

Study of parameters influencing the process of phosphorus recovery in synthetic biologically treated pig effluent in pilot lab scale

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Abstract

A pilot lab scale to recycle phosphorus contained in the solid fraction of biologically treated pig manure was developed. It was shown in previous studies that pH, mixing intensity and ammonium concentration determine the quality of the final effluent as well as the quantity and the composition of the solid. In this study, the influence of HRT and ratio N/P were tested. The phosphorus abatement rate was 91-100%. The HRT had no significant influence on the phosphorus precipitation. Instead, a high ratio N/P influenced the crystal size and the proportion of struvite in the solid.

Introduction

The excessive use of phosphorus contributes to the depletion of resources and its high quantity in some areas favoured the eutrophication of surface waters. Phosphorus removal in wastes through struvite ($\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$) crystallization allows its recovery as fertilizer. Therefore, phosphorus recycling processes on waste water or manure were developed in several countries. However, most of these processes are not suited for the recovery of a significant amount of P in the concentrated effluents such as swine wastewaters. One of the limitations is the P form presents in swine manure : 80% of P is contained mainly under mineral particular form and its recovery requires a first stage of dissolution [1]. Another limiting step is the crystals size which has to be as long and wide as possible to facilitate their recovery by filtration [2]. Within these requirements, an experimental pilot lab scale was designed. The first main step consists in a preliminary P dissolution at pH 4.5 followed by the separation of residual organic matter. The second main step is the P precipitation with MgO and subsequent filtration of struvite crystals. Six parameters on the phosphorus precipitation were studied in a previous work [3]. It was shown that pH, temperature, mixing intensity and ammonium concentration determine the quality of the final effluent as well as the quantity, the composition of the solid and the crystal size. The aim of this study was to precise the influence of two parameters on the crystals size, struvite amount and reactive consumption. Therefore, four hydraulic retention time (HRT) (24, 19, 14 and 7 hours) and the influence of the ratio N:P (1, 1.3 and 1.8) were studied in a synthetic pig effluent with the final aim to increase the volume of treated manure and the crystal size.

Material and Methods

Synthetic swine wastewater (SSW) preparation

40 L to 60 L of SSW were prepared by mixing different salts in tap water to obtain the ionic concentrations observed in the studied swine wastewater (Table I). Formic acid (85%, Carlo Erba) was added in the solution until pH reached 4.5. The salts used for synthetic effluent preparation were: KOH, K_2SO_4 , NaNO_2 , KNO_3 , $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ (Carlo Erba), $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$ (Merck). The ionic concentrations of SSW were controlled by ion chromatography on Dionex DX-120. Concentrations for synthetic and real effluents are shown in Table I. A variable amount of NH_4Cl powder (99%, Carlo Erba) was added after acidification to minimize the possible volatilization of NH_3 . The addition was performed under high stirring.

Table I : ionic concentrations of synthetic and real effluent

<i>Ionic concentrations (mg.L⁻¹)</i>	<i>Real effluent</i>	<i>Synthetic effluent (SSW)</i>
Na ⁺	1368±84	1880±268
K ⁺	2315±82	1825±232
Mg ²⁺	628±24	616±87
Ca ²⁺	1437±100	1283±115
Cl ⁻	2305±310	5666±528
NO ²⁻ -N	1±0	1±0
NO ³⁻ -N	7±1	12±1
PO ₄ ³⁻ -P	850±139	922±79
SO ₄ ²⁻ -S	121±9	131±8

Magnesia preparation

The magnesia used is a by-product of the manufacturing of magnesia for animal feeds (Magal TC, Altilis). Magnesia powder was suspended in tap water at 100 g.L⁻¹.

Equipment

The reactor designed according to the concept described by Valsami-Jones [4] is shown in Figure 1. The lower part of the reactor is the reaction zone (R) The upper part is the settling zone (G) where the smallest particles are kept in suspension. The reaction zone containing the particles was sampled every 24 hours with the valve E. The overflow (O) was collected in a 60 L pre-weighed container emptied after each sampling.

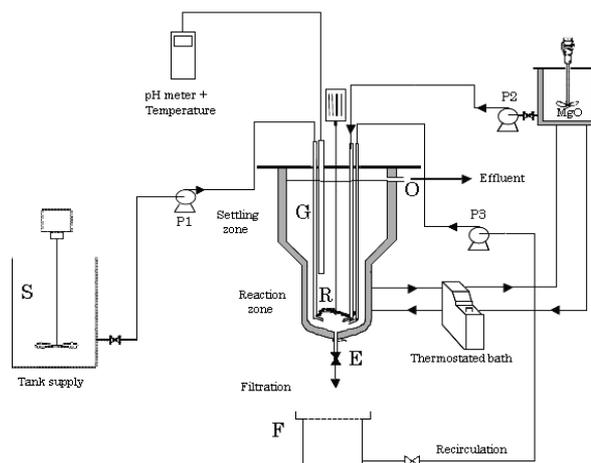


Figure 1 : Continuous crystallization reactor

The SSW stored in the tank (S) was introduced into the thermostated pilot by the peristaltic pump (P1) whose variable flow makes it possible to adjust the hydraulic residence time (HRT). The regulation of the magnesia pump (P2) was programmed to work when the pH value is lower than the instruction.

The magnesia was maintained in suspension under continuous stirring at room temperature. The quantity brought was determined by the operating time of the pump which starts with fixed interval when the pH value is lower than a threshold value fixed according to the pH instruction.

Approximately 20 ml were kept for granulometric analysis and the other part was filtered on a 250 µm sieve or on a filter bag with a 100µm cut-off (F). The liquid was recirculated by the pump P3 in order to reduce MgO consumption. The pH values, the weight of magnesia supply tanks (S) were recorded every 10 minutes. The 250 µm sieve was dried in a drying room (T < 30°C). The solid was then transferred if necessary in a receptacle until complete drying.

Analysis

Samples were sieved on 25 and 100 µm filters. The three solid fractions (<25µm, 25–100µm and >100µm) were weighed and analyzed by ionic chromatography after solid dissolution in formic acid (85%).

Ionic concentration

The composition of the collected fractions were analysed by cation and anion chromatography on Dionex DX-120 with an IonPacTM CS12A column and an IonPacTM AS9-HC column respectively.

Granulometric analysis

The particles analyses were carried out with a morphogranulometer (Occhio, Flowcell FC200M) using an 800 μm thick measuring cell.

Experiments

For all experiments, solid residence time (SRT) was fixed at 24 hours, the temperature at 15°C and the mixing intensity at 250 rpm. SRT, pH consign, mixing intensity and temperature were fixed on the basis of results obtained in a previous work [3]. In each experiment, several values were obtained corresponding to the drawn off volume collected every 24 hours.

Table II presents the conditions and the parameters tested. In experiments A, 4 feed rates were tested. The influence of the type of filtration and the drawn off volume were also studied. In the experiments B, the influence of the N:P ratio was studied. The trial A3-B3 was performed only once but was also used to compare the influence of ratio N:P with trials B1 and B2 for the same feed rate.

Table II : Experimental conditions

Experiment	Overflow average pH	Feed rate (L/d)	HRT (hours)	Feed Mg/N/P ratio	Average drawn off volume (mL)	Type of filtration
A1	7 \pm 0,1	13 \pm 0,8	20	0,8/0,8/1	1014 \pm 21	Filter bag 100 μm
A2	8 \pm 0,1	38 \pm 10	7	0,8/0,9/1	2244 \pm 63	Sieve 100 or 250 μm
A3-B3	7,8 \pm 0,2	19 \pm 0,5	14	0,8/1/1	2084 \pm 30	Sieve 250 μm
A4	8,4 \pm 0,2	11 \pm 0,3	24	0,8/0,9/1	2021 \pm 44	Sieve 250 μm
B1	8,2 \pm 0,0	21 \pm 1,7	12	1/1,3/1	2114 \pm 83	Sieve 250 μm
B2	8,4 \pm 0,2	19 \pm 0,4	14	1/1,8/1	2021 \pm 29	Sieve 250 μm

Results and discussions

Crystallization

The P removal rate varies from 91 to 99 % in the experiments A, and was 100 % in the experiments B. The 91 % corresponds to the trial A1, where the average pH in the reaction zone was lower than 8 in comparison to the others tests.

The solid was composed of struvite, amorphous calcium phosphate (ACP) and MgO. The quantity of the solid product varied from 7 to 11g.kg⁻¹SSW among which struvite was between 28 and 71 % (Table III). In the experiments A, the most substantive differences were observed in the trials A1 and A2. A higher quantity of solid was sieved on the 100 μm filter bag or sieve than in the 250 μm sieve; because the undissolved MgO was trapped into the solid fraction with a 100 μm filter (Table III).

In the trial A1, a low solid quantity was collected because of the low quantity of MgO injected due to the low pH setting and the low drawn off volume. So the quantity of ACP was higher. It is also necessary, in order to extract a significant part of the solid, to collect almost the entire reaction zone (approximately 2L) and to maintain a pH upper than 8 to increase the ratio of struvite in solid.

The quantities of solid were similar in the trials A3 and A4, likewise the proportion of struvite, ACP and MgO. All these observations have shown that increasing feed rates didn't have a significant influence on the proportion of MgO, ACP and struvite in the solid fraction.

The results of the experiment B proved that the ratio N/P influence positively the quantity of struvite.

Table III : composition of the solid

Experiment	Solid (g.kg ⁻¹ SSW)	Dried filtered solid (% of withdrawn SSW)	Struvite	Ca _x H _y (PO ₄) _z (% of solid)	MgO
A1	7 \pm 1	6 \pm 0,4	34 \pm 6	40 \pm 5	26 \pm 8
A2	11 \pm 1	17 \pm 17	28 \pm 5	19 \pm 1	54 \pm 5
A3-B3	9 \pm 3	2 \pm 1	39 \pm 10	20 \pm 4	42 \pm 14
A4	11 \pm 3	2 \pm 1	36 \pm 13	19 \pm 5	45 \pm 17
B1	8 \pm 1	4 \pm 2	57 \pm 10	19 \pm 0,4	24 \pm 9
B2	8 \pm 1	4 \pm 2	71 \pm 7	9 \pm 2	20 \pm 8

Granulometric analysis

The image analyses allowed to confirm that there were less crystalline forms in the trials A1 and A2 (Figure 2). The flow rate appears to have an influence on the crystals size in the experiment A. Indeed, a longer residence time would allow a growth and an agglomeration of crystals. Similarly, higher crystals quantities were obtained in the case of high ratio N/P except in the case of trial B1 where the flow rate was a little bit higher.

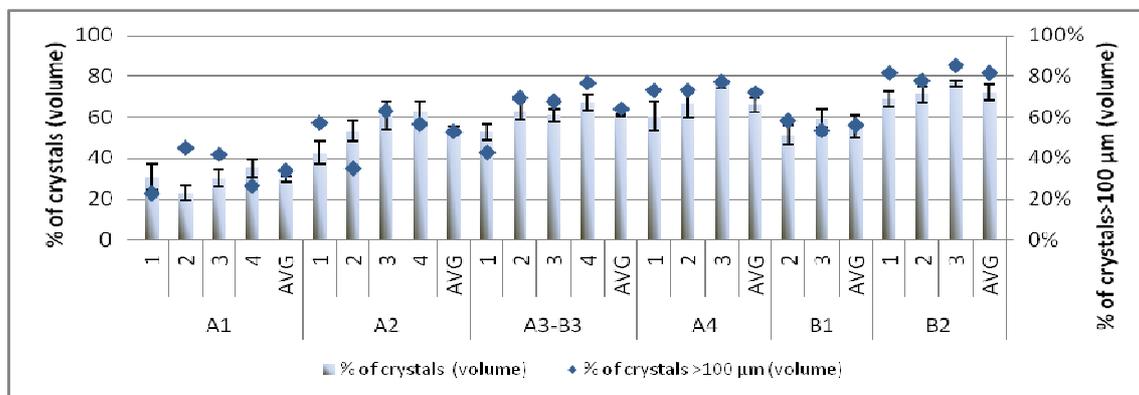


Figure 2 : Percentage of crystals according to the experiments

Conclusion and perspectives

The P removal as struvite was mainly influenced by the low pH in A1 and the filtration device in A2 in the experiments A. The ACP formation was favoured by low pH (near 7) whereas struvite was present in high quantities at pH equal or greater than 8.

The filtration device of the liquid from the reaction zone is crucial for the reduction of MgO amount in the final solid product and for the MgO consumption. A vibration sieve device would be preferred for this step. Higher crystals size and quantities were obtained with high ratio N:P. However this ratio shouldn't be too high to avoid a discharge of N in the surface water and in order to comply with the Nitrate Directive. The hydraulic residence time of 12 hours is a good deal to treat a greater volume of slurry while keeping a suitable crystal size for the filtration step.

The results of the laboratory scale pilot showed that a large amount of P was recovery into struvite. Based on these results, new experiments will occur with a farm scale pilot plant to recycle phosphorus from biologically treated pig slurry. The agronomic value on the final product will be performed this year.

References

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Acknowledgments

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