CHEMICAL ENGINEERING TRANSACTIONS
VOL. 86, 2021

A publication of AIDIC
The Italian Association
of Chemical Engineering
Online at www.cetjournal.it

Guest Editors: Sauro Pierucci, Jiří Jaromír Klemeš

ISBN 978-88-95608-84-6; **ISSN** 2283-9216

DOI: 10.3303/CET2186245

Struvite Crystallisation of Synthetic Urine Using Magnesium Nitrate: Effect of Parameters on Crystal Size Distribution

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Urine diversion toilets have become popular as a means of solving the challenges in sanitation. As a result, the source separated urine must be adequately treated so that it can be disposed of safely and valuable struvite can be extracted for use as fertiliser. Struvite crystallization has been investigated for this purpose, however, for the crystallization process to be viable and economical, a cost effective yet optimal magnesium source is required. Crystallisation must have optimal yield as well as crystal size and morphology (CSD). Crystal size is an important factor in crystallisation as it affects further processing steps such as washing and filtering, therefore CSD must be controlled in crystallisation processes. In this study, synthetic urine was prepared, and struvite crystallisation experiments carried out using Magnesium Nitrate ($MgNO_3$). The effect of parameters on CSD were investigated. Residence time was found to be the parameter with the most effect on CSD. At residence time of 10, 30 and 60 minutes, mean particle sizes were 17, 34 and 53 µm showing that with higher residence times, larger crystal sizes can be achieved. SEM analysis of the crystal showed that the resultant crystals had the typical morphology of struvite crystals.

1. Introduction

Struvite or magnesium ammonium phosphate (MAP) is a mineral which is made up of Magnesium (Mg), Ammonium (NH_4) and Phosphate (PO_4) as the name suggests. It occurs naturally in stored urine (Udert et al., 2006). Struvite has also been found in wastewater treatment systems, where it causes scaling problems (Ariyanto et al., 2014). Struvite has large potential for use as fertiliser and it may be the preferred fertiliser for several reasons some of which are stated below:

- It is slow releasing which enables the plants to take up the nutrients before the fertiliser is leached and therefore less frequent application is required (Munch and Barr, 2001)
- Heavy metals are much lower in struvite fertilisers than other fertilisers (Doino et al., 2011)
- Essential nutrients (N,P, Mg) can be applied to the plants simultaneously (Taiz and Zeiger 1991).

A number of studies have been conducted on struvite precipitation from source separated urine. The rationale behind the studies is because urine naturally contains nutrients present in synthetic fertilisers. On average urine contains 1g/l of P, 9g/l of N and 10g/l of chemical oxygen demand (COD). Human urine makes up approximately 1% of municipal wastewater but it contributes approximately 50% of the phosphorus load (Wilsenach et al., 2007). The abovementioned factors therefore make urine a valuable potential source of nutrients for use as fertiliser (Maurer et al., 2006)

Struvite crystallization is also the subject of various studies aiming at removing phosphates from wastewaters. Discharging of wastewaters containing nitrogen and phosphorus to the environment can lead to eutrophication. This has led to limits being imposed on the amount of P and N that can be discharged to waters in order to prevent this (Doyle and Parsons, 2002). This has encouraged investigation into various methods of extracting these nutrients from wastewaters before discharge to rivers, oceans, lakes etc.

Struvite crystallization occurs through two processes, namely nucleation and crystal growth (Ariyanto et al., 2014). Nucleation is the process whereby ions combine to form crystal embryos (Doyle and Parsons, 2002). Crystal growth then occurs after nucleation, where growth continues until equilibrium is reached. The process occurs when parameters are such that the concentration of Mg^{2+}, NH_4^+ and PO_4^{3-} in the solution exceed the

Paper Received: 6 September 2020; Revised: 2 February 2021; Accepted: 19 April 2021
Please cite this article as: Seodigeng R., Tshilenge J., Rutto H., 2021, Struvite Crystallisation of Synthetic Urine Using Magnesium Nitrate: Effect of Parameters on Crystal Size Distribution, Chemical Engineering Transactions, 86, 1465-1470 DOI:10.3303/CET2186245

solubility product of struvite. The parameters which have an effect on struvite precipitation include pH, Mg:P ratio, supersaturation, temperature, mixing intensity and presence of other ions in the solution (Matynia et al., 2006).

Bhuyian et al. (2007) and Ariyanto et al. (2014) found that supersaturation and pH had the most influence on crystallisation while Barbosa et al. (2016) found that in urine, the factors that had the most effect were stirring speed and Mg:P ratio. Harrison et al. (2011) also found that growth rates increased with an increase in pH, up to 8.5.

An important objective of crystallisation is to produce crystals of the appropriate size or crystal size distribution (CSD) and crystal morphology. Crystal size is an important factor in crystallisation as it affects further processing steps such as washing and filtering, therefore CSD must be controlled in crystallisation processes. In the study by Doino et al., 2011, crystal sizes of 170 µm were obtained in a pilot fluidised reactor, which made the crystals easily filterable. The crystal morphology is affected by pH. Abbona and Boistelle, (1982) found that at pH greater than 8, twinned dendritic structure was formed, between pH 7 and 8, a tabular structure was supported. At pH lower than 6, elongated, needle like crystals formed. Tabular form is the most preferred form for industrial equipment. (Abbona and Boistelle, 1982). Struvite crystals typically exhibit an orthorhombic structure (Doyle and Parson, 2002). Some crystals can exhibit a needle like structure, an x – shape structure or rod-shaped structure. (Wilsenach et al., 2007). Barbosa et al. (2016) found that different Mg sources resulted in different crystal structures. MgO resulted in a combination of irregular shaped and x-shaped crystals while $MgCl_2$ and $Mg(OH)_2$ resulted in an orthorhombic structure, which is a typical pattern for struvite. Similar shapes were reported by Munch and Barr (2001) and Korchef et al.(2011).

The objective of this study is to study struvite crystallization using $Mg(NO_3)_2$ as a Mg source and observe the CSD and morphology of the resultant struvite crystals. This will determine whether $Mg(NO_3)_2$ as a Mg source is suitable for struvite crystallization. In addition, the effect of parameter such as Mg:P ratio, pH, residence time, stirring speed on CSD were also investigated.

2. Materials

A solution of synthetic urine was prepared using a standard recipe from literature. $MgCl_2.6H_2O$, $CaCl_2.2H_2O$ NaCl , Na_2SO_4, $Na_3(C_6H_5O_7).2H_20$ (Sodium citrate), KCl, $C_4H_7N_3O$ (Creatinine), $(NH_2)2CO$ (Urea), NH_4Cl, K_2HPO_4, $Na_2(COO)_2$ (Sodium oxalate), $C_6H_8O_6$ (Ascorbic acid), $C_5H_4N_4O_3$ (Uric acid), Na_2CO_3 Na_3PO_4 were used to prepare the synthetic urine in proportions such that the concentrations mimicked the typical concentration of urine as it leaves the human body. H_2SO_4 was used to preserve the synthetic urine. NaOH was used for pH adjustment. $Mg(NO_3)_2$ was used as the Mg source.

2.1 Design of experiments

The key parameters of the struvite crystallisation were investigated are Mg:P ratio, pH, residence time and stirring speed. The studied key parameters were varied within prescribed range of discrete values as shown in Table 1. Initial experiments were conducted to determine the combined effects of pH, residence time, Mg:P ratio and stirring speed on CSD. Using these preliminary results, Stat-Ease Design Expert® was used to design an optimised set of experiments for studying factor interaction. A set of 20 experiments were designed and carried out at varying conditions.

Table 1: Discretised parameter ranges

Factor	Name	Units	Minimum	Maximum
A	pH	-	9	10
B	Mg:P ratio	-	1	2
C	Stirring speed	RPM	60	120
D	Residence time	Minutes	5	60

2.2 Crystallisation experiments

Batch crystallisation experiments were conducted using 2L of synthetic urine per experimental run. The experiments were carried out in a struvite crystallization vessel equipped with a stirrer. pH was adjusted using NaOH. The stirrer speed was then adjusted as per the predetermined run conditions. A supersaturated solution of $Mg(NO_3)_2$ was prepared and added to the synthetic urine as an Mg source. The amount of $Mg(NO_3)_2$ added was determined based on the targeted final Mg:P ratio. The experiment was done until the required residence time was reached as per run conditions. The residence time was determined from the time the Mg source solution was added. At the required run residence time, the stirrer was stopped, and the crystals were filtered from the solution using a vacuum pump manifold. The solution was filtered through a filter paper.

2.3 Analysis techniques

The filtered crystals were dried in an oven overnight at 35°C and then weighed to determine the yield. The mass of filter paper was subtracted from the total weight. Samples were prepared for particle size distribution (PSD) analysis by suspending them in distilled water. Crystal size distribution was analysed using a Malvern PSD analyser. The precipitate was analysed using SEM to determine the crystal morphology and composition analysed by EDS.

3. Results and Discussion

3.1 Effect of residence time on crystal growth

Figure 1 to Figure 3 show the results for the experiments. The results show crystal size distribution at residence times of 10, 30 and 60 minutes. The mean particles sizes at 10, 30 and 60 minutes were 17, 34 and 53 µm, respectively as shown in Figure 3. The graph shows that at higher residence times larger crystal sizes were achieved. This effect was also observed by Hutnik et al. (2013).

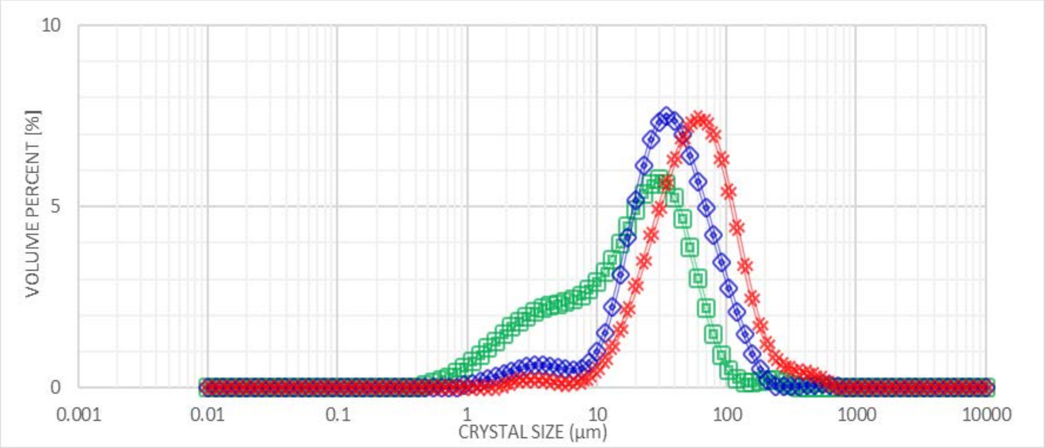

Figure 1: Crystal size distribution at 10 min, 30 min and 60 min

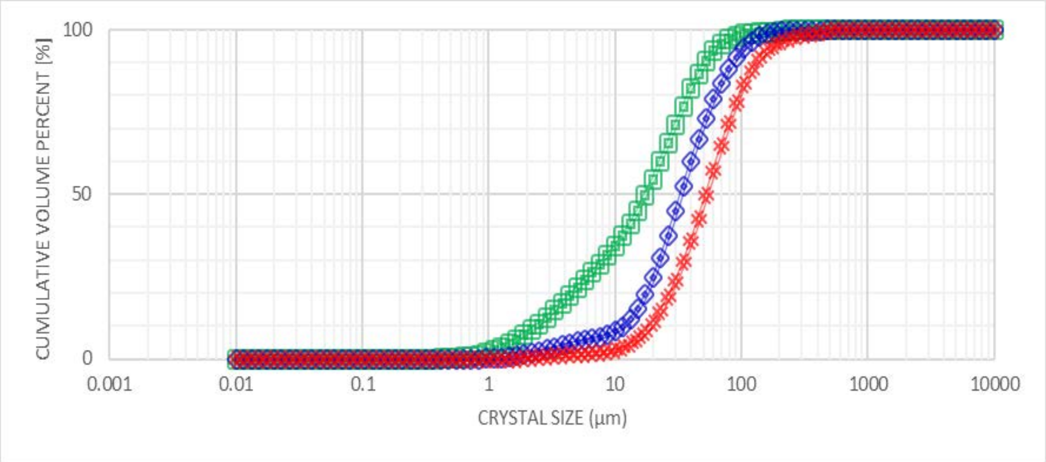

Figure 2: Cumulative crystal size distribution at residence time 10 min, 30 min and 60 min

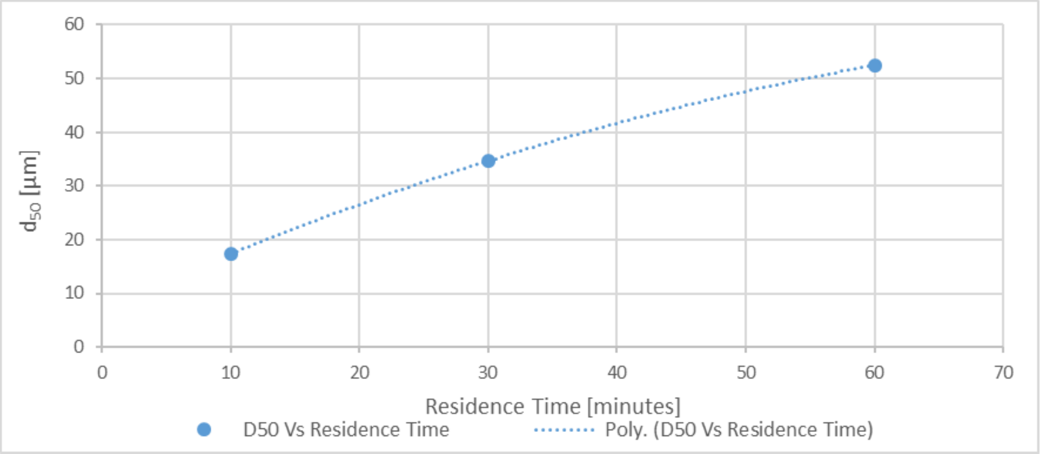

Figure 3: Mean crystal size distribution at residence time 10 min, 30 min and 60 min

3.2 Effect of Mg:P ratio and residence time on crystal growth

Figure 4 shows a graph of the effect of Mg:P ratio on crystal size distribution showing interactions with residence time. At higher Mg:P ratio, the supersaturation of struvite is high which supports faster spontaneous nucleation. When nucleation rates are higher than growth rate, then the average crystal sizes decrease. At low Mg:P ratio, crystal growth is favoured more than nucleation (Bhuiyan et al., 2008). The interaction is analysed at an optimum pH of 9.5 and stirring speed of 90 rpm. The two graphs are plotted for a minimum residence time of 5 min and a maximum residence time of 60 minutes. The graph shows very clear influence of residence time on crystal size. An increase in mean residence time resulted in larger mean crystal size (Hutnik *et al.*, 2013).

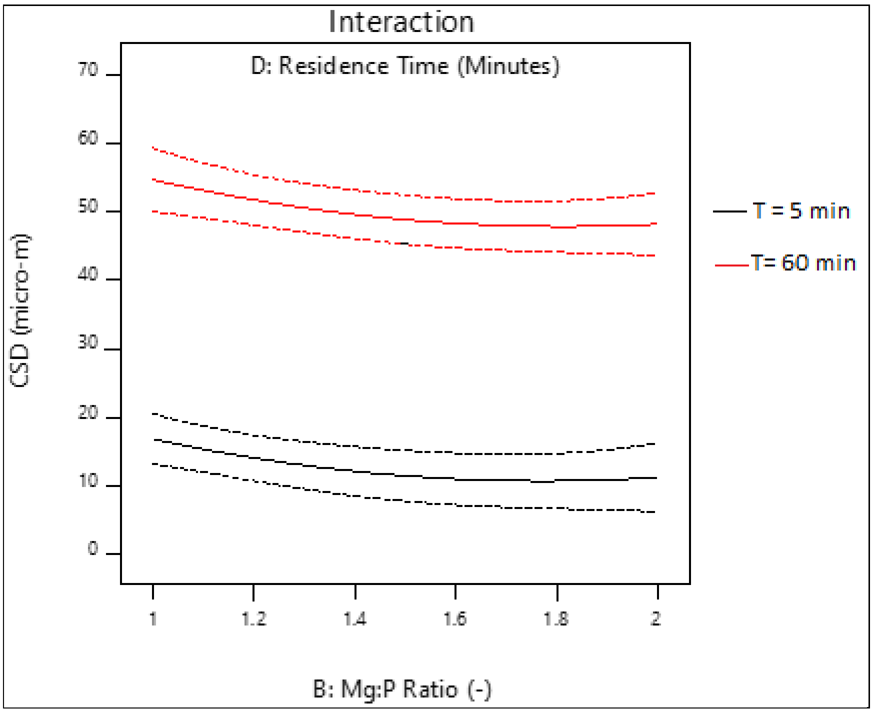

Figure 4: Effect of Mg:P ratio on CSD (d50) showing interaction with residence time, while stirring speed and pH are kept constant

3.3 Struvite elemental analysis

Samples of the collected precipitate obtained after P removal with Mg:P of 1.5 and residence time of 60 was selected for crystals characterization. The content of struvite in the precipitates was confirmed by SEM, SEM–EDS. Figure 5 shows the SEM images of the precipitate which shows the crystal morphology of the precipitate. The elemental analysis of the crystals was also determined by EDS. The SEM images show that the resultant crystals were similar in morphology and displayed the typical rod-shaped morphology of the struvite crystal.

SEM–EDS analyses of the crystals are shown in Table 2. The chemical element composition showed the presence of Mg, P, N and O on the crystals in quantities that are similar to that of theoretical struvite. The EDS elemental analysis also showed similar composition to theoretical struvite with the exception of elements such as Na, K and Ca, which are present in synthetic urine but not in pure struvite. These elements are however present in small quantities (<2%) in the precipitate.

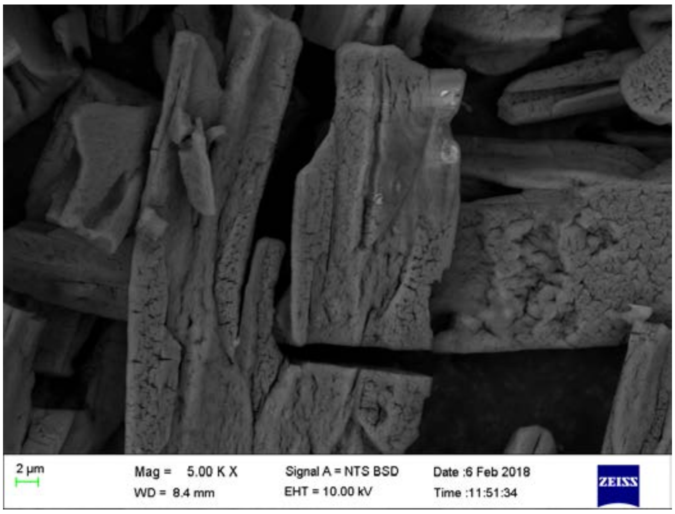

Figure 5: SEM analysis of precipitate at 5000X magnification

Table 2: Precipitate elemental analysis

Element	N K	O K	Na K	Mg K	P K	K K	Ca K	Totals
Weight%	8.70	52.20	0.21	13.74	21.21	2.48	1.36	100
Atomic %	11.85	62.21	0.26	10.78	13.06	1.21	0.65	100

4. Conclusions

It can be concluded that residence time is an influential parameter on struvite crystallization in terms of crystal size distribution. Crystals need to be allowed sufficient time to grow to a suitable size. This means that in crystalliser design and process optimisation, the residence time will be the most important factor as whether all other parameters are at an optimum is immaterial if there is insufficient time given for nucleation and crystal growth to occur. Also, sufficient time must be allowed for the solution to reach equilibrium to ensure maximum yield of crystals. The elemental analysis using SEM-EDS showed that the resultant crystals were similar in composition to theoretic struvite elemental analysis. Elements such as Na, K and Ca which are expected to be present in urine were also detected in trace quantities. Crystal morphology was also analysed with SEM and showed the typical rod-shaped morphology of struvite crystals.

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