

Phosphorus recycling as struvite from pig manure. Influence of process parameters.

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Abstract

Previous studies have shown that it was feasible, at bench scale, to recycle P from pig slurry as mineral fertiliser by a simple acidification/precipitation process. In this study the influence of several parameters on the continuous pilot process designed from the bench scale results were tested. The pH, stirring rate, N/P ratio and solid retention time were the main factors influencing the proportion of struvite in the solid and the crystal size. The P abatement rate was 95-99% both on dissolved and total phosphorus.

Introduction

The issues in the recycling of the phosphorus (P) are twofold i) the protection of a limited resource and ii) the fight against the eutrophication by adapting the application of P to the needs of crops which would minimize the leaks to the aquatic environment. The struvite ($MgNH_4PO_4 \cdot 6H_2O$), a crystalline form obtained from dissolved P of liquid effluents, is marketed as fertilizer in Japan or in Canada. It can be obtained by crystallization of P from livestock waste [1]. However, most of the systems developed at an industrial scale recycle only the dissolved P from urban or agro-industrial effluents. The most wide-spread process is the fluidized bed reactor in which the effluent is mixed with magnesium chloride and sodium hydroxide [2]. But this process is difficult to transpose into the context of the animal waste for several reasons: i) P is present mainly as inorganic particular form and its recycling requires a first stage of dissolution [3]; ii) when the concentration of P is high, as it is the case for animal waste after inorganic particular P dissolution ($1g\ P\ L^{-1}$), the energy necessary to maintain particles in suspension by the recirculation in the fluidized bed reactor increases; iii) the treatment plants are generally located on the farm and managed daily by the farmer himself. The processes must thus be rustic with no dangerous reagent. The technical and economic feasibility of a process of extraction and recycling of P in the form of struvite from pig slurry was previously studied from batch tests in stirred reactor, on small volumes [4]. The process has four stages: i) dissolution of P by acidification to pH 4,5; ii) separation of the liquid, containing dissolved P, from sludge containing the organic matter; iii) P crystallization; iv) filtration and drying of the solid. Two constrictions were highlighted during these previous works: i) the low efficiency of the separation by settling after the stage of acidification which penalizes the global yield of the system and ii) the small size of the crystals of struvite obtained in batch in stirred reactor. But this determines the capacity of retention of the product by a rustic system of filtration. A continuous stirred reactor allowing the separation of the zones of reaction, growth and settling has been developed [5]. It allows to separate the hydraulic residence time (HRT) of the effluent from the residence time of crystals (SRT) which favors the growth within the reactor. In this study, a semi continuous pilot was developed at lab scale to recycle the P contained in the solid fraction of biologically treated pig manure based on this principle. The aim was to measure the performances of the acidification/separation step and to study the effect of temperature, stirring rate, pH, HRT and SRT on struvite crystallization.

Material and Methods

Pig manure: The pig manure came from a biological treatment plant removing nitrogen from the effluent of a breeding–fattening farm, situated in Brittany (France). After dosage of the remaining ammonium, the ratio N/P was adjusted according to the need for the experiments by adding supernatant of untreated settled liquid manure, stemming from the same plant.

P recycling pilot: For practical reasons of storage and supply in liquid manure, the pilot was divided into two modules. The first one in batch is dedicated to the acidification and to the separation of the supernatant enriched with dissolved P. The second one in a continuous reactor is dedicated to the crystallization of P with recovery of the solid on filtering bags. The acidification was performed with formic acid (85%, 405832 Carlo-Erba) to reach a pH of 4.5. A small amount of polymer (Zetag 8140, CIBA) was added before the separation of the acidified pig slurry on a dewatering table equipped with

a 360 μ m filter screen. The liquid (ASW) was stored at 4°C before being used. In the module of crystallization, the liquid from the separation step is pumped into the stirred zone where it is mixed with the magnesia MgO. The inorganic particles formed are maintained in suspension above the stirred zone by the impeller. When they reached a sufficient size, they settle and accumulate at the bottom of the reactor where they are periodically harvested in a filter bag. The liquid from the filtration is recirculated to the stirred zone. The refined effluent goes out through the top of the reactor. The addition of magnesia, which determines the pH of the reaction, is regulated by the pH probe. Magnesia was a by-product of the manufacturing of magnesia for the animal feed. It was brought as a suspension (100g.L⁻¹) maintained under mixing. Two different lots were used during the experiments. The purity of lot 1 (83%) was higher than lot 2 (79%).

Experiments : Three series of experiments were realized. The first one (A) had for objectives to set up the pilot by adjusting the various parameters according to the results of the previous batch trials and to determine the operating parameters of the magnesia pump (duration and frequency) allowing to regulate at best the pH. The second (B), had for objective to study the sensibility of the process to the variations of the parameters. It was based on a screening experimental design combining five factors at two levels (Statgraphics ®). The third (C) allowed to test the optimal conditions on long-term trials. The conditions of the experiments conducted within the framework of these three series are included in table 1.

Table 1: Experimental conditions of the experiments.

Experimentation	Trials	MgO Lot	pH setting	Temp.(°C)	Stirring rate (rpm)	HRT (h)	SRT (h)	N/P
A	A1	1	8.5	20	215	24	24	1.5
B	B1-B25	2	7.5-9.5	5-25	100-300	24-48	4-72	0.9
C	C1	2	8	20	200	24	24	0.7
	C2-C3	2	8	15	200	24	24	0.7
	C4	2	8	15	250	24	24	1.3

Biochemical Analysis: The analyses of TS, TSS, VS, VSS and NTK followed the standard methods. The ammoniacal nitrogen was measured by distillation. Other cations and anions were measured by Ionic chromatography (Dionex, Sunnyvale, the USA). The total P was measured by automated colorimetry (Lachat) after mineralization with a sulphuric and nitric acid mixture under pressure. Unless otherwise specified, all the analyses were realized in triplicates.

Morphometric analysis: These analyses were realized with a morphogranulometer (Occhio, Flowcell 2000) as described by Capdevielle *et al.* [6].

Results and discussion

Acidification / separation

The amount of formic acid required to reach pH \approx 4.5 was 10g.L⁻¹ dissolving 80 \pm 7% of the initial total P. The characteristics of the effluent at this stage are presented in table 2. The TS was at 90% dissolved among which more than 75% was mineral. About 70% of the initial volume containing 50-60% of the total P was collected.

Table 2: Characteristics of the liquid manure before and after the acidification / separation module.* the analysis was realized before the addition of supernatant of raw liquid manure to adjust the ammonium.

	Experiment A		Experiment B		Experiment C	
	Input	Output	Input	Output	Input	Output
pH	8.1	4.8	7.82	4.9 \pm 0.5	7.94	4.7 \pm 0.4
COD(gO ₂ .kg ⁻¹)	25 \pm 3	-	30 \pm 2	5.0 \pm 0,1	30 \pm 2	4.4 \pm
TS (g.kg ⁻¹)	31 \pm 1	-	33 \pm 1	15.8 \pm 0.3	54 \pm 1	18.0 \pm 0.1
VS(g.kg ⁻¹)	16 \pm 1	-	20 \pm 1	4.2 \pm 0.2	31 \pm 1	5.0 \pm 0.1
TSS(g.kg ⁻¹)	25 \pm 1	-	27 \pm 1	2.0 \pm 0.3	47 \pm 1	0.9 \pm 0.3
VSS(g.kg ⁻¹)	15 \pm 1	-	19 \pm 1	1.0 \pm 0.2	30 \pm 1	0.5 \pm 0.2
N-NH ₄ ⁺ (mg.kg ⁻¹)	40 \pm 1*	470 \pm 1	30 \pm 1*	270 \pm 6	70 \pm 1*	247 \pm 6
total P (mg.kg ⁻¹)	837 \pm 70	-	803 \pm 20	-	1115 \pm 82	-
P-PO ₄ ³⁻ (mg.kg ⁻¹)	265 \pm 12	683 \pm 6	268 \pm 4	699 \pm 9	152 \pm 1	809 \pm 5
Mg ²⁺ (mg.kg ⁻¹)	40 \pm 3	332 \pm 3	121 \pm 10	524 \pm 77	153 \pm 4	624 \pm 29
Ca ²⁺ (mg.kg ⁻¹)	39 \pm 5	798 \pm 9	108 \pm 7	1081 \pm 70	124 \pm 20	1439 \pm 135

Crystallization

During the crystallization, whatever the parameters, the P removal in the liquid was between 95 and 99%. The mass of the solid varied from 5 to 18 g.kg⁻¹ of ASW. The solid was a mix of struvite, amorphous calcium phosphate (ACP) and MgO. The results from experiment B showed that the main parameter influencing the mass of total solid was the pH. The pH was regulated by MgO addition. MgO was not totally dissolved during the process and partly recovered in the solid. However, MgO dissolution was also depending on the parameters. High stirring rate decreased the amount of MgO in final product and so increased the ratio of struvite. The stirring rate and the solid retention time were also the crucial parameters to be controlled in order to avoid solid accumulation in the reactor. Struvite in solid increased with pH and decreased with high temperature (table 3).

Table 3: Influence of the parameters on the composition of the solid phase (experiment B). Figures in brackets indicate the value of the probability p when it is lower than 0.05.

	<i>Struvite</i>	$Ca_xH_y(PO4)_z$	<i>solid</i>	<i>struvite</i>	$Ca_xH_y(PO4)_z$	<i>MgO</i>
	g.kg ⁻¹ of ASW			% of solid		
Min-Max	1.0-3.2	1.2-2.2	7.0-18.0	8-35	7-27	46-79
Temperature	-	+		-	+	
	(0.0001)	(0.0000)		(0.00138)	(0.0001)	
Stirring rate				+		-
				(0.0227)		(0.0216)
pH	+		+	-	-	+
	(0.0315)		(0.0000)	(0.0000)	(0.0000)	(0.0000)
HRT						
SRT						

In the experiments C, increasing the initial N/P ratio from 0.7 to 1.3 increased struvite in solid twofold. However, the best result was obtained in the experiment A, with the highest N/P ratio tested (1.5/1) and MgO from lot 1 (table 4). The distribution of P between struvite and ACP could determine the agronomic property of the final product. ACP can be mineralized in hydroxyapatite during drying and storage. Hydroxyapatite is an insoluble compound and so not ready available for plants.

Table 4: Composition of the final solid product

	<i>pH</i>	<i>Solid</i>	<i>Struvite</i>	$Ca_xH_y(PO4)_z$	<i>MgO</i>
	<i>measured</i>				
		g.kg ⁻¹ ASW		% of solid	
A1	8.6±0.5	6±1	66±5	18±2	16±2
B1-B25	7.5-9.5	7-18	8-35	7-27	46-79
C1	8.1±0.5	11±2	19±4	24±5	57±8
C2	8.2±0.2	10±1	19±3	27±3	53±3
C3	7.5±0.5	7±1	12±6	35±5	55±7
C4	8.1±0.2	10±1	38±6	15±2	47±7

Morphometric analysis

Picture analysis combined with a statistical classification method allowed to classify particles in four families. Three of them were different types of struvite crystals (sticks, stars or aggregates) and the fourth one was amorphous calcium phosphate (figure 1).

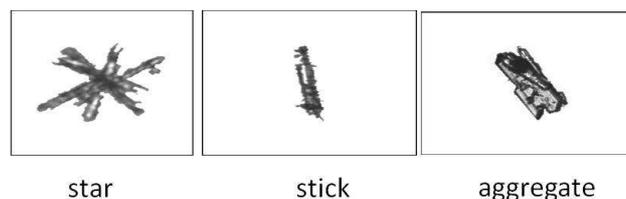


Figure 1 : different types of struvite crystals obtained by recycling P from pig manure.

Previous works having shown that the struvite is under crystalline shape while the calcium phosphate is rather under amorphous shape, a comparative approach of the relative composition of the solid is possible by comparing the surface occupied by the diverse types of particles. A more important proportion of crystalline forms, respectively 71 ± 2 % and 51 ± 3 % of the total surface of particles is present in the trials C4 and A. This is coherent with the composition of the solid calculated previously which demonstrate a more important proportion of struvite in these trials. The crystalline forms are mainly in the form of aggregates excepted for the trial C1 where the quantities of stars and aggregates were identical. The morphometric analysis of the crystals did not show significant difference on the average size of the total populations between the various experiments. However some large aggregates ($L > 100$) were present in the experiment A and C4 while only some aggregates included between 100 and 200 μm were observed in trials C1 and C2 and no aggregate larger than 100 μm was observed in C3 (Figure 2). The number of aggregates was very limited, less than a particle in a million, but their surface was approximately 2 % of the total surface occupied by the crystalline forms for the trial A and 10 % for the trial C4. A high N/P ratio would favor the formation of these compact aggregates which have sometimes the aspect of a single very wide crystal.

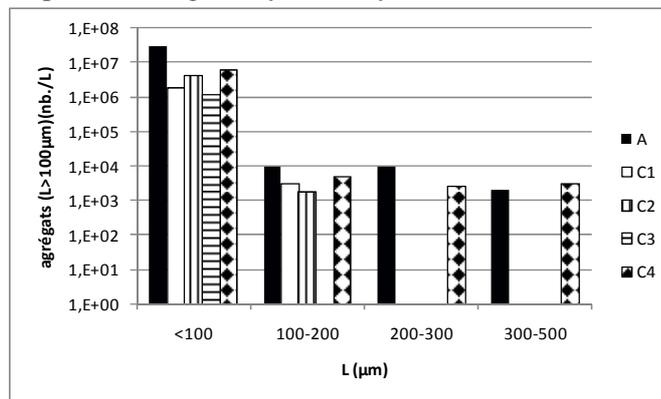


Figure 2: concentration of large aggregates ($L > 100 \mu\text{m}$) (number.L^{-1})

Conclusion and perspectives

These experiments have shown that it was possible to recycle more than 60% of the initial total P of pig slurry as a mineral product containing struvite, ACP and MgO. The proportion and the size of struvite crystals mainly depend on pH, during the crystallization step, and on N/P ratio. The continuous stirred reactor allowed recovering 95-99% of the dissolved P using only MgO which is a cheap by-product easy to handle at a farm level.

The amount of acid required for the acidification step was the same as for the previous batch tests. Because of the cost of the acid and the environmental impact of its production, acidification is the limiting step of the process. To be competitive with chemical mineral fertilizers produced from ore, this step has to be optimized.

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