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Production of slow release crystal fertilizer from wastewaters through struvite crystallization – A review

Md. Mukhlesur Rahman [a,b,*], **Mohamad Amran Mohd. Salleh** [a,c], **Umer Rashid** [a], **Amimul Ahsan** [a,d], **Mohammad Mujaffar Hossain** [b], **Chang Six Ra** [e]

[a] *Institute of Advanced Technology, University Putra Malaysia, UPM 43400 Serdang, Selangor, Malaysia*
[b] *Department of Animal Science, Bangladesh Agricultural University, Mymensingh 2202, Bangladesh*
[c] *Department of Chemical and Environmental Engineering, University Putra Malaysia, UPM 43400 Serdang, Selangor, Malaysia*
[d] *Department of Civil Engineering, University Putra Malaysia, UPM 43400 Serdang, Selangor, Malaysia*
[e] *Department of Animal Life System, Kangwon National University, Chuncheon 200-701, South Korea*

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Abstract Nitrogen and phosphorus in wastewaters are a burning environmental issue of the present world. This review covers the studies conducted on the removal and recovery of phosphorus and nitrogen from wastewaters through struvite crystallization. Wastewater which contains a high amount of phosphorus and nitrogen would be a good source of struvite. Struvite is a phosphate fertilizer, although it contains a significant amount of nitrogen and magnesium, and it is an effective alternative source of rock phosphate to maintain the agricultural production system. The present review deals with the principles and concept of struvite nucleation, crystal growth and the factors that affect on the struvite quality. Struvite precipitation occurs in an equimolecular concentration of Mg^{2+}, NH_4^+ and PO_4^{3-} at slightly alkaline conditions. Addition of a source of Mg is essential to maintain the favorable condition of PO_4 and Mg. Different factors such as Mg:PO_4 molar ratio, pH, aeration rate, reactor types, as well as P and N removal efficiencies were also discussed throughout this review. The slower nutrient leaching loss and its fertilizer quality make struvite an eco-friendly fertilizer. It is possible to overcome the acute shortage of rock phosphate if all the municipal and livestock wastewaters are connected with the wastewater treatment plants.

1. Introduction

Wastewaters contain a high amount of organic matter, nitrogen and phosphorus (Deng et al., 2006), a considerable amount of Mg (Suzuki et al., 2007), different macro and micro elements (Ali, 2005), and heavy metals (Liu et al., 2011a,b,c) due to which it is considered as one of the major polluting agents discharged into the environment. These pollutants come

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[*] Corresponding author at: Institute of Advanced Technology, University Putra Malaysia, UPM 43400 Serdang, Selangor, Malaysia. Tel.: +60 89467502 (O), mobile: +60 102689653; fax: +60 386566061.
E-mail address: mmrahmanz@gmail.com (M.M. Rahman).

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from anthropogenic, livestock, natural or industrial sources (Panizza and Cerisola, 2001). Nitrogen and phosphorus are important organic plant nutrients (ICM, 2000) and also utilized for optimization of animal and plant production. A large amount of nitrogenous and phosphate fertilizers is applied in the soil every year to increase the fertility of the soil. The present consumption of rock phosphorus (P) is over one million tons yearly (Rahman et al., 2011) as fertilizer and Nitrogen (N) fertilizer consumption might be three fold of this. It is known that in addition to the leaching loss of N from urea, large N losses occur through ammonia volatilization (26.5–29.4%), surface runoff (5.6–7.7%), vertical leaching (4.0–5.0%), lateral seepage (4.0–5.3%), and denitrification (4.37–5.0%) after field application (Liang et al., 2007). Moreover, about 10% is unused and only 38.2–44.8% nitrogen is taken up by the rice crop. Thus, a large amount of N and P is added to water stream and then transferred to the environment from this fertilizer source.

Besides crop production, P is one of the vital elements needed for animal growth, milk and egg production as well (Saito, 2001). The daily nutritional requirements for dairy cattle and beef cattle have been stated as 86–95 g day^{-1} and 35–40 g day^{-1}, respectively (CEEP, 2003). Animals cannot utilize the whole amount and are excreted through manure or urine that exists in the wastewater. So, the feeding of excess P increases the phosphate levels in animal wastewaters. Only 14% of corn P and 31% of soybean meal can be digested by swine. A large percentage of phosphorus is unavailable, and most of it is excreted into the environment through manure and urine (Dhakal, 2008). The excreted P is dissolved into the water and transported to the nearby water bodies or infiltrates onto the groundwater (ICM, 2000). The livestock waste stream is therefore, very rich in phosphorus. A significant amount of nitrogen comes out through excreta as a residue of protein supplement as well as dead animals. Improper management of livestock waste creates a nuisance and obnoxious environment which also greatly affect on public health. A lot of currency is expended for importing rock phosphate to fulfill the national demand but proper recovery of phosphate from wastewaters can be reduced with the import of rock phosphate. Municipal wastewater or sewage contains a significant amount of N and P along with organic and inorganic substances (Bashan et al., 2004). Industrial wastewaters are also an important source of phosphorus. Phosphorus is used (i) for stabilization of calcium carbonate to softened waters, (ii) in public water systems in order to control corrosion as well as in steam power plants to control scaling in the boilers, and (iii) in dairy and other food-processing industries (Dhakal, 2008). Fig. 1 showed the sources of P in the wastewaters. Insufficient and improper treatment facilities of these effluents cause serious soil and water pollution, including eutrophication in the surrounding areas. Phosphorus and nitrogen enhance the growth of algal blooms in the water bodies (rivers, lakes and seas) worldwide, which reduce light penetration and available oxygen in the water bodies. Thus, eutrophication leads to aquatic death all over the world (Khan and Ansari, 2005; Lee et al., 2003). Some forms of nitrogen (ammonia, nitrite, and nitrate) and phosphorus (orthophosphate and monophosphate) produce toxicity in the water and affect on aquatic life. It is obligatory to remove nitrogen and phosphorus from wastewaters before discharging it into the water stream to create an eco-friendly, pollution-free environment. So, many countries are paying attention to water pollution resulted from wastewaters, and have tightened legislation and discharging standards.

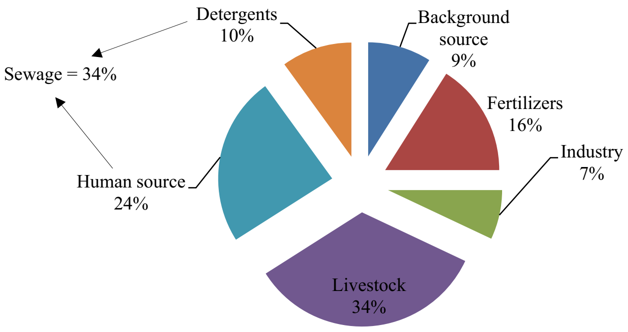


Figure 1 Sources of P in the wastewaters (CEEP, 2003).

Great efforts have been done by researchers for the removal of nitrogen from wastewater through biological nitrification and denitrification (Welander et al., 1998), ammonia-stripping (Bonmati and Flotats, 2003), electrochemical conversion (Kim et al., 2006), ion exchange (Jeong et al., 2006; Liu et al., 2011a), microwave irradiation (Cho et al., 2009) and struvite precipitation (Rahman et al., 2011). Wastewater that contains high concentration of N, and P is an effective source of struvite recovery. In recent years, struvite has been recovered from different types of wastewaters, such as swine wastewater (Nelson et al., 2003; Deng et al., 2006; Suzuki et al., 2005, 2007; Rahman et al., 2011), calf manure wastewater (Schuiling and Andrade, 1999), leather tanning wastewater (Tunay et al., 1997), sewage sludge (Munch and Barr, 2001), dairy wastewater (Massey et al., 2007), wasted sludge (Jaffer et al., 2002), digester supernatant (Battistoni et al., 2000; Pastor et al., 2010), industrial wastewater (Diwani et al., 2007), municipal landfill leachate (Kim et al., 2007), lagoon wastewater (Westerman et al., 2009), poultry manure wastewater (Yetilmezsoy and Zengin, 2009), agro-industrial wastes (Moerman et al., 2009), slaughterhouse wastewater (Kabdasli et al., 2003), anaerobic digester effluents (Celen and Turker, 2001), synthetic wastewater (Adnan et al., 2003), slurry type swine wastewater (Kim et al., 2004), animal manure (Burns and Moody, 2002), urine (Etter et al., 2011) and fertilizer plant wastewater (Yu et al., 2013). Recently, struvite has been produced from wastewaters using microbial fuel cells by Ichihashi and Hirooka (2012). Struvite is a crystalline substance consisting of magnesium, ammonium and phosphorus in equal molar concentrations ($MgNH_4PO_4{\cdot}6H_2O$). The crystals form in an alkaline condition according to the reaction shown below (Bouropoulos and Koutsoukos, 2000).

$$\mathrm{Mg^{2+} + NH_4^+ + H_2PO_4^- + 6H_2O} \\ \rightarrow \mathrm{MgNH_4PO_4 \cdot 6H_2O + 2H^+} \qquad \text{(i)}$$

Generally, wastewaters from anthropogenic, livestock, or municipal leachate contains less magnesium compared with nitrogen and phosphate. So, it is necessary to add a source of Mg to optimize the struvite crystallization process (Tunay et al., 1997; Schuiling and Andrade, 1999; Battistoni et al., 2000; Nelson et al., 2003; Suzuki et al., 2005, 2007; Massey et al., 2007; Diwani et al., 2007; Kim et al., 2007; Westerman et al., 2009; Yetilmezsoy and Zengin, 2009; Moerman et al., 2009). Not only, from wastewaters but the addition of Mg and PO_4 salts during the composting process of manure also precipitated struvite crystals in the compost, which increases the compost quality (Lee et al., 2009, 2010).

The composition of wastewater differs according to their source of origin. A gross composition of wastewaters is shown in Table 1 through which we can get an idea about characteristics of wastewaters. Most of the wastewaters contain a high concentration of organic matter, including N, and the P concentration depends on its source. Different theoretical and experimental processes have been adopted by the researchers for the successful recovery of struvite (Abbona et al., 1982; Ohlinger et al., 1998; Hao and Von Loosdrecht, 2006; Ronteltap et al., 2007; Wilsenach et al., 2007; Pastor et al., 2008). In near future, wastewaters will no longer be a hazardous material; it will be a valuable resource when all wastewaters undergo the treatment process. Therefore, environmental scientists and workers are doing efforts to optimize the factors such as influent concentrations, the molar ratio of NH_4, PO_4 & Mg, pH level, aeration rate, temperature, types of crystallizing reactors, etc. for optimum struvite production. Struvite is an effective alternative source of rock phosphate, and thus it will be the chief P fertilizer in the future after exhaustion of all rock phosphate (Munch and Barr, 2001; Shu et al., 2006; Massey et al., 2007). Struvite has excellent fertilizer qualities under specific conditions when compared with standard fertilizers (Ghosh et al., 1996; Liu et al., 2011a).

In the past decade, struvite precipitation has gained interest as a route to phosphorus recovery (Doyle et al., 2003). Cheaper source of N and P in wastewater makes it a potential raw material for fertilizer industry, provided that its nucleation and the quality of crystals recovered can be controlled. Research in struvite formation is now widespread and includes studies on the prevention of scaling, alternative phosphorus removal and recovery from wastewater effluents, and possible exploitation for the benefit of wastewater companies and industries as a fertilizer. Struvite precipitation has also been studied in the medical field, as it can spontaneously form calculi in human kidneys (Coe et al., 2005) and in agricultural sciences in a way to entrap N and P in compost (Jeong and Kim, 2001; Jeong and Hwang, 2005; Lee et al., 2009, 2010). Not only this, struvite can also be used as a source of P and Mg during microwave treatment of wastewaters to curtail the need of Mg salts. Microwave irradiation dissociates the struvite into Mg, NH_4 and PO_4 that are recycled again to the influent wastewaters for struvite precipitation (Cho et al., 2009) that reduced the struvite production cost. This review paper is an overview of struvite crystallization from different types of wastewaters at different conditions and its quality identification.

2. Physical and chemical nature of struvite

Struvite is a crystal which is formed with an equal molar concentrations of magnesium, ammonium and phosphate combined with six water molecules ($MgNH_4PO_4{\cdot}6H_2O$). Its molecular weight is 245.43 g mol^{-1}, and it is sparingly soluble under neutral and alkaline conditions but readily soluble in acid (Chirmuley, 1994). Solubility value is 0.018 g 100 ml^{-1} at 25 °C in water, 0.033 g 100 ml^{-1} at 25 °C in 0.001 N HCl and 0.178 g 100 ml^{-1} at 25 °C in 0.01 N HCl (Le Corre et al., 2009), and the solubility constant is $10^{-13.26}$ (Ohlinger et al., 1998). Crystallization process occurred under a wide range of alkaline condition. Struvite might be described as a soft mineral with a low specific gravity (1.7), which is not flashed away by rainfall, and hence, can be successfully used as fertilizer in flooded areas (Lee et al., 2009). Pure struvite occurs as white crystalline powder, but also can occurs either as large single crystals, very small crystals, curds or a gelatinous mass (Munch and Barr, 2001). Yellowish or brownish-white, orthorhombic or pyramidal crystals or in platey mica-like structures of MAP are also available (Lee et al., 2009). Orthorhombic is a complex structure indicated by regular PO_4^{3-} octahedral, distorted $Mg(H_2O)_6^{2+}$ octahedral, and NH_4 groups all held together by hydrogen bonding (Abbona et al., 1982). Sometimes it appears as tight aggregates of fine crystals (Adnan et al., 2003), star-like particles (Regy et al., 2002), irregular, unshaped, coarse crystals (Zhang et al., 2009; Westerman et al., 2009; Rahman et al., 2011), elongated structures (Le Corre et al., 2007; Kozik et al., 2011; Hutnik et al., 2013a,b; Matynia et al., 2013) were found as struvite. Struvite crystal size varied on different production conditions and found from 15 µm (Zhang et al., 2009) to 3.5 mm (Adnan et al., 2003) in length. Munch and Barr (2001) found a significant smaller crystal from a pilot-scale MAP reactor compared to the crystals produced from full-scale MAP reactors in Japan. The average sizes of the crystals (2.0 ± 3.8 mm) were found by Kurita Water Industries, Japan (Abe, 1995). He (Abe, 1995) also stated that the crystal size was influenced by the influent phosphorus concentration and particle retention time in the reactor. He reported that the crystal growth rate was 0.173 mm/d with a high influent P concentration (>200 mg/l) and only 0.061 mm/d for a low influent P concentration (34 ± 100 mg/l). A more detail physical shapes and sizes are shown in Table 2, which are found by several researchers. Different types of struvite crystals are shown in Fig. 2 (gross crystals) and Fig. 3 (SEM of crystals). According to compositional structure, it contains 13% P and treated as P fertilizer, although it is also an effective source of nitrogen (6% N) and magnesium (10% Mg). Morphologies of MAP crystals are identified by scanning electron microscopy (SEM), but the compositional quality of the crystals can be identified via X-ray diffraction (XRD) by matching the position and intensity of the peaks with the database model for the reference. Chemically, it is sparingly soluble under neutral conditions, but highly soluble in acidic media and highly insoluble in alkaline media (Chirmuley, 1994). It can increases soil pH (Johnston and Richards, 2003), and hence it is suitable for acidic soils. Rahman et al. (2011) found an increasing tendency of pH in MAP treated soils, whereas a decreasing tendency of pH in commercial N and P fertilizer treated soils.

The thermal characteristic of struvite was studied by several researchers (Ali, 2005; Ali and Schneider, 2008; Bhuiyan et al., 2008) and found the decomposition of struvite, under dynamic temperature conditions. Struvite shows a gradual decrease of some ammonia and was partially transformed into bobierrite when it was boiled (temperature <100 °C) for 24 h. Boiling struvite in excess water resulted in the loss of five water molecules from its structure and transformed into the monohydrate, dittmarite. As a result, dittmarite contains a higher P_2O_5 (45.7%) or P (19.9%) whereas, struvite contains only 28.9% P_2O_5 or 9.8% P (Bhuiyan et al., 2008). The conditions for the transformation of struvite to dittmarite could be exploited for intentional dittmarite formation that would extend the field of P recovery from wastewater. Fig. 4 shows

Table 1 Characteristics of wastewaters.

Parameters ($mg\ L^{-1}$)	Swine wastewater (Liu et al., 2011c)	Municipal wastewater (Kim et al., 2007)	Mixed UASB effluent (Yetilmezsoy and Zengin, 2009)	Nylon industry wastewater (Huang et al., 2012)
COD	ND	1500–2500	1800	1095
TN	2623.50	800–2200	1580	781
TP	31.62	1–45	370	0.20
Mg	ND	ND	ND	0.50
SO_4^{2-}	ND	ND	ND	389
TSS	10.73	100–200	1130	ND
VSS	2.21	ND	970	ND
pH	8.31	7.2–8.7	7.95	7.9

N. B.: COD = chemical oxygen demand, TN = total nitrogen, TP = total phosphorus, TSS = total suspended solids, VSS = volatile suspended solids, ND = not detected.

the detail transformation pathways of struvite under different temperature conditions. However, the economics associated with this transformation have yet to be proven as cost-effective. Studies involving the effect of ammonia pressure, water vapor pressure and simultaneous use of temperature and ultrasonic on the decomposition of struvite are recommended to understand more about struvite. With quantification of water in each compound and quantification of each element in a compound, derivation of a phase diagram of the relationship between struvite, bobierrite, and dittmarite is also recommended. The decomposition temperature of dittmarite was found to be around 220 °C in the same study (Bhuiyan et al., 2008) under static air and a heating rate of 5 $°C\ min^{-1}$. Around 80% of ammonia losses from dittmarite under above condition through the reaction shown below:

$$\underset{\text{(Dittmarite)}}{MgNH_4^+PO_4 \cdot H_2O} \rightarrow \underset{\text{(Amorphous)}}{MgHPO_4} + NH_3 \uparrow + H_2O \uparrow \tag{ii}$$

3. Background theory of struvite nucleation

The struvite crystal development occurs in two chemical phases: nucleation or crystal birth and crystal growth. Predicting these mechanisms is complex, as it is controlled by a combination of factors such as the crystal state of initial compounds, thermodynamic of liquid–solid equilibrium, phenomena of mass transfer between solid and liquid phases (Jones, 2002) and kinetics of reaction (Ohlinger et al., 1999). The nucleation corresponds to the apparition of new particles. Several mechanisms are possible for struvite crystallization depending on the supersaturation level in the crystallizer. Homogeneous primary nucleation corresponds to nuclei apparition directly in the supersaturated solution. Heterogeneous primary nucleation takes place on foreign surfaces, which can be dust in suspension or parts of the crystallize itself. Surface secondary nucleation, also called true secondary nucleation, needs to have already suspension particles of the same specie as the solid which is crystallized. Indeed, surface secondary nucleation corresponds to the nuclei formation on the surface of these particles. The new-born surface nuclei are then detached by the shear exerted by the fluid or by shocks undergone by the particles (Regy et al., 2002). Among the different nucleation mechanisms, homogeneous primary nucleation requires the highest super saturation level to spontaneous development. It is followed by heterogeneous primary nucleation and surface secondary nucleation, respectively.

Several physico-chemical parameters also influence these mechanisms such as pH of the solution (Bouropoulos and Koutsoukos, 2000), supersaturation (Doyle et al., 2002), mixing energy (Ohlinger et al., 1999), temperature (Aage et al., 1997), and presence of foreign ions (Le Corre et al., 2005). Free Mg^{2+}, $NH_4{}^+$ and PO_4^{3-} ions react to form struvite are subject to a range of speciation in a standard pH. It is therefore, important to understand the equilibrium to calculate the free ion concentrations and other thermodynamic properties during crystallization. Mixing effect occurs if the reaction and crystallization kinetic rates are faster or of the same order of magnitude than the mixing process rates, resulting in competition among mixing, reaction, and nucleation. In this case mixing kinetics show a strong effect on the number of crystals formed and consequently, on their size (Regy et al., 2002). The effects of foreign ions (Fe^{2+}, PO_4^-, NO_3^{2-}) and organic impurities presence were investigated and presented in literatures, both for individual species and many species in various mixtures (Hutnik et al., 2012; Hutnik et al., 2013a,b; Kozik et al., 2011). These foreign ions can also co-precipitate in the form of sparingly soluble hydroxides or phosphates in alkaline environment along with the struvite precipitation, which deteriorate the chemical composition of struvite. The presence of calcium ions in the continuous struvite reaction crystallization process showed a lower homogeneity, and smaller crystal size (Hutnik et al., 2011).

Several researchers investigated the thermodynamical properties of Mg^{2+}, $MgOH^-$, NH_4^+, NH_3, PO_4^{3-}, HPO_4^{2-}, $H_2PO_4^-$, H_3PO_4, $MgNH_3^{2+}$ and $Mg(NH_3)_2^{2+}$ species (Snoeyink and Jenkins, 1980; Bouropoulos and Koutsoukos, 2000). Thermodynamical calculation of these reagents expanded the subsequent research for MAP precipitation (Ali, 2007; Ali and Schneider, 2008). Ohlinger et al. (1999) studied the nucleation properties of MAP from the previous thermodynamic calculations and showed the equations for equilibrium reactions. Supersaturation is the state of a solution where the solute concentration is greater than its value at equilibrium. As struvite contains three specific ions (Mg^{2+}, NH_4^+ and PO_4^{3-}), and its solute concentration can be defined by the ion activity product (IAP). When the IAP is greater than the solubility product (K_{sp}) the system is supersaturated and struvite may nucleate and grow, returning the system to equilibrium (Galbraith and Schneider, 2009). Nelson et al. (2003) stated that

Table 2 An overview of struvite crystallization.

Source of waste/ wastewater	Additional chemicals	PO_4:Mg molar ratio	pH range	Reactor type	NH_4 removal (%)	PO_4 removal (%)	Crystal type	References
Swine wastewater	$MgCl_2$	1: 1.2	8.0–9.0	Continuous flow reactor	31	93	Irregular shaped, coarse	Rahman et al. (2011)
Swine wastewater	$MgCl_2$	1:0.8	7.82–8.92	Batch test in CFR	65	67	Irregular shaped, coarse	Liu et al. (2011a)
Synthetic wastewater	$MgCl_2$	2:1	8.5–10.5	Pilot scale Continuous flow reactor	56	81	Elongated crystals (50–100 μm)	Le Corre et al. (2007)
Anaerobic digester sidestream	$Mg(OH)_2$ slurry	1:1.3	8.0–9.0	Pilot-scale MAP reactor	–	94	Trapezoidal shape crystal	Tunay et al. (1997)
Swine manure	$MgCl_2$, KH_2PO_4	1:1.2	8.0–9.5	Batch test in aerobic reactor	–	–	–	Lee et al. (2009)
Swine manure	$MgCl_2$	1:1.2	8.0–8.5	Batch test	–	–	Irregular shaped crystal	Lee et al. (2010)
Swine manure slurry	MgO, $Mg(Cl)_2.6H_2O$	1:1.6	7.0–11.0	Bench scale reactor	–	91	Irregular shaped, white crystal	Burns and Moody (2002)
Sewage wastewater	By-product of magnesium oxide production (BMP)	1.6:1	8.28–8.41	Full scale sewage treatment plant	30	90		Quintana et al. (2008)
Landfill leachate	$MgCl_2$, MgO, Na_2HPO_4	1: 1.1	8.4–9.0	Batch reactor	–	85.5	Coarse, irregular crystals (15–40 μm)	Zhang et al. (2009)
MAP containing slurry	$MgCl_2$, KH_2PO_4	1:1	8.0–9.0	Batch reactor (microwave irradiation)	40	87	Cube granules	Cho et al. (2009)
Poultry manure wastewater	$MgCl_2$,$MgSO_4$,MgO, KH_2PO_4	1:1	9.0	Batch reactor	–	85.4		Yetilmezsoy and Zengin (2009)
Slurry-type swine wastewater	MgO, H_3PO_4	1: 1.5	8.0–11.0	Anaerobic digester	20	99	Irregular white crystals	Kim et al. (2004)
Synthetic wastewater	$NaCl_2$, $(NH_4)_2HPO_4$, NH_4Cl	1:1.2–1:2.4	7.5–8.7	Bench-scale reactor	42	90	2.5–3.5 mm	Adnan et al. (2003)
Digested swine wastewater	Bittern	1.0:0.6	8.0–11.0	Batch reactor	23–29	90	Irregular mixed crystals	Ye et al. (2011)
Swine wastewater	N, P and Mg in wastewater	–	8.0–9.0	Batch mode reactor connected with MFC	–	79–82	Irregularly shaped, hexagonal crystals	Ichihashi and Hirooka (2012)
Synthetic wastewater	$NH_4H_2PO_4$, $MgCl_2$, $NaNO_3$	1:1, 1:1.2	9.0–11.0	Continuous flow reactor	–	–	Rod shaped crystals (18–55 μm)	Hutnik et al. (2013a)

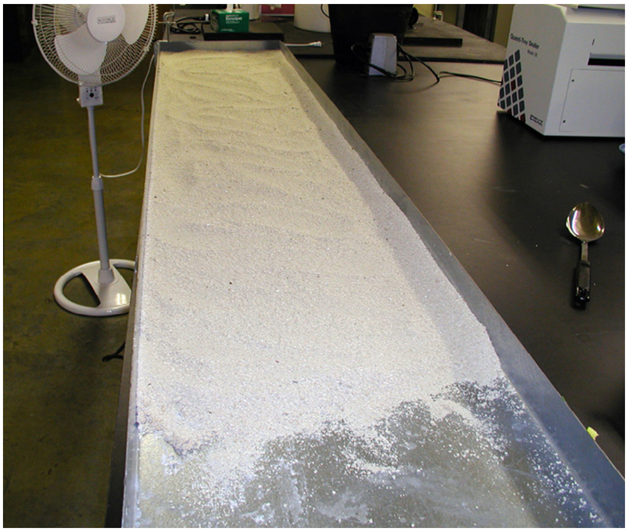


Figure 2 Struvite crystal produced from lagoon wastewater (Westerman, 2009).

the IAP value was 7.08×10^{-14}. The IAP, saturation index (SI), saturation ratio (S_a) and K_{sp} can be explained by the following formula:

$$\mathrm{IAP} = \mathrm{Mg}^{2+}\{\mathrm{NH}_4^+\}\{\mathrm{PO}_4^{3-}\} \quad \text{(iii)}$$

$$\mathrm{SI} = \log\left(\frac{\mathrm{IAP}}{K_{sp}}\right) \quad \text{(iv)}$$

$$\mathrm{S_a} = \left(\frac{\mathrm{IAP}}{K_{sp}}\right)^{1/3} \quad \text{(v)}$$

Ohlinger et al. (1998) showed the minimum solubility product (K_{so}) of struvite as $10^{-13.26}$, and the value was used by Ohlinger et al. (1999) and Bouropoulos and Koutsoukos (2000). Bhuiyan et al. (2007) found that the K_{so} value was $10^{-13.36}$, and the value was applied for further MAP products. Most commonly used apparent value of K_{so} is $10^{-12.6}$ (Snoeyink and Jenkins, 1980) that might be resulted from the lowest reagent concentration. A smaller K_{so} than the calculated value indicates that the solution is supersaturated for struvite precipitation. On the other hand, a higher calculated value than the K_{so} indicates that the solution is undersaturated. SI and (S_a) would be required for dealing with non-ideal, multi-component systems. Both the expressions are incorporated into the ion activity product and the minimum solubility product.

Nucleation is the first step of the struvite crystallization process. It occurs when Mg^{2+}, NH_4^+ and PO_4^{3-} molecules come in contact with each other in clusters and grow by accretion in a favorable pH. Then, they come in contact with each other quickly to form a larger nucleus of crystals in a new phase (Mullin, 1993). The required time between the achievement of super saturation and the starting of the crystal nuclei is called the induction time. Ali and Schneider (2008) estimated the struvite growth kinetics using four different approaches. The kinetic equation of struvite growth incorporates a mathematical relation with the increase of mean particle size and the solution supersaturation. In approach 1 and 2, they incorporated relative supersaturation to compute supersaturation solution; on the other hand, they incorporated saturation index to compute the supersaturation solution in approach 3 and 4. Different expressions of supersaturation were employed for the kinetic estimation to verify the responses of the struvite growth model. Regy et al. (2002) stated that the struvite crystal growth was generally a two-step process: a mass transfer process across the diffusion layer surrounding the crystal, followed by a surface integration mechanism of the solute into the crystal. The global growth kinetics depends on the kinetics of each step. Thus, if the mass transfer kinetic is greatly lower than the integration kinetics, growth is controlled by diffusion. On the contrary, struvite crystal growth will be controlled by surface integration if the solute transfer is much more rapid than the solute surface integration. The nucleation of struvite can be completed within one minute when the required ions are present in equal molar concentrations (Booker et al., 1999). The reaction kinetics of struvite is as given below (Zhang et al., 2009):

$$\mathrm{Mg}^{2+} + \mathrm{NH}_4^+ + \mathrm{PO}_4^{-3} + 6\mathrm{H_2O} \rightarrow \mathrm{MgNH_4PO_4} \cdot 6\mathrm{H_2O} \downarrow \quad \text{(vi)}$$

$pK_s = 12.6$ at 25 °C. The kinetics of chemical reactions can be written as:

$$-d[\mathrm{C}]dt = k[C]^{\mathrm{n}} \quad \text{(vii)}$$

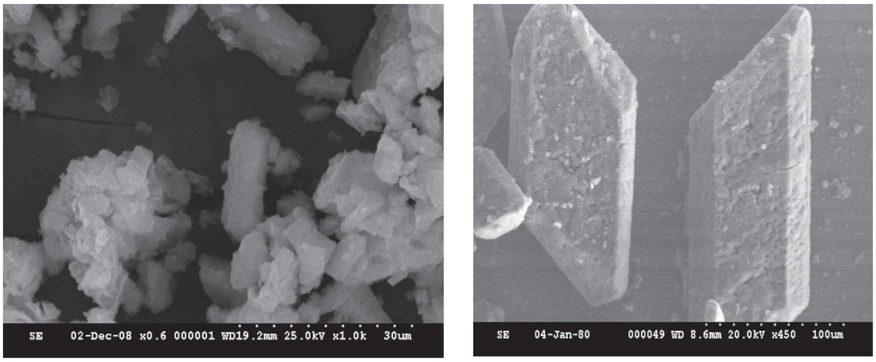
where C is the molar concentration of reactant, t is the reaction time, k is the rate constant and n is the order of reaction.

Zhang et al. (2009) also stated that the first, second and third-order kinetic models were fitted through the struvite precipitation data, and its respective R-square value was 0.99, 0.93 and 0.79, respectively. Some other researchers have furthermore studied the kinetics of struvite precipitation reaction. Nelson et al. (2003) reported that the struvite formation fitted well to the first-order kinetics with the rate constants 3.7 h^{-1} at pH 8.4, 7.9 h^{-1} at pH 8.7 and 12.3 h^{-1} at pH 9.0. Ohlinger et al. (2000) stated that the struvite precipitation fitted to the first-order kinetics with the rate constant 4.2 h^{-1}. They all used the Mg^{2+} to study the kinetic reactions.

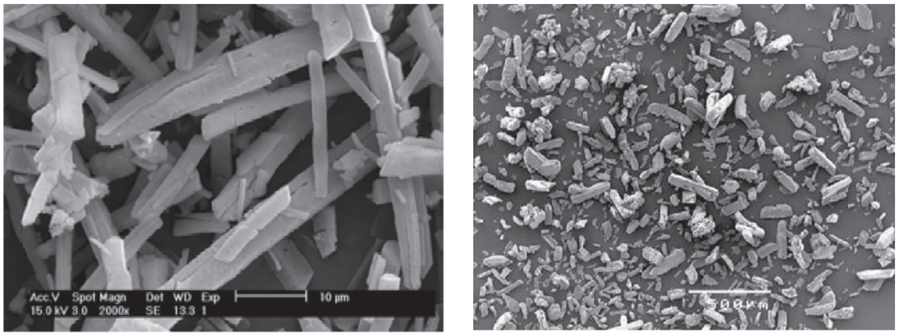
4. Conditions for struvite precipitation

4.1. Molar ratio

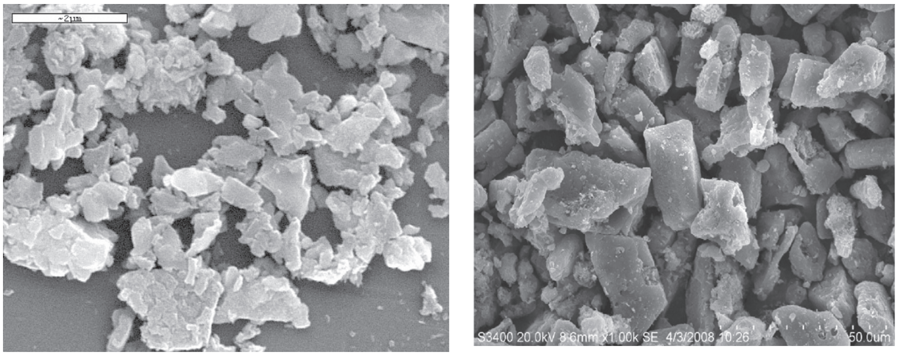
Recently, researchers have tried to identify the factors that influence the struvite precipitation. A lot of factors such as types of chemicals added, $\mathrm{PO_4}$:Mg molar ratio, pH, type of the reactors and the removal efficiency of P and N by several researchers are shown in Table 2. Most of the researchers used $\mathrm{MgCl_2}$ as a source of magnesium for struvite precipitation, but only few of them used $\mathrm{MgSO_4}$, MgO and $\mathrm{Mg(OH)_2}$. Yetilmezsoy and Zengin (2009) found no significant differences between $\mathrm{MgCl_2}$ and $\mathrm{MgSO_4}$ in case of $\mathrm{NH_4}$-N, COD and color removals. However, a much lesser $\mathrm{NH_4}$-N, COD and color removal occurred when MgO was used as a source of magnesium. Kim et al. (2007) stated that magnesium hydroxide attributed to increased TSS in the solutions that lead to a lower $\mathrm{NH_4}$-N removal. From the esthetic point of view, it might be stated that the addition of $\mathrm{MgCl_2}$ as a source of magnesium is more suitable to achieve highest efficiencies of $\mathrm{NH_4^+}$-N, COD and color removals. Therefore, $\mathrm{MgCl_2}$ may be proposed as the best option to achieve the maximum removal of $\mathrm{NH_4^+}$-N through recovery from wastewater. The presence of calcium ion



(a) Irregular crystal (Rahman et al., 2011) (b) Cube like crystal (Cho et al., 2009)



(c) Rod lioke irregular crystal (Le Corre et al., 2007) (d) Irregular crystal (Ali, 2007)



(e) Irregular crystal (Kim et al., 2004) (f) Cube like irregular crystal (Zhang et al., 2009)

Figure 3 SEM of struvite crystals.

(Ca^{2+}) in the wastewater might preferentially react with PO_4 to produce hydroxyapatite, dicalcium phosphate, and octacalcium phosphate. Correspondingly, low level of residual PO_4 was observed by Kim et al. (2007) where Ca^{2+} concentration was approximately 224 mgL^{-1}. Le Corre et al. (2005) found an amorphous calcium phosphate in struvite when high concentration of Ca^{2+} ions was presented in the solution. Doyle and Parsons (2002) also stated that struvite formation can be inhibited by the formation of calcium phosphates. The presence of residual Ca^{2+} in the solution might be the cause of impure struvite. Therefore, it might be stated that highly pure struvite can be achieved by the addition of magnesium and orthophosphate in an ammonia rich wastewater.

It is found that a wide range of PO_4 and Mg ratio was applied for struvite precipitation, but in most cases, the effective ratio was 1:1 or 1:1.2 (Rahman et al., 2011). The addition of chemicals to the wastewaters would be needed to provide an equimolecular condition of PO_4 and Mg. Yetilmezsoy and Zengin (2009) conducted a series of experiments to see the effect of Mg, NH_4 and PO_4 ratio on struvite precipitation and nitrogen removal efficiency. They found a lesser N and COD removal at under dose conditions of molar ratios of $Mg:NH_4:PO_4$ (0.5:1:1, 0.8:1:1, 1:1:0.5, 1:1:0.8) compared to higher molar concentrations (1.2:1:1, 1.5:1:1, 1:1:1.2, 1:1:1.5). Actually, lesser N and COD removal occurred when the molar concentrations of Mg^{2+} or PO_4^{3-} were lower than 1, compared to higher molar concentrations (1.5:1:1 and 1:1:1.5). They concluded that the Mg^{2+}:NH_4^+-N:PO_4^{3-}-P molar ratio of 1:1:1 would be enough for the residual N removal and struvite precipitation. Zhang et al. (2009) stated that suitable Mg^{2+}:NH_4^+:PO_4^{3-} would be 1.15:1:1 in order to remove ammonium effectively and avoid higher concentration of PO_4^{3-} in the effluent. Kozik et al. (2011) found that an average crystal size was 42 µm when the pH was 9.0 and the PO_4:Mg molar ratio

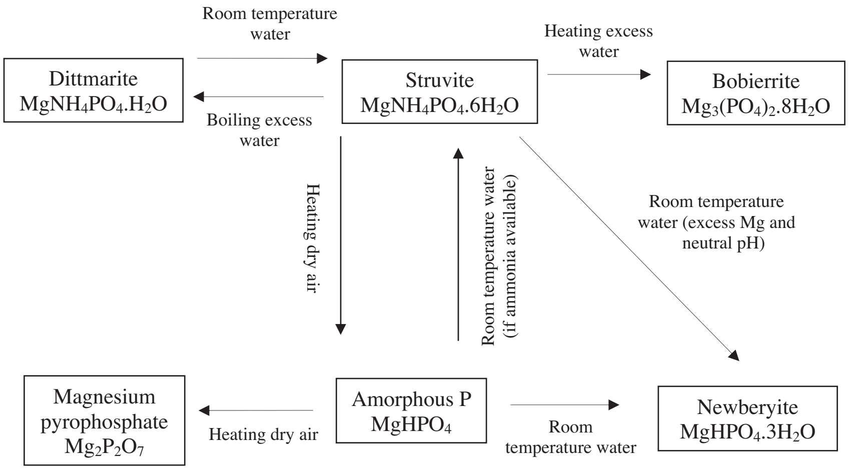


Figure 4 Possible transformation mechanisms of various phases associated with struvite (Bhuiyan et al., 2008).

was 1:1, but the crystal size increased at 58 µm when the molar ratio was increased to 1:1.2 within 30 minutes. The crystal growth was 67 and 80 µm when the PO_4:Mg was 1:1 and 1:1.2, respectively in one-hour reaction at the same operational conditions. Larger crystals were also found by several other researchers with a higher molar ratio (1.2 mole) of magnesium based on the PO_4 of the wastewaters (Koralewska et al., 2009; Matynia et al., 2013; Hutnik et al., 2012, 2013a,b).

Struvite crystallization also occurred in swine manure composting when 1.2 mole Mg was added based on the TN of the manure (Lee et al., 2009, 2010). Lee et al. (2009) found an interesting behavior of the ortho phosphate/total phosphate (OP/TP) ratio in struvite formation during composting of swine manure. They found that the OP/TP ratio decreased when both Mg and PO_4 were added for struvite formation, and the decreasing rate was proportional to the amounts of Mg and PO_4 up to 0.05 molar ratio of Mg. The added Mg and PO_4 react with aboriginal NH_4 or the NH_4 produced during organic matter decomposition, resulting from the formation of struvite and subsequently the OP/TP decreased. In case of addition of only Mg, continuous struvite formation was not found during composting when Mg was below 0.06 molar ratio due to Mg deficiency. Whereas, Lee et al. (2010) stated that a decrease of OP/TP and a clear increase of TP content in the finishing compost might be due to the struvite formation in the finishing compost; because, they added 1.2 mole Mg according to the TN of the swine manure. Finally, they concluded that continuous formation of struvite during composting can be achieved if more than 0.06 molar ratio of Mg according to TP of the manure was added. However, further study is needed to identify the maximum amount of Mg for optimum struvite formation.

4.2. pH

The pH plays an important role during the struvite precipitation process. Struvite or MAP can be precipitated at a wide range of pH (7.0–11.5), but the suitable pH ranges between 7.5 to 9.0 (Hao et al., 2008). Efficiency of MAP precipitation depends on the concentration and molar ratios of Mg^{2+}, NH_4^+, & PO_4^{3-}, pH, aeration rate, temperature, and presence of Ca^{2+} in the reacting media (Stratful et al., 2001; Le Corre et al., 2005; Hao et al., 2008; Yetilmezsoy and Zengin, 2009). The rate of pH decrease reflects the speed of crystal growth rate and also influences the quality of precipitated crystals. So, pH might be used as an indicator of struvite nucleation (Bouropoulos and Koutsoukos, 2000; Kabdasli et al., 2004). Influent pH is also important in transforming of NH_4^+ ions into gaseous ammonia through ammonia stripping. Various researchers have investigated the effect of pH on the removal efficiency of P and N (Ohlinger et al., 1999; Celen and Turker, 2001; Stratful et al., 2001; Battistoni et al., 2001; Dastur, 2001; Adnan et al., 2003). All these investigations have found a higher P and N removal with the increasing of pH. This might establish the fact that the solubility of struvite decreases with increasing of pH (Snoeyink and Jenkins, 1980), thus facilitating higher P & N removal and recovery for a given feed strength. Adnan et al. (2003) also stated that the operating pH should be raised up to 8.3 to get more than 90% P removal. They increased the pH gradually to a higher value and found a smoother operation of the reactor. Theoretically, there should be a direct relationship between pH and the P removal to some limiting value. Steady operation condition in struvite crystallization could be obtained by maintaining the pH, molar ratios, influent flow rate, and temperature. Systematic studies on successful steady-state operation of struvite were obtained both in bench scale operation (Lee et al., 2010; Adnan et al., 2003) and continuous reaction crystallization process (Matynia et al., 2013; Hutnik et al., 2012; Hutnik et al., 2013a,b). It can also be observed that comparable removal efficiencies were obtained in low and medium phosphorus concentrations, since for both feed strengths it was possible to achieve high P removal rates at more or less similar operating conditions.

Solution pH also influences the growth rate of struvite crystal. Ohlinger et al. (1999) showed that the accumulation of struvite on stainless steel coupons in contact with supernatants of anaerobically digested sludge was influenced by the pH. An increase in pH caused an increase of supersaturation and a resultant increase in the growth rate (Le Corre et al., 2009). Ali (2007) stated that the formation of struvite depends upon the reactant concentration and solution pH. He (Ali, 2007) found a mean particle size of 127.77 µm and 133.25 µm where the growth rate of struvite was 1.625 and 0.83 µm h^{-1} and the operating supersaturations were 0.23 and 0.17, respectively. Thermodynamic modeling and simulation along with crystal growth are a function of solution supersaturation. Moreover, pH has also a significant effect on struvite crystal size and purity. Matynia et al. (2006) demonstrated that an increase of pH from 8 to 11 could decrease five times the mean crystal size of struvite formed in synthetic solutions ($NH_4H_2PO_4/MgCl_2/NaOH$). Matynia et al. (2013) also stated that an increase of pH from 9 to 11 decreased the crystal size by more than 2-times in a continuous flow struvite crystallizer (from 20.2 to 9.2 μm, in 15 min where V_w was 1.2 dm^3). It is established through several researches that a comparative higher pH reduces the struvite crystal size within the same reaction time (Kozik et al., 2011; Hutnik et al., 2011, 2012). Struvite precipitation potential significantly increases due to its solubility and decreases with the increasing of pH. Increase in pH produces higher nuclei population densities that might be the cause of producing smaller crystals. Higher pH in the crystallizer is not only responsible for smaller particles, but also higher size diversity. On the other hand, prolonged contact time of crystal suspension with supersaturated condition increased the struvite crystal size significantly.

Le Corre et al. (2007) have also shown that pH was responsible for the change in struvite zeta-potential, hence influencing struvite agglomerative properties. They showed that the crystal size increased from 33.57 ± 0.7 to 84.07 ± 11.2 mm as the zeta-potential decreased in magnitude from -23.37 ± 0.6 to -17.57 ± 1.1 mV. Crystal's size is not only depended on the pH, but also on other factors such as aeration rate (Liu et al., 2011b,c), influent concentration and crystal retention time (Adnan et al., 2003). They (Adnan et al., 2003) furthermore, stated that larger struvite crystal can be achieved when the crystals spend sufficient time within the reactor. They found a linear increase in the mean crystal size with an increase in crystal retention time (CRT). Optimum CRT of 8–12 d is sufficient to achieve the required size (3.5 mm) and structural strength of the crystals.

Hao et al. (2008) stated that transparent rods like crystals were obtained in the ultra-pure water solutions within the pH range of 7.5–9.0 and in the tap water solutions within the pH range of 7.0–8.5. In both solutions with higher pH (more than 9.0), the precipitations became white and even colorful powders, but not crystals. Therefore, the precipitations at higher pH values are not pure struvite. When pH was higher than 9.0, some impurities such as $Mg(OH)_2$ and Mg_3PO_4 probably emerged in the precipitations, which indicates more noisy XRD patterns with reduction in peak intensities and change in peak positions and which also shows more irregular patterns in the microscopic images. In other words, the existence of Ca^{2+} in the tap water solutions at higher pH values would contribute to more impurities like Ca_3PO_4 and even $CaHPO_4$ (Yigit and Mazlum, 2007), besides $Mg(OH)_2$ and Mg_3PO_4 found in the ultra-pure water solutions.

Very recently, Hao et al. (2013) described a little different statement about the pH properties during struvite formation. They found that XRD data misled the researchers into believing that the harvested crystals were struvite, but in fact, it was amorphous phosphorus. Struvite precipitation is a pH dependent reaction and pure struvite is form near neutral pH. From the elemental analysis of the crystals, they confirmed that the highly purified (99.7%) struvite was formed at pH 7.0–7.5 at a longer period of time (three months) under ambient temperatures (25–30 °C) and controlled conditions. They also found that the struvite content decreased to around 30–70% at pH 8.0–9.0, and over pH 9.5, the content decreased sharply to $< 30\%$. Higher pH levels (> 10.5) resulted in the complete disappearance of struvite in the precipitates.

4.3. Aeration rate

Air flow plays an important role in the removal of NH_4-N from the solution. Air flow agitates the solution and creates a removal pathway for dissolved ammonia to volatilize from the solution. Moreover, air flow dilutes the concentration of gas-phase NH_4-N and increase the driving force for dissolving NH_4-N to separate the gaseous phase. So, there is an increasing tendency for ammonia volatilization with increasing air flow rate. Yetilmezsoy and Zengin (2009) stated that a sufficient aeration time should be provided to achieve high removal efficiencies. They obtained about 93.4% NH_4-N removal with an aeration rate of 0.6 L min^{-1} within a period of 24 h. They also found the highest NH_4-N removal (95.3%) in 12 h reaction time with an aeration rate of 10 L min^{-1}. Lei et al. (2006) found about 60.2% ammonia removal with an aeration rate of 0.6 L min^{-1} in a reaction time of four hours. On the contrary, they achieved the same removal efficiency without aeration in a period of 24 h. Liu et al. (2011b,c) found that struvite formation is proportional to the aeration rate and reached a plateau at around 0.73 L min^{-1}. Suzuki et al. (2007) stated that aeration rate enhanced the CO_2 stripping that helps to raise the pH of the aeration column. They found the pH ranged between 7.5 and 8.0 when the aeration rate was 12 m^3 h^{-1}, but a higher pH (range between 8.0 and 8.5) was found when the aeration rate was 16 m^3 h^{-1}. Higher aeration also enhances the foam formation in the aeration column during crystallization process, and it is necessary to use defoaming agent.

4.4. Operation mode of crystallization process

The operation mode of crystallization process has an important role on the performances of struvite production. Researchers are trying to get the highest removal of PO_4 and NH_4 through struvite precipitation from wastewaters through different types of reactors (Table 2 and Fig. 5). Cost involvement in preparation of reactors also influenced the production cost of struvite. Le Corre et al. (2007) designed a pilot-scale crystallization reactor continuously fed with synthetic liquors with two concentric stainless steel meshes that were immerged in the upper section (Fig. 5a). They found that the system combining two concentric meshes placed in the enlarged section of the pilot-scale crystallization reactor could accumulate struvite at a rate of 7.6 g m^{-2} h^{-1} under optimum conditions of precipitation and also to achieve 81% PO_4 removal. Suzuki et al. (2007) constructed a continuous flow reactor with three layers of stainless steel wire mesh providing aeration and settling zones (Fig. 5b). They produced 65.0 kg struvite in 70 days operation where influent loading rate was 5.3 m^3 day^{-1} and the struvite recovery rate was 171 g m^{-3} wastewater.

Bhuiyan et al. (2008) precipitated a comparative larger struvite crystal (0.5–3.5 mm) with a fluidized bed reactor consisting of an external clarifier, a storage tank for receiving anaerobic digester supernatant (PO_4 and NH_4 rich wastewater), several pumps for controlling feed materials, $MgCl_2$ and NaOH solutions. $MgCl_2$ and NaOH solutions were added into the reactor through the injection ports, just above the feed and recycle flows. Ali and Schneider (2008) designed a batch reactor with auto control of feed and temperature (Fig. 5c). Volume of the reactor was 44 L, made with clear perspex allowing the seed to keep in uniform and full suspension. A pH controller controlled the pH set point and triggered feed addition when solution pH dropped below the set point. Two dosing pumps were operated for the addition of feed solution based upon the output signal sent from the pH controller. They controlled the temperature through encompassing a plastic-coated copper-cooling coil, resistive temperature device and solenoid valves. They try to estimate the struvite growth kinetics using four different approaches with this highly controlled reactor. They also establish the kinetics of struvite growth and the mathematical relation between mean particle size and the solution supersaturation.

A simple reactor was designed by Rahman et al. (2011) where continuously feeds were added in a Plexiglas reactor (12.3 L). Influent wastewater and $MgCl_2$ solutions were added to the reaction zone through the pump where air flow rate was 0.73 L min^{-1} (Fig. 5d). Irregular white crystals were produced with 93% PO_4 and 31% NH_4 removals with this crystallizer. A glass made continuous flow type cylindrical tank equipped with heating/cooling jacket was developed by Hutnik et al. (2013a,b). The process was also equipped with a draft type circular tube with a three-paddled propeller (Fig. 5e). PO_4, Mg and NH_4 were added in a ratio of 1:1:1 and 1:1.2:1 in a varied pH and fixed temperature. High-quality elongated crystals were produced through this crystallizer. It was also found that the unit process yield was small with this process condition and thus, a lower economic efficiency of a whole production plant was reported. Successful steady-state operation in the continuous reaction crystallization process was found where continuous struvite reaction crystallization process ran in original jet-pump crystallizers of various scales, which operate successfully in a continuous regime (Matynia et al., 2013).

5. Fertilizer quality of struvite

5.1. Nutrient leaching rate

Struvite is an effective fertilizer as its nutrient releasing rate is very slow. Rate of N release also depends on the size of the crystals. Nelson (2000) studied the N releasing pattern by measuring N uptake rate from three different sizes of struvite crystals (< 2 mm, 2–3 mm, and 4–8 mm) on ryegrass grown as a greenhouse. He found that the struvite particle size affected N release in the first 3–6 weeks after planting, when the smaller particle sizes released more N than the coarser particles did. After 6–9 weeks, the N release was similar for all particle sizes. Johnston and Richards (2004) also stated that struvite was the typical control released fertilizer, after testing the growth of potted ryegrass. It was found from the investigation that the uptake rate of P of struvite was 100% (Westerman et al., 2009).

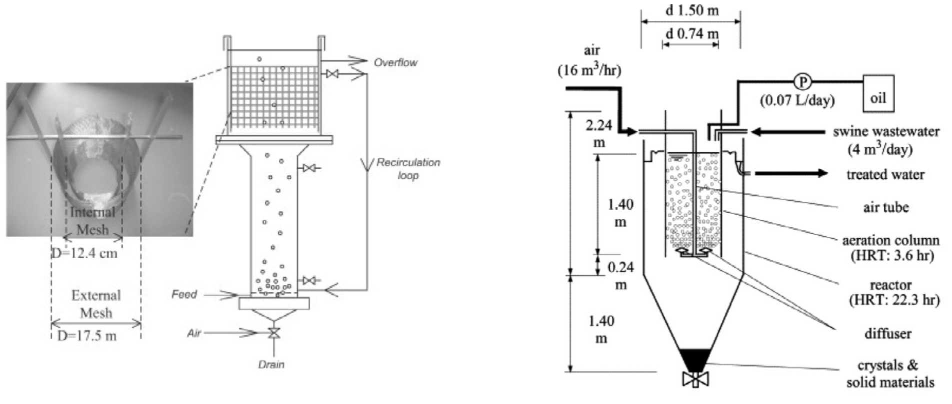
Struvite has been successfully used on turf grass, tree seedlings, ornamentals, vegetables, flower boards and garden grass as fertilizer (Munch and Barr, 2001; Nelson et al., 2003; Gonzalez Poncer and Garcialopez, 2007; Yetilmezsoy and Zengin, 2009), and found it as an excellent fertilizer. Moreover, struvite would be the most alternative fertilizer for a few crops, like sugar beet that needs magnesium (Gaterell et al., 2000). Over application of struvite does not burn the roots due to its slow releasing characteristics, which is common with traditional ammonium–phosphate fertilizers (Scope Newsletter, 2003). It has a long residual effect on the root zone of plant that makes it more advantageous on soluble fertilizers. Highly soluble fertilizers are undesirable in grasslands and forests, where fertilizers are applied once in every several years. A slow-releasing fertilizer would be effective in such environments. According to Bashan and Bashan (2004), struvite may have a low leaching rate and slowly releases nutrients during the plant growing season. Small quantities of recovered struvite are currently being tested on ornamental plants as fertilizer. It is essential to evaluate the efficiency of struvite on different types of crops and plant growth as an alternative source of fertilizer. The fertilizer properties of struvite have been investigated by several researchers (Schuiling and Andrade, 1999; Li and Zhao, 2003; Yetilmezsoy and Zengin, 2009; Liu et al., 2011a). From the last decade, struvite had been commercially produced in Japan, and sold to fertilizer companies (Ueno and Fujii, 2001). It is very effective for those crops, which needs low-soluble fertilizers. The presence of magnesium makes struvite useful for sugar beets because sugar beet needs magnesium ions (Bashan and Bashan, 2004). This slow-release behavior is ideal for coastal agriculture.

Rothbaum and Rohde (1976) found that struvite showed the higher growth of grass, fruit and various crops, compared with conventional fertilizers. It is well suited for fertilizing turf grass not only providing the N and P, but also for the presence of the Mg, because it is the vital element of chlorophyll, which is responsible for the green coloration of the plants. Fernandez-Escobar et al. (2004) found that less than 20% of the urea N was recovered by fruit trees. They also stated that the annual application rate of N fertilizer for olive orchards is 350 kg ha^{-1}. Low N recovery by the fruit trees might be due to higher N loss by leaching and evaporation that results in a negative impact in the environment. Thus, urea fertilization increases the global warming issue. In that situation, struvite would be an effective eco friendly fertilizer for fruit trees.

5.2. Soil type and struvite

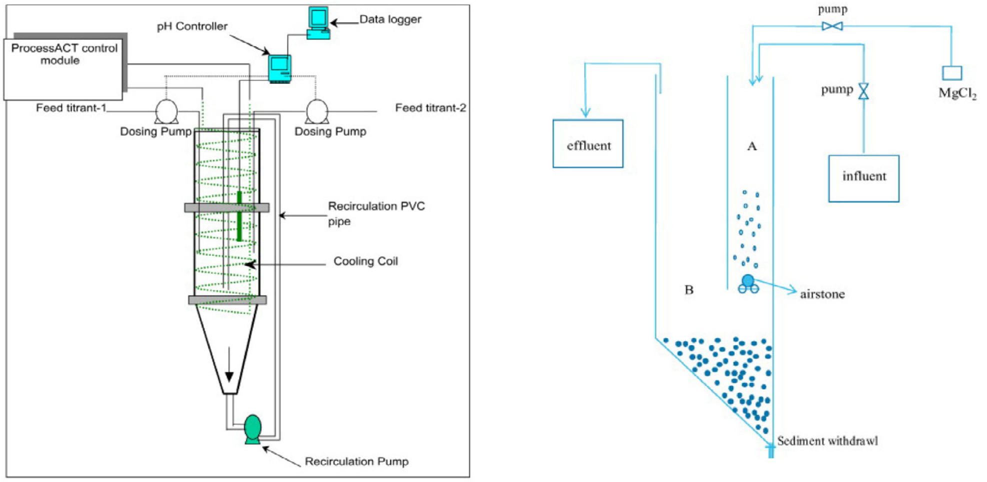
Gonzalez Poncer and Garcialopez (2007) studied the effectiveness of struvite as a P source compared to that of phosphate rock, mono ammonium phosphate and calcium superphosphate on potted ryegrass. The doses applied with each source were 0, 8, 16, 24, 32 and 40 mg of P kg^{-1} of soil. They found that plant P concentration was greater than all of these fertilizers compared to no fertilizer applied. Moreover, struvite treated ryegrass achieved greater P concentration than that of any other P sources. It might be revealed that the P uptake rate is higher from struvite than that of any other PO_4 fertilizers.

Calcareous soil contains high concentrations of Ca phosphate that substantially decreases the solubility of rock phosphate. Manure and compost could be used for organic production in calcareous soil; rock phosphate and bone meal might also be used as fertilizer, but they are ineffective as fertilizers in calcareous soil. So, development of a sustainable, effective alternative P fertilizer for calcareous soils is important



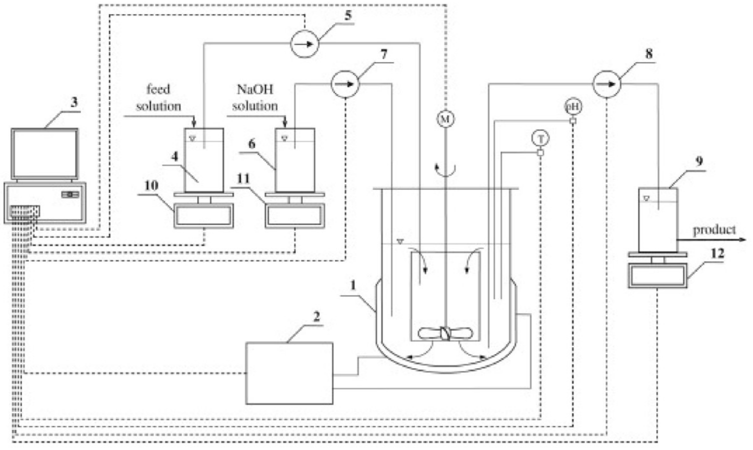
(a) Continuous flow reactor (Le Corre et al., 2007)

(b) Continuous flow reactor (Suzuki et al., 2007)



(c) Batch reactor (Ali and Schneider, 2008)

(d) Continuous flow reactor (Rahman et al., 2011)



(c) Continuous flow reactor designed by Hutnik et al. (2013a), where 1- DT MSMPR type crystallizer with internal circulation of suspension, 2- thermostat, 3- PC computer, 4- feed reservoir: wastewater, $MgCl_2$ and NH_4Cl, 5- feed proportioner (pump), 6- alkalinity agent tank: aqueous solution of NaOH, 7- proportioner (pump) of NaOH solution, 8- receiver (pump) of product crystal suspension from the crystallizer tank, 9- storage tank of a product crystal suspension, 10, 11, 12- electronic balances, M- stirrer speed control/adjustment, pH- alkaline/acid reaction control/adjustment, T- temperature control/adjustment.

Figure 5 Recently adopted struvite crystallizers.

for organic agriculture in semi-arid environments. According to Lindsay (1979), struvite is substantially more soluble than Ca phosphates at alkaline pH, and hence it is a potential P fertilizer in calcareous soils. Massey et al. (2007) conducted a greenhouse trial for organic wheat production in calcareous soil to investigate the effectiveness of recovered struvite as a fertilizer in different types of soil conditions. They found that struvite is very effective in moderately acidic and moderately alkaline soils. Increased P concentration within the plant as well as higher yield was found in struvite applied plants in semiarid environment (Massey et al., 2009). Pastor et al. (2008) also stated that struvite was an effective fertilizer source in acidic and hilly lands. The presence of access heavy metals in the fertilizers reduced the crop yield (Islam et al., 2010). Struvite also contains some heavy metals, because wastewater contains a significant amount of heavy metals. Heavy-metal ions can be incorporated into the struvite crystalline network not only by nucleation, but also during the crystal growth process. Although the struvite contains heavy metals, it is perfectly maintained the legal limits for fertilizers (Munch and Barr, 2001; Antakyali et al., 2006; Guney et al., 2008; Qiu et al., 2011; Liu et al., 2011b,c). So, it is also an eco-friendly fertilizer regarding heavy-metal situation. Pretreatment with membrane filtration might be an effective method of reducing heavy metal contamination in struvite. Use of the Donnan membrane process can successfully remove metal ions from P rich wastewaters by the help of a Nafion 117 membrane after dissolution in the acidic media (Prakash et al., 2004; Guney et al., 2008). Table 3 shows the heavy-metal situation of struvite with its legal limit.

Table 3 Heavy metal concentrations in MAP compared with the limit value of heavy metals in fertilizer.

Heavy metals (mg/kg)	Legal limit		MAP from anaerobic digester (Munch and Barr, 2001)	MAP from digested Sludge (Weidelener et al., 2005)	MAP from digested sludge Liquor (Antakyali et al., 2006)	MAP from ILDS (Guney et al., 2008)	MAP from Swine wastewater (Liu et al., 2011b)
	German fertilizer regulation, 2003	Queensland regulation, Australia					
Copper	70	–	ND	1.8	1.67	34	16.06
Cadmium	1.5	350	<4	<0.5	<0.4	0.9	ND
Nickel	80	–	–	1.1	<0.4	0.9	ND
Zinc	1000	–	ND	5.2	7.7	49	81.44
Lead	150	100	<5	<0.5	<0.4	2	ND
Chromium	2	–	ND	8.6	0.45	1.6	ND
Mercury	1	5	0.2	0.05	0.06	0.01	ND

ND = not detected.
$<$ = is less than.

Application of struvite in the agricultural sector would be a profitable investment. Generation of 1 kg of struvite per day is enough to fertilize 2.6 ha of arable land by applying phosphorus (as P_2O_5) at the rate of 40 kg ha^{-1} per annum (European Fertilizer Manufacturers Association, 2000; Zheng et al., 2004). Shu et al. (2006) stated that 100 m^3 wastewater could recover 1 kg MAP per day that would lead to an increase of nine tons in dry grain yield. Furthermore, it helps to create an eco-friendly environment by reducing the need of rock phosphate.

5.3. Eco-friendly crop/agricultural production

Agricultural soil contributes only 1% of the global CO_2 whereas, CH_4 and N_2O emissions were 39 and 60%, respectively (OECD, 2000), and nitrogen fertilization is the chief source of NO, N_2O and CH_4 emission from the soil (Matson et al., 1998; Perala et al., 2006; Chu et al., 2007; Aguilera et al., 2013). Greenhouse gases (CH_4, CO_2, NO, N_2O) are the key elements for global warming and presently efforts are going on to reduce these gases. Urea is widely used as nitrogen fertilizer worldwide that released N rapidly to the soil, from which only 40% is recovered by plant and 60% is lost by different ways (Liang et al., 2007) and maximum loss was estimated as evaporative loss (26.5–29.4%) that contributed to greenhouse-gas emission. Methane contributes to climatic change by trapping outgoing terrestrial infrared radiation 20 times more effectively than CO_2 (Getachew et al., 2005), whereas N_2O is 300 times more potent than CO_2 in absorbing terrestrial thermal radiation (IPCC, 2001) in the troposphere that enhances global warming. Application of struvite as fertilizer may reduce the risk of global warming, although it contains only 6% N. Due to slow releasing characteristics (Nelson, 2000) of struvite, plant can uptake most of the N without any wastes (Lee et al., 2009; Westerman et al., 2009) after application in the soil. A controlled-release N fertilizer is the best solution to minimize the N_2O emission from soil (Chu et al., 2007). Nitrous oxide production by nitrification and denitrification of agricultural nitrogen that is lost from the field through leaching and runoff is directly influenced on global warming (Nevison, 2000). One kg of volatilized NH_3-N contributes approximately 0.01 kg of N_2O (Mkhabela et al., 2008). A large amount of N_2O is emitted every year through urea fertilization throughout the world. From this perspective, struvite would be a useful alternative to traditional N fertilizers because reducing the greenhouse-gas emissions might be possible due to its slow releasing pattern. Mao et al. (2005) stated that slow releasing N fertilizers would be the best alternative to traditional N fertilizer as they reduce N loss through leaching and volatilization. Not only this, production of struvite simultaneously reduced the P and N from wastewaters that help to reduce the risk of eutrophication in water bodies. Liu et al. (2011a) stated that MAP might be the ideal eco-friendly fertilizer for crop production. They conducted a comparative experiment with MAP and commercial P and N fertilizer for maize forage growth. They used MAP as P and N source; on the other hand, equivalent weight of P was used from FSP, and N was used from urea fertilizer. The results revealed that biomass yield and crude protein percentage were significantly higher in MAP treated groups compared to FSP-urea treated groups. At the same time, N_2O emission was 3-fold higher in FSP-urea treated group than in MAP treated group. A similar study (Rahman et al., 2011) also found that N leaching was also 3-fold lower in MAP than in commercial N fertilizer. Slow solubility rate might be the cause of a lower leaching tendency in MAP treated groups. Lower leaching rate of N and lower emission of N_2O made the struvite as an eco-friendly fertilizer (Ueno and Yamamuro, 1996). Finally, it could be said that struvite was an ideal slow-release fertilizer, and thus, application of it as a fertilizer could create an eco-friendly environment by reducing the greenhouse-gas emissions.

6. Essentials of struvite recovery

It is estimated that the present reserve of mined phosphate rocks is 7000 million tons as P_2O_5, in which 40 million tons of P rock are used for fertilizer production and human consumption every year (Florida Institute of Phosphate Research, 2005). Rock phosphate is used as raw materials for the production of phosphate fertilizer, which are not evenly distributed throughout the world. Morocco and China are called the reservoir of P rock that reserves about 68% of the total P rock around the world. Fig. 6 shows the distribution of P rock around the world where Morocco is clearly on the driver's seat. There is a growing demand for sustainable phosphorus resources in the industrialized world for fertilizer production. It is predicted that the demand of P will increase by 1.5% each year (Steen, 1998). So, it might be stated that the mined P rocks will be exhausted within 90 years, assuming a 1.5% annual increase of utilization. Shu et al. (2006) stated that all reserved P rocks would be exhausted by the year 2090 at 1.5% increasing utilization trend. In contrast, mined P rock will be continued up to the year 2200, if the utilization decreases 1.5% each year. Decreasing of P rock utilization is impossible without the recovery of organic phosphate. Because agricultural production depends on P utilization, and currently there are only a few alternative sources of P for crop production (Sharpley, 2001). Very recently, Elser and Bennett (2011) described that the maximum production of reserved rock P will continue up to 2030 and then will be started to decrease, which might increases its price. They suggested taking the immediate recycling program of P from wastewaters. It is possible to remove 93% P (Rahman et al., 2011) and 40% N (Cho et al., 2009) through struvite crystallization from wastewaters. The utilization of MAP as fertilizer would help to reduce the application of rock phosphate in the agricultural sector.

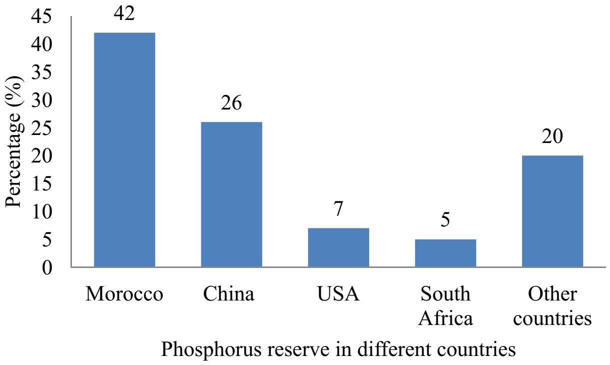


Figure 6 Phosphate rock reserve in the world.

At present, the average world P fertilizer application rate is 21.62 kg ha^{-1} $year^{-1}$ as P_2O_5 over arable land of 1.48 billion ha (Wild, 1993). This already indicates a shortage in the utilization of P as fertilizer, because the required rate of application is 40 kg ha^{-1} $year^{-1}$. Once the P resources are exhausted, application rates would have to be reduced to around 1 kg ha^{-1} $year^{-1}$, depending upon the population (Shu et al., 2006). This situation is very alarming for the crop production, and also to feed the fast-growing world population, and hence, P recovery from organic sources is an urgent need to optimize crop production and human consumption. Phosphorus recovery from wastewaters is an effective way to overcome this situation. Research is currently going on to recover phosphorus from wastewater, since domestic sewage offers a great potential for phosphorus to be recovered and recycled (Driver et al., 1999; Massey et al., 2009).

It is assumed that a wastewater treatment plant (WWTP) can recover one kg of MAP from 100 m^3 of wastewater (Munch and Barr, 2001), considering that the wastewater contains 7 mg PO_4^{3-} L^{-1} and the phosphorus recovery rate is 55.3%. It is possible to recover 0.63 million tons of phosphorus annually as P_2O_5, if 50% of the global population (6 billion) is connected with wastewater treatment plant (WWTP), assuming that each person generates 2.5 g phosphorus yearly, and the recovery rate is 55% (Shu et al., 2006). It is also assumed that a 3.6-folds increase of P recovery is possible if the entire human population connected to WWTPs and the phosphorus recovery rate is 100%. It is equally important to recover all P from livestock and industrial wastewaters. So, struvite crystallization is simultaneously beneficial for the mankind by providing slow-releasing, high-quality fertilizer, and reducing the risk of soil and water pollution by recovering the N and P from wastewaters.

7. Conclusion

Struvite crystallization process is an effective eco-friendly process that removes and recovers P and N from wastewaters. The hazardous elements in wastewaters (mainly NH_4 and PO_4) might be converted to a valuable resource through this process. So, the optimization of Mg molar ratio, pH level, aeration rate, reaction time and temperature would enhance the quality as well as production. About 90–94% P and half of the N are recovered as struvite during the crystallization process. Although the amount of N is less in struvite, a huge amount of N is removed from wastewaters through ammonia stripping during the struvite crystallization process. Struvite would be the principal P fertilizer after exhaustion of all mined P rock in near future. It is a slow-release valuable fertilizer that reduces the cost of production in agriculture. So, it is necessary to develop the optimum conditions for small-scale and commercial production of struvite.

8. Future prospect

i. Production of struvite from wastewaters will reduce the hazard of eutrophication in the water bodies by removing N and P.
ii. Struvite will be the most effective alternative source of P that will help to continue agricultural and animal production after exhaustion of all mined phosphate rock.
iii. Small-scale and commercial struvite production plant will be established at the wastewater production site throughout the world.
iv. Production of struvite from wastewater and its utilization as fertilizer would partially help to reduce global warming and thus, it would be an effective eco-friendly fertilizer.

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