Phosphorus recovery as struvite from farm, municipal and industrial waste: feedstock suitability, methods and pretreatments

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Abstract

Global population growth requires intensification of agriculture, for which a sustainable supply of phosphorus (P) is essential. Since natural P reserves are diminishing, recovering P from wastes and residues is an increasingly attractive prospect, particularly as technical and economic potential in the area is growing. In addition to providing phosphorus for agricultural use, stripping P from waste residues and effluents lessens their nutrient loading prior to disposal. This paper critically reviews published methods for P recovery from waste streams (municipal, farm and industrial) with emphasis on struvite (MgNH₄PO₄·6H₂O) crystallization, including pretreatments to maximize recovery. Based on compositional parameters of a range of wastes, a Feedstock Suitability Index (FSI) was developed as a guide to inform
researchers and operators of the relative potential for struivite production from each waste.

Keywords: struvite, phosphorus, anaerobic digestion, nutrients, pre-treatments

1. Introduction

1.1. Phosphorus: Concerns and possibilities

The global population is projected to rise by 40% from 7.2 billion individuals in the year 2013 to 9.6 billion by the year 2050 (UN, 2014) with food consumption increasing at a rate of 3.1% per year (Heffer and Prud’homme, 2014). Requirements for food security necessitate the sustainable intensification of agricultural production towards supporting productivity gains and income generation (Zapata and Roy, 2004); to meet this demand agricultural productivity is expected to grow by 60% (FAO, 2013). Fertile soils are the key to sustainable production of crops for food, feed and fibre and essential for supporting rural livelihood needs, however few soils are fertile without the addition of plant-available nutrients from organic matter (manure) and commercial fertiliser (Dawson and Hilton, 2011). Commercial fertilisers depend upon the continuing availability of rock phosphate reserves (Heckenmüller et al., 2014); however it has been predicted that the global supply of phosphorus (P) will run out in under 70 years. P is readily fixed by other chemical constituents (e.g. Ca, Fe, Al, Mg, K) making it a key limiting factor in soils globally (Shen et al., 2011), with consequences including reduced yields, delayed maturity and lowered disease resistance across 40% of the world’s arable soils (Vance, 2001). Agro-ecosystems account for 80-90% of the world’s total P consumption (Childers et al., 2011) with 41.8Mt of P fertiliser consumed in 2013 globally (Heffer and Prud’homme, 2014). Global P demand is forecast to grow at an annual rate of 1.9% over the period 2013 to 2018 (Heffer and Prud’homme, 2014) with
consumption stabilized in the developed countries, but demand increasing in the
developing world (Heffer and Prud’homme, 2010). In this context, recovery of P
through efficient and economically viable processes from non-conventional P-rich
sources such as wastes and residues is clearly a priority for sustainable development.

Understanding of the sedimentary biogeochemical cycle of P is helpful to
identify the possible P sinks in nature for effective P management. During the cycling of
P in the terrestrial and aquatic environment, significant amounts of P end up in P-rich
waste from farms, municipal wastes and industrial processes, prompting recent calls for
changes in waste management strategies to promote recycling of waste P. The most
common method of P recovery is through production of mineral or salt precipitates from
P-rich sources such as the mineral struvite (magnesium ammonium phosphate;
MAP/MgNH$_4$PO$_4$.6H$_2$O) (de Bashan and Bashan, 2004). Struvite by mass is 44%
crystal water, 39% phosphate, 10% magnesium, and 7% ammonium (Gell et al., 2011)
and its precipitation requires the presence of three ionic species, magnesium (Mg$^{2+}$),
ammonium (NH$_4^+$) and orthophosphate (PO$_4^{3-}$) in an alkaline solution with an optimum
molar ratio of 1:1:1 (Rahaman et al., 2008). The factors that govern the precipitation of
struvite in P-rich sources include: pH, the ionic strength of solution (Nelson et al.,
2003), the presence of impurities or non-participating ions (Le Corre, 2007), the mixing
energy (Wang et al., 2006), the residence time of suspension during crystallization
(Kozik et al., 2013) and the nature of the reactor used for crystallization (Koralewska et
al., 2009).

Struvite is an ideal alternative fertilizer since it is a non-odorous, non-sludgy
crystal which releases nutrients slowly (Bouropoulos and Koutsoukos, 2000) and has
low solubility in water thus avoiding eutrophication problems that may arise from other
P fertilizers (Zhang et al., 2012). Woods et al. (1999) demonstrated that P recovery from
sewage sludge via formation of calcium phosphate granules resulted in reduced biosolid
concentrations of 11-49% when a Crystalactor® fluidized bed reactor was used as a
tertiary application following conventional biological treatment, compared to
conventional treatment without the P recovery step. When sidestream Crystalactor
technology was applied with enhanced biological nutrient removal (EBNR), reductions
in biosolids ranged from 5-30% compared to EBNR only. Technologies that reduce the
disposal volume of sludge are environmentally useful since the waste becomes suitable
for environmental disposal (Gell et al., 2011). Integration of a nutrient recovery plan
with a waste management system will result in cost efficient relocation of excess
nutrients (Burns and Moody, 2002).

While struvite recovery has been widely investigated as a waste water treatment
method (Munch et al., 2001), it is only recently that its prospects as an alternative P-rich
fertilizer source have been realised. Here we review the different approaches taken for
struvite recovery, i.e. suitability of sources from farm, municipal and industrial origin,
scales and method of pre-treatments and production to enhance struvite recovery.

1.2. Spontaneous struvite precipitation and issues concerning prevention

Spontaneous struvite precipitation in pipes and containers in wastewater
treatment processes is often seen as a nuisance which can reduce system efficiency and
increase operational cost (Jaffer, 2002). Struvite scale formation is found frequently in
anaerobic digester units, digester liquor discharge line, heat exchangers and in
centrifuge dewatering units downstream of the digester system of wastewater plants.
Struvite occurs in regions of high turbulent flow (e.g. in valves, pipe joints and aeration
assemblies) when concentrations of Mg$^{2+}$, NH$_4^+$ and PO$_4^{3-}$ are favourable and the
mixing energy is appropriate (Bhuiyan, 2007). In such zones, degassing of carbon
dioxide results in localised increase in pH favouring struvite formation (Wu et al.,
During anaerobic digestion of waste water sludges, mineralization of nutrients bound to organic matter occurs (Seadi et al., 2012) forming phosphate (also known as orthophosphate). NH$_4^+$ becomes available from the degradation of nitrogenous material in organic wastes and this increases the potential of struvite formation (Bhuiyan et al., 2007). Sometimes recirculation of digested effluent from an advanced treatment unit to a previous treatment unit is carried out to obtain a lower concentration of total solids and biochemical oxygen demand, which subsequently causes nutrient looping (Evans, 2007; Fattah and Chowdhury, 2014). Returning of sludge dewatering liquors to previous treatment units has been reported to contribute 20% of the total nitrogen and phosphorus load of the effluent (Evans, 2007). This also creates suitable conditions for struvite formation. In a recent study by Maab et al. (2014), production of struvite in a wastewater treatment plant and its application as fertilizer, added value to the process for both operator and end users.

Where struvite scaling is problematic, various (physical and chemical) strategies have been taken to minimize the risk of its formation. These include: (a) elimination of super-saturation by precipitating out one of the constituents of struvite by chemical dosing (Mamais et al., 1994); (2) removal of the phosphate by external addition of chloride and sulphate salts of iron (Fe) or aluminium (Al) forming Fe$_3$(PO$_4$)$_2$.8H$_2$O and Al$_2$(PO$_4$)$_3$ respectively (Mamais et al., 1994); (3) phosphate fixation into the dewatered sludge cake by addition of magnesium hydroxide (Mg(OH)$_2$) which increases the alkalinity of the sludge, favouring availability of P as PO$_4^{3-}$ and (HPO)$_4^{2-}$ which may be fixed by Mg$^{2+}$ and calcium (Ca$^{2+}$), thus decreasing P availability for struvite formation (Wu et al., 2005); (4) use of chemical inhibitors and chelating agents (nitrilo-tri-acetic acid, acetyl acetone, ethylenediaminetetraacetic acid (EDTA) (Doyle et al., 2003), which selectively bind the constituents of struvite and do not allow its formation;
6) use of ultrasonic technology, which prevents struvite scale formation by employing ultrasonic vibration to keep the pipelines continuously in motion. Ultrasonic technology is commercially in use in sewage treatment plants in Korea.

The methods to control struvite scaling may be effective, but have drawbacks in terms of cost (labour, materials and time) which can make them impractical (Ohlinger et al., 1998); in addition they may have negative environmental impacts and only alleviate the problem rather than removing it completely. For instance, chemical P removal by adding Fe and Al salts increases the total solid content of the sludge and further recovery of P from the resultant precipitates is difficult (Wu et al., 2005). Agricultural application of the remaining sludge then becomes a matter of concern (Wu et al., 2005).

Deposition of struvite scale is responsible for reductions in wastewater treatment efficiency. However, efficient and controlled production of struvite can be economically beneficial because of its potential fertilizer value. Therefore, in the absence of an affective struvite mitigation strategy, controlled and intentional precipitation has been aimed for as a means of ‘harvesting’ the P-rich struvite. Designed precipitation of struvite can alleviate the scaling problem and produce a high value fertilizer.

2. Struvite recovery: Feedstock sources

A range of feedstock sources has been reported for the precipitation and recovery of struvite (Table 1). These feedstocks can be categorized into three groups viz. farm waste, municipal waste and industrial waste depending upon their occurrence or origin. Abundance of a source and need for its treatment are two main deciding factors that make it suitable for struvite recovery. Some inexhaustible and easily accessible natural P sinks such as animal manure and urine represent potential sources for struvite production in addition to some industrial wastes with high P concentrations (for example, carmine dye industry, semiconductor industry, fertilizer
industry, Cola beverage industry and wastewater. However, some sources need to undergo pre-treatment in order to release P into an available form to make the recovery process effective (Shen et al., 2011) due to the presence of limiting ions such as \( \text{Ca}^{2+} \) and \( \text{Fe}^{3+} \) which minimize recovery (Le Corre et al., 2009). Further, for sources with lower availability of participating ions (\( \text{NH}_4^+ \) and \( \text{PO}_4^{3-} \)), the struvite recovery process requires chemical supplementation. In this review, 23 potential sources for recovery of struvite are identified. Human urine and wastewater sludge are the only two sources where commercial scale recovery has been demonstrated. In a further 21 sources, feasibility of recovery has been reported only at laboratory scale.

(Table 1 Sources used for recovery of struvite and process conditions)

2.1. Laboratory feasibility studies

Several waste sources have been suggested as potentially feasible for struvite recovery at the laboratory scale (Table 1), but have yet to be up-scaled. In general, these feasibility studies all ensure the availability of \( \text{P}, \text{Mg}^{2+} \) and \( \text{NH}_4^+ \) in alkaline solution along with some form of energy for mixing, although specific compounds and reaction conditions vary. The pH range reported to be favourable for struvite precipitation varies from 8-11 (Kabdasli et al., 2009). P recovery efficiency is generally high and often >90% (Table 1) with municipal wastewater averaging 95% (Pastor et al., 2010; Uysal et al., 2010) and landfill leachate (Iaconi et al., 2010), human urine (Ganrot et al., 2007) and carmine dye industry (Chimenos et al., 2003) wastewater processes reporting 100% recovery. Struvite also captures \( \text{NH}_4^+ \) with recovery efficiency as high as 98% for municipal wastewater and semiconductor wastewater (Suscha and Polawski, 2003; Kim et al., 2009).
2.1.1. Farm wastes

Improper management of farm wastes through unintended release into the environment can lead to a range of pollution problems (e.g. emissions, eutrophication) and struvite recovery could serve as an effective means of recycling the excess nutrients. Out of the 49 studies included here (Table 1), six reported use of farm waste as a struvite recovery source. Farm waste represents the most inexpensive and abundantly available stock for struvite recovery. Among farm wastes, successful struvite recovery has been reported in cattle manure (Demirer et al., 2005; Zhao et al., 2010; Shen et al., 2011), swine manure (Burns et al., 2001, 2003; Nelson et al., 2003; Suzuki et al., 2007; Perera et al., 2007; Ryu and Lee, 2010; Liu et al., 2011; Huang et al., 2011; Zhang et al., 2012), poultry manure (Yetilmaz et al., 2009) and cattle urine (Prabhu and Mutnuri, 2014). In general manures are rich in P and $\text{NH}_4^+$, which is desirable for struvite recovery, however, composition varies depending upon animal species, rearing conditions (diet, dietary supplements and bedding), manure handling, storage and treatment method. Total P concentration varies in the range of 100-460 mg L$^{-1}$ in dairy manure, 370-600 mg L$^{-1}$ in poultry manure and 90-200 mg L$^{-1}$ in swine manure (Table 1). Farm based wastes contain soluble nitrogen mainly in the form of $\text{NH}_4^+$ (200-1400 mg L$^{-1}$).

The high P content of manure makes it a suitable source, however its available P fraction remains only in the range of 35% (poultry manure) to 63% (dairy manure) of total P (Barnett, 1994). P predominantly present in particulate form remains unavailable for recovery (Sharpley and Moyer, 2000; Chapuis-Lardy et al., 2003). Average P recovery efficiency achieved is 75% from dairy manure and 90% from swine waste. The higher recovery efficiency from swine waste might be due to its lower Ca content (~150 mg L$^{-1}$) compared to that of dairy manure (~1700 mg L$^{-1}$) (Table 1).
Due to the presence of particulate P, farmyard wastes need to undergo pre-treatment prior to P recovery. Acid leaching (for dairy manure and poultry litter), use of chelating agents (dairy manure), microwave treatment (dairy manure), anaerobic digestion (dairy manure) are the key pre-treatment methods used for farm based waste (Szogi et al., 2008; Moody et al., 2009; Zhang et al., 2010; Qureshi et al., 2008).

2.1.2. Municipal waste

The spontaneous precipitation of struvite in municipal sewage systems led to the concept of controlled struvite recovery using other wastes. Effluent generated in the anaerobic sludge digestion process of municipal wastewater (Uysal et al., 2010; Pastor et al., 2010; Latifian et al., 2012) (Table 1) is the most widely investigated struvite source. Municipal wastewater has PO$_4^{3-}$ concentrations of 21-270 mg L$^{-1}$ and 168-1400 mg L$^{-1}$ NH$_4^+$ For struvite precipitation, chemical supplements in terms of P salts (H$_3$PO$_4$, KH$_2$PO$_4$) are required when orthophosphate concentrations are low (<55 mg L$^{-1}$) (Turker and Celen, 1997; Uysal et al., 2010; Latifian et al., 2012), however, no NH$_4^+$ supplementation has been reported. Fixation of P in wastewater sludge particles requires use of some pre-treatment methods (acidic, basic, microwave, enhanced biological phosphorus removal) to enhance struvite formation (Stark, 2005; Pan et al., 2006; Pastor et al., 2008).

Landfill leachate (average 2430 mg L$^{-1}$ NH$_4^+$) (Li and Zhao, 2003; Kim et al., 2006; Iaconi et al., 2010) and human urine (average 3000 mg L$^{-1}$ NH$_4^+$) (Ganrot et al., 2007; Morales et al., 2013, Hug and Udert, 2013) (Table 1) are two other sources of municipal origin, where struvite recovery has been recommended as a treatment method to reduce its high NH$_4^+$ content. However, because of low orthophosphate concentrations in landfill leachate (~ 11 mg L$^{-1}$) (Kim et al., 2006) supplementation of P salts is
required for struvite precipitation (Li and Zhao, 2003; Iaconi et al., 2010). Urine can be used without any pre-treatment prior to P recovery. Further, urine-derived struvite is free of heavy metals and its inherent alkaline nature requires no addition of an external base (Hug and Udert, 2013; Morales et al., 2013).

Apart from liquid waste, ash from municipal sewage sludge generated by incineration is P-rich and has potential for struvite recovery (P constitutes 13-25% of the total mass) (Hong et al., 2005; Xu et al., 2012). However, it requires mechanical, thermal (incineration) or chemical (acid/base leach) pre-treatments to allow for P recovery because of its strong retention with other elements like Ca, Mg, Al and Fe (Hong et al., 2005).

2.1.3. Industrial wastes

Industrial wastewater effluent commonly contains nutrients that need to be reduced before it is released into the environment. Struvite recovery is an alternative consideration in stripping both P and NH$_4^+$ from industrial effluents to meet set environmental standards. Out of the 49 studies (Table 1), 20 used effluent of industrial origin to recover struvite.

Successful struvite recovery has been reported from wastewater from the following industries: Tannery (Tunay et al., 1997), textile (Kabdasli et al., 2000, Huang et al., 2012), carmine dye (Chimenos et al., 2003), semiconductor (Kim et al., 2009), slaughterhouse and meat packing (Kabdasli et al., 2009), food processing (potato processing and molasses based) (Moerman et al., 2009; Turker and Celen, 2010), rare-earth (Huang et al., in 2011), coking (Zhang et al., 2009; Kumar et al., 2013), 7-amino cephalosporanic acid (Li et al., 2012) and yeast production (Uysal et al., 2013). For these sources, struvite recovery simultaneously reduces high NH$_4^+$ contents. However, the
orthophosphate concentrations in several of these industrial wastes (Abattoir wastewater, Yeast industry wastewater, Textile wastewater, Rare-earth wastewater etc.) are relatively low (Table 1) P and supplementation is required for effective struvite crystallization. For sources with limiting NH$_4^+$, such as the Cola beverage and fertilizer industry wastewater, NH$_4^+$ is added as NH$_4$Cl or NH$_4$OH (Xu et al., 2012; Hutnik et al., 2012; Folleto et al., 2013). Unlike farm waste, no pre-treatment requirements have been reported for industrial waste prior to struvite recovery.

2.2. Pilot and commercial scale recovery of P

Recovery of struvite from urine has been demonstrated at the pilot scale in Nepal (Ronteltap et al., 2007; Gell et al., 2011; Grau et al., 2012) without the need for any pre-treatments. Human urine contains 156-460 mg L$^{-1}$ of P and is low in heavy metals (Ganrot et al., 2007; Morales et al., 2013). Struvite can easily be precipitated from urine urea by addition of Mg, since it is naturally deficient in Mg. Commercial struvite recovery units handling municipal wastewater sludge are in operation in countries like Japan, Canada, England, USA, Australia, Germany, The Netherlands and Italy (Britton et al., 2009; Gantenbein and Khadka, 2009). Descriptions of some commercially available struvite recovery technologies viz. Phosnix (Japan), Pearl Ostara (North America, UK), Phospaq, (Netherlands), Seaborne (Germany), AirPrex (Germany, Netherlands) and Multiform (America) are given below.

Pearl$^\text{®}$ Technology (North America, UK): The US patented Pearl$^\text{®}$ Technology was developed by the University of British Columbia, Canada. The technology was first implemented at a pilot scale at the Gold Bar Wastewater Treatment Plant in 2007 in North America. Durham Advanced Wastewater Treatment Facility of Clean Water Services, Portland, Oregon (USA) installed the first commercial full-scale plant in 2009. The technology is suitable as a side-stream treatment for effluent containing high
phosphorus and ammonium concentrations and recovers struvite in a fluidized-bed reactor. Process performance of the technology was further modified through incorporation of additional process (WASSTRIP®, where, in an anaerobic zone before digestion, phosphate is stripped from activated sludge and added to the reject water. The process has an average recovery efficiency of 80% for phosphate and 10-15% for nitrogen with an average per year production of 600 ton which is marketed under the commercial name Crystal Green. Full details of the technology can be found at http://www.ostara.com/.

Phospaq™, (The Netherlands): Phospaq™ technology was developed by Paques (The Netherlands) and is in commercial use in The Netherlands at Lomm (for processing potato factory effluent), at Olburgen (for processing sewage sludge effluent following dewatering, combined with potato factory effluent) and in the UK at Severn Trent’s Stoke Bardolph wastewater treatment works (Driessen, n.d., Phospaq™ Process; Durose and Jeffcoat, 2014, Stoke Bardolph STW Centrate Scheme; both reports available at www.WaterProjectsOnline.com). Crystallized struvite is harvested from the bottom of an aerated reactor amended with MgO. Aeration strips CO₂ from the effluent and increases the pH which encourages struvite precipitation and simultaneous reduction of COD (Schultz, 2009). The process recovers up to 80% of the PO₄-P (Schultz, 2009; Remy, 2013). To increase retention of precipitating struvite particles within the reactor and minimize flushing of fine particles, the reactor is equipped with a patented internal separator (Remy, 2013). The process is further enhanced by another step which converts ammonium into nitrogen gas via nitrification and the action of anammox bacteria (Driessen et al., 2009). This Anammox® process results in 90% NH₄-N recovery and Phospaq and Anammox reactors are in use in The Netherlands (Olburgen) and the UK (Stoke Bardolph).
**Phosnix (Japan):** The Phosnix process was developed by Unitika Ltd. (Katsuura, 1998) and has been in operation in Japan since 1987 (Münch and Barr, 2001). Despite its relative longevity, little information is available in the literature about the process. The reactor consists of an aerated column into which returned water from sewage sludge treatment is fed, magnesium hydroxide is supplied and the pH adjusted to 8.5-8.8 using NaOH. Aeration ensures that struvite crystals are fluidized allowing them to act as seed material to encourage adherence of new particles and crystal formation. Struvite is removed from the bottom of the column (Nawa, 2009). First full scale implementation was done in 1998 in lake Shinji Eastern Clarification Center of Shimane Prefecture of Japan (Nawa, 2009). The technology allows for transfer of the effluent back to the initial wastewater treatment step thereby reducing the requirement for chemical supplementation (Ueno and Fuji 2001; Nawa, 2009). The system has a treatment capacity of 1000 m$^3$ d$^{-1}$ and a PO$_4$-P recovery rate of 80-90%.

**Seaborne (Germany):** The Seaborne process was developed by the Seaborne Environmental Research Laboratory, Germany in 2000 to recover nutrients from slurry. Most available information describes the first large scale installation at the Gifhorn wastewater treatment plant in 2007 which used a modification of the original Seaborne process (Müller et al., 2007). This combined treatment technology with multiple unit operations uses anaerobic digestion, following which sludge is acidified by sulphuric acid to extract nutrients and heavy metals from the solid phase, followed by heavy metal precipitation as metal sulphide using anaerobic digester biogas rich in hydrogen sulphide gas (Müller et al., 2007) after increasing the pH to pH 5.6 using NaOH. After that, struvite is precipitated by addition of magnesium hydroxide and NaOH (to increase the pH to pH 9) in a continuous stirred tank reactor. Finally, ammonia is recovered as ammonium sulphate from the still ammonium-rich reject water (Bayerle, 2010). A
problem with separating the metals was reported by Müller et al. (2007) because of the
colloidal size of the heavy metal sulphides. Whilst the average concentration of heavy
metals in samples of thickened sludge was below German legal requirements during
tests (Günther et al., 2008), this may not be the case in other scenarios, either in terms of
location or treated waste. The Gifhorn site produces 270 kg struvite per day but is

*AirPrex™ (Germany, Netherlands)*: The AirPrex™ technology was developed by
Berliner Wasserbetriebe as a solution to struvite incrustations in wastewater treatment
plants in Germany and was implemented at the Wassmannsdorf wastewater treatment
plant (Heinzmann and Engel, 2006). The technology precipitates and collects struvite
from digested sludge before it is dewatered. The process utilizes magnesium chloride
which may be added to the sludge storage tank after digestion; the tank is aerated from
the bottom to remove CO₂ and increase the pH to around pH 8 which results in struvite
precipitation (Heinzmann and Engel, 2006) with a percentage recovery of 90-95%
(Forstner, 2015). Process installation after anaerobic digestion and prior to dewatering
enhances sludge dewatering and prevents downstream struvite precipitation. The
process is restricted to wastewater treatment plants with enhanced biological P removal
with two operating in Germany and one in the Netherlands (P-Rex, AirPrex Technical

*Multiform (America)*: The patented Multiform technology was developed by
Multiform Harvest Inc. and in 2012 two were established at wastewater treatment plants
in Boise, Idaho and the City of Yakima, Washington. The technology is also suitable for
food processing and swine farm waste; trials are being undertaken at two dairies in the
USA. The process occurs after the anaerobic digestion and dewatering stage and the
Multiform Harvest cone is designed to run the wastewater through only once with a
retention time of 15 minutes or less for the wastewater and two to three days for the
struvite. Struvite is harvested from the bottom of the cone shaped fluidized bed reactor
resulting in an 80% and a 20% reduction in phosphate and nitrogen from wastewater
respectively. There is little published information about Multiform Harvest cones apart
from that on the company website (www.multiformharvest.com) although research
carried out on laboratory scale cones resulted in the development of the commercial
process (e.g. Bowers and Westerman, 2005).

2.3. Effects of non-participating ions on crystallization

For precipitation of struvite, the three main components, Mg\(^{2+}\), NH\(_4^+\), and PO\(_4^{3-}\)
must be available in solution (Burns and Moody, 2002; Zhang et al., 2010). Most waste
sources comprise a heterogeneous mix of nutrients and ions and certain non-
participating ions can limit the struvite precipitation process. In typical wastes P can
exist in particulate or suspended form and in soluble and insoluble form, often in
association with other components (Le Corre et al., 2005; Marti et al., 2008). Inorganic
particulate P attached to mineral particles can be converted to dissolved P during
physico-chemical changes associated with changes of pH; however, particulate P which
is bound with Ca, Fe and Al ions is more resistant to solubilisation. There are various
impurities including aluminium ions, alkali metal ions (potassium, sodium), alkali
earths (calcium), transition metals (iron, copper, zinc), anions (sulphates, chlorides,
nitrates, fluorides, carbonates) and organic impurities (lactic acid) which impact on
crystal growth kinetics (Table 2). Most of the metals ions form their respective
phosphate or hydroxide salts in the alkaline environment necessary for struvite
formation (see section 3 below). In this way metal ions compete for phosphate ions and
co-precipitation of their salts along with struvite can reduce product purity (de Bashan,
2004). Further, the increase in growth of crystals is inhibited because of blockage of
active growth sites through adsorption of impurity ions onto the surface of struvite crystals (Jones, 2002; Kabdasli et al., 2006). In the presence of calcium, iron and nitrates ($\text{NO}_3^{-}$), crystal size decreases by up to 46% (Hutnik et al., 2011). There is also an increase in induction time when non-participating cations are present, because of cationic accumulation around the anionic species of struvite (Kabdasli et al., 2006). However, the increase in induction time is insignificant in the presence of carbonate ($\text{CO}_3^{2-}$), sodium and sulphates ($\text{SO}_4^{2-}$) (Kabdasli et al., 2006). Table 2 summarizes the effect of different impurities on struvite precipitation along with the concentration at which the effect was studied.

Calcium is the most widely investigated non-participating element in struvite recovery. Calcium concentrations are relatively high in many wastewaters and animal manures where inorganic calcium phosphates (such as apatite) may be precipitated. The source of calcium in animal wastes may be variously attributed to animal feed and bedding materials (Gungor and Karthikeyan, 2008). This tends to lead to a very low concentration of soluble phosphates ($\text{PO}_4^{3-}$) in animal manure (Sharpley and Moyer, 2000; Chapuis-Lardy et al., 2003; Gungor and Karthikeyan, 2005; Le Corre et al., 2005) and dairy manure (both undigested and anaerobically digested) typically displays less than 20% of total P remaining in solution (Barnett, 1994; Gungor and Karthikeyan, 2008). Wastewater from municipal and industrial sources also contains relatively high concentrations of calcium and P may preferentially bind to the calcium fraction making struvite recovery a challenge (Wang et al., 2005; Marti et al., 2008).

Interference from calcium can be minimized and the purity of recovered struvite can be increased in a calcium-rich source by either thermodynamically driven re-dissolution of calcium phosphate or by removing it via chemical precipitation at elevated pH (Huichzermeier and Tao, 2012). This will help to reduce effective
Ca$^{2+}$:PO$_4^{3-}$ and Ca$^{2+}$:Mg$^{2+}$ activity ratios to below 1 and 0.5 respectively, which have been suggested as optimum for struvite precipitation (Wang et al., 2005; Huichzermeierand and Tao, 2012).

Whilst magnesium is a constituent of struvite, an excess may limit precipitation because a high Mg: total P ratio increases the potential for Mg to complex with organic matter (Bowers and Westerman, 2005).

(Table 2 Effect of non-participating ions on struvite precipitation)

3. Feedstock Suitability

Given the various requirements for successful precipitation and recovery of struvite, a ‘Feedstock Suitability Index’ (FSI) was calculated to provide a measure of the suitability of a particular waste for struvite recovery based on its chemical composition specifically PO$_4^{3-}$, NH$_4^+$, Ca and Fe. Data were obtained from published papers which demonstrated struvite precipitation and which provided compositional data for the waste studied (i.e. PO$_4^{3-}$, NH$_4^+$, Ca and Fe concentrations, Tables 1 and 2). In some cases the number of papers fulfilling these criteria is limited, but nevertheless the FSI (Table 3) provides a novel means of compiling the data and evaluating the potential of a wide range of wastes and can be the basis for further study and development of the technologies. To determine the FSI, it was assumed that high concentrations of PO$_4^{3-}$ and NH$_4^+$ were beneficial for struvite recovery whilst low, rather than high, concentrations of Ca and Fe were favourable. Apart from Ca, the most influencing inhibiting ion in struvite precipitation, influence of Fe could be identified as inhibiting (Table 2) as it can limit P availability and therefore struvite formation.

However, Fe concentrations were not generally specified in the selected papers and for the purposes of calculating the FSI, were taken from other published sources relevant to the named wastes. The Mg concentrations were not taken into account in the FSI.
calculations since in all cases addition of Mg was routinely required for struvite
recovery (Table 1). For wastes with variable composition, an FSI range was calculated
(Table 3). Values for $\text{PO}_4^{3-}$, Ca, $\text{NH}_4^+$ and Fe concentrations were normalized to a scale
of 0-1 and the FSI calculated as the median of the normalized values was considered to
rank the waste sources for their suitability as struvite source.

Of the waste streams considered, rare-earth, fertilizer (phosphate fertilizer)
carmine dye and nylon wastewater had the highest FSIs suggesting their suitability for
struvite recovery, although since little data are available for these sources, caution
should be exerted because the variability of the effluent chemistry and effect on P
recovery is unknown. Further, abundance of such waste source is a matter of concern
for commercial scale struvite recovery. In contrast, struvite recovery from human urine
has been relatively well studied and maximum FSI of 0.322 for urine is indicative of the
relative ease with which struvite is precipitated from this resource (Table 3). Presence of
desirable ingredients $\text{PO}_4^{3-}$ (average 260 mg L$^{-1}$) and $\text{NH}_4^+$ (average 4000 mg L$^{-1}$) in
relatively higher concentration, at the same time relatively lower concentration of
inhibiting ions Ca (average 90 mg L$^{-1}$) and Fe (average 0.07 mg L$^{-1}$) make it a suitable
consideration for struvite production. Considering its inexpensive and reliable stock,
human urine holds potential as a favourable struvite source. Abattoir or slaughterhouse
wastewater is the least suitable source with FSI index range of 0.006-0.014 due to low
$\text{PO}_4^{3-}$ (5.5-10 mg L$^{-1}$) and high Ca concentrations (53-71 mg L$^{-1}$), although it also
contains a complex of organic components which are likely to inhibit struvite
crystallization.

The FSI index is a potentially useful tool for identifying comparative suitability
of different waste sources for struvite production, but for effective use, compositional
status of a particular waste must be known.
4. Pre-treatments for maximizing struvite precipitation

P recovery from wastes may be limited because of fixation with other ions (e.g. Ca, Fe, Al) and it is necessary to understand P dynamics in terms of its speciation and distribution between soluble and particulate forms before recovery. From the liquid fraction of agricultural, municipal and industrial wastes, only 40% recovery of total P is thought possible (Petzet and Cornel, 2011) and thus a major portion of P is lost if the solid fraction is not considered in the recovery process. Therefore, to achieve maximum P recovery, it is important to mobilize P into an available form by releasing it from the solid fraction by use of pre-treatments. Although the feasibility of pre-treatments has been established experimentally, there is scope to study economic aspects of the processes in order to optimize recovery. Pre-treatments aim to selectively reduce the impacts of non-participating ions and are discussed below.

4.1. Anaerobic digestion

The spontaneous deposition of struvite in anaerobically digested wastewater sludge led to the idea of using anaerobic digestion as a pre-treatment for struvite recovery. Compared to undigested manure, availability of N, P and Mg is enhanced in anaerobically digested pig, cattle and poultry manure (Wu et al., 2005; Masse et al., 2007; Marti et al., 2008) due to hydrolysis and mineralization of organic nutrients (Seadi et al., 2012). Thus anaerobic digestion increases the potential for struvite formation as indicated by previous studies (Beal et al., 1999; Bhuiyan et al., 2007; Moody et al., 2009; Hidalgo et al., 2015).

Struvite precipitation from untreated swine waste resulted in 92% phosphate recovery, a figure that rose to 98% following pre-treatment by anaerobic digestion (Beal et al., 2007).
Moody et al. (2009) reported PO$_4^{3-}$ and Mg increases of 26% and 254% respectively in anaerobically digested swine wastewater compared to undigested waste. When these authors compared struvite precipitation from the digested and undigested swine waste, 61% less PO$_4^{3-}$ remained in the digested manure, the removal indicating greater struvite precipitation.

### 4.2. Acid-base leaching

Acidification (using hydrochloric or sulphuric acid) releases P into solution thereby enhancing P availability for subsequent struvite formation. Acidification causes protonation of phosphate ions from bound phosphates (Ca/Mg/Fe phosphate), which lowers their ionic product below their equilibrium solubility product. This results in higher dissolution of particulate phosphate into solution increasing its availability (Zhang et al., 2010).

P availability is affected by the pH and composition of the material (Stark, 2005). Lowering the pH of anaerobically digested dairy manure to pH 3.8 increased P availability by 500% (Zhang et al., 2010), whilst a lesser decrease to pH 4.5 resulted in 43-100% of the total P present in dairy manure becoming available (Shen et al., 2011). Szogi et al. (2008) demonstrated that 60-80% of the total P in poultry manure was released from organically bound P following acid treatment. Treating with a base to increase alkalinity also enhances P availability as demonstrated by a 50-70% increase in available P in dried sewage sludge (Stark, 2005). However, acid treatment also releases metal ions which may result in contamination of the crystallized struvite if both metals and P are available in the waste effluent (Stark, 2005).

### 4.3. Use of a chelating agent

Chelating agents (e.g. ethylenediaminetetraacetic acid (EDTA) and oxalic acid) have been proposed as a pre-treatment method for minimizing the inhibitory effect of
calcium on struvite precipitation (Zhang et al., 2010). In mechanically separated liquid dairy manure, EDTA sequesters calcium thereby suppressing formation of calcium phosphate compounds (Shen et al., 2011) resulting in higher concentrations of available P. The ligands react with Ca-PO$_4$ to form Ca-EDTA complexes and PO$_4^{3-}$ is released (Zhang et al., 2010). In digested dairy manure, use of EDTA increased available P up to 93% (Zhang et al., 2012). Addition of oxalic acid leads to formation of calcium oxalate, which is precipitated as white powder along with struvite. A combination of microwave treatment followed by oxalic acid amendment to dairy manure resulted in a 95% recovery of the total P as struvite, because 90% of the Ca was removed from solution whilst 90% of the Mg was not (Zhang et al., 2015).

Use of EDTA to chelate Ca and consequently enhance struvite formation needs optimising. Excess EDTA might subsequently bind to Mg thereby limiting Mg availability which is a requirement for struvite formation (Zhang et al., 2010). The optimum concentration of EDTA is that which results in maximum EDTA-Ca complex formation without also complexing Mg (Shen et al., 2011). Since calcium concentrations are high in many farm wastes, use of chelating agents is particularly attractive, although concerns relating to environmental toxicity and expense will limit the sustainability of this approach.

4.4. Microwave heating

Microwave irradiation has been suggested as a pre-treatment method to release particulate P for enhanced struvite recovery (Liao et al., 2005; Pan et al., 2006; Chan et al., 2007; Qureshi et al., 2008; Lo et al., 2011) and the extent of P release depends upon the forms of P present in the source materials (Pan et al., 2006). The degree of P solubilisation depends upon microwave operating temperature and duration of heating (Liao et al., 2005) with 120$^\circ$C considered to be the optimum temperature for releasing
both NH$_4^+$ and P in sewage sludge (Chan et al., 2007). Pan et al. (2006) showed an 80% release of P following microwave treatment (170°C) of liquid dairy manure. The advantages of microwave treatment over conventional heating include uniform heating throughout the material, precise control over process temperature and no direct contact between heating source and materials (Lo et al., 2011).

Pre-treatment with microwave heating has been further modified by incorporation of chemically assisted microwave digestion (Pan et al., 2006; Chan et al., 2007; Qiao et al., 2008; Qureshi et al., 2008). The common chemicals used are oxidants, acids and bases. Combined microwave-chemical treatment is more effective at releasing P than microwaving only (Qureshi et al., 2008; Lo et al., 2011). The 80% release of P demonstrated by Pan et al. (2006) after microwaving dairy slurry was increased to 85% when H$_2$O$_2$ treatment was incorporated. From microwave treated P enhanced dairy manure, up to 90% of orthophosphate recovery as struvite is possible (Qureshi et al., 2008). Use of H$_2$O$_2$ reduces the required temperature for optimum P release and hydroxyl radicals react with organic particulate P to release P into solution (Lo et al., 2011). Xiao et al. (2015) more recently showed that microwaving activated sludge as a pre-treatment prior to anaerobic stirring for 1 h maximized phosphate release with a recovery efficiency of 95% in the form of amorphous calcium phosphate and struvite.

4.5. **Enhanced biological phosphorus removal (EBPR)**

Enhanced biological phosphorus removal (EBPR) in wastewater plants is based on the ability of the microbial biomass to sequester P from the surrounding medium. EBPR is an increasingly utilized technology where alternating anaerobic and aerobic steps result in sludge bacteria respectively releasing and uptaking large quantities of PO$_4^{3-}$ as a means of increasing P removal from effluents (Batista and Jeong, 2006). The P concentration in EBPR sludge can be up to 12% whilst in conventional sludge its
concentration is 2 - 3% (Liao et al., 2005) which allows for more efficient struvite recovery (Britton et al., 2005; Pastor et al., 2008; Shen, 2010). The enhanced $\text{PO}_4^{3-}$ concentrations in sewage sludge and the ease with which it is released from the microbial biomass increases the risk of struvite scale formation in the treatment plant’s pipelines. Intentional struvite precipitation is therefore recommended as a means of limiting these operational problems (Marti et al., 2008).

It has been reported that 58-94% P recovery is possible through formation of struvite from EBPR in wastewater treatment plants (Munch and Barr, 2001; Britton et al., 2005; Marti et al., 2008). However, the recovery efficiency varies depending upon sludge characteristics (Pastor et al., 2008). Recovery is less efficient from wastes with higher calcium contents, as calcium limits P availability (Pastor et al., 2008) and therefore this process would not be suitable for many farm wastes.

5. Methods of struvite recovery

Chemical precipitation methods are the most widely utilized methods of struvite recovery. However, alternative techniques using established principles of electrochemistry, ion exchange separation and biomineralization (Figs 1-4), have been tested, but these require sophisticated and dedicated facilities. Although the basic mechanism of struvite crystallization remains the same, there are differences in cost and energy demand between methods and here we provide a comparative assessment of the performance, advantages and limitations of each approach (Table 4).

(Table 4 Recovery methods of struvite)

5.1. Chemical precipitation methods in agitated reactor

The approach aims to precipitate struvite from a waste source following addition of external Mg in a mechanically agitated reactor (Fig. 1). A narrow range of process
conditions in terms of type of Mg salt, pH and pH adjustment method have been reported (Table 1). pH may be adjusted to create the alkaline conditions required for struvite precipitation (Bouropoulos and Koutsoukos, 2000) using NaOH (most commonly used), MgO, KOH, NH₃ or by CO₂ stripping (Chimenos et al., 2003; Suzuki et al., 2007; Zhao et al., 2010). Limitations of these approaches include the fact that MgO and KOH have limited solubility, the CO₂ stripping method is energy intensive and loss of ammonia may occur from aeration (Cusick et al., 2014). MgCl₂, MgSO₄ and MgO are commonly used magnesium amendments, although alternative and renewable Mg sources are under investigation such as bittern, sea water, wood ash, magnesite and struvite pyrolysate which would be more cost effective (Suzuki et al., 2007; Huang et al., 2011; Sakthivel et al., 2011; Yu et al., 2012).

To provide adequate mixing energy, stirred batch reactors are most frequently used, particularly in small-scale laboratory investigations as they are simple to operate and install (Table 3) (Kabdasli et al., 2000; Kim et al., 2006; Xu et al., 2012; Folleto et al., 2013). At a larger scale, fluidized bed reactors are commonly used as these provide solution turbulence and a greater reactive surface area (Seckler et al., 1996) thereby reducing crystallization induction time (Bhuiyan, 2008).

The main advantage of chemical precipitation methods is their operational simplicity. However, precipitation often results in the production of non-recoverable, fine struvite particles because of the high mixing energy commonly found in stirred reactors (Adnan et al., 2003). To reduce this problem, recycling of struvite fines back to the precipitating reactor to act as seeding agents for new crystal growth is recommended (Ueno and Fuji, 2001; Le Corre et al., 2009). In a fluidized bed reactor, this problem is not as marked, as the fluidized struvite particles found in suspension act as seed for further crystal growth. Moreover, when multi-component heterogeneous sources such as
manure and wastewater sludge are used, this technique often results in co-precipitation of other salts (such as calcium phosphate) which result from the presence of non-participating ions (Capdevielle et al., 2013).

Other issues include the need to use chemicals for pH adjustment, magnesium salts and sometimes NH\(_4^+\) or P salts, depending on waste type, to supplement the deficient component in order to achieve struvite precipitation. These inputs can account for a large share of the total production cost and can outweigh the revenue value of the struvite to a producer (Barak and Stafford, 2006). For example, Dockhorn (2009) estimated the cost of struvite production using chemical precipitation to be around $3500 tonne\(^{-1}\) of P which was significantly higher than the market value of P at the time ($765 tonne\(^{-1}\)$).

5.2. Electrochemical methods

In this approach struvite precipitation is induced by an electrochemical reaction. An electrochemical cell is used with an anode formed of inert material such as platinum, graphite or carbon-felt discs and a cathode of nickel, a platinum-carbon catalyst, or a steel plate. Deposition of struvite takes place on the cathode from an analyte solution containing Mg, PO\(_4^{3-}\) and NH\(_4^+\) ions (Fig. 2). During the process, electrochemical reduction of water or oxygen takes place at the cathode forming hydroxide ions (O\(_2+2H_2O+4e^-\rightarrow 4OH^-\)), while hydrogen gas (H\(_2\)) is released (H\(_2O+e^-\rightarrow 1/2 H_2+OH^-\)) (Moussa et al., 2006; Wang et al., 2010). This reaction elevates the pH in the vicinity of the cathode into the alkaline range and results in rapid precipitation of struvite (Wang et al., 2010).

This method has the advantage that chemicals are not required for pH adjustment purposes (Wang et al., 2010). The concurrent production of hydrogen during the electrolytic reduction of water at the cathode is another advantage since hydrogen
recovery for other uses could offset the operational costs involved in the process (Cusick and Logan, 2012). A disadvantage is that the electrochemical precipitation of struvite needs energy to develop the required potential (~1.23V) for the reduction of water. While some anaerobic digester effluents have been studied (Fischer et al., 2011; Cusick et al., 2014) for struvite recovery using this method, a range of farm, municipal and industrial wastes remains currently untested.

To reduce process costs further, struvite precipitation in a microbial electrochemical cell was investigated; a fuel cell converts chemical energy to electrical energy by the catalytic activity of microbes under anaerobic conditions. The electric current required for splitting water is supplied by the microbes which produce electrical energy using organic matter as fuel and convert it to inorganic matter through oxidation at the anode. The electrons are transferred to an external circuit and at the cathode the electrons and protons combine by reducing oxygen to water or by producing hydrogen gas (Wang et al., 2010). Struvite recovery from sewage sludge treated in microbial fuel cells is higher than from the starting feedstock (Fischer et al., 2011) because inorganic phosphates (e.g. FePO$_4$, Al(PO$_4$)$_3$) are reduced resulting in increased P availability (up to 48% of the total P). An advantage of this method is that, unwanted heavy metals are retained in the sludge matrix in immobilized forms (Fischer et al., 2011).

In the case of a small, decentralized reactor requiring a high automated dose of Mg, it is possible that the Mg itself can be used as the sacrificial anode (Hug and Udert, 2013; Kruk et al., 2014) which is thought to be of comparable outlay from the use of MgCl$_2$ and MgSO$_4$ salts (Hug and Udert, 2013). Here electrochemical dissolution of Mg into solution from the Mg electrode takes place through oxidation (Hug and Udert, 2013) and Mg ions released into solution react with the P and N to form struvite. Effective
anode potential for Mg electrode to release Mg is more than the pitting potential of Mg
i.e. the potential enough to create irregular corrosion pit at Mg anode surface.

Struvite obtained through electrochemical deposition can have a high purity (97%) with P recovery efficiencies of up to 96% (Wang et al., 2010). Limitations include the use of precious metals like platinum, issues with performance of the cathode which deteriorates when struvite particles accumulate on its surface and formation of microbial biofilms which block active sites and inhibit mass transfer, thus limiting struvite precipitation and necessitating addition of cleaning and scrubbing stages to the process (Hirooka and Ichihashi, 2013; Cusick et al., 2014).

5.3. Ion exchange methods

These methods are based on the principle that nutrients from wastewaters are selectively exchanged in ion exchangers and struvite is precipitated after addition of Mg\(^{2+}\) at controlled pH (Liberti et al., 1986, 2001; Mijangos et al., 2004, 2013; Ortueta et al., 2014). Sodium chloride is used as a regenerating solution in ion exchange columns; \(\text{NH}_4^+\) is commonly exchanged for \(\text{Na}^+\) ions in a cationic exchanger (zeolite based) and \(\text{PO}_4^{3-}\) ions are exchanged for \(\text{Cl}^-\) ions in an anionic exchanger (sulphonic/carboxylic based) (Liberti et al., 1986) (Equations 1 and 2). Regenerates from the ion exchangers are then allowed to react with externally added MgCl\(_2\) in a stoichiometric ratio of Mg:NH\(_4^+\)::PO\(_4^{3-}\)= 1:1:1 resulting in struvite precipitation (Fig. 3).

\[
\text{CationicNa} + \text{NH}_4^+ \rightleftharpoons \text{CationicNH}_4 + \text{Na}^+ \quad (1)
\]

\[
\text{AnionicCl} + \text{HPO}_4^{2-} \rightleftharpoons \text{AnionicC}_2\text{HPO}_4 + 2\text{Cl}^- \quad (2)
\]

In the case of waste with imbalanced N and P concentrations, spontaneous precipitation does not effectively occur and stoichiometric chemical additions are necessary (Table 1). For example, to overcome this issue in wastes containing high \(\text{NH}_4^+\) concentrations (e.g. sewage sludge liquors) the process was modified to allow
exchange of all \( \text{PO}_4^{3-} \) present in the waste and only its equimolar amount of \( \text{NH}_4^+ \), thus leaving excess \( \text{NH}_4^+ \) in the source (Liberti et al., 2001). The modification involves regulating the flow through the cation exchanger to achieve a desired level of \( \text{NH}_4^+ \) exchange, while for \( \text{PO}_4^{3-} \), the whole stream is processed for selective anion exchange (Liberti et al., 2001). Availability of specific anion exchangers for \( \text{PO}_4^{3-} \) sorption is the main limitation of this process (Petruzzieli et al., 2004). Moreover, the high suspended solid content of regenerated effluent may cause fouling of the exchange columns (Gonder et al., 2006).

Conventional ion exchange has been further modified by the use of ion exchange isothermal supersaturation (Mijangos et al., 2004; Ortueta, 2014). The principle is to facilitate concentration of the precipitating solution beyond its solubility level at a given temperature and enabling spontaneous crystallization of struvite. The important factors influencing the process are the eluent concentration and selection of ion exchange resin, in particular, resin functional groups and the ion exchanger matrix (Mijangos et al., 2013; Ortueta et al., 2014). At higher concentrations of the precipitating ions, degree of super-saturation increases and formation of intermatrix crystalline deposits are likely to block resin surfaces.

5.4. Biomineralization methods

Biomineralization is the natural process of deposition of minerals by microorganisms for hardening their structural tissue which leads to microbial production of struvite (Da Silva et al., 2000). Certain bacterial strains (e.g. *Myxococcus xanthus*, *Staphylococcus aureus*) can precipitate struvite in a medium containing \( \text{PO}_4^{3-} \) and Mg (Table 4). \( \text{NH}_4^+ \) required for precipitation is produced from microbial metabolism of the nitrogenous compounds present in the medium or precipitating solution (Omar et al., 1998). Release of \( \text{NH}_4^+ \) from nitrogen metabolism results in
increased pH which favours precipitation of struvite (Gonzalez-Munoz et al., 1996; Omar et al., 1998) (Fig. 4).

Apart from living microbial cells, dead cells, disrupted cells and isolated bacterial structures (e.g. cell membranes) can also induce struvite crystallization by acting as substrates for heterogeneous nucleation for crystallization (Gonzalez-Munoz et al., 1996; Omar et al., 1998). The organic matrix of disrupted bacterial cells is rich in negatively charged multi-molecular complexes (proteolipids, phospholipids, glycoprotein, proteoglycan) and attracts positive ions like Mg, resulting in struvite precipitation (Gonzalez-Munoz et al., 1996; Omar et al., 1998).

In living microorganisms, precipitation of struvite is initiated at the exponential growth phase and a peak is reached at the start of the stationary phase (Da Silva et al., 2000). There is a link between struvite morphologies, microbial species and specific physicochemical conditions of the culture medium (Lopez et al., 2007). The presence of Ca in culture media inhibits struvite formation (Beavon and Heatley, 1962). Table 5 summarizes the findings of different struvite recovery studies using microorganisms.

Table 5 Microbial species reported in struvite precipitation

6. Conclusions

Here we analysed waste sources, methods and pre-treatments used during struvite recovery processes and developed a Feedstock Suitability Index to rank potential sources. Feasibility of recovery has been established at the laboratory scale for a range of wastes with relatively high P recovery efficiencies (~85-99%). However, full-scale installations are limited and focus dominantly on the municipal wastewater industry. Development of a targeted and cost-effective recovery method is still a challenge due to the inherent heterogeneous nature of waste sources. The overall
impacts of such technological successes would be profound and the benefits for global
food security in terms of alternative and sustainable fertilizers are enormous.

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**References**


Madison, Wisconsin.


Heinzmann, B., Engel, G. 2006. Induced magnesium ammonium phosphate precipitation to prevent incrustations and measures for phosphorus recovery, Water Practice & Technol. IWA Publishing online, DOI: 10.2166/WPT.2006051.


Katsuura, H., 1998. Phosphate recovery from sewage by granule forming process (full scale struvite recovery from a sewage works at Shimane Prefecture, Japan. International conference on phosphorus recovery from sewage and animal waste, Warwick University, UK.


Syafalni, Abdullah, R., Abustan, I., Nadiah, A., Ibrahim, M., 2013. Wastewater treatment using bentonite, the combinations of bentonite-zeolite, bentonite-alum,


Highlights:

- Development of a *feedstock suitability index* to rank P recovery potential of range of wastes
- Comprehensive review of struvite recovery methodologies
- Pre-treatments for maximizing struvite recovery reviewed
Fig. 1. Schematic diagram of chemical precipitation of struvite.
Fig. 2. Schematic diagram of electrochemical precipitation of struvite.
Fig. 3. Schematic diagram of ion exchange method of struvite precipitation.
Fig. 4. Schematic diagram of struvite precipitation through biomineralization.
Table 1

Sources used for recovery of struvite and process conditions.

<table>
<thead>
<tr>
<th>#</th>
<th>Sources</th>
<th>Type of reactor</th>
<th>Total P/PO$_4$-<em>P</em> (*mg L$^{-1}$)</th>
<th>TN/NH$_4$-N (*mg L$^{-1}$)</th>
<th>Ca (*mg L$^{-1}$)</th>
<th>Mg source</th>
<th>Additional chemical</th>
<th>pH</th>
<th>pH adjustment by</th>
<th>P recovery (%)</th>
<th>NH$_4^+$ recovery (%)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Leather tanning wastewater</td>
<td>Closed stirred batch reactor</td>
<td>NR/12.3</td>
<td>2405</td>
<td>370</td>
<td>MgCl$_2$</td>
<td>Na$_3$HPO$_4$</td>
<td>9</td>
<td>NaOH</td>
<td>90</td>
<td>85</td>
<td>Tunay et al., 1997</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Closed stirred batch reactor</td>
<td>NR/2.5-8</td>
<td>NR/119-1076</td>
<td>178-245</td>
<td>MgCl$_2$</td>
<td>Na$_3$HPO$_4$</td>
<td>9</td>
<td>NaOH</td>
<td>NR</td>
<td>≤ 89</td>
<td>Tunay and Kabdasli, 2001</td>
</tr>
<tr>
<td>2</td>
<td>Textile printing industry wastewater</td>
<td>Stirred reactor</td>
<td>NR/NR</td>
<td>30-1765/20-368</td>
<td>NR</td>
<td>MgCl$_2$</td>
<td>KH$_2$PO$_4$</td>
<td>8-9.5</td>
<td>NaOH/H$_2$SO$_4$</td>
<td>NR</td>
<td>84</td>
<td>Kabdasli et al., 2000</td>
</tr>
<tr>
<td>3</td>
<td>Abattoir waste water/ meat packing industry effluent</td>
<td>Closed stirred batch reactor</td>
<td>NR/5.5-10</td>
<td>NR/83-208</td>
<td>53-56</td>
<td>MgCl$_2$</td>
<td>Na$_3$HPO$_4$</td>
<td>9</td>
<td>NaOH</td>
<td>NR</td>
<td>≤ 78</td>
<td>Tunay and Kabdasli, 2001</td>
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<td></td>
<td></td>
<td>Closed stirred batch reactor</td>
<td>NR/6</td>
<td>250-260 / 210-220</td>
<td>71</td>
<td>MgCl$_2$</td>
<td>NaH$_2$PO$_4$</td>
<td>9.5</td>
<td>NaOH</td>
<td>NR</td>
<td>89.5</td>
<td>Kabdasli et al., 2009</td>
</tr>
<tr>
<td>4</td>
<td>Cochineal insects processing wastewater (Carmine Dye industry)</td>
<td>Agitated batch reactor</td>
<td>NR/3490</td>
<td>NR/2320</td>
<td>42</td>
<td>MgO</td>
<td>Na$_3$HPO$_4$</td>
<td>8.5-9</td>
<td>MgO</td>
<td>100</td>
<td>89</td>
<td>Chimenos et al., 2003</td>
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<td>5</td>
<td>AD effluent of molasses-based industrial wastewater</td>
<td>Stirred batch reactor</td>
<td>NR/24</td>
<td>NR/1400</td>
<td>21</td>
<td>MgCl$_2$</td>
<td>-</td>
<td>8-9</td>
<td>NaOH/HCl</td>
<td>78-95</td>
<td>95</td>
<td>Turker and Celen, 2007</td>
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<td>6</td>
<td>Semiconductor wastewater</td>
<td>Jar test with paddle</td>
<td>NR/286</td>
<td>NR/100</td>
<td>5-12</td>
<td>MgCl$_2$</td>
<td>-</td>
<td>9</td>
<td>NaOH</td>
<td>70</td>
<td>98</td>
<td>Kim et al., 2009</td>
</tr>
<tr>
<td>7</td>
<td>Anaerobic effluent from potato processing industries</td>
<td>Continuous aerated stirred reactor</td>
<td>NR/43-127</td>
<td>NR/208-426</td>
<td>36-65</td>
<td>MgCl$_2$</td>
<td>-</td>
<td>8.5-8.7</td>
<td>NaOH</td>
<td>19-89</td>
<td>NR</td>
<td>Moerman et al., 2009</td>
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<td>8</td>
<td>Coking/coke oven wastewater</td>
<td>Stirred batch reactor</td>
<td>NR/NR</td>
<td>NR/520</td>
<td>NR</td>
<td>MgCl$_2$</td>
<td>Na$_3$HPO$_4$</td>
<td>9.5</td>
<td>NaOH</td>
<td>NR</td>
<td>84</td>
<td>Zhang et al., 2009</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Continuous stirred reactor</td>
<td>NR/56</td>
<td>NR/3500</td>
<td>NR</td>
<td>MgCl$_2$</td>
<td>Na$_3$HPO$_4$, Ca(H$_2$PO)</td>
<td>9.5</td>
<td>NaOH/HCl</td>
<td>NR</td>
<td>95</td>
<td>Kumar et al., 2013</td>
</tr>
<tr>
<td>9</td>
<td>Rare-earth wastewater</td>
<td>Stirred jar apparatus</td>
<td>7.8/ NR</td>
<td>NR/4535</td>
<td>0.7</td>
<td>Brucite</td>
<td>H$_3$PO$_4$</td>
<td>8.5-9.5</td>
<td>NaOH</td>
<td>97</td>
<td>95</td>
<td>Huang et al., 2011</td>
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<tr>
<td>#</td>
<td>Sources</td>
<td>Type of reactor</td>
<td>Total P/PO₄-P (*mg L⁻¹)</td>
<td>TN/NH₄-N (*mg L⁻¹)</td>
<td>Ca (*mg L⁻¹)</td>
<td>Mg source</td>
<td>Additional chemical</td>
<td>pH</td>
<td>pH adjustment by</td>
<td>P Recovery (%)</td>
<td>NH₄⁻ recovery (%)</td>
<td>Reference</td>
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<tr>
<td>10</td>
<td>Nylon wastewater</td>
<td>Closed stirred jar test apparatus</td>
<td>0.2/NR</td>
<td>781/550</td>
<td>0.8</td>
<td>Brucite, MgSO₄</td>
<td>H₂PO₄, Na₃HPO₄</td>
<td>8.5</td>
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<td>7-Aminocephalosporanic Acid Wastewater</td>
<td>Variable speed jar test apparatus</td>
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<td>MgCl₂, MgO, MgSO₄</td>
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<td>Fertilizers industry wastewater</td>
<td>Stirred batch reactor</td>
<td>NR/NR</td>
<td>NR/1197</td>
<td>NR</td>
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<td>Draft Tube Mixed type continuous crystallizer</td>
<td>NR/4.45 %</td>
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<td>NH₄Cl</td>
<td>9-11</td>
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<td>Yeast Industry Wastewater</td>
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<td>25.6</td>
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<td>NR/10.8</td>
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<td>H₃PO₄</td>
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<td>87.55</td>
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**Farm Waste**

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<th>Total P/PO₄-P (*mg L⁻¹)</th>
<th>TN/NH₄-N (*mg L⁻¹)</th>
<th>Ca (*mg L⁻¹)</th>
<th>Mg source</th>
<th>Additional chemical</th>
<th>pH</th>
<th>pH adjustment by</th>
<th>P Recovery (%)</th>
<th>NH₄⁻ recovery (%)</th>
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<td>Poultry manure waste water</td>
<td>Manually stirred reactor</td>
<td>NR/572</td>
<td>NR</td>
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<td>MgCl₂</td>
<td>-</td>
<td>9</td>
<td>NaOH</td>
<td>91</td>
<td>NR</td>
<td>Burns et al., 2001</td>
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<td>Continuously stirred batch reactor</td>
<td>370/NR</td>
<td>1580/1318</td>
<td>NR</td>
<td>MgO, MgSO₄, MgCl₂</td>
<td>NaHPO₄, KH₂PO₄, H₃PO₄</td>
<td>9</td>
<td>NaOH</td>
<td>NR</td>
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<td>Yetilmissoy et al., 2009</td>
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<td>16</td>
<td>Dairy manure</td>
<td>Continuously stirred batch reactor</td>
<td>100-450/ NR</td>
<td>255-519</td>
<td>NR</td>
<td>MgCl₂, Mg(OH)₂</td>
<td>Na₃HPO₄</td>
<td>8.5-9.2</td>
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<td>Fluidized bed reactor</td>
<td>275-317/NR</td>
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<td>-</td>
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<td>460/19</td>
<td>2845/1405</td>
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<td>Ca (*mg L&lt;sup&gt;-1&lt;/sup&gt;)</td>
<td>Mg source</td>
<td>Additional chemical</td>
<td>pH</td>
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<td>P Recovery (%)</td>
<td>NH&lt;sub&gt;4&lt;/sub&gt;&lt;sup&gt;+&lt;/sup&gt; recovery (%)</td>
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<td>17</td>
<td>Cattle urine</td>
<td>Stirred batch reactor</td>
<td>305/NR</td>
<td>NR/7732</td>
<td>NR</td>
<td>Brine</td>
<td>-</td>
<td>9</td>
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<td>Prabhu and Mutnuri, 2014</td>
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<td>Demonstration crystallization reactor</td>
<td>145/72</td>
<td>NR/532</td>
<td>255</td>
<td>Bittern</td>
<td>-</td>
<td>7.5-8.5</td>
<td>CO&lt;sub&gt;2&lt;/sub&gt; stripping</td>
<td>73</td>
<td>NR</td>
<td>Suzuki et al., 2007</td>
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<td>Agitated bench scale reactor</td>
<td>NR/42</td>
<td>NR/234</td>
<td>61</td>
<td>MgCl&lt;sub&gt;2&lt;/sub&gt;</td>
<td>KH&lt;sub&gt;2&lt;/sub&gt;PO&lt;sub&gt;4&lt;/sub&gt;</td>
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<td>NaOH</td>
<td>89</td>
<td>70</td>
<td>Perera et al., 2007</td>
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<td>Intermittently aerated reactors</td>
<td>105-222/30-56</td>
<td>959-1120 /732-931</td>
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<td>MgCl&lt;sub&gt;2&lt;/sub&gt;</td>
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<td>Ryu and Lee, 2010</td>
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<td>Jar test</td>
<td>182/161</td>
<td>1212/985</td>
<td>135</td>
<td>Struvite pyrolysate</td>
<td>H&lt;sub&gt;3&lt;/sub&gt;PO&lt;sub&gt;4&lt;/sub&gt;</td>
<td>8-8.5</td>
<td>NaOH</td>
<td>96</td>
<td>80</td>
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<td>18</td>
<td>Swine waste water</td>
<td>Stirred batch reactor</td>
<td>89-189/55-139</td>
<td>1381-2001/1013-1426</td>
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<td>MgCl&lt;sub&gt;2&lt;/sub&gt;</td>
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<td>99</td>
<td>87</td>
<td>Zhang et al., 2012</td>
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<td>Composting equipment</td>
<td>28000 mg kg&lt;sup&gt;-1&lt;/sup&gt; DM /3000 mg kg&lt;sup&gt;-1&lt;/sup&gt; DM</td>
<td>26400 mg kg&lt;sup&gt;-1&lt;/sup&gt; DM /1900 mg kg&lt;sup&gt;-1&lt;/sup&gt; DM</td>
<td>NR</td>
<td>MgCl&lt;sub&gt;2&lt;/sub&gt;</td>
<td>H&lt;sub&gt;3&lt;/sub&gt;PO&lt;sub&gt;4&lt;/sub&gt;</td>
<td>7.3</td>
<td>NR</td>
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**Municipal Waste**

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<th>Total P/PO&lt;sub&gt;4&lt;/sub&gt;-P (*mg L&lt;sup&gt;-1&lt;/sup&gt;)</th>
<th>TN/NH&lt;sub&gt;4&lt;/sub&gt;-N (*mg L&lt;sup&gt;-1&lt;/sup&gt;)</th>
<th>Ca (*mg L&lt;sup&gt;-1&lt;/sup&gt;)</th>
<th>Mg source</th>
<th>Additional chemical</th>
<th>pH</th>
<th>pH adjustment by</th>
<th>P Recovery (%)</th>
<th>NH&lt;sub&gt;4&lt;/sub&gt;&lt;sup&gt;+&lt;/sup&gt; recovery (%)</th>
<th>Reference</th>
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<tr>
<td>19</td>
<td>Swine compost</td>
<td>Stirred glass batch reactor</td>
<td>NR/240</td>
<td>NR/6963</td>
<td>28</td>
<td>MgCl&lt;sub&gt;2&lt;/sub&gt;</td>
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<td>9</td>
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<td>96</td>
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<td>Ronteltap et al., 2007</td>
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<td>Fluidized bed reactor</td>
<td>NR/460</td>
<td>NR/40</td>
<td>234</td>
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<td>9.4</td>
<td>NaOH</td>
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<td>NR</td>
<td>Wilsenach et al., 2007</td>
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<td>Stirred beaker</td>
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<td>NR/7220</td>
<td>NR</td>
<td>MgCl&lt;sub&gt;2&lt;/sub&gt;</td>
<td>Na&lt;sub&gt;3&lt;/sub&gt;HPO&lt;sub&gt;4&lt;/sub&gt;</td>
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<td>NaOH</td>
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<td>400/NR</td>
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<td>MgO</td>
<td>-</td>
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<td>Stirred single component reactor</td>
<td>NR/197</td>
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<td>Hug and Udert, 2013</td>
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<td>NR/156-194</td>
<td>NR/3200-4990</td>
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<td>MgO</td>
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<td>Closed batch reactor</td>
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<td>NR/245</td>
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<td>Latifian et al., 2013</td>
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<td>NR/2750-2900</td>
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<td>MgCl$_2$, MgO, MgSO$_4$</td>
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<td>Li and Zhao, 2003</td>
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<td>Stirred Jar test apparatus</td>
<td>NR /10.5</td>
<td>NR /1795</td>
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<td>MgCl$_2$</td>
<td>KH$_2$PO$_4$</td>
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<td>H$_3$PO$_4$</td>
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<td>Municipal wastewater</td>
<td>Stirred batch reactor</td>
<td>NR/200</td>
<td>NR/1150</td>
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<td>MgO</td>
<td>Triple Superphosphate, H$_3$PO$_4$</td>
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<td>Demirer and Othman, 2009</td>
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<td>NaOH</td>
<td>≤ 95%</td>
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<td>1043/949</td>
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<td>Uysal et al., 2010</td>
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<td>NR/795</td>
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<td>KH$_2$PO$_4$</td>
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<td>Latifian et al., 2012</td>
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<td>Sewage sludge ash</td>
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<td>NR</td>
<td>Xu et al., 2012</td>
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NR = Not reported; * = mg L$^{-1}$ unless stated otherwise
### Table 2

Effect of non-participating ions on struvite precipitation.

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<th>Ion</th>
<th>Source of occurrence</th>
<th>Concentration</th>
<th>Effect on struvite recovery</th>
<th>Reference</th>
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<tbody>
<tr>
<td>Ca</td>
<td>Animal Manure, Municipal wastewater</td>
<td>Mg:Ca=2:1 &amp; 1:2; 40-160 mg L(^{-1}); 0.01-0.20 mass %</td>
<td>Formation of amorphous Ca phosphate when Mg:Ca&gt;1:1; Decrease in struvite purity when Ca:Mg&gt;1; Precipitation of Ca phosphate at pH&gt;10; With increase in Ca concentration, decrease in mean crystal size (by 46%); Formation of tubular crystal; Co-existence of hydroxyl-apatite in product</td>
<td>Le Corre, 2005; Wang et al., 2005; Hutnik et al., 2011</td>
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<td>Na</td>
<td>Leather tanning industry, Landfill leachate</td>
<td>(1012 – 35765) (\times 10^5) mg L(^{-1}); 30-60 mg L(^{-1});</td>
<td>Marginal increase in induction time; Increase in smaller sized particles (&lt;1 um) with increase in Ca concentration</td>
<td>Kabdasli et al., 2006; Lee et al., 2013</td>
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<td>CO(_3)(^{2-})</td>
<td>Anaerobically digested dairy manure</td>
<td>(1200–3000) (\times 10^5) mg L(^{-1}); 3309-6567 mg L(^{-1});</td>
<td>Marginal increase in induction time; Removes Ca as CaCO(_3) &amp; increases struvite formation potential</td>
<td>Kabdasli et al., 2006; Huichzermeier and Tao, 2012</td>
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<tr>
<td>SO(_4)(^{2-})</td>
<td>Textile industry wastewater</td>
<td>(12000 – 72000) (\times 10^8) mg L(^{-1});</td>
<td>Increase in induction time</td>
<td>Kabdasli et al., 2006</td>
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<td>Lactic acid</td>
<td>Municipal, household, agricultural wastewater</td>
<td>0.03-0.06 mass %; (1012 – 35765) (\times 10^5) mg L(^{-1});</td>
<td>Formation of untypical long &amp; thin crystals; No adverse impact on crystal development</td>
<td>Kozik et al., 2011</td>
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<td>Fe</td>
<td>Phosphoric acid manufacturing industry, Municipal wastewater</td>
<td>0.0001-0.001 mass %; 0.2-0.5 mg kg(^{-1});</td>
<td>Co-precipitation of Fe hydroxides; With increase in Fe(^{2+}) concentration decrease in mean crystal size (by &gt;20%); Moderate increase in crystal size (by 6%); Presence of Cu hydroxide in product</td>
<td>Hutnik et al., 2012; Hutnik et al., 2013</td>
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<td>NO(_3)(^{-})</td>
<td>Industrial wastewater</td>
<td>0.0443 – 0.886 mass %; 2.05 (\times 10^{-5}) mass %;</td>
<td>With increase in NO(_3)(^{-}) concentration, decrease in mean crystal size (by 29%); Appearance of Zn impurity in product as hydroxides, phosphates, other salt; Appearance of K impurity in product as hydroxides, phosphates, other salt; Appearance of Al impurity in product as hydroxides, phosphates, other salt</td>
<td>Hutnik et al., 2013; Kozik et al., 2013; Kozik et al., 2013</td>
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<td>Cu</td>
<td>Liquid manure, fertilizer industry wastewater</td>
<td>0.2-0.5 mg kg(^{-1}); 0.025 mass %; 0.002 mass %</td>
<td>Moderate increase in crystal size (by 6%); Presence of Cu hydroxide in product; Appearance of Cu hydroxide in product</td>
<td>Hutnik et al., 2013; Kozik et al., 2013; Kozik et al., 2013</td>
</tr>
<tr>
<td>Zn</td>
<td>Municipal sludge</td>
<td>2.05 (\times 10^{-5}) mass %</td>
<td>Appearance of Zn impurity in product as hydroxides, phosphates, other salt</td>
<td>Kozik et al., 2013</td>
</tr>
<tr>
<td>K</td>
<td>Municipal sludge</td>
<td>0.025 mass %</td>
<td>Appearance of K impurity in product as hydroxides, phosphates, other salt</td>
<td>Kozik et al., 2013</td>
</tr>
<tr>
<td>Al</td>
<td>Municipal sludge</td>
<td>0.002 mass %</td>
<td>Appearance of Al impurity in product as hydroxides, phosphates, other salt</td>
<td>Kozik et al., 2013</td>
</tr>
</tbody>
</table>
Table 3

Ranking and Feedstock Suitability Index (FSI) of potential struvite recovery sources

<table>
<thead>
<tr>
<th>Rank</th>
<th>Feedstock</th>
<th>O-Phosphate, mg L⁻¹</th>
<th>NH₄⁺, mg L⁻¹</th>
<th>Ca, mg L⁻¹</th>
<th>Fe, mg/l (Reference)</th>
<th>FSI Range</th>
<th>Median FSI</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Rare-earth wastewater</td>
<td>5</td>
<td>4535</td>
<td>0.7</td>
<td>0.06-0.10 (Palmer et al., 2015)</td>
<td>0.430-0.444</td>
<td>0.437</td>
</tr>
<tr>
<td>2</td>
<td>Fertilizers industry wastewater</td>
<td>4528*</td>
<td>1197</td>
<td>70*</td>
<td>121-144 (Bosslar et al., 2009)</td>
<td>0.294</td>
<td>0.294</td>
</tr>
<tr>
<td>3</td>
<td>Cochinel insects processing Wastewater (Carmine Dye industry)</td>
<td>3490</td>
<td>2320</td>
<td>42</td>
<td>10 (Ghaly et al., 2014)</td>
<td>0.277</td>
<td>0.277</td>
</tr>
<tr>
<td>4</td>
<td>Nylon wastewater</td>
<td>0.2</td>
<td>550</td>
<td>0.8</td>
<td>10 (Ghaly et al., 2014)</td>
<td>0.238</td>
<td>0.238</td>
</tr>
<tr>
<td>5</td>
<td>Human Urine</td>
<td>156-460</td>
<td>40-7220</td>
<td>16-234</td>
<td>0.07 (Salih and Jafaar, 2013)</td>
<td>0.046-0.322</td>
<td>0.184</td>
</tr>
<tr>
<td>6</td>
<td>Leather tanning wastewater</td>
<td>2.5-12.3</td>
<td>119-2405</td>
<td>178-405</td>
<td>0.01-0.08 (Shegani, 2014)</td>
<td>0.035-0.334</td>
<td>0.184</td>
</tr>
<tr>
<td>7</td>
<td>Cola beverage</td>
<td>415</td>
<td>2900</td>
<td>75</td>
<td>1-2 (Haroon et al., 2013)</td>
<td>0.126-0.128</td>
<td>0.128</td>
</tr>
<tr>
<td>8</td>
<td>Landfill leachate</td>
<td>10.5-663</td>
<td>1795-2900</td>
<td>240-1557</td>
<td>2.92-32.5 (Lee et al., 2010)</td>
<td>0.062-0.138</td>
<td>0.101</td>
</tr>
<tr>
<td>9</td>
<td>Coking/coke oven Wastewater</td>
<td>56</td>
<td>510-3500</td>
<td>88</td>
<td>2.2-7.5 (Mieleczarek et al., 2011)</td>
<td>0.023-0.127</td>
<td>0.075</td>
</tr>
<tr>
<td>10</td>
<td>Poultry manure waste water</td>
<td>370-572</td>
<td>1318</td>
<td>976</td>
<td>6 (Aldrich et al., 1997)</td>
<td>0.066-0.077</td>
<td>0.072</td>
</tr>
<tr>
<td>11</td>
<td>AD effluent of molasses-based industrial wastewater</td>
<td>24</td>
<td>1400</td>
<td>21</td>
<td>12.8 (Poddar and Sahu, 2015)</td>
<td>0.058</td>
<td>0.058</td>
</tr>
<tr>
<td>12</td>
<td>Dairy Manure</td>
<td>209-572</td>
<td>255-1405</td>
<td>227-1735</td>
<td>21.62-300 (Rostami and Ahangar, 2013)</td>
<td>0.020-0.081</td>
<td>0.051</td>
</tr>
<tr>
<td>13</td>
<td>Semiconductor wastewater</td>
<td>286</td>
<td>100</td>
<td>5-12</td>
<td>3 (Wong et al., 2013)</td>
<td>0.034-0.055</td>
<td>0.045</td>
</tr>
<tr>
<td>14</td>
<td>Textile printing industry wastewater</td>
<td>36</td>
<td>1128</td>
<td>460</td>
<td>1.2 (Zamiraei et al., 2015)</td>
<td>0.043</td>
<td>0.043</td>
</tr>
<tr>
<td>15</td>
<td>Municipal wastewater</td>
<td>50-391</td>
<td>168-949</td>
<td>21-1049</td>
<td>2.72-4.7 (Syafalni et al., 2013)</td>
<td>0.009-0.063</td>
<td>0.036</td>
</tr>
<tr>
<td>16</td>
<td>Swine wastewater</td>
<td>32-161</td>
<td>234-1426</td>
<td>61-255</td>
<td>75 (Meneghetti et al., 2012)</td>
<td>0.012-0.061</td>
<td>0.036</td>
</tr>
<tr>
<td>17</td>
<td>Yeast industry wastewater</td>
<td>10.8-17.4</td>
<td>161-528</td>
<td>26-258</td>
<td>0.54 (Farooq et al., 2013)</td>
<td>0.011-0.030</td>
<td>0.021</td>
</tr>
<tr>
<td>18</td>
<td>Anaerobic effluent from potato processing industries</td>
<td>43-127</td>
<td>208-426</td>
<td>36-65</td>
<td>3748 (Nayono et al., 2012)</td>
<td>0.012-0.026</td>
<td>0.019</td>
</tr>
<tr>
<td>19</td>
<td>Textile printing industry wastewater</td>
<td>10</td>
<td>20-368</td>
<td>19</td>
<td>10 (Ghaly et al., 2014)</td>
<td>0.010-0.022</td>
<td>0.017</td>
</tr>
<tr>
<td>20</td>
<td>Abattoir waste water/Slaughterhouse wastewaters</td>
<td>5.5-10</td>
<td>83-220</td>
<td>53-71</td>
<td>0.6-1.1 (Sarainih and Jamrah, 2008)</td>
<td>0.007-0.015</td>
<td>0.012</td>
</tr>
</tbody>
</table>

*Reference: Gouider et al., 2014
<table>
<thead>
<tr>
<th>Specifications</th>
<th>Chemical precipitation</th>
<th>Electrochemical Deposition</th>
<th>Ion exchange</th>
<th>Biomineralization</th>
</tr>
</thead>
<tbody>
<tr>
<td>Principle</td>
<td>Precipitation of P and NH$_4^+$ in solution with addition of Mg and mixing</td>
<td>Deposition of struvite on a cathode in a solution containing Mg, PO$_4^{3-}$, NH$_4^+$ through electrochemical reaction</td>
<td>P and NH$_4^+$ are exchanged in ion exchangers and precipitated as struvite upon Mg addition</td>
<td>Precipitation through biomineralization in medium containing PO$_4^{3-}$ &amp; Mg, utilising NH$_4^+$ from N metabolism by microbes</td>
</tr>
<tr>
<td>pH</td>
<td>Chemical additive (NaOH, KOH)</td>
<td>Self establishment of alkalinity</td>
<td>Chemical additive (NaOH)</td>
<td>Self established alkalinity</td>
</tr>
<tr>
<td>Mixing</td>
<td>Stirring, fluidizing</td>
<td>Stirring, fluidizing</td>
<td>Not applicable</td>
<td>Not applicable</td>
</tr>
<tr>
<td>Reactor</td>
<td>Stirred batch, fluidized bed</td>
<td>Electrochemical cell</td>
<td>Ion exchange column</td>
<td>Batch culture</td>
</tr>
</tbody>
</table>
| Limitation     | 1. Co-precipitation of impurity as salt  
2. Ineffective crystallization for not meeting suitable conditions  
3. Production of fines | 1. Co-precipitation of impurity  
2. Use of costly material like Pt  
3. Scale formation on cathode | 1. Co-precipitation of impurities  
2. Regeneration of resin at regular intervals  
3. Limited availability of specific anion exchangers for PO$_4^{3-}$ sorption | 1. Co-precipitation of impurity  
2. Slow precipitation |
| Advantage      | Easy to install, operate  
Does not employ use of sophisticated equipment | No need of alkali addition, concurrent production of potential H$_2$ fuel | Fast precipitation | No external addition of alkali |
| Installation   | At commercial/laboratory scale | At laboratory scale | At laboratory scale | At laboratory scale |
| Demonstration  | In real (manure, sludge, ash) and synthetic wastes | In real (sludge, digestate)/synthetic waste | In synthetic waste | In synthetic waste |
| Large share of cost | Alkali source, Mg source | Cathode material, electrical energy | Ion exchange resin | Mg source |
### Table 5

Microbial species reported in struvite precipitation

<table>
<thead>
<tr>
<th>#</th>
<th>Microbial sp.</th>
<th>Key findings</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td><em>Staphylococcus aureus</em></td>
<td>Increase Mg concentration in culture medium increases crystal formation; Ca addition prevents it.</td>
<td>Beaven and Heatley, 1962</td>
</tr>
<tr>
<td>2</td>
<td><em>Ureaplasma urealyticum</em></td>
<td>Inoculation with <em>U. urealyticum</em> in urine causes alkalisation and crystallization.</td>
<td>Grenabo et al., 1984</td>
</tr>
<tr>
<td>3</td>
<td><em>Trypanosoma cruzi</em></td>
<td>It excretes NH$_4^+$ into growth medium and when contain Mg$^{2+}$ and PO$_4^{3-}$ struvite is precipitated.</td>
<td>Adroher and Osuna, 1987</td>
</tr>
<tr>
<td>4</td>
<td><em>Arthrobacter</em> and <em>Pseudomonas</em> sp.</td>
<td>Morphology of crystals formed under agitation differs from those formed when cultures not agitated.</td>
<td>Perez et al., 1990</td>
</tr>
<tr>
<td>5</td>
<td><em>Bacillus pumilus</em></td>
<td>Precipitation of struvite after 6-20 days of bacterial growth in medium containing Mg$^{2+}$ and PO$_4^{3-}$.</td>
<td>Struble et al., 1991</td>
</tr>
<tr>
<td>6</td>
<td><em>Myxococcuscoralloides</em></td>
<td>Extra-cellular production of struvite (1$^*$ report on struvite production by <em>Myxococcus</em>).</td>
<td>Gonzalez-Munoz et al., 1993</td>
</tr>
<tr>
<td>7</td>
<td><em>Myxococcusxanthus</em></td>
<td>Dead cells or cell debris can act as seed for crystal growth.</td>
<td>Omar et al., 1995</td>
</tr>
<tr>
<td>8</td>
<td><em>Myxococcuscoralloides</em> and <em>M.xanthus</em></td>
<td>Intact bacterial cells did not act as sites for crystal formation. Changes in environmental conditions or autolysis create debris and exudates rich in proteolipids and phospholipids that attract Mg$^{2+}$ promoting crystallization.</td>
<td>Omar et al., 1998</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Culture medium chemistry influences struvite formation, with maximum crystallization occurring at the beginning of the stationary growth phase.</td>
<td>Da Silva et al., 2000</td>
</tr>
<tr>
<td>9</td>
<td><em>Myxococcusxanthus</em></td>
<td>Precipitation efficiency depends upon culture age. Culture physico-chemical condition and crystal morphology are linked.</td>
<td>Lopez et al., 2007</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Autolyzed bacterial debris acted as heterogeneous nuclei.</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td><em>Brevibacteriumantiquum</em></td>
<td>90% of P uptake from medium, accumulated P was mostly in orthophosphate form.</td>
<td>Smirnov et al., 2005</td>
</tr>
<tr>
<td>11</td>
<td><em>Idiomarinasp.</em></td>
<td>Produce extra-cellular polymeric substances that provide reactive sites to bind dissolved ions for struvite precipitation.</td>
<td>Gonzalez-Munoz et al., 2008</td>
</tr>
<tr>
<td>12</td>
<td><em>Proteus mirabilis</em></td>
<td>Extracellular proteins interact with Mg$^{2+}$ and induce nucleation and growth of struvite crystals.</td>
<td>Sun et al., 2012</td>
</tr>
</tbody>
</table>