Study of the crystallisation reaction behaviour to obtain struvite

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Abstract

In the present work, the behaviour of the struvite crystallisation reaction from the nutrients present in pig manure in a fluidised bed reactor was studied. The most influential parameters in the crystallisation reaction were studied: concentrations of phosphorus and magnesium in the reaction medium (using the Mg/P and N/P ratios), fluidising agent flow rate and reaction time. The study was carried out using the Taguchi methodology. Three levels of each parameter were used in the work. The parameters that had the greatest influence on the struvite crystallisation reaction yield were: concentration of phosphorus and concentration of magnesium. Air flow rate and reaction time had little influence on the reaction yield. Struvite crystals were analysed by scanning electron microscopy. The fluidised bed reactor achieved higher reaction rates than using mechanical stirring reactors. Finally, it has been found that the pH and reaction temperature had a strong influence on the release of nitrogen in the form of ammonia gas from the liquid phase ammonium ion.

Introduction

Modern industrial agriculture relies on continuous inputs of a range of non-renewable nutrients to synthesise fertilisers. Among these nutrients is phosphorus. The reserves of phosphate rock used to make fertilisers are finite and there are concerns about their depletion. Phosphorus is an essential, non-renewable and irreplaceable resource (only 2% of applications have a viable substitute) as a raw material of essential nutrients to sustain agriculture in a competitive manner.

Therefore, an adequate supply of fertilisers is a key element in achieving the goal of improved yields from farming and food processing in order to maintain favourable growth worldwide.

One of the ways to recover nutrients is the valorisation of livestock droppings (such as pig manure), which is a waste management and environmental problem.

Commonly, livestock dropping is used for the production of biogas. In addition to biogas itself, biogas plants produce digestate, which is an excellent fertiliser, rich in organic matter as well as in macro and micronutrients. There is a strong dependence between the physico-chemical characteristics of the digestate and the nature and composition of the substrates digested in the anaerobic digestion process, as well as the operational parameters of the process.

Digestate is normally used as a crop fertiliser without any further processing, replacing industrially produced mineral fertilisers. However, the need for efficient nutrient management, required by restrictions on the application of livestock waste in areas with high livestock density, coupled with the depletion of the world's natural reserves of phosphorus and potassium, means that the recovery and recycling of nutrients from livestock and agricultural waste and has an increasingly important role to play in the agro-livestock industry.

The nutrients contained in the digestate can be extracted and concentrated through the application of different technologies and processes. Nutrient recovery technologies are those that result in a final product with higher nutrient concentrations than the unprocessed digestate, or technologies that are capable of separating nutrients into mineral form or creating another marketable final product suitable for use as a biofertiliser; thus closing the nutrient cycle.

For digestate processing, membrane, evaporation, stripping, ion exchange or struvite precipitation technologies can be used.

The struvite precipitation of phosphorus and nitrogen in the digestate is one of the most promising nutrient recovery techniques. Ammonium and phosphate can be removed from the digestate by precipitation of struvite, also known as MAP (ammonium magnesium phosphate). The reaction that takes place is described by Eq 1:

$$Mg^{2+} + NH_4^+ + PO_4^{3-} + 6H_2O \rightarrow MgNH_4PO_4 \cdot 6H_2O \quad (1)$$

The resulting struvite is a good fertiliser because nitrogen, phosphorus and magnesium are valuable nutrients for plants. The struvite crystallisation reaction yield is influenced by various parameters (concentration of phosphorus, nitrogen and magnesium in the reaction medium, pH, temperature, reaction time, presence of foreign ions, etc.), so it is necessary to study the most important parameters to have a correct understanding of the behaviour of the crystallisation reaction mechanism.

Materials and methods

Design of experiments

In the present work, the digestate produced in the anaerobic digestion process has been recovered as a slow-release fertiliser through the crystallisation process as struvite. Once the process was analysed, the operating variables or factors that affected the most significantly were identified and the levels required for each of the variables were determined.

Given the large number of parameters involved in the process, as well as its interrelationship, a design of experiments was carried out that allowed the number of experiences to be reduced to a minimum without this entailing a loss of relevant information.

Taguchi's Experiment Design is the most economical, fast and efficient way to optimise a process. Parameter design allows:

- Determine the optimal levels of the factors influencing a process.
- Ensure with a certain level of confidence, the influence of each of the different factors on the process.
- Determine which factor levels ensure less process variability in the face of uncontrolled external changes, i.e., ensure the robustness of the process.
- To set the levels of the factors that offer a more linear behaviour of the process.

The first step in carrying out the Taguchi methodology is to identify the variables to be optimised. The reaction yield was the variable selected for this study. For the reaction yield, the type of optimisation sought has been higher-better, i.e. the struvite production yield is sought to be as high as possible.

The second step was the selection of the influencing factors in the process. The control factors selected were:

- Influence of magnesium.
- Influence of phosphorus.
- Fluidising agent flow rate.
- Reaction time.

This selection is mainly due to the fact that they are the factors that have the greatest influence on the struvite solubility product (concentration of species in the reaction medium) and that they greatly affect the fluidised bed reaction (reaction time and fluidisation air flow rate). Each of the factors selected above can be modified within certain limits (levels). All factors were tested at 3 levels.

The selected levels and their justification are as follows:
Influence of Mg: The influence of magnesium concentration was studied using the Mg/P ratio. This is the molar relation of the two elements involved in the crystallisation reaction. Thus, the study of the variable was carried out in the form of a ratio, facilitating the comparison between each of the experiments, as well as the analysis of their results. The levels of this variable varied between 1.0 and 2.0, so that the effect that saturation may have on the crystallisation reaction can be felt.

- Level 1: Mg/P = 1.0
- Level 2: Mg/P = 1.5
- Level 3: Mg/P = 2.0

Influence of P: The influence of the phosphorus concentration was studied in a similar way to magnesium, by means of the N/P ratio. Since nitrogen is the third species that is part of the struvite crystallisation reaction. The levels of this variable varied between 4.0 and 12.0, so that, once again, the effect that saturation may have on the crystallisation reaction can be felt.

- Level 1: N/P = 4.0
- Level 2: N/P = 8.0
- Level 3: N/P = 12.0

Reaction time: The selected reaction times (0.5-2.0 h) are within the typical time range according to the kinetic model of the reaction.

- Level 1: t = 0.5 h
- Level 2: t = 1.0 h
- Level 3: t = 2.0 h

Fluidising agent flow rate (air flow rate): In a fluidised bed process, the fluidising agent (in this case air) acts as a driving force in the homogenisation of the reaction mixture. The selected level range (2.0-12.0 NL/min) corresponds to the upper and lower flow limits at which the pilot crystallisation plant can operate.

- Level 1: Q_{air} = 2.0 NL/min
- Level 2: Q_{air} = 6.0 NL/min
- Level 3: Q_{air} = 12.0 NL/min

From the analysis of the digestate, the necessary information is available to fix each of the levels at which the different parameters to be studied in the crystallisation tests varied.

Table 1. Design of experiments

Factors	Levels		
Mg/P ratio	1.0	1.5	2.0
N/P ratio	4.0	8.0	12.0
Air flow rate (NL/min)	2.0	6.0	12.0
Reaction time (h)	0.5	1.0	2.0

On the other hand, all the experiments were carried out at a temperature of 25°C and a pH value of 9.0. These values have been selected on the basis of previous studies at laboratory scale [1] as the most optimal from a technical and economic point of view. Since, better results are obtained at higher temperature and pH values, but most of the nitrogen contained in the digestate is removed in the form of gaseous ammonia, which prevents its recovery in the form of struvite.

From the definition of the factors to be studied and the levels of these, the orthogonal matrix L_9 was obtained according to the Taguchi methodology, to carry out a reduced design of experiments (Table 2).

Table 2. Orthogonal design of experiments (L_9)

Exp. number	Mg/P ratio	N/P ratio	Air flow rate (NL/min)	Reaction time (h)
1	1.0	4.0	2.0	0.5
2	1.0	8.0	6.0	1.0
3	1.0	12.0	12.0	2.0
4	1.5	4.0	6.0	2.0
5	1.5	8.0	12.0	0.5
6	1.5	12.0	2.0	1.0
7	2.0	4.0	12.0	1.0
8	2.0	8.0	2.0	2.0
9	2.0	12.0	6.0	0.5

In the present work, all the designs and analysis have been carried out using Minitab 17 statistical software.

The signal to noise (S/N) ratio indicates the effect of each factor on the reaction yield.

For reaction yield S/N ratio is calculated using "larger is better" criteria and the equation for the calculation of S/N ratio is shown in Eq. 2.

$$\left(S/_{N}\right) = -10 \cdot log\left(\frac{1}{n} \cdot \sum_{i=1}^{n} \frac{1}{y_i^2}\right) \qquad (2)$$

where n is the number of tests in a experiment, y_i is the experimental response at i-repetition.

The range of S/N ratio values (delta) is calculated for each factor and a larger range signifies a higher influence on reaction yield. Delta is the difference between the highest and the lowest S/N ratio value of the three levels studied for a given factor. The higher delta value, the greater variability of S/N ratio values (for a given factor) is. Therefore, a factor with a high delta value will have a great influence on the process.

The struvite crystallisation reaction yield was calculated taking into account the amount of crystal obtained and the amount of reagent fed, considering the limiting reagent. In all cases the limiting reagent is phosphorus, so the reaction yield is also a direct measure of the amount of phosphorus that has been removed from the digestate.

Eq. 3 defines the material balance (molar) in the crystallisation reactor for an i-component of the crystallisation reaction.

$$(\text{initial mole})_{\text{i}} - (\text{reactive mole})_{\text{i}} = (\text{final mole})_{\text{i}} \quad (3)$$

Hence, reaction yield is calculated according to Eq. 4.

$$\text{Reaction yield } (\%) = \frac{(\text{final mole})_{\text{limiting reagent}}}{(\text{initial mole})_{\text{limiting reagent}}} \cdot 100 \qquad (4)$$

Thus, in each experiment, the amount of nitrogen that is lost in the form of NH_3 has been determined by a balance of matter to that element, as can be seen in Eq. 5.

$$(\text{N mole removes as NH}_3) = (\text{Initial N mole digestate}) - (\text{N mole remaining mother liquor}) - (\text{N mole obtained solid crystal}) \qquad (5)$$

Temperature and pH affect the struvite crystallisation reaction yield, but also influence the NH_3/NH_4^+ chemical balance. In order to study this influence, the experiments in Table 2 were repeated maintaining the conditions except pH and temperature. pH and temperature used in these experiments were 10.5 and 30 ºC, respectively.

Crystallisation reactor

A fluidised bed reactor was used for the experiments (Fig 1). It was a 50 L reactor made of borosilicate glass with a cylindrical shape. It has an internal diameter of 20 cm and a total height of 2 m, so that the ratio L/D = 10 recommended for fluidised bed reactors was achieved. Inside the reactor there was a methacrylate cylinder of 10 cm diameter and similar height to the outside. The reactor had four peristaltic pumps for the dosing of the raw material and the required reagents (pig manure, phosphorus salt, magnesium salt and sodium hydroxide). In the lower part of the interior of the reactor there was a diffuser for the introduction of air that acts as a fluidising agent. When it came into contact with the raw material and the reagents (reaction mixture) at the bottom, the air pushed them vertically through the interior of the methacrylate cylinder. When it reached the top, the reaction mixture descended by gravity, between the reactor walls and the methacrylate cylinder. When it reached the bottom, the mixture was pushed upwards again through the interior of the methacrylate cylinder, so that a continuous stirring movement was produced, which favoured contact between the components of the mixture, increasing the speed and efficiency of the reaction and avoiding the formation of preferential flow paths. In this upper part was the reactor outlet, which in continuous operation, is produced by overflow. As a result of the reaction, crystals were generated and grow, increasing their particle size and thus their weight, so that the accessional force of the air was not sufficient to overcome the action of gravity and the weight of the particle at a given moment and therefore the particle was deposited at the bottom of the reactor. Thus, the crystal harvest was collected in the lower part of the reactor. This part had a conical shape to facilitate the emptying of the reactor. The crystals were collected by a solid valve.

Finally, the reactor was equipped with a pH and temperature sensor to control the reaction parameters and a heating jacket (also made of borosilicate glass) to maintain the reaction temperature. All system parameters was controlled and recorded by a PLC.

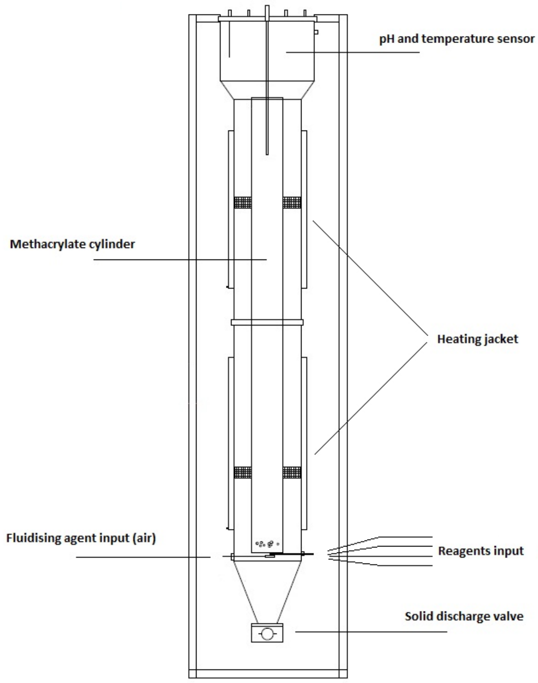

Fig 1. Fluidised bed crystallisation reactor diagram

Methodology

The experiments for the struvite crystallisation study were performed in a discontinuous fluidised bed reactor (50 L). The experiments were performed at pH 9.0, 25 ºC temperature and different reaction times (0.5, 1.0 and 2.0 h) and fluidising agent flows (2.0, 6.0 and 12.0 NL/min). Digestate from the anaerobic pig slurry digestion plant in Almazán (Spain) was used in the experiments. The composition of the digestate is shown in Table 3.

Table 3. Digestate composition

Experiment No.	NH_4^+ (mg/L)	PO_4^{3-} (mg/L)	Mg^{2+} (mg/L)	Ca^{2+} (mg/L)
1	3383.28±314.65	239.69±1.44	n.d.	n.d.
2	3328.01±309.50	211.85±1.27	n.d.	n.d.
3	3368.12±313.24	182.64±1.10	n.d.	n.d.
4	3508.66±326.31	270.46±1.62	n.d.	n.d.
5	3708.57±344.90	228.76±1.37	n.d.	n.d.
6	3926.87±365.20	182.21±1.09	n.d.	n.d.
7	3926.87±365.20	182.21±1.09	n.d.	n.d.
8	3926.87±365.20	182.21±1.09	n.d.	n.d.
9	3926.87±365.20	182.21±1.09	n.d.	n.d.

n.d: not detected

Prior to the reaction, the samples were centrifuged to remove any solids that might be contained in the digestate and thus facilitate the interaction of the reagents to produce struvite crystallisation and avoid fouling and clogging in the reactor. The nitrogen, phosphorus and magnesium that will later crystallise as struvite are dissolved in the liquid phase. The samples were centrifuged in a GEA Westfalia centrifuge model OTC 3-03-107. The sample was continuously centrifuged, obtaining the solid-free digestate at the outlet of the centrifuge. The removed solid was deposited inside the centrifuge drum.

Once the sample was centrifuged, digestate and the necessary amount of magnesium salt and phosphorus salt (depending on the experiment) were added to the reactor so that each sample had its corresponding Mg/P and N/P ratio (Table 4). The magnesium salt used was $MgCl_2 \cdot 6H_2O$, while the phosphorus salt was $NaH_2PO_4 \cdot 12H_2O$. Finally, the pH of the samples was 8.5, so it was necessary to add a concentrated alkali (50% NaOH solution) to raise the pH value to 9.0.

Table 4. Mass of $MgCl_2 \cdot 6H_2O$ and $NaH_2PO_4 \cdot 2H_2O$ added in each experiment

Experiment No.	Mg/P molar ratio	N/P molar ratio	$MgCl_2 \cdot 6H_2O$ mass added (g)	$NaH_2PO_4 \cdot 12H_2O$ mass added (g)
1	1.0	4.0	61413	943.41
2	1.0	8.0	302.05	409.72
3	1.0	12.0	203.79	253.51
4	1.5	4.0	955.34	965.73
5	1.5	8.0	504.88	460.80
6	1.5	12.0	356.40	313.31
7	2.0	4.0	1425.61	1150.44
8	2.0	8.0	712.81	522.59
9	2.0	12.0	475.20	313.31

Once the reactor was fully loaded. The reactor air flow rate (between 2 and 12 NL/min depending on the experiment) was activated and the reaction time was between 0.5 and 2.0 hours.

After the reaction time had elapsed, the crystals were harvested using the solids discharge valve of the reactor and the sample was separated by centrifugation to obtain the struvite crystals formed. A laboratory centrifuge model Jouan B4i was used in the operation.

The sedimented phase (crystals) was subjected to a stove drying process at 50 ºC for 24 hours to remove moisture. Since struvite can be degraded at temperatures above 55 °C [2]. The total nitrogen of these samples were analysed.

On the other hand, the supernatant (mother liquor crystallisation process) was removed for further analysis of its concentration in N, P and Mg. The concentration of N, P and Mg in the mother liquor crystallisation process determined the amount of these elements in the struvite crystals and therefore the reaction yield.

The analyses performed to quantify the physico-chemical parameters considered in the follow-up of the crystallisation test were ammoniacal nitrogen, phosphorus and magnesium concentrations.

Once these experiments were completed, they were repeated maintaining the same levels and factors but increasing the pH and reaction temperature to 10.5 and 35 ºC. The purpose of these experiments was to study the influence of pH and temperature on the NH_3/NH_4^+ equilibrium.

All the experiments were conducted in duplicate.

Analytical methods and instrumentation

A Jouan centrifuge model B4i was used to carry out the centrifugation of the samples obtained in the fluidised bed reactor. The samples of mother liquor from the centrifugation step were analysed according to American Public Health Association (APHA), American Water Works Association (AWWA) and Water Pollution Control Federation (WPCF). Phosphorus was analysed by spectrophotometry with a spectrophotometer (Shimazu, UV-1603), nitrogen was analysed by titrimetric method using a distiller (Selecta, RAT 2), a digester (Selecta) and a digital burette (Bran). Mg concentration was measured with an Inductively Coupled Plasma Optical Emission Spectrophotometer (ICP-OES) (Shimadzu AA-6800, Japan). The morphology of the crystals obtained was observed by using Scanning Electron Microscope (SEM) analysis (FEI QUANTA 200). For the determination of the total nitrogen content in struvite crystals, an elemental analysis unit (LECO brand, model TruSpec CHN) was used. The analysis procedure is based on the combustion of the solid sample at a temperature of 950 ºC, and on the subsequent determination of the N content of the combustion gases through a heat conductive cell.

Results

Table 5 shows the reaction yield and the percentage of nitrogen lost as NH_3 for the experiments carried out at pH 9.0 and 25 ºC of temperature.

Table 5. Results for the experiments carried out at pH 9.0 and 25 ºC of temperature

Experiment No.	Reaction yield (%)	N lost as NH_3 (%)
1	89.84	8.62
2	84.27	6.00
3	82.36	3.44
4	97.78	22.07
5	95.84	5.18
6	90.45	13.43
7	97.90	35.88
8	93.31	17.70
9	91.43	14.82

<u>Influence of Mg on reaction yield</u>
For the study of the effect of Mg concentration on struvite crystallisation at pilot scale, three Mg/P molar ratios were selected for the study 1.0, 1.5 and 2.0.

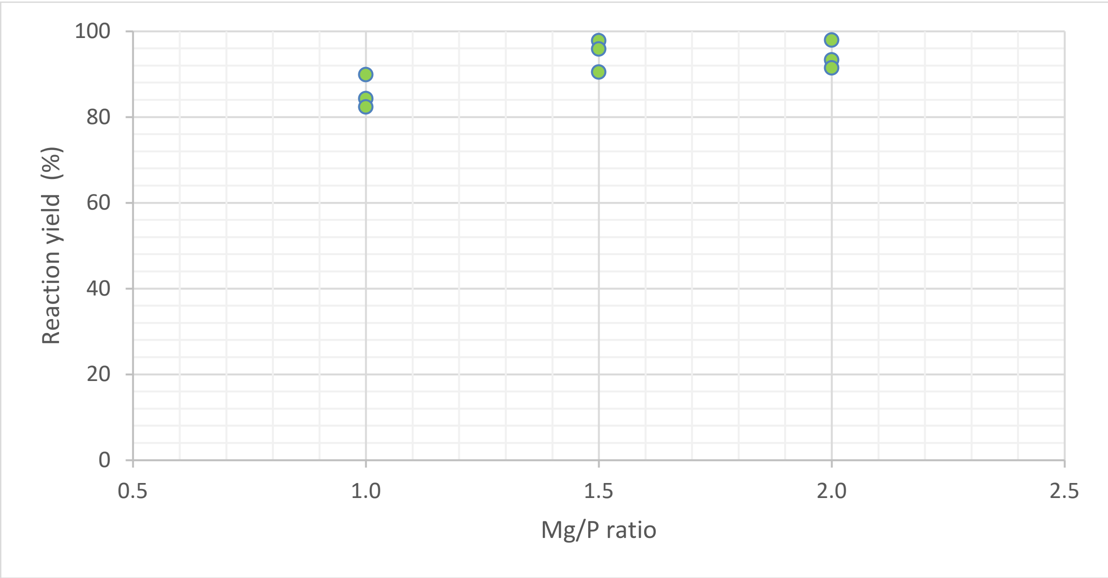

Fig 2. Influence of Mg concentration on struvite crystallisation reaction

The influence of Mg concentration on the reaction yield is shown in Fig 2 using Mg/P ratio. As was the case in laboratory-scale experimentation [1], the reaction yield generally increases with the increase in the Mg/P ratio. However, the reaction yields are very similar when Mg/P ratios of 1.5 and Mg/P ratios of 2.0 are used.

<u>Influence of P on reaction yield</u>
To determine the effect of P on struvite crystallisation, different N/P molar ratios were analysed (4.0, 8.0 and 12.0).

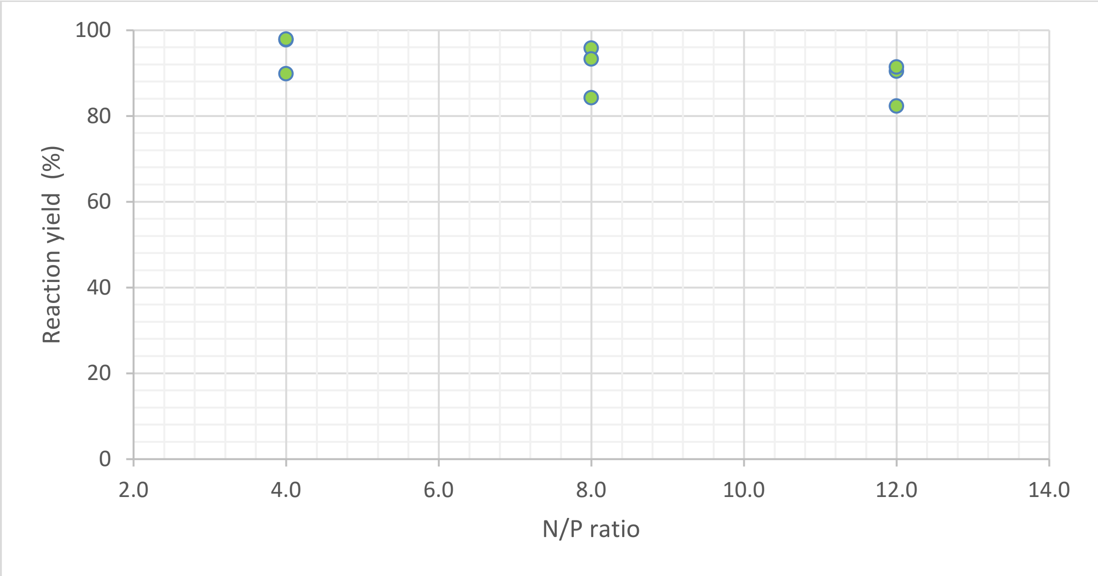

Fig 3. Influence of P concentration on struvite crystallisation reaction

According to Fig 3, in general, there is an inverse relationship between the reaction yield and the N/P ratio. As the value of the N/P ratio increases, the reaction yield decreases.

<u>Influence of fluidising air flow rate on reaction yield</u>

One of the most important factors in a fluidised bed reaction is the flow rate of the fluidising agent being processed. In this case, the agent used was air and the levels at which its influence was studied were 2.0, 6.0 and 12.0 NL/min.

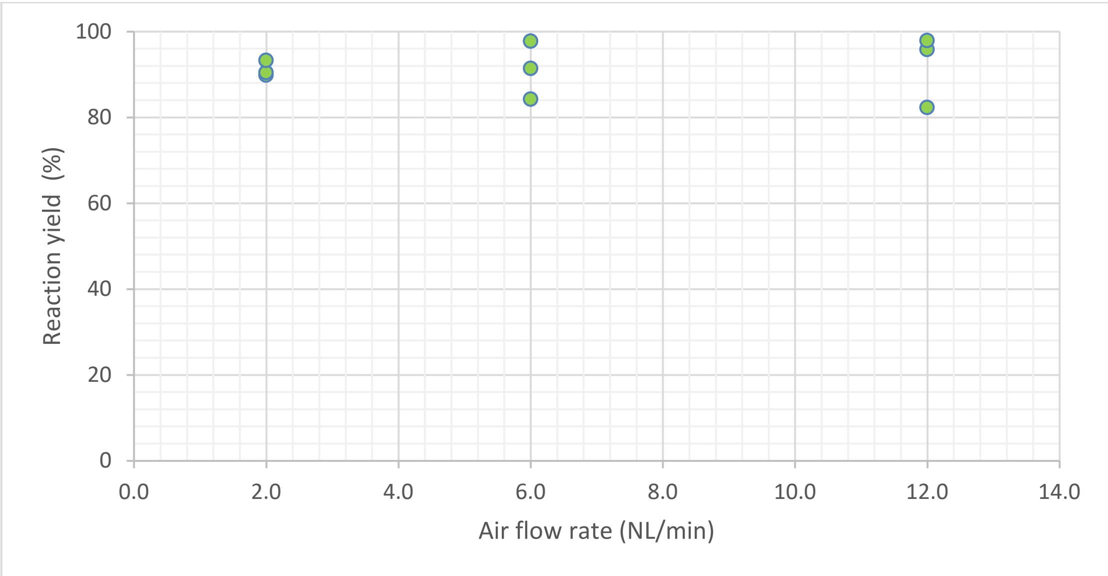

Fig 4. Influence of airflow rate on struvite crystallisation reaction

With some exceptions, the crystallisation reaction yield increases as the airflow rate increases (Fig 4).

<u>Influence of reaction time on reaction yield</u>

To study the influence of reaction time on struvite reaction yield, experiments were conducted with three time levels (0.5, 1.0 and 2.0 h).

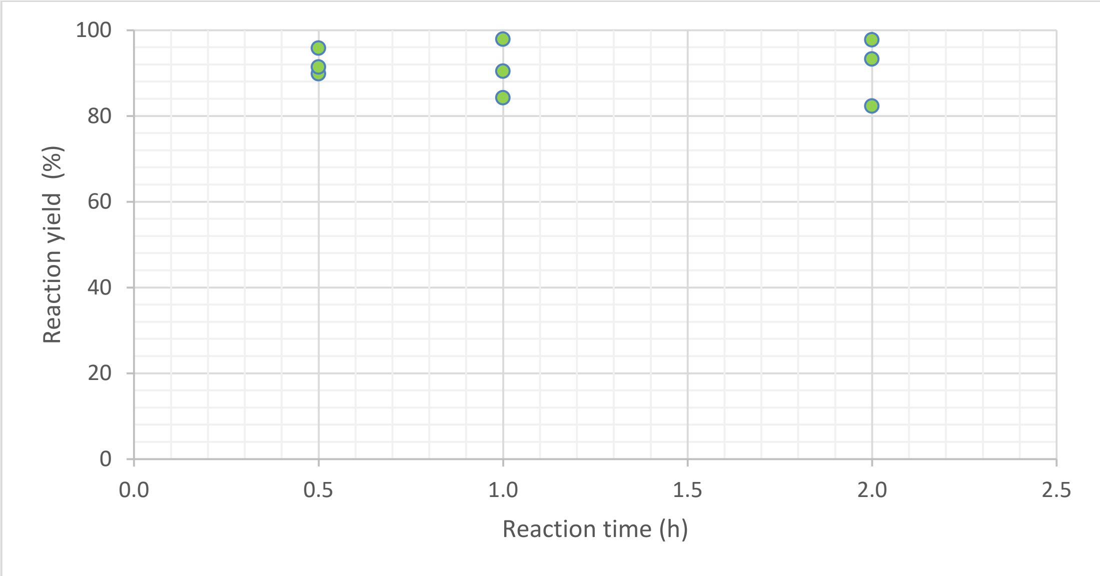

Fig 5. Influence of the reaction time on the crystallisation reaction yield

Again, in general, the reaction yield increases as the reaction time increases (Fig 5). However, the differences in reaction yield are very small for 1.0 h and 2.0 h (the highest reaction time levels considered).

With respect to the associated experimental errors, it should be noted that the standard deviation of each experiment is less than 10% for duplicate reaction yield results.

Influence of pH and temperature on NH_3/NH_4^+ chemical equilibrium

In order to study the influence of pH and temperature on NH_3/NH_4^+ chemical equilibrium, new experiments were performed with the same conditions of Mg/P ratio, N/P ratio, air flow rate and reaction time, but in all cases the pH was changed to 10.5 and the reaction temperature to 35 ºC. The results of the percentage of nitrogen lost as NH_3 are presented in Table 6.

Table 6. Results for the experiments carried out at pH 10.5 and 35 ºC of temperature.

Experiment No.	N lost as NH_3 (%)
1	71.65
2	90.27
3	68.36
4	77.63
5	85.46
6	67.00
7	85.90
8	75.72
9	74.37

It is clear that the loss of nitrogen increased drastically compared to the reactions in which a lower pH and temperature were used (Table 5).

Finally, Fig 6 shows a Scanning Electron Microscope (SEM) image of the struvite crystals obtained in this study. As can be seen, the crystals obtained have the characteristic shape of struvite crystals, that is, needle-shaped crystals.

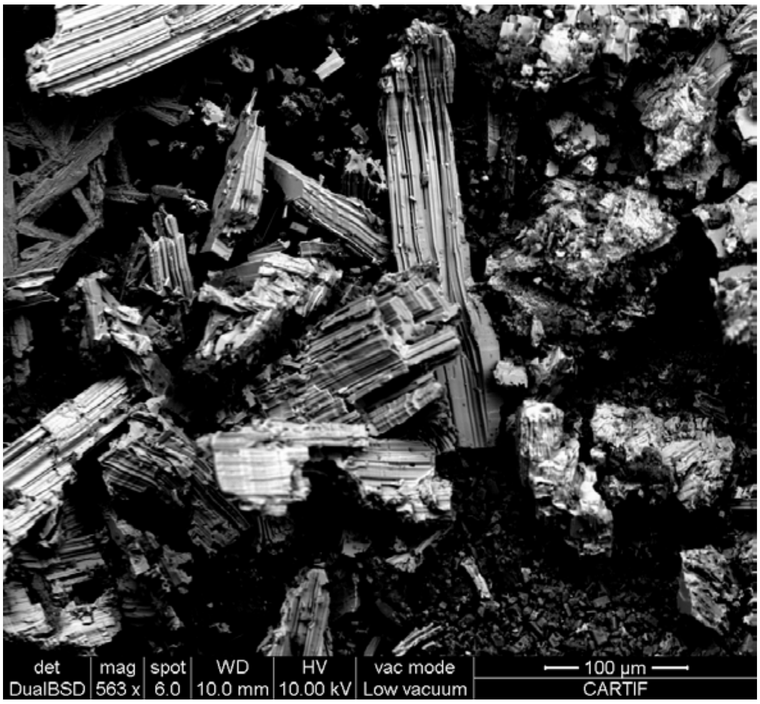

Fig 6. SEM picture of struvite obtained in the study

Discussion

In the present work the effect, of different process parameters under study of the struvite crystallisation reaction yield has been calculated. The mean values of the S/N ratio (the mean of the duplicate experiments for the nine different experimental conditions) have been calculated to quantify the effects of the different parameters and their levels. The use of both the S/N ratio and the Analysis of Variance (ANOVA) method facilitates the analysis of the results and therefore allows a quick conclusion to be reached. Interactions between factors have not been considered in this work.

The S/N ratio expresses the relationship between the expected value of the characteristic under study (signal) and the variability of that characteristic (noise). Thus, the higher the value of the S/N ratio, the better the performance of the system is.

In Table 7, the values of the S/N ratio for the reaction yield of each experiment are shown.

Table 7. S/N ratios for reaction yield

Experiment No.	S/N ratio for reaction yield
1	39.07
2	38.51
3	38.31
4	39.81
5	39.63
6	39.13
7	39.82
8	39.40
9	39.22

According to Table 8, the highest value of the S/N ratio is the Mg/P ratio, followed by the N/P ratio, reaction time and airflow rate. This means that the Mg/P ratio has the greatest influence on reaction yield, as a change in factor causes a greater impact on reaction yield, resulting in a greater range of the S/N (delta) ratio. This trend can be clearly seen in Fig 7.

Table 8. Response of S/N ratios for reaction yield

Levels	Mg/P ratio	N/P ratio	Air flow rate	Reaction time (h)

			(NL/min)	
L1	85.49	95.17	91.20	92.37
L2	94.69	91.14	91.16	90.87
L3	94.21	88.08	92.03	91.15
Delta	9.20	7.09	0.87	1.50
Rank	1	2	4	3

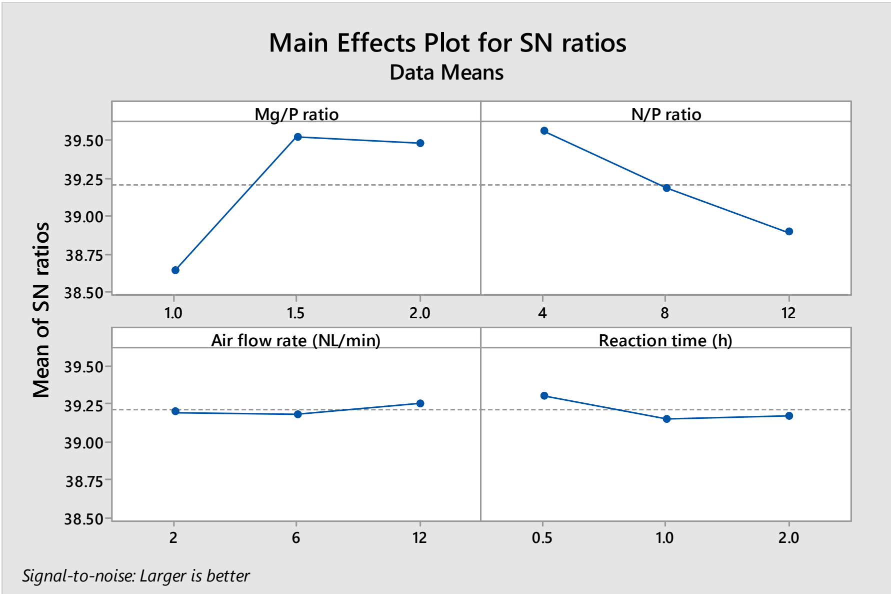

Fig 7. Effects of process parameters on reaction yield

The struvite crystallisation reaction is influenced by several parameters such as initial concentration of ion species in the solution, flow rate of the fluidising agent (mixing speed), reaction time, temperature, pH, presence of foreign ions, etc. [3]. In the present work, some of these factors were examined to assess the reaction yield in a fluidised bed reactor. According to Fig 2, Fig 3, Fig 4 and Fig 5, reaction yields (phosphorus removal) of up to 97% are achieved.

According to the stoichiometry of the struvite crystallisation reaction, 1 mol of Mg reacts with 1 mol of P and 1 mol of N, making it necessary to work with molar ratios Mg/P = 1 or higher [4], [5]). In accordance with [6] and [7], there is an increase in the efficiency of phosphorus removal through crystallisation by increasing the Mg/P molar ratio. In the present work, the influence of the Mg/P molar ratio has been evaluated in a range between 1.0 and 2.0. When working with a Mg/P molar ratio of 1 (stoichiometric ratio), reaction yields of up to 90% were achieved. However, when the Mg/P molar ratio increased from 1.0 to 1.5 and 2.0, reaction yields of 97% were achieved.

In addition, the effect of the molar ratio N/P on the crystallisation reaction was studied. For a molar N/P ratio = 4, reaction yields of 97% were achieved, however for higher molar N/P ratios the reaction yields obtained were considerably lower (up to 95% for N/P ratios = 8 and up to 91% for N/P ratios = 12). All this is in accordance with what has been reflected in previous works [8].

The positive effect of the increase in reagent concentrations (P and Mg) on reaction yield is given by the direct relationship between these concentrations and the saturation index of the reaction [9]. Logically, as the Mg/P molar ratio increases and the N/P molar ratio decreases, the concentrations of Mg and P in the reaction are increased, this will encourage the equilibrium of the reaction to shift to struvite formation, which will cause an increase in the reaction yield. However, it should be noted that excessive increase in the concentration of Mg and P in the reaction may lead to supersaturation which would cause an impediment in the growth of the crystals and most of them would remain in their primary phase as nuclei [10]. Obviously, a supersaturation situation is not desired in the crystallisation reaction.

With regard to the influence of the fluidising air flow rate on the reaction yield, it can be seen that the reaction yield has increased as the air flow rate has increased from 2 to 12 NL/min. According to [11], this may be because air influenced the effectiveness of phosphorus removal (precipitating as struvite) by the increased agitation of the reaction medium, which favours the interaction between the different reagents to form the crystal. On the other hand, it should be noted that of all the parameters studied in this work, airflow has the least influence on reaction yield. These results are in line with [12]. Finally, the values reached in the reaction yield (phosphorus removal) in the fluidised bed reactor, with air flow rates between 2 and 12 NL/min, were much higher than those obtained by mechanical or magnetic agitation (between 69% and 82%) [13], [14].

For the reaction time, 0.5, 1.0 and 2.0 h were considered for the crystallisation reaction. The results showed a reaction yield of over 90% for most cases. Thus, the effect of the reaction time on crystallisation was very small, especially when the reaction time was increased from 1.0 to 2.0 h. These results coincide with those obtained in previous works [15], [3], [16], [17]. According to [3] and [16] an increase in phosphorus removal to obtain struvite for hydraulic residence times (HRT) greater than 1.0 hour was practically negligible.

Based on the results presented in Table 5 and Table 6, temperature and pH were found to have a significant effect on ammonia stripping. With an increase in temperature and pH, the release of gas-phase nitrogen in the form of NH_3 is promoted. Increasing the temperature from 25 to 35 °C and the pH from 9.0 to 10.5 increases the loss of nitrogen from the reaction medium in the form of NH_3 from 30% to 90%. Furthermore, the increase in temperature favours the struvite crystallisation reaction, since it increases the molecular diffusion coefficient of ammonia in the liquid and gas phases, but on the other hand, it causes a significant increase in the desorption of ammonia from water, which in turn increases the transfer of matter. The results obtained are in accordance with the suggestion of [18]. According to these authors, the equilibrium between NH_3 and NH_4^+ in an aqueous solution depends on the pH and temperature of the solution and its concentration can be calculated according to Eq. 6, since the amount of ammonia removed from a solution depends mainly on two thermodynamic balances: the liquid ammonia dissociation equilibrium and the ammonia gas/liquid equilibrium.

$$[NH_3] = [NH_4^+] \cdot \left(1 + \frac{10^{-pH}}{10^{-\left(0.1075+\left(\frac{2725}{T(K)}\right)\right)}}\right)^{-1} \quad (6)$$

According to Eq. 6, for a pH of 10.5 and a reaction temperature of 35°C, the loss of nitrogen in the form of NH_3 gas would be 96%, while at pH 9.0 and 25°C the loss of nitrogen in the form of NH_3 gas would be 36%.

<u>Model predictions</u>

Table 9 shows the predicted reaction yield for other combination of factors and levels and the results from the nine experimental runs. This information has been obtained from the results of Taguchi's method applied in this work.

From the predicted results, it can be seen that the maximum reaction yield of is obtained using 1.5 Mg/P ratio, 4.0 N/P ratio, 12.0 NL/min of air flow rate and 0.5 h of reaction time as reaction conditions.

Table 9. Reaction yield based on Taguchi's L_9 Orthogonal Array's prediction (the results from the nine experimental runs are marked in bold, the other yields are predicted from Taguchi's method)

No.	Mg/P ratio	N/P ratio	Air flow rate (NL/min)	Reaction time (h)	Reaction yield (%)
1	**1.0**	**4.0**	**2.0**	**0.5**	**89.84**
2	1.0	4.0	2.0	1.0	88.34
3	1.0	4.0	2.0	2.0	88.62
4	1.0	4.0	6.0	0.5	89.80
5	1.0	4.0	6.0	1.0	88.30
6	1.0	4.0	6.0	2.0	88.58
7	1.0	4.0	12.0	0.5	90.67
8	1.0	4.0	12.0	1.0	89.18
9	1.0	4.0	12.0	2.0	89.45
10	1.0	8.0	2.0	0.5	85.81
11	1.0	8.0	2.0	1.0	84.31
12	1.0	8.0	2.0	2.0	84.59

13	1.0	8.0	6.0	0.5	85.77
14	**1.0**	**8.0**	**6.0**	**1.0**	**84.27**
15	1.0	8.0	6.0	2.0	84.55
16	1.0	8.0	12.0	0.5	86.64
17	1.0	8.0	12.0	1.0	85.14
18	1.0	8.0	12.0	2.0	85.42
19	1.0	12.0	2.0	0.5	82.75
20	1.0	12.0	2.0	1.0	81.25
21	1.0	12.0	2.0	2.0	81.53
22	1.0	12.0	6.0	0.5	82.71
23	1.0	12.0	6.0	1.0	81.21
24	1.0	12.0	6.0	2.0	81.49
25	1.0	12.0	12.0	0.5	83.58
26	1.0	12.0	12.0	1.0	82.08
27	**1.0**	**12.0**	**12.0**	**2.0**	**82.36**
28	1.5	4.0	2.0	0.5	99.04
29	1.5	4.0	2.0	1.0	97.54
30	1.5	4.0	2.0	2.0	97.82
31	1.5	4.0	6.0	0.5	99.00
32	1.5	4.0	6.0	1.0	97.50
33	**1.5**	**4.0**	**6.0**	**2.0**	**97.78**
34	1.5	4.0	12.0	0.5	99.87
35	1.5	4.0	12.0	1.0	98.38
36	1.5	4.0	12.0	2.0	98.65
37	1.5	8.0	2.0	0.5	95.01
38	1.5	8.0	2.0	1.0	93.51
39	1.5	8.0	2.0	2.0	93.79
40	1.5	8.0	6.0	0.5	94.97
41	1.5	8.0	6.0	1.0	93.47
42	1.5	8.0	6.0	2.0	93.75
43	**1.5**	**8.0**	**12.0**	**0.5**	**95.84**
44	1.5	8.0	12.0	1.0	94.34
45	1.5	8.0	12.0	2.0	94.62
46	1.5	12.0	2.0	0.5	91.95
47	**1.5**	**12.0**	**2.0**	**1.0**	**90.45**
48	1.5	12.0	2.0	2.0	90.73
49	1.5	12.0	6.0	0.5	91.91
50	1.5	12.0	6.0	1.0	90.41
51	1.5	12.0	6.0	2.0	90.69
52	1.5	12.0	12.0	0.5	92.78
53	1.5	12.0	12.0	1.0	91.28
54	1.5	12.0	12.0	2.0	91.56
55	2.0	4.0	2.0	0.5	98.56
56	2.0	4.0	2.0	1.0	97.07
57	2.0	4.0	2.0	2.0	97.34
58	2.0	4.0	6.0	0.5	98.52
59	2.0	4.0	6.0	1.0	97.03
60	2.0	4.0	6.0	2.0	97.30
61	2.0	4.0	12.0	0.5	99.40
62	**2.0**	**4.0**	**12.0**	**1.0**	**97.90**
63	2.0	4.0	12.0	2.0	98.18
64	2.0	8.0	2.0	0.5	94.53
65	2.0	8.0	2.0	1.0	93.03
66	**2.0**	**8.0**	**2.0**	**2.0**	**93.31**
67	2.0	8.0	6.0	0.5	94.49
68	2.0	8.0	6.0	1.0	92.99
69	2.0	8.0	6.0	2.0	93.27
70	2.0	8.0	12.0	0.5	95.36
71	2.0	8.0	12.0	1.0	93.87
72	2.0	8.0	12.0	2.0	94.14
73	2.0	12.0	2.0	0.5	91.47
74	2.0	12.0	2.0	1.0	89.97
75	2.0	12.0	2.0	2.0	90.25
76	**2.0**	**12.0**	**6.0**	**0.5**	**91.43**
77	2.0	12.0	6.0	1.0	89.93
78	2.0	12.0	6.0	2.0	90.21
79	2.0	12.0	12.0	0.5	92.30

80	2.0	12.0	12.0	1.0	90.81
81	2.0	12.0	12.0	2.0	91.08

Conclusions

- Concentrations of magnesium and phosphorus in the reaction medium are the parameters that have the greatest influence on the struvite crystallisation reaction yield. The higher concentrations of magnesium and phosphorus, the higher the reaction yield, although very high values of these concentrations will favour the phenomenon of supersaturation, which will cause a decrease in the particle size of the crystals and therefore in the reaction yield. Therefore, the optimum Mg/P ratio and N/P ratio levels are 1.5 and 4.0 respectively.
- Air flow rate of the fluidising agent is the parameter that has the least influence on the reaction yield. Therefore, moderate air flows would be sufficient for a correct development of the struvite crystallisation reaction.
- The reaction time has little influence on the crystallisation reaction. Therefore, reaction times between 0.5 and 1.0 hour are sufficient to achieve high reaction yields.
- The struvite crystallisation reaction in fluidised bed reactors generally achieves better results (higher efficiencies) than in mechanical stirring reactors.
- High values of pH and temperature reaction favour the increase of the reaction yield but also an increase in the loss of nitrogen in the form of NH_3 gas is obtained. Due to the displacement of the NH_4^+/NH_3 equilibrium.

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