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Struvite Crystallisation of Synthetic Urine Using Magnesium Nitrate: Effect of Parameters on Yield

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Urine diversion toilets and waterless urinals have received much attention lately to solve sanitation challenges in water scare countries. Separating the urine at source and treating the urine and solids separately has the impact of reducing water usage and reducing the burden on wastewater treatment systems. Source separated urine can be valorised by extracting struvite as fertiliser through crystallisation. A cost-effective magnesium (Mg) source is required for the process and depending on factors such as location and availability, an Mg source may be the difference between an economically viable process and one that is not. Different kinds of sources for Mg have been investigated, but none investigated fertiliser grade magnesium nitrate ($Mg(NO_3)_2$). In this study, struvite crystallisation using $Mg(NO_3)_2$ was investigated. The effect of four parameters namely residence time, pH, Mg: P ratio and stirring time on yield were studied. Residence time was determined to be the most influential parameter. The optimal pH, stirring speed, residence time and Mg:P ratio were found to be 9.5, 90 rpm, 24 min and 1.5 respectively. Stirring speed was found to have the least effect on yield and a minimal effect on crystal size distribution.

1. Introduction

According to the latest report on the status of sanitation services in South Africa, 11% of households in South Africa do not have suitable sanitation services. Approximately 1.4 million households in informal settlements do not have access to sanitation services while over half a million households in informal settlements use interim services (Department of Water Affairs, 2012). Some of the reasons cited for these challenges include scarcity of water resources, the high cost of infrastructure for installation of waterborne sewage systems and the high cost of infrastructure maintenance and operation.
Recent studies in developing countries, have identified urine diversion as a plausible sanitation solution in water scarce countries. Waterless urinals and urine diversion toilets separate urine and faecal solids at source facilitating drastic reduction in water usage and reducing economic and technological requirements for wastewater treatment (Etter et al.,2011). Furthermore, valuable nutrients can be removed from waste to be reused as fertilizer.
Nitrogen (N), phosphorus (P) and potassium (K) are some of the important macro-nutrients required for plant growth (Mehta and Batstone, 2013). Urine is naturally rich in these three nutrients, which also happen to be the three components used in most synthetic fertilisers (Mercola, 2014). Urine excretion accounts for the bulk of the daily human nitrogen excretion at approximately 88% as well as 67 % of the phosphorus excretion (Karak and Bhattacharyya, 2011). Human urine contains approximately 1g/L of phosphorus and 9g/L of nitrogen (Barbosa et al., 2016), which makes it an excellent source of nutrients for plants.
Raw urine has been studied as a fertiliser for more than twenty different plant species (Karak and Bhattacharyya, 2011). Applying raw urine directly to the soil is however controversial owing to issues of hygiene, perception, and effects on soil health (Lind, Ban and Byden, 2000). Some potential risks of applying raw urine include soil contamination from antibiotics and endocrine disruptors such as hormones, soil contamination from bacteria, parasites and viruses, potential crop failure due to spreading of urine at the incorrect time during growth season or unevenly spreading the urine on the field (Karak and Bhattacharyya, 2011).
Struvite is an orthophosphate which is composed of magnesium (Mg), ammonium (NH_4^+) and phosphate (PO_4^3). It is very effective as a fertiliser. It precipitates naturally in urine that has been stored for a period of time (Udert,

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Larsen and Gujer, 2006). The crystallisation of struvite from urine is a method through which fertiliser can be extracted from urine and be applied to crops without the potential harmful effects. Struvite crystallisation has also been investigated for recovery of nutrients from anaerobically digested supernatants from zootechnical wastewaters and sludge lines of urban wastewater treatment plants (Santinelli et al., 2013). It is widely studied as a promising method of recovering nutrients from various wastewaters such as rubber wastewaters (Huy et al., 2019)

Struvite crystallisation occurs through chemical reaction described in Equation (1) (Wilsenach, Schuurbiers and van Loosdrecht, 2007):

$$Mg^{2+} + NH_4^+ + H_2PO_4^- + 6H_2O \rightarrow MgNH_4PO_4 \cdot 6H_2O + 2H^+ \quad (1)$$

It is the process of crystallising Mg^{2+}, NH_4^+ and PO_4^{3-} in a solution. Urine in its natural state is supersaturated with nitrates (NO_3^-) and phosphates PO_4^{3-}, and only needs addition of Mg to achieve the state of struvite supersaturation followed by spontaneous nucleation and crystallisation.

Struvite crystallization is an inexpensive method of extracting struvite from urine, however, the need for a low-cost Mg source can often render the process uneconomical depending on the location. Currently, industrial processes are used to extract struvite from various wastewaters, and they use different Mg sources. The NuReSys process (Belgium), Airprex (Germany) and Multiform (America) use $MgCl_2$ as an Mg source, while Phosphaq process (Netherlands) use MgO as an Mg source. The Phosnix process in Japan uses $Mg(OH)_2$ as an Mg source (Munch and Barr, 2001). Etter et al. (2011) investigated the cost of different sources of Mg to determine which is more economical for Nepal. Sources such as magnesite rock ($MgCO_3$), magnesium sulphate ($MgSO_4$) and bittern, a waste brine remaining after extraction of salt from seawater were investigated.

$Mg(NO_3)_2$ is a water-soluble salt which occurs naturally in mines and caverns as nitro-magnesite. The $Mg(NO_3)_2$ used commercially is synthesised by the reaction of nitric acid and various magnesium salts. It is commonly used as a dehydration agent, but some grades can be utilised as fertilizer. $Mg(NO_3)_2$ may be easily available depending on location, for instance, fertilizer grades are available in India for export to many countries. This may be a suitable Mg source for the South African context. However, its suitability for struvite crystallization needs to be determined and optimised. In this study, $Mg(NO_3)_2$ was used as an Mg source for crystallisation of struvite from synthetic urine and optimal parameters were determined.

2. Materials and Methods

2.1 Materials

A solution of synthetic urine was prepared using a standard recipe from literature. The resultant concentrations were determined so that they were similar to the typical concentration of urine as it leaves the human body. The chemicals used to prepare the synthetic urine and the resultant concentration are shown in Table 1.

Table 1: Synthetic urine preparation chemicals and concentrations

Chemical	MW (g/mol)	Concentration (mM)
$MgCl_2.6H_2O$	203.3	3.2
$CaCl_2.2H_2O$	147.02	4.4
NaCl	58.44	78.7
Na_2SO_4	142.04	16.2
$Na_3(C_6H_5O_7).2H_20$ (Sodium citrate)	294.1	2.6
KCl	74.55	21.5
$C_4H_7N_3O$ (Creatinine)	113.12	9.7
$(NH_2)2CO$ (Urea)	60.6	330.0
NH_4Cl	53.49	18.7
K_2HPO_4	136.08	30.90
$Na_2(COO)_2$ (Sodium oxalate)	134	0.15
$C_6H_8O_6$ (Ascorbic acid)	176.12	0.57

2.2 Design of experiments

The key parameters of struvite crystallisation that were investigated are Mg:P ratio, pH, residence time and stirring speed (Seodigeng, Tshilenge and Rutto, 2021). The studied key parameters were varied within a prescribed range of values as shown in Table 2. Stat-Ease Design Expert® was used to design an optimised set of 20 experiments with varying experimental conditions for studying factor interaction (Seodigeng, Tshilenge and Rutto, 2021).

Table 2: 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	Min	5	60

2.3 Crystallisation experiments

Batch crystallisation experiments were conducted using 2L of urine per experimental run. Experiments were conducted using a similar methodology to that detailed in Seodigeng, Tshilenge and Rutto, 2021. pH was adjusted using NaOH. 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 Mg:P ratio is the ratio of the amount of Mg in the form of Mg^{2+} to the amount of P in PO_4^{3-} form. The Mg was added in solution form to eliminate any particles which could interfere with the experiment by promoting the nucleation process. The experiment was run until the required residence time was reached as per run conditions at which point the stirrer was stopped, and the crystals were filtered from the solution. Figure 1 shows the experimental setup for crystallisation experiments (Seodigeng, Tshilenge and Rutto, 2021).

Figure 1: Experimental setup with beaker and vacuum manifold

2.4 Analysis techniques

The filtered crystals were dried in an oven overnight at 35°C and then weighed to determine the yield.

3. Results and Discussion

For the yield, the optimal pH, stirring speed, residence time and Mg:P ratio were found to be 9.5, 90 rpm, 24 min and 1.5 respectively. Figure 2 to Figure 4 show graphs of the effect of Mg:P ratio on crystal yield showing interactions with residence time, stirring speed and pH. An increase in Mg:P ratio results in higher yields, however this effect decreases at Mg:P ratio above 1.5. Beyond this ratio, the yield does not increase further. This is because the amount of phosphate and ammonium ions become depleted. Adding more Mg will not have any effect.

Figure 2 shows the interaction of the effect of Mg:P with residence time on yield while the pH and stirring speed were kept constant at optimum values of 9.5 and 90 rpm respectively. The solid lines on the figure indicate the model results showing the interaction of the parameters, while the dashed lines indicate the 95% tolerance levels. Higher residence time resulted in higher yields. The two graphs are plotted for a minimum residence time of 5 min and a maximum residence time of 60 min. The graph shows very distinct differences in yield between the two residence times, which indicates a strong effect of residence time on yield. This is similar to the findings of Hutnik et al (2013).

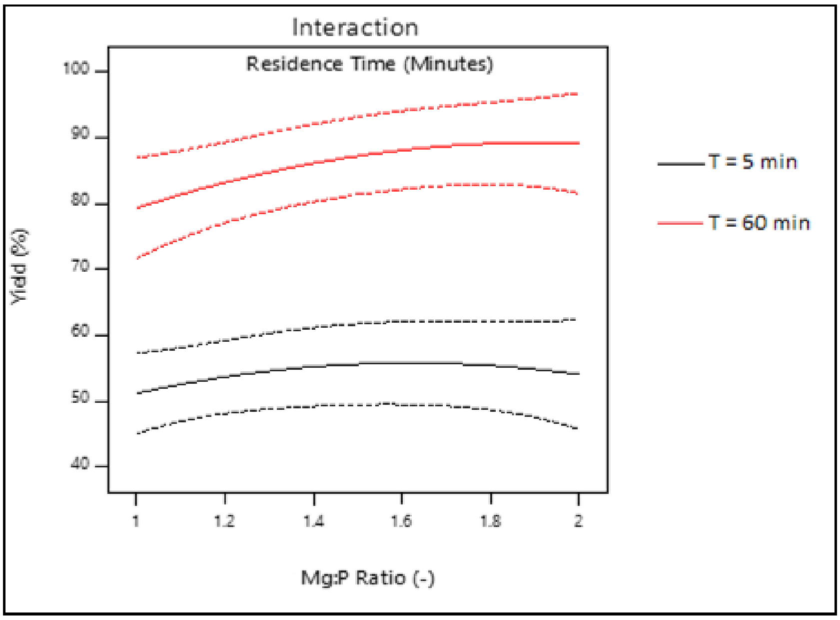

Figure 2 Effect of Mg:P ratio on crystal yield showing interaction with residence time, while stirring speed and pH are kept constant at 90rpm and 9.5 respectively

Figure 3 shows a graph of the effect of Mg:P ratio on crystal yield showing interaction with pH while stirring speed and residence time were kept constant at 90 rpm and 24 min respectively. The graph shows the interaction at minimum pH value of 9 and a maximum pH of 10.

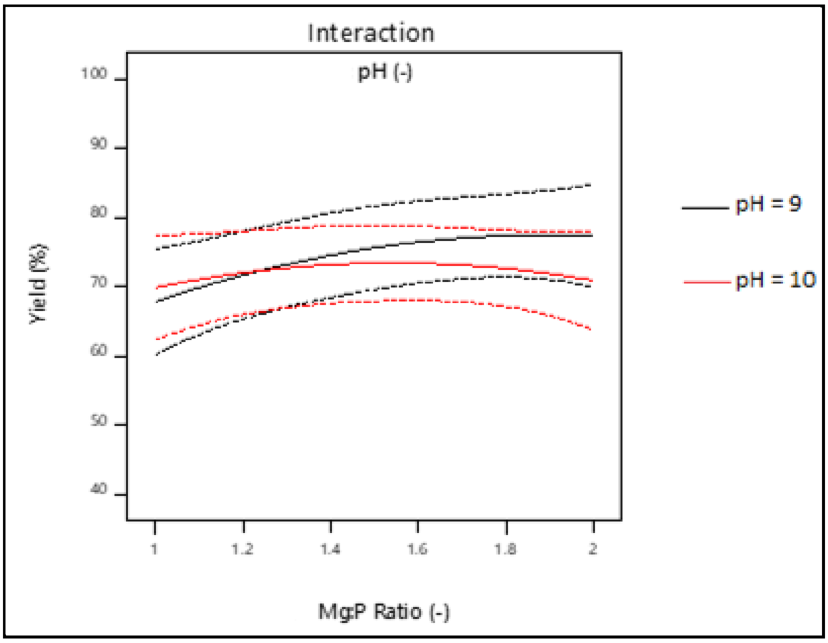

Figure 3: Effect of Mg:P ratio on crystal yield showing interaction with pH, while stirring speed and residence time are kept constant at 90rpm and 24 min respectively

The graphs show that yield increases with increasing Mg:P ratio. At pH of 9, an increase in Mg:P ratio to results in an increase in yield, the yield is minimally affected by Mg:P ratio. This could be because crystallisation is favoured at high pH and regardless of the amount of Mg added to the solution, the effect of pH dominates that of Mg:P ratio. This phenomenon is shown in situations when urine is stored over time and urea decomposes to form ammonium, resulting in an increase in pH which leads to spontaneous crystallisation of struvite without addition of Mg. Bhuiyan, Mavinic and Beckie (2008) and Ariyanto, Sen and Ang (2014) also concluded that pH has a greater effect on crystallisation.
Figure 4 shows the effect of Mg:P ratio on crystal yield showing interaction with stirring speed, while pH and residence time are kept constant at 9.5 and 24 min respectively. The graph shows that while yield increases with increasing Mg:P ratio, the interaction with stirring speed did not have an effect on yield as the graphs are similar for both 60 rpm and 120 rpm. Bhuiyan, Mavinic and Beckie (2008) found that induction time is minimally affected by stirring speed.

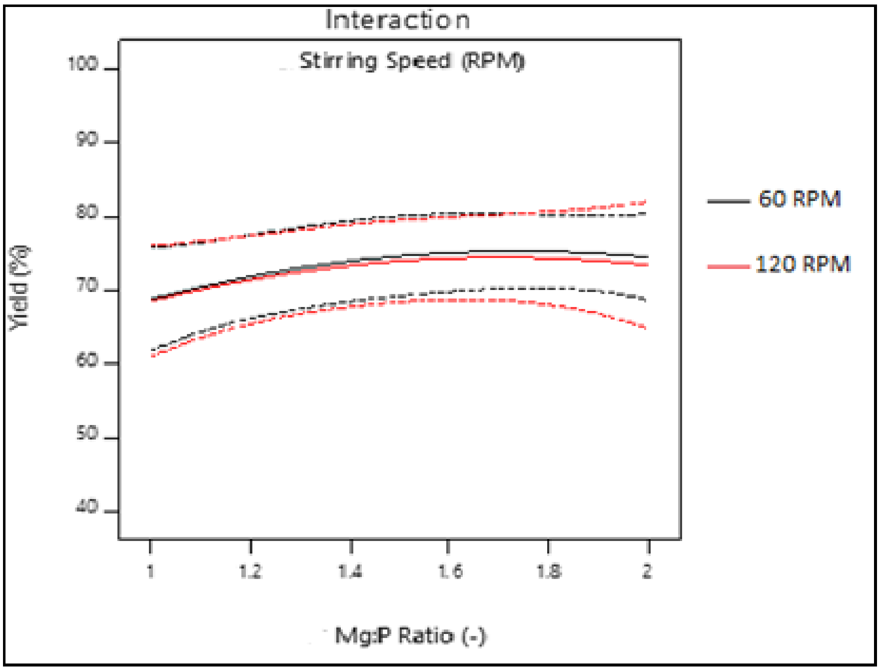

Figure 4 Effect of Mg:P ratio on crystal yield showing interaction with stirring speed, while pH and residence time are kept constant at 9.5 and 24 min respectively

4. Conclusions

In this study, the most influential parameter on struvite crystallization in terms of yield was found to be residence time. This means that in crystalliser design and process optimisation, the residence time will be the most important factor which will allow for the solution to reach equilibrium and produce the maximum yield of crystals. If there is not enough residence time, even if other parameters are optimal, maximum yield cannot be reached. In general, high Mg:P ratio results in higher yields up to an optimum point, after which, no further increase in yield is possible as then the limiting reagents become ammonium and phosphate. In crystalliser design, the optimal Mg:P ratio will determine the amount of excess Mg required so as to minimise cost of the reagent. One of the cost considerations for struvite crystallisation process is the Mg source and optimisation of this parameter as well as utilising cheaper Mg sources can go a long way in making the process economically feasible.

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