Study of the crystallisation reaction behaviour to obtain struvite

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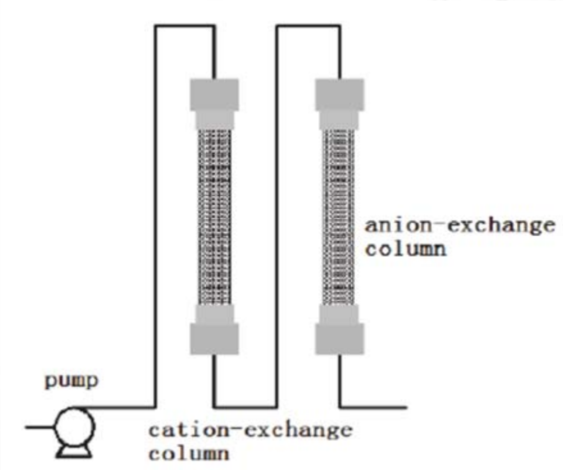
Introduction

- The wide application of anaerobic digestion for the treatment of organic waste streams results in the production of **high quantities of anaerobic effluents**.
- Such effluents are characterised by **high nutrient content** (N and P).
- Consequently, **adequate post-treatment** is required in order to comply with the existing land application and discharge legislation in the European Union countries.

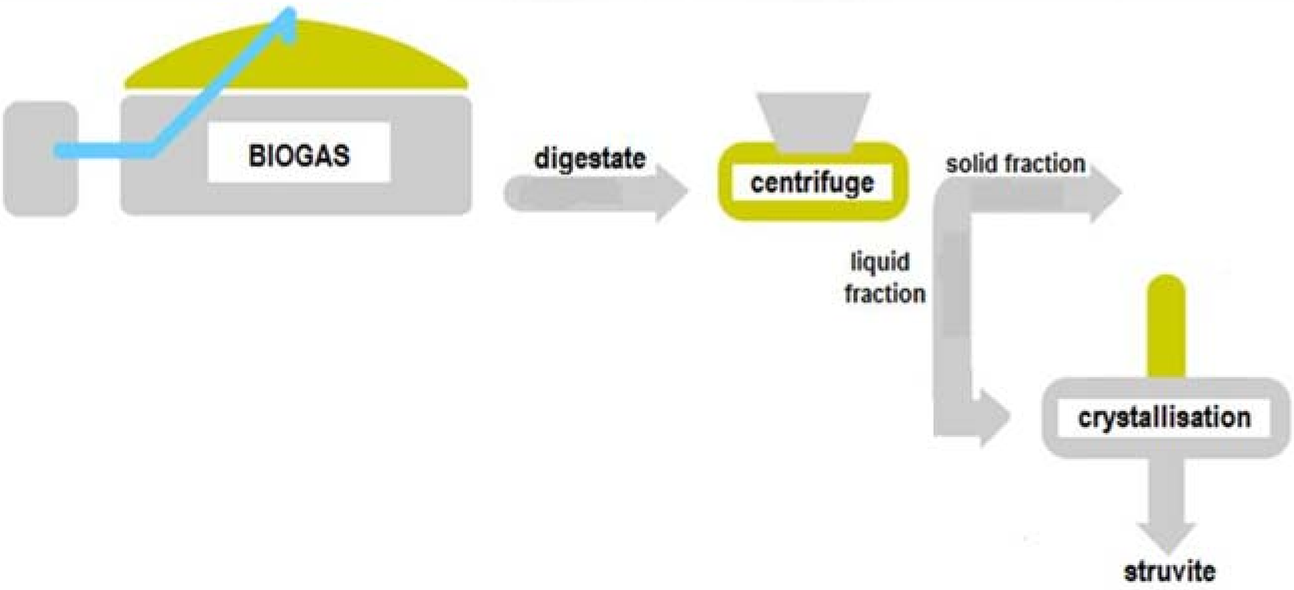
Introduction

- There are several **technologies** for **digestate processing**:
  - Membrane technologies.
  - Evaporation.
  - Stripping.
  - Ion exchange.
  - Struvite precipitation.



Introduction

- **Struvite precipitation** is one of the most promising digestate treatment techniques.
- Unlike other techniques, not only digestate is treated, but also **recovery of nutrients** present in digestate is carried out.



Introduction

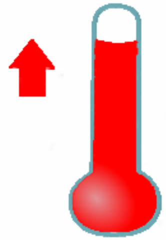
- Ammonium and phosphate can be **removed** from the digestate by precipitation of **struvite**, also known as MAP (ammonium magnesium phosphate).

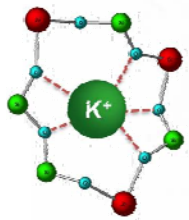
$$Mg^{2+} + NH_4^{+} + PO_4^{3-} + 6H_2O \longrightarrow MgNH_4PO_4 \cdot 6H_2O$$

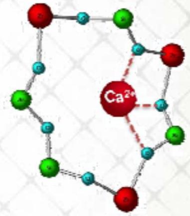
- The resulting **struvite** is a **good fertiliser** because nitrogen, phosphorus and magnesium are valuable nutrients for plants.

Introduction

- The struvite crystallisation **reaction** yield is influenced by various **parameters**:
  - Phosphorus, nitrogen and magnesium concentrations in the reaction medium.
  - pH.
  - Temperature.
  - Reaction time.
  - Strirring rate.
  - Presence of foreign ions.



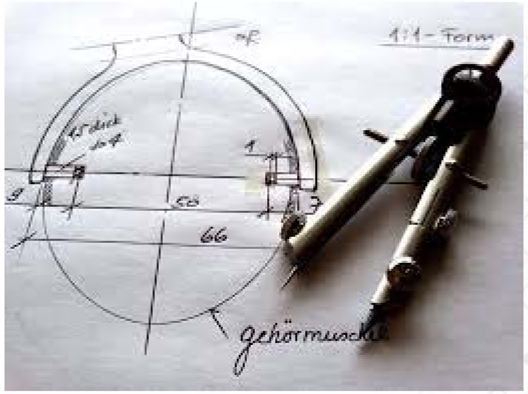


- So it is necessary to **study** the **most important parameters** to have a correct understanding of the crystallisation reaction mechanism.

Design of the experiments

- An **experiment design** was carried out that allowed the number of experiences to be reduced to a minimum without losing relevant information.

Factors	Levels		
Mg/P molar ratio	1.0	1.5	2.0
N/P molar 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



- Mg and P **concentrations** are expressed in **molar ratios** to facilitate comparison of experiments.
- **Fluidised bed reactor** was used. The stirring speed is given by the flow rate of the fluidising agent (air).
- All the experiments were carried out at a **temperature** of **25 ºC** and a **pH** value of 9.0.

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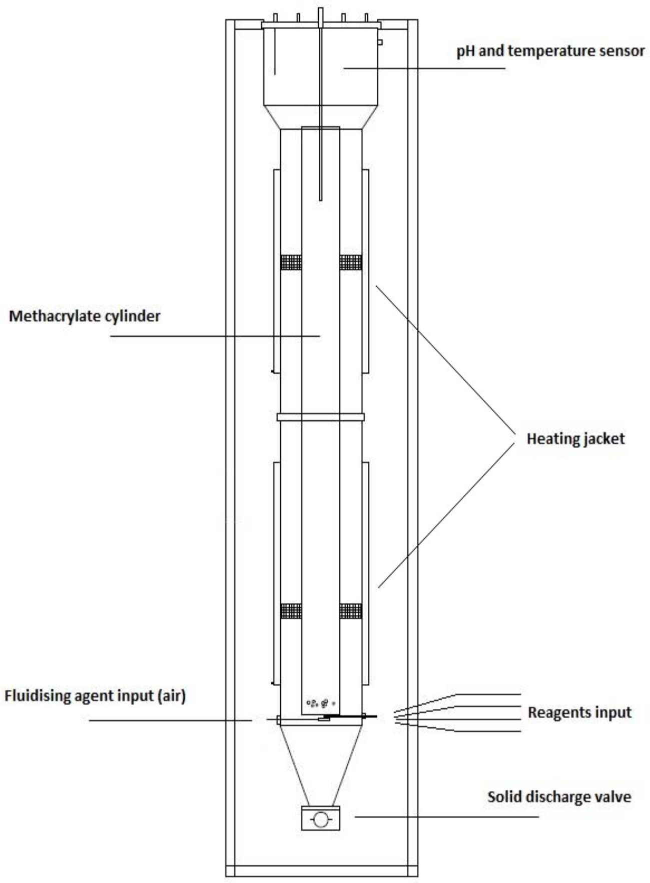
Design of the experiments

- 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**.

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

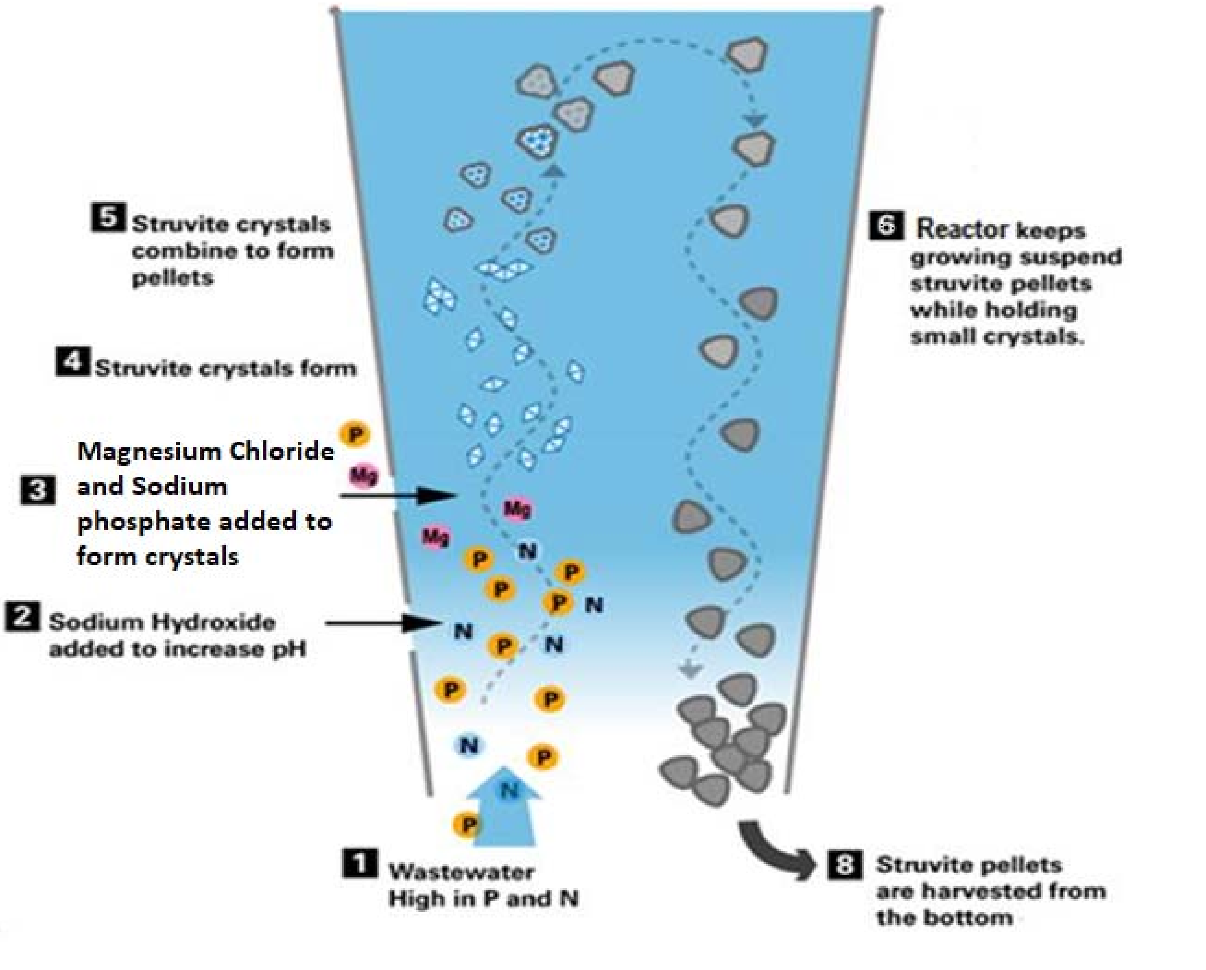
- The experiments were conducted in duplicate.

Crystallisation fluidised bed reactor



- 50 L reactor made of borosilicate glass with a cylindrical shape.
- Internal diameter of 20 cm and a total height of 2 m (L/D =10).
- Magnesium chloride ($MgCl_2 \cdot 6H_2O$) was used as Mg source.
- Sodium phosphate ($NaH_2PO_4 \cdot 12H_2O$) was used as P source.
- 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.

Crystallisation reaction



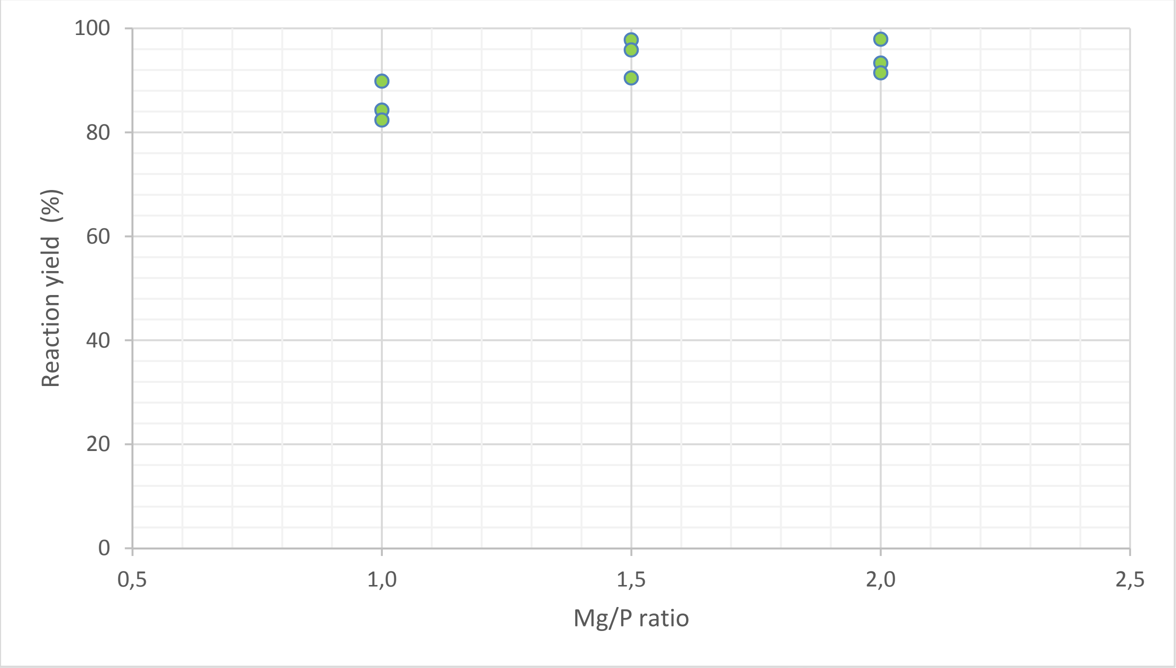
Crystallisation reaction

- 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 (**needle-shaped crystals**).

Results

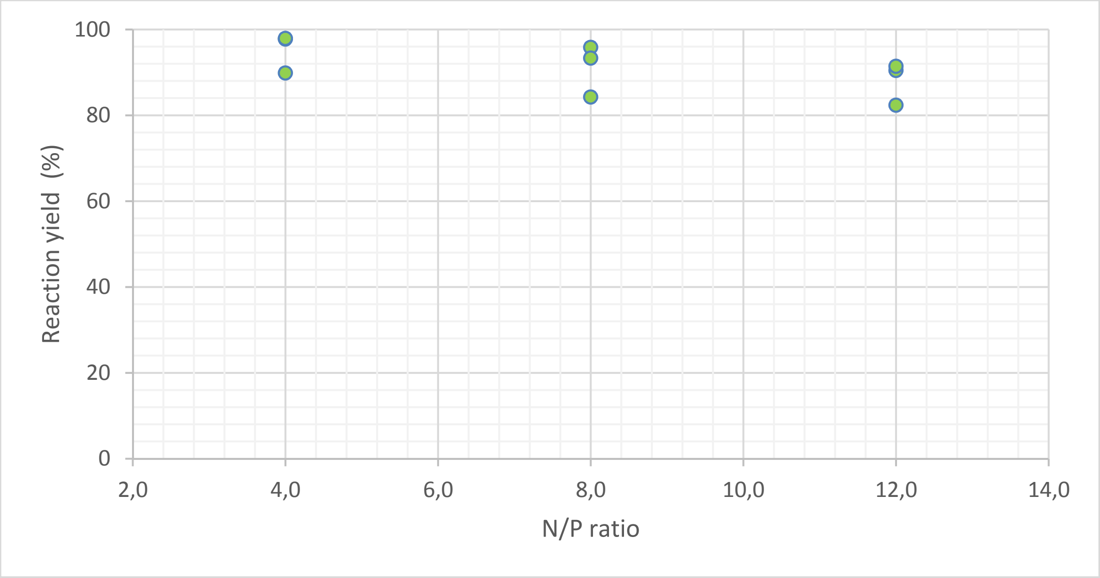
- Influence of Mg on reaction yield.



- 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 **2.0** are used.

Results

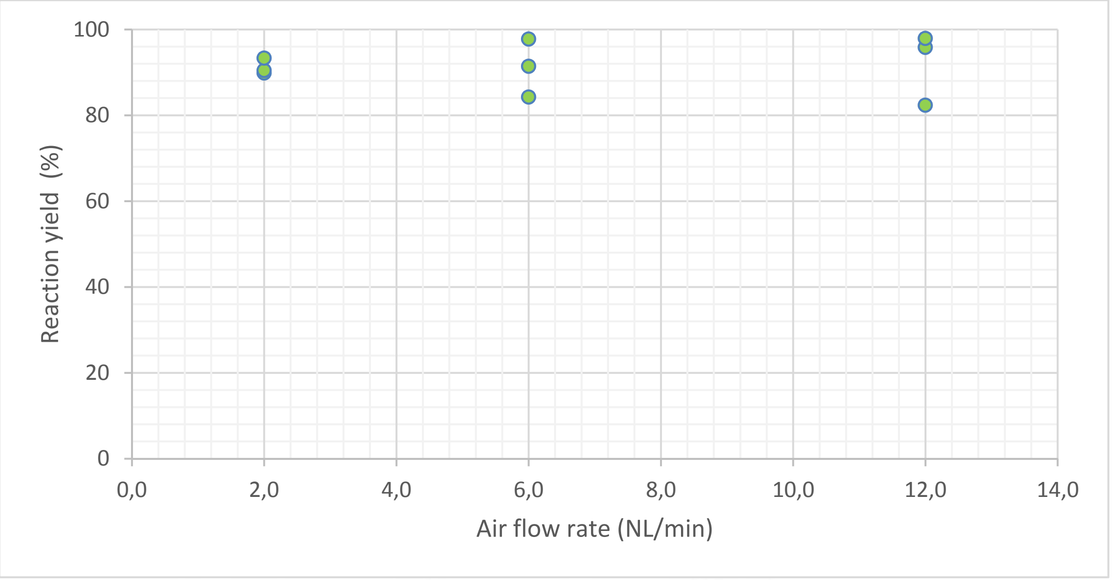
- Influence of P on reaction yield.



- 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.

Results

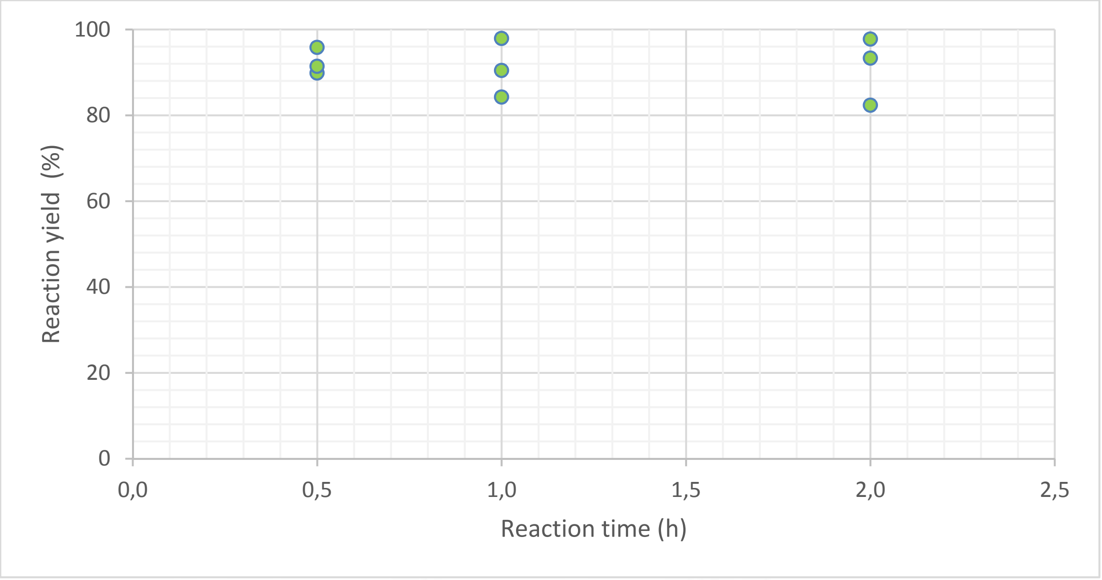
- Influence of **fluidising air flow rate** on reaction yield.



- With some exceptions, the crystallisation **reaction yield increases** as **the air flow rate** increases.

Results

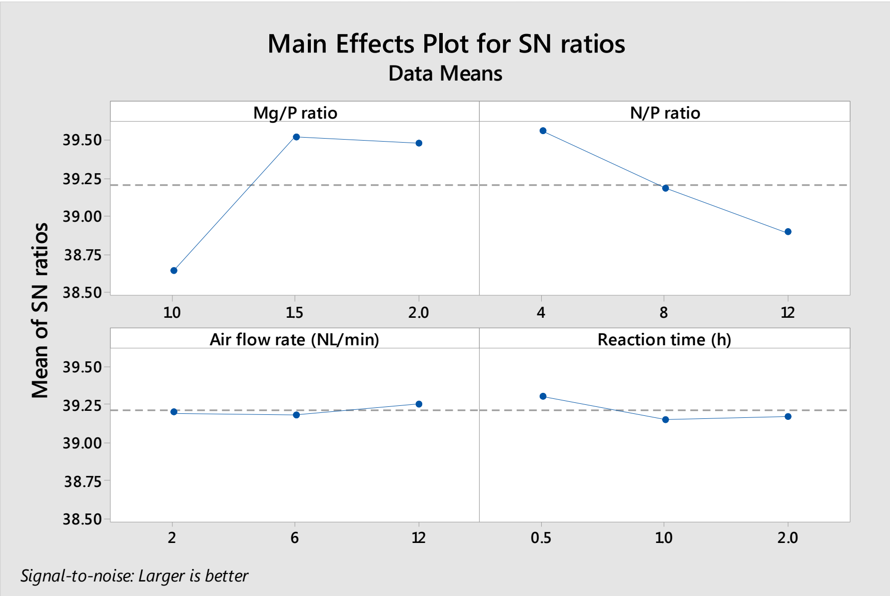
- Influence of **reaction time** on reaction yield.



- The **reaction yield increases** as the reaction **time increases**. However, the **differences** in reaction yield are very **small** for **1.0** h and **2.0** h.

Results

- The effect of the process parameters was analysed by Taguchi methodology using **Signal to Noise ratio** (S/N) **method**.



- The parameters that had the **greatest influence** on the struvite crystallisation reaction yield were: Mg and P **concentrations.**
- **Air flow rate** and **reaction time** had **little influence** on the reaction yield.

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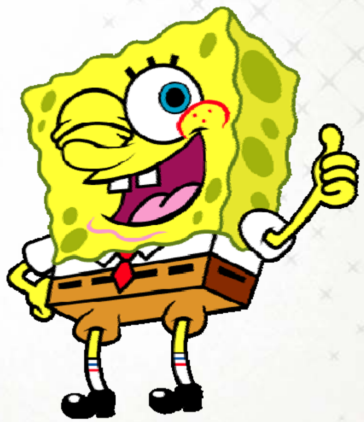
Conclusions

- **Concentrations** of Mg and P in the reaction medium are the parameters that have the **greatest influence** on the struvite crystallisation reaction yield. The higher concentrations of Mg and P, the higher the reaction yield. Therefore, the optimum Mg/P 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.

- **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.

- Struvite crystallisation reaction in **fluidised bed reactors** generally achieves **better results** (higher efficiencies) than in **mechanical stirring reactors**.



Future works

- Study the **growth rate** of struvite crystals.
- **Optimise** struvite crystallisation reaction by **continuous operation**.
- **Field tests** of struvite to check its properties as a **slow-release fertiliser**.

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Thank you for your attention

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If you have any question, do not hesitate to contact me

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