

# SCALE DEPOSITS FROM PALM OIL MILL EFFLUENT (POME) TREATMENT AND VARIOUS OTHER INDUSTRIES: A DEVELOPMENTAL REVIEW

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## ABSTRACT

*The palm oil mill effluent (POME) treatment process is exposed to the formation of crystal-like deposits where their accumulation could create a significant threat to achieving an efficient POME treatment. This article reviewed similar occurrences in other industries, discussed factors influencing the crystal formation and suggested possible solutions to be applied in the oil palm industry. From the review, it was found that crystal deposits have always been a nuisance and sometimes a significant threat to similar industries such as industrial, agricultural and municipal wastewater treatment facilities. Other industries where there is a handling process of certain type of fluids such as heat transfer and oil reservoir drilling fluids also faces similar problems. The article also presented the spectrum of methods for mitigation and removal of the crystal formed. For many cases, nutrient recovery through struvite precipitation has become attractive as it not only reduces crystal growth but at the same time prevents excessive nutrients discharge to the environment. Further exploitation of the recovered struvite as a fertiliser source could possibly generate additional income to the oil palm industry.*

**Keywords:** industrial wastewater, palm oil mill effluent, struvite precipitation, crystallisation, nutrient recovery.

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## INTRODUCTION

The Malaysian oil palm industry has been growing at a rate of 3%-5% based on yearly oil palm planted area. The number of mills has also increased to 453 nationwide (MPOB, 2016). In line with the growth, there is also a growing concern on the environmental performance of the industry. Government policies,

industry initiatives, environmental certification programmes and active research have been the focus of efforts to raise the environmental profile of the industry. One particular effort in recent years in the milling process is to bring down the level of biological oxygen demand (BOD) in the palm oil mill effluent (POME) final discharge (Loh *et al.*, 2013). In order to do this, palm oil millers are either encouraged or in some cases required to install a polishing plant or a tertiary treatment system to further treat the POME. However the introduction of this polishing plant, where it involves heavy usage of piping set-up, has created another concern which is the gradual crystals formation in the pipeline. This kind of formation has also been reported earlier in the secondary stage of POME treatment utilising retention ponds. It reduces the piping diameter thus

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reducing the efficiency in POME treatment process. It is also being referred to as scaling or fouling (Blandin *et al.*, 2015; Steinhauer *et al.*, 2015).

The crystal deposits found in most of the agricultural, farming and municipal wastewater are identified as struvite mineral (Doyle and Parsons, 2002; Lahav *et al.*, 2013; Zhou *et al.*, 2015). Struvite is basically an ammonium magnesium phosphate hexahydrate ( $\text{NH}_4\text{MgPO}_4 \cdot 6\text{H}_2\text{O}$ ) (Moed *et al.*, 2015) that has a distinctive orthorhombic crystal structure (Doyle and Parsons, 2002). The struvite formed in the wastewater from anaerobically digested dairy manure presents itself in a commonly found pyramidal form (Figure 1) as examined by the scanning electron microscopy (SEM) (Tao *et al.*, 2016). In groundwater reservoir facilities and desalination plants, crystal deposits found are called limestones (Ruelo *et al.*, 2013), which mainly consist of calcium carbonate ( $\text{CaCO}_3$ ) with iron (Fe), silicon (Si), sodium (Na), chlorine (Cl) and sulphur (S) as other constituents. Ketrane *et al.* (2010) have reported finding limestone after analysing the Ouargla region groundwater scale deposits in Algeria. Further analysis using energy dispersive spectrometry (EDS) also discovered carbon (C), oxygen (O) and potassium (K) elements. The groundwater scale precipitates present themselves in needle forms (Figure 2) under the SEM analysis (Ketrane *et al.*, 2010).

In industries where the application of a heat exchanger is involved, it is identified as calcium sulphate dehydrate ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) (Kazi *et al.*, 2013) or gypsum as it is normally called. These crystal deposits act as a thermal insulator, which could reduce the heat transfer rate, decrease its flow rate thereby increasing the pressure drop across the heat exchanger (Hasan *et al.*, 2012). Recent findings show a variety of struvite types named as struvite-K

and struvite-Na where the original composition of ammonium is replaced accordingly; either by K or Na (Chauhan and Joshi, 2014).

### HISTORICAL CRYSTALS FORMATION IN WASTEWATER AND PROCESS WATER

Among the early discoveries of scale deposits were: 1) in 1939 when a British scientist, A M Rawn, detected a crystalline material in the digested supernatant pipelines (Doyle *et al.*, 2001), 2) in 1968 where the Hyperion wastewater treatment plant, among the world's largest in treating 1.32 million  $\text{m}^3$  wastewater per day, experienced a decreased gravity flow of the effluent due to a 50% loss of its piping original diameter of 304.8 mm (12 inches). That eventually forced the plant operators to use additional pumps to meet the required flow rate and led to major pipe replacement works (Borgerding, 1972), and 3) in 1989 where the formation of struvite caused operation and maintenance problem in the newly commissioned Ponggol Pigwaste Plant in Singapore (Bhattarai *et al.*, 1989).

In oil explorations, crystal deposits can occur in the formation pores near the wellbore thus reducing formation porosity and permeability (Crabtree *et al.*, 1999). It would then block the oil flow by clogging the perforations or form a thick lining in the production tubing. In a worst-case scenario, it can also coat and damage down-hole completion equipments, such as safety valves and gas-lift mandrels. In North Sea oil well, in the 1990s, the oil production fell from 30 000 barrels per day to zero in just 24 hr. In another case, the South District Wastewater Treatment Plant operated by the Miami-Dade Water and Sewer Department faced the clogging of pipes and reduction of its available treatment volume due

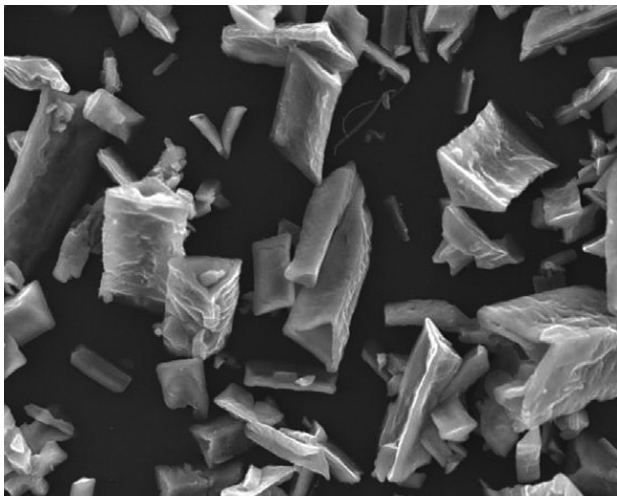


Figure 1. Orthorhombic pyramidal struvite crystal.

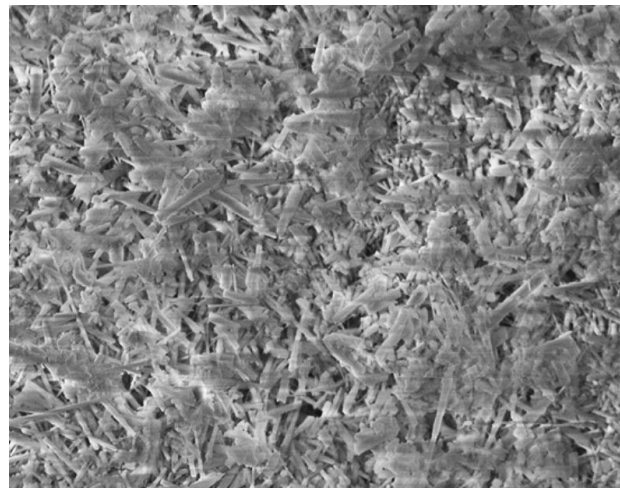


Figure 2. Needle form limestone crystal.

to the formation and accumulation of struvite thus upsetting the plant performance (Mudragada *et al.*, 2014).

### FORMATION AND SOLUBILITY OF CRYSTAL DEPOSIT

The formation of crystal can be categorised into its nucleation and growth stage (Doyle and Parsons, 2002). According to Ariyanto *et al.* (2014), dissolved wastewater constituents such as  $Mg^{2+}$ ,  $NH_4^+$  and  $PO_4^{3-}$  ions which are released during the anaerobic digestion and sludge dewatering operation can combine, if condition permits to form an orthorhombic crystalline mineral. This mineral which is often described as tenacious (Doyle and Parsons, 2002) begins to form when the state of any fluid is perturbed such that the solubility limit for one or more of its minerals is exceeded (Crabtree *et al.*, 1999).

#### Nucleation

The crystal nucleation process is considered as complex and difficult to predict (Buckhurst *et al.*, 2002). There have been a number of theories to describe the formation of crystals. These theories are often referred to as the Classical Nucleation Theory. The easiest way to understand nucleation is to note that it is a phase transition where liquid transforms into a solid phase. A solubility curve as shown in Figure 3 describes the transition zone of a saturated, unsaturated and supersaturated conditions of several salt solutions. The area below any of the curve in the graph represents unsaturated solutions while the area above the curve represents supersaturated solutions. The curve itself represents the values where the solution becomes saturated. For example, based on the solubility curve of  $NaNO_3$  in Figure 3, a solution that has 90 g of  $NaNO_3$  in 100 g of  $H_2O$  with a temperature of  $40^\circ C$  is considered as an unsaturated solution. However, if the temperature of the solution is reduced to  $15^\circ C$  with the same amount of  $NaNO_3$ , the solution becomes supersaturated. This curve is useful in understanding the required condition for a salt to transform into crystalline solid. Transition of the solution phase is subjected to external factors that will drive a solute in a highly saturated solution into crystalline solid or amorphous solid. Crystalline solid will have a higher degree of regular molecular arrangement called Bravais lattice (Mullin, 2001).

Nucleation can be classified into primary and secondary nucleation. Primary nucleation is where the nucleation process occurs in the absence of any grown crystal while in secondary nucleation it happens with the influence from an existing crystal (Buckhurst *et al.*, 2002). Nucleation starts with the arrangement of atoms and molecules in a unit

cell of Bravais lattice which is called crystal nuclei (Wondratschek *et al.*, 2008). There are seven types of crystal lattice pattern distinguished by their unit cell; cubic, tetragonal, rhombohedral, hexagonal, orthorhombic, monoclinic and triclinic as shown in Figure 4.

Nucleation is considered an energy-consuming process due to the organised structure with defined surfaces from randomised solution constituents (Chen, 2012). It can redissolve if the physical requirements of crystal growth are not met (Roberts *et al.*, 2011). Nucleation can be categorised into homogenous and heterogeneous nucleation. Homogeneous nucleation occurs without the influence of foreign particles while heterogeneous nucleation is catalysed by foreign solid particles (Chen, 2012). Crystal grows rapidly under heterogeneous nucleation due to additional nucleation sites provided by foreign particles (Cahn, 1960). Secondary nucleation of a struvite was recorded to grow at the range of  $0.03-1.2 \times 10^6$  nuclei  $litre^{-1} s^{-1}$  (Mehta and Batsone, 2013). In real application *e.g.* wastewater treatment, having a rough surface mimicking foreign particles in considerably high concentration in contact with the source of crystal serves as a heterogeneous nucleation and may assist in its growth. Therefore, in trying to mitigate this, having a smooth tank surface to contain a wastewater is recommended to suppress excessive growth of crystals.

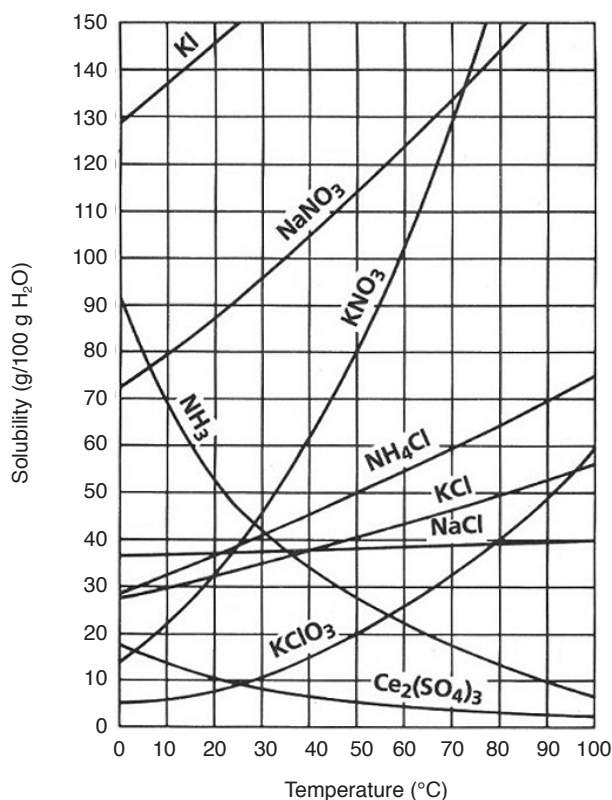


Figure 3. Examples of solubility curves of several salt solutions.



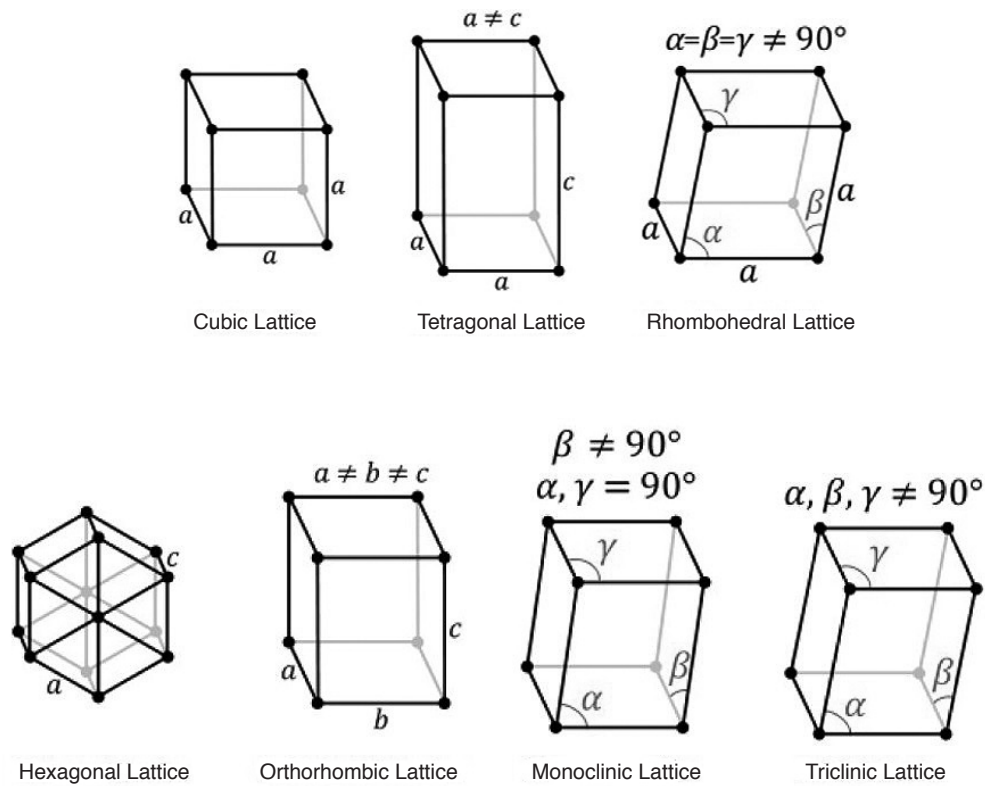


Figure 4. Seven types of crystal lattice pattern.

### Crystal Growth

Crystal growth is the stage where the crystal nuclei created during the nucleation process starts being deposited by precipitation (Chen, 2012). The molecules or atoms at the depositing surface interact with constituents of a solution where chemical reaction takes place. The types of force or interaction depend on the chemistry between the surface and the fouling liquid (Fletcher, 1991). A layer of deposit will form and multiply infinitively in a three-dimensional array as described by the Bravais lattice formula (Wondratschek *et al.*, 2008) (Equation 1).

$$R = n_1 a_1 + n_2 a_2 + n_3 a_3 \dots + n_i a_i \quad \text{(Equation 1)}$$

where:

$n_i$  = any integer.

$a_i$  = a vector that lies in different direction to span the lattice.

$R$  = a vector to describe the crystal array.

This formula defines the crystal growth in terms of its crystalline arrangement and frontiers. The overall growth mechanism depends very much on the nano-scale surface topography of the crystal faces (Roberts *et al.*, 2011). Measuring crystal growth can be challenging as it depends on a complex pattern of temperature, supersaturation, behavior of the crystal constituents, flow dynamics and mechanics, pH, *etc.* It is much more convenient

to measure crystal growth rate in terms of mass deposited per unit time per unit area of crystal surface as measuring individual faces is possible (Mullin, 2001). This can be done via agitated vessel and fluidised bed by measuring mass deposition on a known mass of sized seed crystal under carefully controlled conditions based on Equation 2 (Mullin, 2001).

$$G = \frac{M_i^{1/3} - M_f^{1/3}}{(\alpha \rho N)^{1/3} t} \quad \text{(Equation 2)}$$

where:

$M_i$  = initial crystal mass.

$M_f$  = final crystal mass.

$N$  = the number of individual crystals.

$\alpha$  = volume shape factor.

$\rho$  = density of the grown crystal.

$t$  = time for complete growth in second.

This theory was used by Mwaba *et al.* (2006) to establish a correlation that matches crystal growth and several regions of the thermal fouling resistance of a heat exchanger in order to develop a more accurate heat exchanger maintenance schedule.

### Solubility

Understanding the solubility of struvite enables a researcher to make an assessment on the prerequisites for struvite formation. It is

also important for further exploration into the valorisation of struvite for fertiliser. The solubility of struvite is often reported in the form of the solubility constant as it indicates the balance between dissolved ions from the salt and undissolved salts in order to represent the solubility equilibrium. Struvite solubility is mainly dependent on the ionic strength, temperature and pH. Theoretically, under high ionic strength conditions, struvite solubility increases due to the decreased activity coefficients of  $Mg^{2+}$ ,  $NH_4^+$  and  $PO_4^{3-}$  (Zhang *et al.*, 2016a). Bhuiyan *et al.* (2007) found the solubility of struvite in deionised water to be 169.2 mg litre<sup>-1</sup> at 25°C, with the maximum value of 212.7 mg litre<sup>-1</sup> at 35°C. He also reported, with respect to varying temperatures, that the solubility value also varies from 14.36 to 14.01 for a temperature range of 10°C-60°C with a minimum value of 13.17 at 30°C. A similar value was also reported by Ronteltap *et al.* (2003), Pastor *et al.* (2008) and Zhang *et al.* (2016a), where at around a temperature of 25°C to 30°C the solubility values were 13.40, 13.31 and 13.06 respectively.

#### SPECTRUM OF CRYSTAL STUDY IN WASTEWATER AND RECENT DISCOVERIES

Crystallography is a vast emerging field involving the fundamental investigation into atomic materials and molecular structures formed in an arranged manner. To date, it is the focused area when dealing with the problem of scale deposits. Many studies focus on the struvite precipitation technology to remove not only the scale deposit but also to recover valuable nutrients from the wastewater as biofertiliser. The successful implementation of this could benefit the relevant stakeholders in terms improved wastewater treatment plant cost effectiveness and better crop yields, as well as a reduced environmental impact caused by the discharged nutrients.

#### Struvite Precipitation for Nutrients Recovery (natural occurrence)

Recently, there is a growing interest in nutrient recovery from wastewaters using crystallisation. Wastewater crystal deposition has received much attention as a source of mineral fertiliser. In many cases, phosphorous (P) was found to be one of the highest compositions among the minerals present in wastewater crystals. Modern agriculture welcomes fertilisers enriched with additional P in order to support plant growth and yield. This finite mineral sourced from phosphate rock is fast depleting and may last only until next century (Xu *et al.*, 2012; Stolzenburg *et al.*, 2015). Mostly struvite precipitation is applied to extract and recover this

mineral because of the ease of assembling cation (*e.g.*  $Mg^{2+}$ ,  $NH_4^+$ , *etc.*) and  $PO_4^{3-}$  in equal molar ratios (Escudero *et al.*, 2015).

Zhang *et al.* (2015) reported a 97% recovery rate of PO from a concentrated desorption effluent of a proprietary hydrated ferric oxide nanocomposite system (HFO-201). Similar recovery rate (98%) was achieved when applying struvite precipitation to urine separated wastewater (Triger *et al.*, 2012). Wang *et al.* (2015) managed to achieve 100% recovery of  $NH_4^+$  and 94% for P from a concentrated anaerobically digested excess sludge using a struvite reactor and electro dialysis technology. Rahaman *et al.* (2014) utilised a customised fluidised bed crystalliser to reduce the content of struvite minerals in the effluent discharge, and high percentage of  $PO_4^{3-}$  recovery (> 90%) was achieved. In India, struvite has already been introduced as an important ingredient to increase the percentage of P in final compost by up to 39% (Karak *et al.*, 2015). P is also the main targeted renewable resource with >90%  $PO_4^{3-}$  recovery in the treatment of swine wastewater (Capdevielle *et al.*, 2013). Struvite precipitation in an activated sludge system was found to be able to lower the concentration of free ammonia of swine wastewater in subsequent biological reactor and thus avoided the accumulation of nitrite (Ryu and Lee, 2010). In another case, struvite precipitation also provided alternative renewable sources of nitrogen (N) and  $PO_4^{3-}$  that can be used as nutrients for the cultivation of algae (Davis *et al.*, 2015).

Ye *et al.* (2014) concluded that struvite precipitation or crystallisation is able to reduce the intensity of P and  $NH_4^+$  in the wastewater thus potentially reducing eutrophication. The underlying issue is to get the optimum degree of crystal growth and proper formation of crystal fines. This is due to the fact that struvite fines could be easily flushed out of a reactor thus decreasing P recovery efficiency (Ye *et al.*, 2014). Through analysing the characteristics of struvite aggregates using fractal geometry and controlling their growth development, it is possible to retain the struvite fines. Similarly, Fukumoto *et al.* (2011) precipitated struvite in swine manure attempting to trap the N and reduce nitrogenous emission ( $NH_3$ ,  $N_2O$ , NO) during the composting process so that the nitrogenous element can be maintained in the final compost. A total of about 50% was recovered.

A modelling framework for the precipitation-based nutrient recovery system was developed by Galbraith *et al.* (2014). The model incorporated non-ideal solution thermodynamics, and a dynamic mass and population balance to track the development of struvite precipitates - nucleation, growth and aggregation in response to solution pH, and the evolving particle size distribution. The model was claimed to be able to explain other more complex nutrients recovery system.

### Struvite Precipitation (assisted by foreign seeding)

In some cases, Mg is added to assist in struvite production. Escudero *et al.* (2015) for example used this technique for the removal of  $\text{NH}_4^+$  from anaerobically treated swine effluent. The foreign Mg and P sources added were  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  and  $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$  which were able to remove 96% of the initial  $\text{NH}_4^+$  content in the wastewater. Therefore, a cheaper source is equally important for this purpose. In Nepal, a locally found magnesite ( $\text{MgCO}_3$ ) was used as a cheaper Mg source in struvite production from urine (Krähenbühl *et al.*, 2016). Alternatively, the reagent cost is reduced by pre-treating magnesium oxides ( $\text{MgO}$ ) with phosphoric acid ( $\text{H}_3\text{PO}_4$ ), which increases its dissolution to almost 100% compared to its original ~40% (Romero-Guiza *et al.*, 2015). This provides both the  $\text{Mg}^{2+}$  and  $\text{PO}_4^{3-}$  at the same time for struvite precipitation which enables removal of total ammonia nitrogen (TAN) up to 80%.

### Pre- and Post-struvite Treatment and Other Techniques

Another method is decomposing the produced struvite itself using chlorination ( $\text{NaClO}$ ) and recycling the struvite by up to five times in treating a landfill leachate in a municipal sanitation center in Beijing, China (Huang *et al.*, 2015). This approach has successfully reduced 92% of ammoniacal nitrogen ( $\text{NH}_3\text{-N}$ ) and saved about 34% of the reagent cost. Gamma ray irradiation was used to pre-treat a livestock wastewater prior to struvite precipitation (Kim *et al.*, 2014). It has proven to be able to reduce the concentration of  $\text{NH}_3$  and PO and has further reduced the dependency of chemical dosage during the process.

Some other studies approached differently *i.e.* gearing towards preserving the environment by getting rid of the harmful discharge. The most recent discovery is struvite as a stabilising agent for high-activity nuclear waste stream (Wagh *et al.*, 2016). K in struvite is replaced with cesium (Cs) using Ceramicrete resulted in a matrix stable enough (due to immobilisation of Cs) to host radioactive substances. In the steel-making industry, a huge amount of water is consumed in producing metallurgical coke (USEPA, 1995). The waste stream of the process contains hazardous substances that are still laden with  $\text{NH}_3\text{-N}$  and P contents after being treated biologically. Research has discovered the potential of utilising struvite to recover these substances with about 95% to 98% recovery of  $\text{NH}_3\text{-N}$  (Kumar and Pal, 2012; 2013).

Struvite precipitation was found to be useful in harnessing the potential of the semi-conductor wastewater as fertiliser. A significant improvement in fresh weight of almost 200% was recorded when

the struvite was applied to grow Chinese cabbage (Ryu *et al.*, 2012).

### ECONOMIC FEASIBILITY AND ENVIRONMENTAL IMPACT OF STRUVITE PRECIPITATION TECHNOLOGY

An economic study carried out by Maaß *et al.* (2014) concluded that the integrated value chain of wastewater treatment and crop production can have a higher return via establishing struvite-P and other nutrients into the cultivation cycle. It was reported that a profit of € 35 000 added-value gains per year for crop producers who replaced conventional ( $\text{PO}_4^{3-}$ )-based fertiliser with struvite generated from the associated wastewater. Earlier in 2007, Türker and Çelen calculated the cost for single step precipitation work for  $\text{NH}_4^+$  removal from molasses wastewater at USD 7.7  $\text{kg}^{-1}$  of  $\text{NH}_4^+$ . Applying this formula to POME which has about 36  $\text{mg litre}^{-1}$  of  $\text{NH}_4^+$  (Loh *et al.*, 2013), it is estimated that struvite precipitation from POME could cost about USD 0.28  $\text{t}^{-1}$  of POME subjected to crystallisation.

Shu *et al.* (2006) estimated about 1 kg of struvite can be crystallised from 100  $\text{m}^3$  of wastewater in general. In addition, Pastor *et al.* (2008) informed that 13.7 g of P  $\text{kg}^{-1}$  of treated sludge can be harvested from the municipal wastewater treatment plant. A typical 60  $\text{t hr}^{-1}$  palm oil mill processing for 8 hr per day could produce about 300  $\text{m}^3$  of POME per day, considering 0.65 as the ratio for processing capacity ( $\text{t hr}^{-1}$ ) to effluent generation ( $\text{m}^3 \text{hr}^{-1}$ ). Thus, there is a potential production of about 3 kg of struvite per day or 60 kg of struvite per month from a palm oil mill. In general, a hectare of well-managed oil palm plantation requires about 84 kg of rock phosphate that usually contains between 4%-20% of phosphorous pentoxide ( $\text{P}_2\text{O}_5$ ) with frequency of application at two rounds per year (Rankine and Fairhurst, 1999). Assuming struvite generated from POME has similar composition of P, it could possibly be a good and potentially cheaper alternative to rock phosphate. Usage of chemicals in the precipitation process could contribute highly to the total process cost. In tackling this issue, dosing Mg via electrochemical process using a sacrificial electrode can be helpful (Hug and Udert, 2013). In this case, a cost reduction of 34% was recorded compared to that using soluble Mg salts. Furthermore, Etter *et al.* (2011) found that it is feasible to produce low-cost struvite in Nepal at industrial scale provided that the source of Mg and waste are locally and readily available. However in terms of financial profitability, it is not possible to make this struvite production self-sustaining.

A life cycle assessment study was carried out by Ishii and Boyer in 2015, comparing different approaches in managing urine wastewater. The



resulting struvite precipitation process where the addition of MgO was applied reduces the environmental costs as calculated by the Tool for the Reduction and Assessment of Chemical and Other Environmental Impacts. Antonini *et al.* (2012) conducted an environmental impact assessment on the production of struvite from urine and concluded that it is a hygienically safe form of alternative fertiliser. Besides, the microbiological health risk in handling struvite precipitation was assessed by Decrey *et al.* (2011) since this was always associated with 'harmful' wastewater. As the inactivation of phage increases linearly with decreasing of moisture content of the struvite, this impresses that dry condition is preferred to prevent any activation of existing pathogen.

## FACTORS INFLUENCING SCALE DEPOSITION

Many chemical and physical factors are involved in determining the characteristic of the scale deposition (Table 1). Hanhoun *et al.* (2011) pointed out that pH, ionic strength and temperature are among the factors influencing struvite scale solubility. The severity of crystallisation fouling and scale formation are depending on the type and concentration of the mineral salts involved in the concerned fluid as well as the operating conditions where the fluid gets into contact with solid parts (Hasan *et al.*, 2012).

### pH

Control of pH is very important in precipitation of scale in wastewater treatment. This is due to the fact that the relating ions, in the case of struvite precipitation ( $Mg^{2+}$ ,  $NH_4^+$  and  $PO_4^{3-}$ ) are highly dependent on pH value (Huang *et al.*, 2014a). Increment in the pH value of the wastewater subject would decrease the formed crystal size (Hutnik *et al.*, 2013). It will also decreases the crystal growth rate (Mazienczuk *et al.*, 2012) and reduced its purity (Kruk *et al.*, 2014). On the other hand, low pH was reported to have decrease the struvite precipitation (Lee *et al.*, 2013a).

### Reaction Time

Reaction time or contact time is a parameter of concern for a typical crystalliser. By increasing the reaction time, one would induce the crystal growth size (Hutnik, 2013). However, the growth rate was reported to decrease with the elongation of reaction time.

### Temperature

Increased temperatures would causes a reduction in particle size and would have an impact on the crystal morphology. Rouff (2013) has reported

a change from elongated to rhombohedral when the temperature was increased from 25°C to 300°C. Apart from that, the particle size was also reduced.

## Ionic Concentration

Ionic activity of the wastewater may or may not affect the scale formation. Struvite formation can be increased in its yield by increasing the concentration of  $Mg^{2+}$  (Korchef *et al.*, 2011; Matynia *et al.*, 2013). On the other hand, the existence of  $Ca^+$ ,  $Fe^{3+}$  and  $Cu^{2+}$  could hamper and retard struvite precipitation (Le Corre *et al.*, 2005; Pastor *et al.*, 2010; Lee *et al.*, 2013b; Huang *et al.*, 2014b; Muryanto and Bayuseno, 2014).

In addition, Rodriguez and Smith (2007) recognised that the wall temperature and flow velocity may also have a significant effect on the scaling deposition rate. For normal solubility salt system, increasing wall temperature will decrease the deposition rate, while for inverse solubility salt system, *vice versa*. Besides that, surface roughness has also long been identified to enhance the initial deposition rate by providing sites for crystal nucleation (Taborek *et al.*, 1972). It was later reaffirmed by Crittenden and Aldermann (1988), and Bott (2011) where they reported increasing deposition rates on higher surface roughness.

## STRUVITE PRECIPITATION TECHNIQUES

Fluidised bed reactor (FBR) is one of the common methods used in recovering struvite. Guadie *et al.* (2014) concluded that an improved shape of a FBR could reduce the loss of crystal by up to 67%. Meanwhile, Su *et al.* (2014) investigated the effects of influent pH and Mg:P molar ratio on magnesium ammonium phosphate crystallisation in FBR. Continuously stirred tank reactor (CSTR) is another method for the precipitation of struvite. Ronteltap *et al.* (2010) found that the CSTR is a reliable and stable process to precipitate struvite crystal without requiring any pH control, however the struvite particle size is affected by supersaturation and temperature. Wang *et al.* (2010) previously worked on forming struvite at a neutral pH introduced electrochemical deposition to improve the precipitation rate. Cusick *et al.* (2014) used microbial electrolysis cells to convert wastewater organics into hydrogen gas and struvite which can later be easily separated. Microbial fuel cells (MFC) on the other hand are used to recover nutrients *e.g.* P while forming struvite and producing water (Ichihashi and Hirooka, 2012). Similarly, Fischer *et al.* (2011) used MFC with *Escherichia coli* as the reducing bacteria and successfully obtained up to 82% or 600 mg litre<sup>-1</sup> of ( $PO_4^{3-}$ -based fertiliser). The subsequent electrolysis process could potentially further remove

TABLE 1. INFLUENCES OF RELATED PARAMETERS ON STRUVITE FORMATION AND PRECIPITATION IN WASTEWATER TREATMENT

Factor	Key result	Reference
pH	Increase in pH decreased the mean crystal size by 5.4%	Hutnik <i>et al.</i> (2013a)
	Low pH decreased the struvite precipitation High pH with foreign Ca source activated Ca-PO <sub>4</sub> precipitation, but reduced its purity	Lee <i>et al.</i> (2013b) Kruk <i>et al.</i> (2014)
	pH control is important as the relating ions (Mg <sup>2+</sup> , NH <sub>4</sub> <sup>+</sup> and PO <sub>4</sub> <sup>3-</sup> ) are highly dependent on pH value Growth rate decreases by two-fold with pH increases	Huang <i>et al.</i> (2014a) Mazienczuk <i>et al.</i> (2012)
Reaction time/contact time (mean residence time)	Increasing reaction time induces crystal growth size by 20%. Growth rate decreases triply with the elongation of mean residence time	Hutnik <i>et al.</i> (2013) Mazienczuk <i>et al.</i> (2012)
	Temperature	Increased temperature causes a reduction in particle size and a change in crystal morphology from elongated to rhombohedral
Molar ratio of reagents	Excess Mg <sup>2+</sup> in a continuous crystallisation process increases the crystal yield	Matynia <i>et al.</i> (2013)
Type of nucleation	Homogenous nucleation with increase in relative supersaturation results in a decreased maximum crystal size; but increases the volumetric percentage	Hanhoun <i>et al.</i> (2013)
Concentration of Ca <sup>+</sup>	Higher concentration of Ca <sup>+</sup> can hamper the crystallisation of struvite	Lee <i>et al.</i> (2013a) Le Corre <i>et al.</i> (2005)
Concentration of Fe <sup>3+</sup>	Fe <sup>3+</sup> presence could negatively affect the struvite precipitation	Huang <i>et al.</i> (2014b)
Concentration of Cu <sup>2+</sup>	Cu <sup>2+</sup> presence could significantly retard struvite growth rate	Muryanto <i>et al.</i> (2014)
Concentration of Mg <sup>2+</sup>	Increase of Mg <sup>2+</sup> concentration significantly yields higher PO <sub>4</sub> <sup>3-</sup> removal	Korchef <i>et al.</i> (2011)
Aeration rate (for aerated crystalliser reactor)	Struvite formation increases in proportion to the aeration rate and can reach a plateau at around 0.73 litre min <sup>-1</sup> of aeration. Aeration cleans struvite crystals from suspended solids which is useful in the separation process	Liu <i>et al.</i> (2011b) Pastor <i>et al.</i> (2010)
	Mixing intensity	Increasing the multiple values of mixing intensity ( $Gt_d$ ) and mixing duration ( $t_d$ ) <i>i.e.</i> , $Gt_d$ to above 10 <sup>5</sup> has resulted in almost pure struvite Agitated crystalliser shows a satisfactory - up to 85% precipitation and recovery efficiencies



the element of  $\text{NH}_3\text{-N}$  after the produced struvite being re-dissolved (Liu *et al.*, 2011). A similar process to explore metallophilic bacterium *Enterobacter* sp. which is resistant to heavy metal for the recovery of P was attempted (Sinha *et al.*, 2014).

## MITIGATION METHODS OF VARIOUS TYPES OF SCALES ACROSS SEVERAL INDUSTRIES

### Electropolarisation

This mitigation method is associated with membrane filtration. The membrane itself is made of nanocarbon material which is electroconductive, making it possible to be polarised into electric fields. This technology has proven to mitigate scale formation in membrane filter and able to increase the permeation flux of the membrane above 1 and 8 times for filtration of wastewater containing natural organic matters and feed water containing bacteria, respectively (Fan *et al.*, 2016).

### Mechanical Scouring

Wu *et al.* (2017) studied the effect of mechanical scouring by granular activated carbon (GAC) to mitigate fouling on membrane filter. The GAC with diameter ranging from 0.9 to 4.6 mm was directed to scour the surface of a membrane by a magnetic stirrer. The membrane threshold flux values were improved significantly especially for membrane with larger pore. This process requires less energy as compared to other conventional mechanical methods of fouling mitigation (Wang *et al.*, 2016).

### Scale Inhibiting Chemicals

Chauhan *et al.* (2008) discovered that by adding the extract of *Commiphora wightii*, a common herbal plant found in northern India, struvite deposition could be inhibited. Prior to that, he also tested the juice of *Citrus medica* Linn. a traditional medicinal material used in Indian culture on struvite growth and found that the inhibition of struvite crystal was successful. Wierzbicki *et al.* (1997) studied the role of phosphocitrate in suppressing the struvite crystal formation at a molecular phase. He found that phosphocitrate presents a strong affinity to faces of struvite crystals resulted in alteration of expression of these faces and the development of characteristic arrowhead struvite morphology. Researchers in University of Science and Technology of China utilises polyaspartic acids (PASP) and found it is effective in the growth inhibition of struvite crystals. Its inhibitory capacity was found proportional to its concentration and it has a significant impact on morphological modification of struvite crystals (Li *et al.*, 2015).

### Electronic Anti-fouling Technology (EAF)

Zhang *et al.* (2016b) investigated the effect of EAF to prevent scaling in a heat transfer industry. EAF is a type of electromagnetic water treatment device that produces pulsing current to create time-varying magnetic fields inside the pipe of a heat exchanger which then creates induced electric field exerting its energy to the depositing scales. In that study, the fouling resistance of the heat exchanger was successfully reduced to 8% compared to 25% without EAF.

### Ozonation

A solution was proposed to control the formation of scaling in membrane filter by applying *in situ* ozonation (Wei *et al.*, 2016). This treatment can effectively mitigate membrane fouling with 76% improvement in transmembrane pressure. It indicates a clearer membrane pore from any scale deposit blockage.

### Catalytic Reaction

The efficacy of using catalytic materials such as tourmaline, zinc (Zn) and aluminum (Al) in mitigating  $\text{CaCO}_3$  scaling of carbon steel was studied (Ruelo *et al.*, 2013). The introduction of these materials was found able to reduce the deposition of scale by 21% on a carbon steel surface.

### Electro-coagulation

Hua *et al.* (2015) studied the efficiency of fouling reduction using electro-coagulation method involving Al electrodes in a membrane bioreactor (MBR). A substantial eight times reduction of the fouling rate compared to normal MBR operation was attainable. No chemical is used during the entire operation of the then termed 'electro-MBR'.

### Ultrasound

Heath *et al.* (2013) reviewed several attempts through ultrasound cavitation technology. The application of ultrasound to perform cavitation erosion on  $\text{CaCO}_3$  deposits has been intimately associated with the scale material bulk properties as well as its microstructure. The complexity of the situation escalates as the macro- and micro-properties of  $\text{CaCO}_3$  scale are dependent on many factors relating to its depositional environment.

### Turbulence Generation

Hasan *et al.* (2012) employed four types of turbulence generators in a piping system in an attempt to suppress the crystallisation build up

in a heat exchanger system. The application of turbulence flow increases the surface temperature of the piping in a cross flow heat exchanger which will then affect crystals formation. So far, an 85% reduction of fouling resistance is obtained using turbulence generators with an 80% blockage area.

### Fibre Seeding

Kazi *et al.* (2013) tested a fibre seeding method by adding natural fibres into a supersaturated  $\text{CaSO}_4$  solution to investigate its effect on scale deposition in a heat exchanger pipe surface. Fibres from pine, spruce and eucalypt pulp were used in that study. The scaling in the heat exchanger was retarded with as low as 0.1% to 0.25% fibre concentrations.

### Ultrasonic Irradiation

Hou *et al.* (2015) investigated the effect of ultrasonic irradiation in mitigating humic acid fouling during membrane distillation. However, there is still much to improve as the reduction in permeate flux resistance is < 5%.

## FORMATION OF CRYSTALS IN POME TREATMENT FACILITY AND ITS TREATMENT APPROACH

The current practice in palm oil mill relating to crystal formation in POME treatment facility is to identify the affected component and determine the performance of each deteriorated component. The follow up action would be either to add relevant mechanical devices based on the component's deterioration degree in assisting the affected component to continue working or to replace totally the items. In the case where the crystal is breakable, hacking tools are used to get rid of it. However, certain areas that are not reachable *e.g.* diffuser, valve and pump will normally be replaced. There was also some effort to perform acid cleaning, hydrokinetic blasting as well as ultrasonic cleaning. While most of the scales can be removed, the pipes are physically affected thus their structural strength is reduced. This has led to the increase of maintenance cost and downtime of the system that may affect the operation of the fruit processing mill which ultimately makes management of the POME polishing plant more difficult and challenging.

As the crystal formation continues to occur in POME treatment facility, the oil palm industry is currently looking for scientific-based solutions and potential recommendations. There is no cost-effective solution forthcoming as yet as knowledge gaps remain in understanding what constitutes the POME crystal, how it is formed, how it can be removed or reduced as well as the related cost

involved in crystal removal/nutrients recovery. The other industries' experiences dealing with similar scale or crystal deposits in this review serve as a learning platform where some potential advanced, economical and practical techniques *e.g.* chemical and mechanical cleaning for crystal growth inhibition and struvite precipitation for nutrient recovery, may be applied to the oil palm industry in dealing with this issue during wastewater treatment and management.

## CONCLUSION

From the review, struvite precipitation was found to be the popular method in solving scaling deposits issue in wastewater treatment plant around the world. This method can be imitated in POME treatment plant due to the benefit of not only having the ability to maximise nutrients recovery and fertilisation value from POME such as the N, P and Mg, its formation in the subsequent process in the treatment plant could also be reduced. Given the recondite subject of struvite precipitation utilising POME, it is notably a research area worth giving attention to. It could opportunistically open up a new path to the industry gearing towards proper POME management in terms of treatment efficiency, cost-effectiveness as well as the impact to environment. The current scarcity of mined P could also be the driving factor for more thorough study into recycling of this nutrient from POME which is wasteful as it is currently being discharged into water streams.

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