	Similar P uptake and grain yield compared to chemical fertilizer/rock phosphate	Comparable P availability with chemical fertilizer	Perez et al., 2009
14	Lettuce (<i>Lactuca sativa</i> L.)	Anaerobically digested	Greenhouse pot	Single superphosphate	P-deficient loamy sand	More efficient than chemical fertilizer in increasing yield &	Comparable to chemical fertilizers or	Gonzalez et al., 2009

		municipal sludge liquor			P uptake	even better		
15	Garden rocket (<i>Eruca sativa</i>)	Anaerobic Sludge of poultry manure	Greenhouse pot	Ammonium nitrate+ Potassium dihydrogen orthophosphate	Garden soil (pH 5.5-6)	More gain in plant wet, dry weight and height compared to chemical fertilizer	Comparatively more effective than chemical fertilizer	Yetilmezsoy et al., 2013
16	Dill (<i>Anethum graveolens</i>),	Anaerobic Sludge of poultry manure	Greenhouse pot	-	Garden soil (pH 5.5-6)	Increase in dry weight by 191% compared to no fertilizer	Effective slow release fertilizer	Yetilmezsoy et al., 2013
17	Fennel (<i>Foeniculum vulgare</i>)	Anaerobic Sludge of poultry manure	Greenhouse pot	-	Garden soil (pH 5.5-6)	Increase in dry weight by 208% compared to no fertilizer	Effective slow release fertilizer	Yetilmezsoy et al., 2013
18	Parsley (<i>Petroselinum crispum</i>)	Anaerobic Sludge of poultry manure	Greenhouse pot	-	Garden soil (pH 5.5-6)	Increase in dry weight by 379% compared to no fertilizer	Effective slow release fertilizer	Yetilmezsoy et al., 2013
19	Canola	Swine manure	Pot	Monoammonium phosphate, polymer-coated monoammonium phosphate	Sandy loam	Similar P uptake but lower biomass yield/unit of P uptake compared to chemical fertilizer because of lower solubility at basic soil	Supplement with chemical fertilizer might need depending upon soil type	Ackerman et al., 2013
20	Tomato	Yeast industry wastewater	Pot	Potassium phosphate, ammonium nitrate	Light alkali nutrient poor soil (pH 8.4)	Higher N, P and Mg uptake of plant for double/triple and quadruple dose of struvite compared to NPK treatment	Higher (more than double) dose of struvite is essential for optimum effect	Uysal et al., 2014

NR: Not Reported