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Additional Information

Alternatives For The Management Of Pig Slurry: Phosphorous Recovery And Biogas Generation

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Abstract

Pig slurry is highly polluted waste stream characterized by its high nutrients content and its high organic matter concentration. In this research, two alternatives in the management of this wastewater were studied. On the one hand, removal of nutrients from piggery wastewater by struvite precipitation was evaluated. Different molar ratios Mg^{+2}/PO_4^{-3}, pH and temperatures were tested. On the other hand, an anaerobic treatment was performed with and without previous struvite crystallization and the methane production was analyzed. Results showed that the optimal experimental conditions to achieve the highest ammonium nitrogen and phosphate removal percentages (62.01% and 66.96%, respectively) were a molar concentration ratio (Mg^{+2}/PO_4^{-3}) of 2.8, pH of 10 and temperature of 22ºC. In addition, images from FE-SEM microscopy demonstrated that the struvite morphology was orthorhombic. Concerning the anaerobic digestion, the chemical oxygen demand removal efficiencies were 59.87% and 52.25% for the treatment without previous struvite precipitation and with previous struvite precipitation, respectively. Furthermore, the maximum biogas potential was found when no previous struvite precipitation was carried out, with a biogas generation around 4 $mL·h^{-1}$ and a percentage of methane in the biogas between 32.37 and 59.73%.

Keywords: pig slurry; nutrients; struvite; anaerobic digestion.

1. Introduction

In Europe, the pig population for human consumption was about 186 million heads in 2014 [1]. Specifically, in Spain, the number of heads was about 27 million [1] generating an annual production about 6.5 Hm^3 of slurries [2]. Pig slurry is a liquid fraction that includes cleaning water, urine and animal feces [3]. The pig livestock farming causes a big environmental problem due to the highly polluting character of the pig slurry. This waste has high nutrients content and high organic matter concentration [4,5]. The intensification of livestock production leads to large quantities of livestock slurries. Thus, the high number of farms for meat production also causes the need of a suitable pig slurry management [5].

Traditionally, these slurries were stored in farms for several months until they could be used in agricultural applications because of their high content in fertilizer elements and organic matter [6]. However, their storage implies significant amounts of gaseous emissions to the atmosphere, which leads to severe environmental problems and can also damage the health of the animals [5,7]. For these reasons, the study of new technologies and alternatives for the pig slurry management is of paramount importance.

Among these technologies, phosphorous recovery and biogas production from pig slurry management have been developed in the recent years. On the one hand, animal by-products are substrates very attractive for biogas production mainly due to the high lipid content [4]. In fact, Hamelin et al. [8] reported that biogas generation from animal slurry is the most cost-efficient and socio-economic technology for reducing greenhouse gas emissions and for the recovery of plant nutrients. On the other hand, controlled struvite precipitation from pig slurry has a relevant importance because it is achieved both the production of a valuable slow release fertilizer and the reduction of the phosphorous concentration in pig slurry [9,10].

The demand of fossil fuels has increased progressively in the recent years. However, the trend to be limited and the importance of controlling the greenhouse effect gases generated by the use of this technology make increase the development of new technologies and strategies for energy production [11]. In this way, Edstorm et al. [12] estimated that the total biogas potential of wastes generated during pig slaughter was 140 MJ/pig. Salminem and Rintala [13] published that methane yields production is about 0.52-0.55 $m^3 \cdot kg^{-1}$ VS for an anaerobic digestion process under mesophilic conditions for a reactor of 2 dm^3 operated at 0.8 $kgVS \cdot m^{-3} \cdot d^{-1}$ and with a hydraulic retention time (HRT) of 50 days.

Concerning to struvite ($MgNH_4PO_4 \cdot 6H_2O$) precipitation, this phenomenon is produced when the concentration of Mg^{+2}, NH_4^+ and PO_4^{-3} exceed the struvite solubility product [10,14]. Because of it, it is necessary the addition of chemical compounds to carry out the struvite precipitation from pig slurry, since the concentration of Mg^{+2} is very low in

comparison with the concentration of the other ions in the pig slurry. Struvite has a potential use as a fertilizer, is a highly effective source of nitrogen, magnesium and phosphorus and is a slow release N-P fertilizer [15]. However, the pure or high-grade magnesium compounds added in the process are very expensive, limiting its full-scale application [16].

In this work, both techniques (phosphorous recovery by struvite precipitation and anaerobic treatment of pig slurry) have been studied at laboratory scale. Different molar ratio Mg^{+2}/PO_4^{-3}, pH and temperatures were tested and ammonium nitrogen and phosphate removal percentages were evaluated. The anaerobic treatment was carried out with and without previous struvite precipitation and the methane production was measured to compare the results of both processes. In this way, this work is a step forward in the study of the valorization of the pig slurry.

2. Materials and methods

2.1. Characterization of raw and treated pig slurry

Pig slurry samples were collected from the entrance point to the pig slurry pond in a piggery of 1,500 pigs located at a distance of 70 km from Valencia (Spain). Once in the laboratory, the sample was filtered with a mesh size of 1 mm to remove the coarse particles and refrigerated at 4ºC prior to use. The characterization of the raw pig slurry included the analysis of pH, conductivity, total solids (TS), volatile total solids (VTS), total COD (chemical oxygen demand) and ammonium nitrogen (NH_4^+-N). In addition, raw samples were also pretreated in order to measure the following parameters in the soluble fraction: COD, total nitrogen (TN), nitrates (NO_3-N), total phosphorous (TP), calcium (Ca^{+2}) and magnesium (Mg^{+2}). The pre-treatment consisted in centrifuging at 10.000 rpm for 16 min and filtering the clarified water.

pH and conductivity measurements were carried out with pHMeter GLP 21+ and EC-Meter GLP 31+ (CRISON), respectively. TS and VTS were measured according to Standard Methods [17]. COD, TN, NO_3-N, PT, Ca^{+2} and Mg^{+2} were analyzed using kits and the spectrophotometer DR600 both provided by Hach Lange (Spain). NH_4^+-N content was determined by a "Pro-Nitro M" distiller (P-Selecta, Spain).

2.2. Struvite precipitation

2.2.1. Ammonium nitrogen and phosphorous removal

The struvite precipitation experiments were performed in a crystallizer of 1 L of capacity. The crystallizer (Fig. 1) was equipped with a mechanical stirrer (Velp Scientifica, Italy), a peristaltic pump (Aiguapres, Spain) and a thermostatic bath to keep constant the fixed pig slurry temperature during the experiment.

The experiments were performed varying the pig slurry pH, the temperature and the Mg^{+2}/PO_4^{-3} molar ratio. The values of these parameters were selected according to Secondes et al. and Li et al. [18,19]. The pH values tested were 9 and 10, the temperatures were 22°C and 35°C and the Mg/PO_4^{-3} molar ratio was varied between 2.0 and 3.6. The set of experiments carried out is summarized in Table 1:

Table 1: Experimental conditions tested for struvite precipitation.

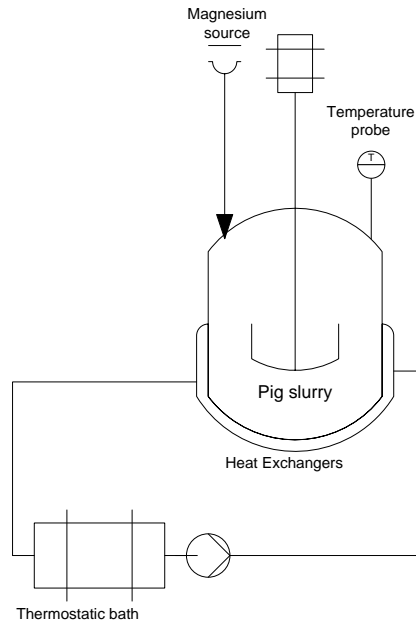| Test	pH	Molar ratio Mg^{+2}/PO_4^{-3}	Temperature (ºC)
1	pH 9	2	22
2	pH 9	2	35
3	pH 10	2	22
4	pH 10	2	35
5	pH 9	2.8	22
6	pH 9	2.8	35
7	pH 10	2.8	22
8	pH 10	2.8	35
9	pH 9	3.6	22
10	pH 9	3.6	35
11	pH 10	3.6	22
12	pH 10	3.6	35

Figure 1: Crystallizer used for struvite precipitation.

The volume of pig slurry employed for each experiment was 200 mL. The reactor was continuously stirred at 800 rpm, meanwhile the magnesium source ($MgCl_2 \cdot 6H_2O$ solution, Panreac, Spain) was added according to the required amount to reach the Mg/PO_4^{-3} molar ratio fixed. Once the appropriate amount of magnesium was added to the reactor, the mixture was shaken during 5 minutes for reaction and then it was allowed to settle for 4 h. The supernatant was centrifuged (10.000 rpm for 16 min), filtered (60 μm) and analyzed. PO_4^{-3}, Mg^{+2} and NH_4^+-N concentrations were determined as previously detailed in Section 2.1.

2.2.2. Struvite purification and microscopy analysis

The precipitate was collected and struvite purification was carried out following the experimental procedure described by Liu et al. [20]. Finally, the morphology and the elemental composition of the precipitated solid from the reactor (no purified) and of the purified struvite were examined using Field Emission Scanning Microscopy (FE-SEM) model Ultra 55 (Zeiss, Oxford Instruments).

The NH_4^+-N and PO_4^{-3} removal efficiencies were calculated according to Eq. 1 and Eq. 2, respectively:

$$NH_4^+ - N\ removal\ (\%) = \frac{NH_4^+ - N_{ini} - \ NH_4^+ - N_{sup} - NH_4^+ - N_{stripping}}{NH_4^+ - N_{ini}} \cdot 100 \qquad \text{(Eq. 1)}$$

$$PO_4^{-3} \; removal \; (\%) = \frac{PO_4^{-3}{}_{ini} - PO_4^{-3}{}_{sup}}{PO_4^{-3}{}_{ini}} \cdot 100 \qquad\qquad (Eq.\ 2)$$

Where NH_4^+-N_{ini} and $PO_4^{-3}{}_{ini}$ are the initial concentrations in the pig slurry sample (mg/L), NH_4^+-N_{sup} and $PO_4^{-3}{}_{sup}$ is the concentration in the supernatant after struvite precipitation (mg/L) and NH_4^+-$N_{stripping}$ is the ammonium nitrogen concentration eliminated by stripping due to the generated turbulence and the pH adjustment (pH 9 or pH 10) for struvite precipitation.

2.2.3. Statistical analysis

As previously explained in Section 2.2.1, a series of runs was performed varying the experimental conditions for struvite crystallization. In this way, two different temperatures (22 and 35ºC), two different pH values (9 and 10) and three different molar ratios Mg^{+2}/PO_4^{-3} (2, 2.8 and 3.6) were tested. Each experiment was repeated at least twice and if the difference in the PO_4^{-3} and NH_4^+ removal percentages were higher than 5%, the experiment was repeated three times. A statistical analysis was carried out with STATGRAPHICS Centurion XVI to study if there were significant differences with the different factors by means of an ANOVA multifactorial analysis with a confidence level of 95%. In this case, the dependent variables were PO_4^{-3} and NH_4^+ removal percentages and the factors studied were the followings ones: temperature, pH and molar ratio Mg^{+2}/PO_4^{-3}.

2.3. Anaerobic treatment

The anaerobic digester consisted of a cylindrical glass reactor of 15 cm diameter and capacity of 2 L. The digester was placed in a thermostatic bath to ensure a temperature of 40ºC. Continuous mixing was carried out by a magnetic stirrer. Fig. 2 shows a chart flow of the laboratory plant employed. The digester was initially inoculated with 1750 mL (87.5% of the digester volume) of sludge from an anaerobic digester of a municipal wastewater treatment plant. The reactor was operated at a HRT of 28 days (feeding the reactor twice a week with 250 mL of pig slurry). The characteristics of the effluent were measured twice a week to evaluate the anaerobic treatment. In this way, the effluent was centrifuged at 10.000 rpm for 16 min and then filtered at 60 µm previously to be analyzed following the procedures described in Section 2.1. In addition, the biogas production ($m^3CH_4 \cdot m^{-3} \cdot d^{-1}$) was measured by liquid displacement and the methane quantification was carried out by absorption using KOH solution 1M (Fisher Scientific, Spain) and further titration with HCl 0.1 M from VWR (Spain) [17].
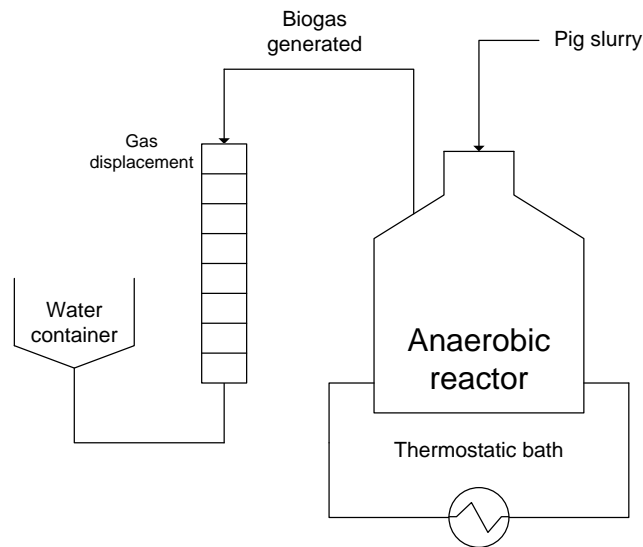
Figure 2: Anaerobic reactor employed for the experiments.

3. Results

3.1. Pig slurry characterization

The composition of the pig slurry samples collected during the study is presented in Table 2. All the precipitation tests were performed with the same pig slurry sample; meanwhile 4 different samples were used as anaerobic reactor feed.

In general, manures have high P and NH_4^+-N content, which is very favorable for struvite recovery. However, composition varies depending on several factors such as the animal species, rearing conditions (mainly diet), manure handling, storage and treatment type [20]. In this case, the pig slurry characteristics shown in Table 2 was very similar to those reported by Romero-Güiza et al., Cerrilo et al. and Zhang et al. [9,11,21].

In addition, it is observed in Table 2 that there were not great differences among the different samples used. As expected, most of the nitrogen content was present in NH_4^+-N form since the amount of TN was very similar to the NH_4^+-N. This phenomenon is very common in livestock wastewater.

Table 2: Samples employed for struvite precipitation and for anaerobic treatment.

Parameters	Sample for struvite precipitation	Samples for anaerobic treatment
sTN (mg/L)	1270	900-1270
sN-NO$_3$ (mg/L)	18.74	9.72-18.74
NH$_4^+$-N (mg/L)	1224	1096-1224
sPO$_4^{-3}$-P (mg/L)	42.7	42.7-70.56
COD (mg/L)	5970	5970-6550
sCOD (mg/L)	3910	3105-4959
sCa^{+2} (mg/L)	129.6	129.6-140.7
sMg^{+2} (mg/L)	43.6	43.6-50.7
sHardness (ºdH)	25.59	25.59-31.5
pH	8.04	7.54-8.14
Conductivity (mS/cm)	13.1	13.32-9.63
TS (g/L)	10.04	6.92-11.84
VTS (g/L)	5.95	3.88-6.5

3.2. Struvite precipitation

3.2.1. Ammonium nitrogen and phosphorous removal efficiencies

Table 3 shows the percentages of NH$_4^+$-N and PO$_4^{-3}$ removal efficiencies across the full series of experiments. According to Sommer et al. and Balsari et al. [22,23], the amount of ammonia volatilization by stripping in stored digested or undigested slurries without surface cover varies between 1.3 to 30 gN·m^{-2}·d^{-1}. However, in this study, as previously was described in Eq.1 and Eq. 2, the amount of ammonia volatilization was measured and included in the calculation, since the increase of the pH for struvite precipitation enhances ammonia stripping. Capdevielle et al. [24] also included the ammonia volatilization in their work.

Results showed that the ammonium nitrogen and phosphate removal efficiencies ranged from 37.89% to 62.01% and from 32.74% to 68.14%, respectively. Similar results were

reported by Romero-Güiza et al. [9], who studied the ammonium nitrogen removal as struvite precipitation from pig manure. They observed that percentages of ammonium nitrogen removal varied from 47 to 72%.

The optimal experimental conditions (test number 7) were pH 10, temperature of 22ºC and molar concentration ratio (Mg^{+2}/PO_4^{-3}) of 2.8, since the highest ammonia nitrogen and phosphate removal percentages in this experiment were reached. The percentages of NH_4^+-N and PO_4^{-3} removal for these optimal experimental conditions were 62.01% and 66.96%, respectively.

Table 3: PO_4^{-3} and NH_4^+-N removal efficiencies (%).

% Removal	1	2	3	4	5	6	7	8	9	10	11	12
NH_4^+-N	49.18	39.50	56.90	37.89	46.64	52.41	62.01	48.63	48.63	55.31	61.90	44.12
PO_4^{-3}	56.64	53.98	52.21	32.74	67.55	65.78	66.96	49.85	66.96	68.14	64.60	66.96

Regarding the optimal experimental conditions, Capdevielle et al. and Zhang et al. [21,24] also studied the optimal experimental conditions for struvite precipitation from pig slurry. The first group of authors published that the maximal phosphorous removal occurred with a Mg:Ca molar ratio of 2.25:1, N:P molar ratio of 3:1 and temperature of 20ºC. The second group of researchers found that the best experimental conditions for struvite crystallization were pH 10 and P:Mg:N molar ratio of 1:1:1.2.

Fig. 3 shows the Tukey diagrams for the factors temperature, molar ratio Mg^{+2}/PO_4^{-3} and pH. Results from variance analysis showed that the factors pH, temperature and molar ratio Mg^{+2}/PO_4^{-3} were not statistically significant in the tested ranges since the p-values were higher than 0.05.
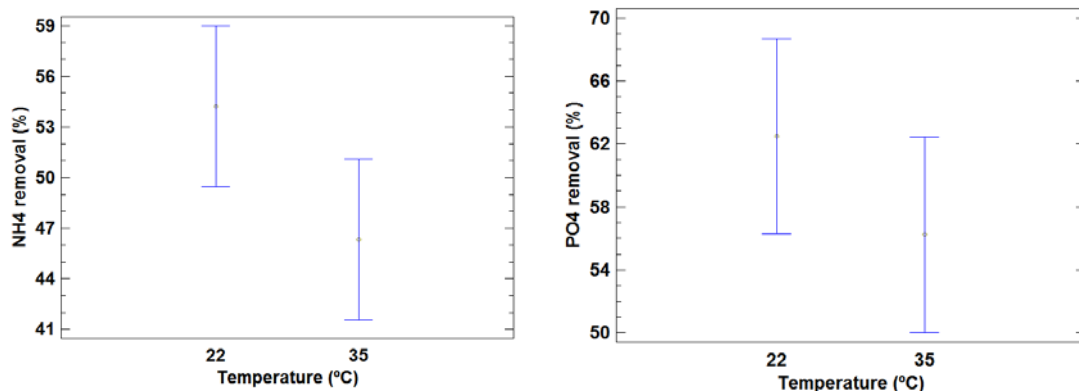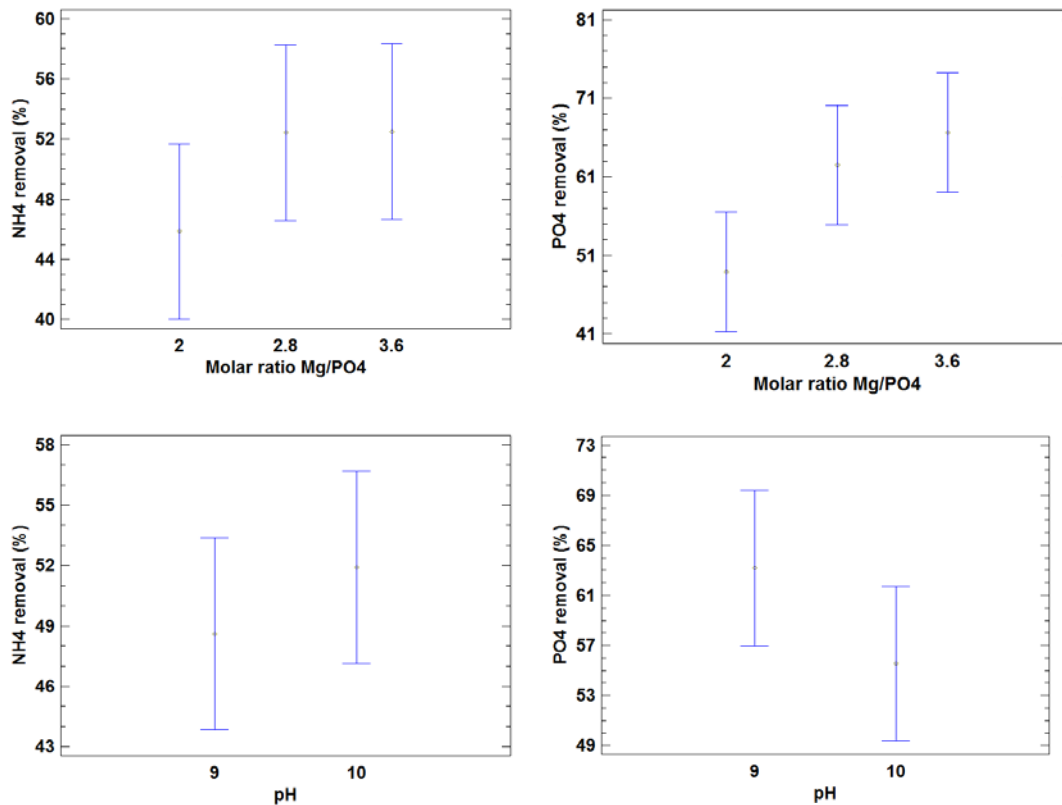
Figure 3: Tukey diagrams for temperature, molar ratio Mg^{+2}/PO_4^{-3} and pH.

3.2.2. Struvite purification

After struvite precipitation, samples were observed and analyzed with FE-SEM microscopy to recognize their morphology and elemental composition. The reported results were focused on the precipitate from test number 7, which yielded the highest ammonium nitrogen and phosphates removal efficiencies. Fig. 4 shows struvite morphology before and after purification at different zoom levels. It is observed in Figure 4.a and 4.b that struvite before the purification process had an amorphous structure. However, after purification process (Fig. 4.c and 4.d), it presented clearly a prismatic structure typical of struvite mineral. The reason of this orthorhombic shape is due to its atomic arrangement [25]. The enlarged FE-SEM images (Fig. 4.c and 4.d) shows struvite crystals, which are rod-shaped crystals very similar to those published by Münch et al., Ye et al. and Korchef et al. [26–28].

Regarding with elemental composition, Table 4 shows the weight percentages of the different elements in the samples analyzed (from test number 7) before and after the purification process. As expected, it is observed that after the purification process samples increased significantly the phosphorous and magnesium concentration, since impurities, mainly organic, were removed. The measured carbon concentration was not due to the sample composition, but to the graphite used in the sample pretreatment for

FE-SEM observation. Furthermore, it has to be taken into account that nitrogen content is difficult to detect due to the conductive character of the sample; therefore the struvite characterization has to be carried out in terms of Mg and P. Finally, it has to be commented that the percentage of Mg is lower than the theoretical one (9.79%), which is due to co-precipitation of calcium. These theoretical values were calculated from the struvite molecular weight and formula (245 $g\cdot mol^{-1}$ and $NH_4MgPO_4\cdot 6H_2O$), respectively. These results were in concordance with Lu et al. and Yan et al. [29,30] who also studied the purity of struvite precipitatated from wastewater under several experimental conditions. The reported purities of struvite were around 90% and 95%, respectively.
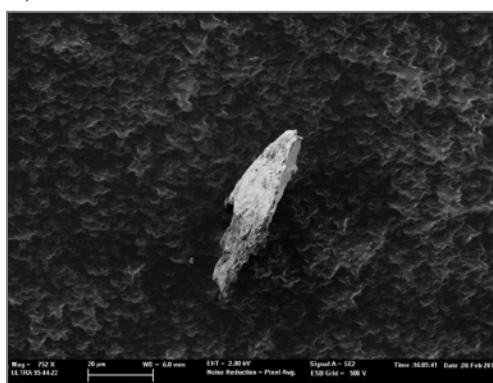
Table 4: Weight percentage of the elements in the struvite samples.

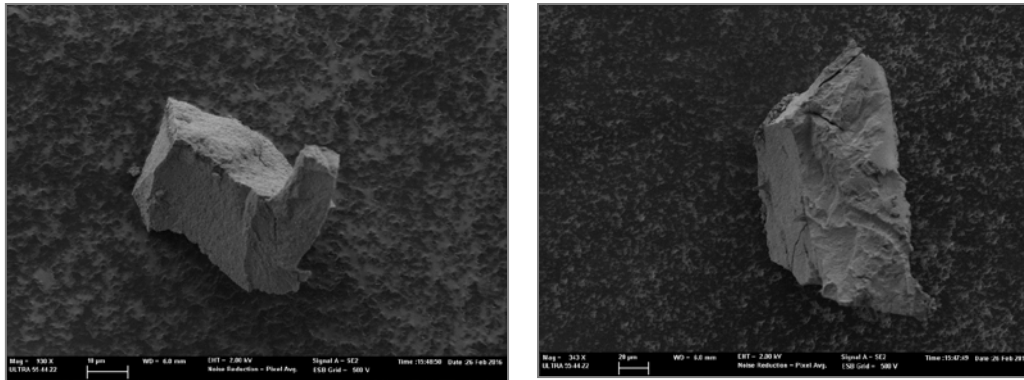| Element	No purified sample (%)	Purified sample (%)
C	28.03	28.01
N	3.01	0.18
O	33.55	48.97
Na	5.79	0.5
Mg	0.59	3.32
P	0.82	7.91
S	3.85	-
Cl	1.75	0.2
K	8.60	-
Ca	10.19	10.92

a)
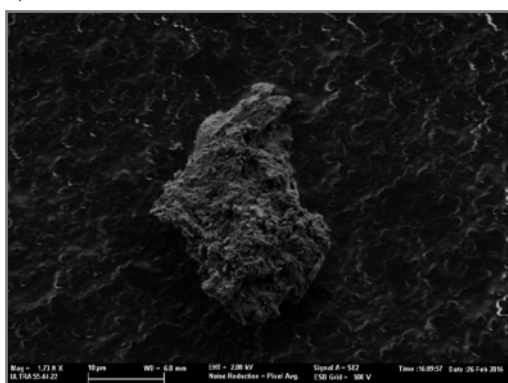
b)

c)

d)

Figure 4: Struvite morphology before and after purification. a) unpurified scale 10 µm, b) unpurified scale 20 µm, c) purified scale 10 µm and d) purified scale 20 µm.

3.3. Anaerobic treatment

3.3.1. Anaerobic treatment without previous struvite precipitation

Fig. 5 shows the evolution of TN, NO_3-N, NH_4^+-N and TP during the experiment. Total nitrogen was lower than ammonia nitrogen since the first one was measured in the soluble fraction, meanwhilethe ammonium nitrogen refers to the total fraction. The four compounds presented the same trend; the concentrations were decreasing in the first 25 days of the experiment. Nitrogen and phosphorous were assimilated by the anaerobic biomass, meanwhile nitrates were reduced to N_2. From the day 25th of the experiment on, TP and TN increased slightly because a different sample of pig slurry, which presented higher pollutant load, was used and in addition to it biomass debris accunlated in the digester. Similar results published Krishna et al. [31], who obtained that NO_3-N concentration is lower in the digestate in comparison with the fresh slurry, the NH_4^+-N and TP concentration are higher in the digestate comparing with the pig slurry and the NT content is very similar in the digestate and in the pig slurry.

Regarding organic matter removal, Fig. 6 shows the evolution of tCOD and sCOD during the experimentañ period. It is observed that tCOD increased significantly in the first days due to the addition of the sludge inoculum for the reactor start-up. It is also important to highlight that sCOD decreased during the anaerobic treatment and the percentage of sCOD removal was 59.87%. Kawai et al. [32] also obtained COD removal efficiencies around 60-70% during the first 35 days of operation.

Fig. 7 presents the evolution of TS and TVS. As expected, the concentration of TS and TVS decreased during the period of the test.

It can be observed in Fig.8 that the volume of generated biogas was about 4 mL·h^{-1} and the percentages of methane in the biogas were between 32.37 and 59.73%. The highest

biogas generation corresponded with the days in that the reactor was fed. However, comparing results with Krishna et al. and Borowski et al. [31,33], it seems clear that the biogas potential was not very high due to the low C/N (around 3) of the pig slurry. Authors such as Zhu et al. and Cerrilo et al. [34,35] have published that the optimal C/N relation for biogas generation is between 15 and 20.
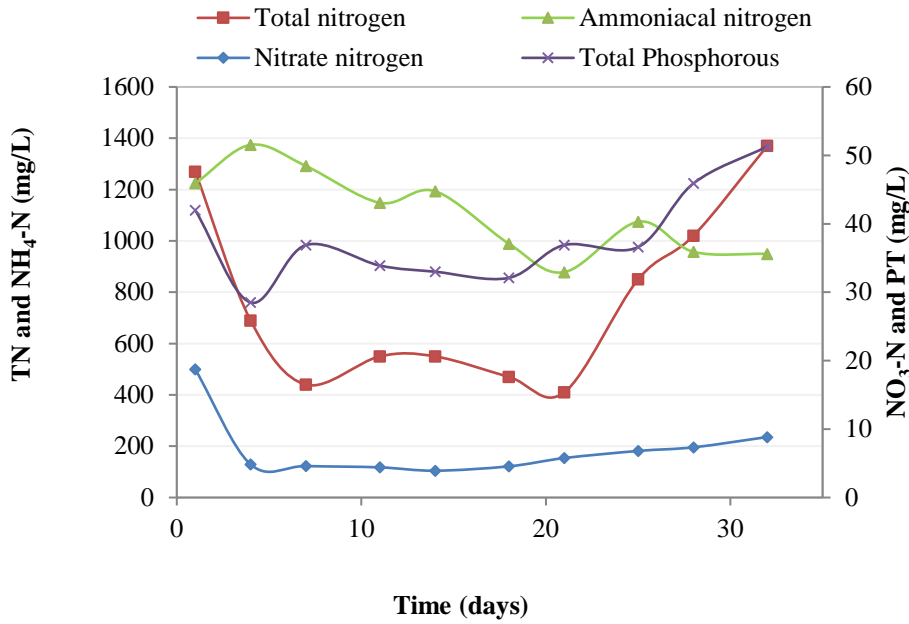

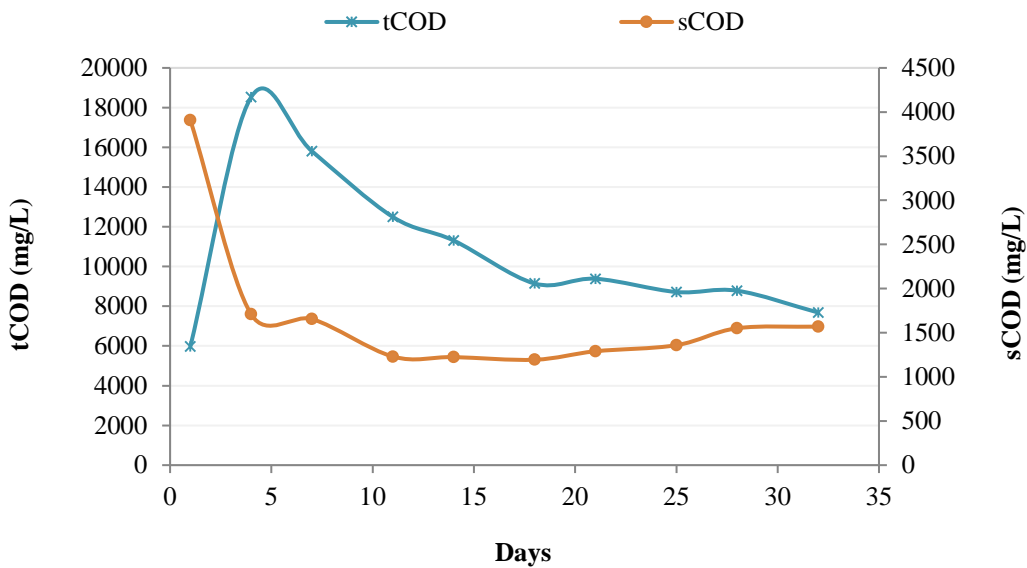**Figure 5: Nitrogen compounds and phosphorous evolution during anaerobic digestion.**

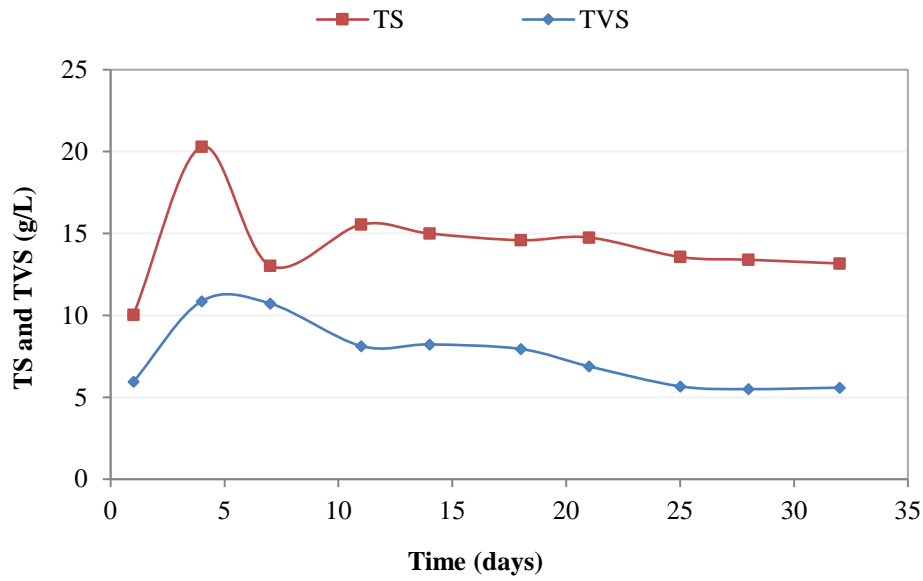**Figure 6: COD removal during anaerobic digestion.**

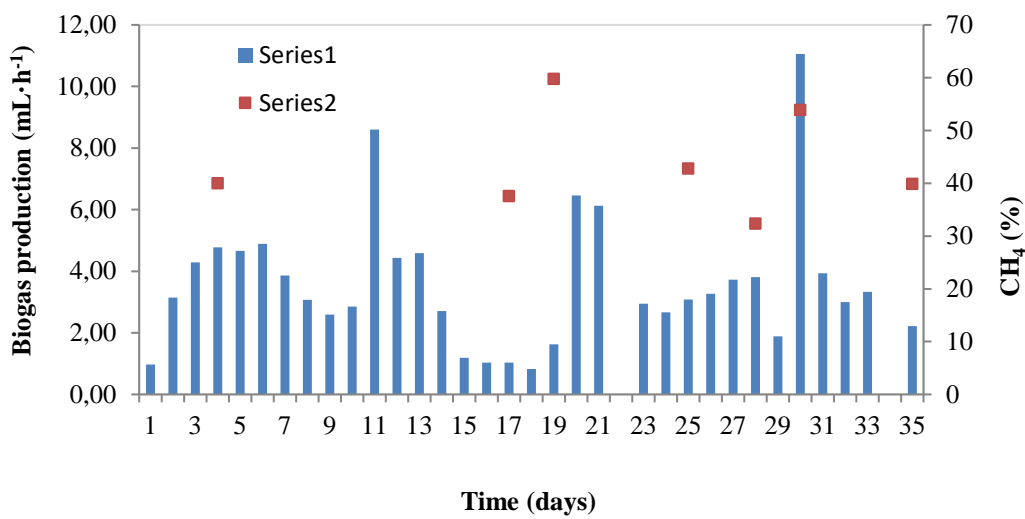**Figure 7: Solids removal during anaerobic digestion.**

Figure 8: Biogas production and methane content during anaerobic digestion.

3.3.2. Anaerobic treatment with previous struvite precipitation

Fig. 9 shows the evolution of COD during the anaerobic treatment with previous struvite precipitation. It is important to note that sCOD removal was higher for the anaerobic digestion without previous struvite precipitation (59.87%) than for the anaerobic treatment with previous struvite precipitation (52.25%).

In addition, biogas generation for anaerobic treatment with previous struvite precipitation was very low (much lower than for anaerobic treatment without struvite precipitation showed in Fig. 8) due to the low relation C/N of the samples. It was due to the organic matter settled in the struvite precipitation process.
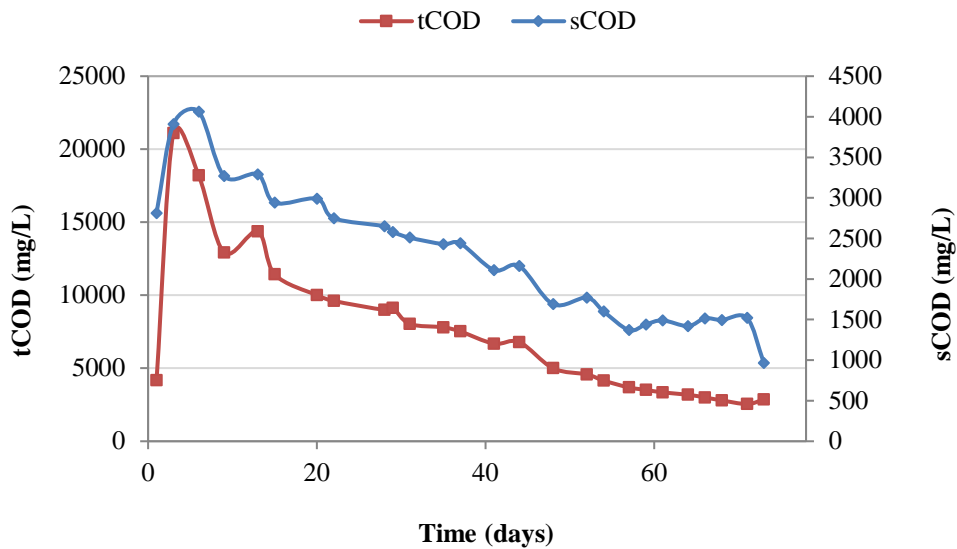

Figure 9: COD removal during anaerobic digestion with previous struvite precipitation.

4. Conclusions

From the results, conclusions about phosphorous recovery from pig slurry by struvite precipitation and anaerobic digestion of the pig slurry have been obtained.

Regarding nutrients removal (phosphorous recovery) by struvite formation, the optimal experimental conditions to obtain the highest nitrogen ammonia and phosphate removal percentages (62.01% and 66.96%, respectively) were molar concentration ratio (Mg^{+2}/PO_4^{-3}) of 2.8, pH 10 and temperature of 22ºC. However, statistical analysis showed that none of these three parameters were statistically significant in the range of values studied. The morphology of the crystals formed according to FE-SEM analysis demonstrated that the structure was typical of struvite crystals, orthorhombic. A purification process was necessary for the separation of the struvite from the carried down organic matter

On the other hand, anaerobic digestion results showed that sCOD removal efficiency were 59.87% and 52.25% for pig slurry without and with previous struvite precipitation,

respectively. Finally, the maximum biogas generated volume was around 4 mL·h^{-1} and the percentages of methane in the biogas were relatively low, ranging between 32.37 and 59.73%. No more biogas generation was obtained due to the low COD/N-NH$_4^+$ relationship in the pig slurry (around 3). A previous struvite precipitation did not improved the biogas generation. In fact, the produced biogas volume was even lower.

Summarizing, the pig slurry could be an important nutrient source by struvite precipitation. However, co-digestion is necessary for the increase of the C/N relationship for biogas production, especially if struvite is previously separated.

Acknowledgements

References

[1] Food and Agriculture Organisation of the United Nations, FAOSTAT, http://faostat.fao.org, 2016 (accessed 10.05.16).

[2] Ministry of Agriculture, Food and Environment. http:// www.marm.es., 2016 (accessed 15.06.16).

 [3] E. Ortega-Martinez, C. Zaldivar, J. Phillippi, H. Carrere, A. Donoso-Bravo. Improvement of anaerobic digestion of swine slurry by steam explosion and chemical pretreatment application . Assessment based on kinetic analysis, J. Environ. Chem. Eng. 4 (2016) 2033–2039. doi:10.1016/j.jece.2016.03.035.

[4] S. Borowski, P. Kubacki, Co-digestion of pig slaughterhouse waste with sewage sludge, Waste Manag. 40 (2015) 119–26. doi:10.1016/j.wasman.2015.03.021.

 [5] J. Bayo, M.D. Gómez-López, A. Faz, A. Caballero, Environmental assessment of pig slurry management after local characterization and normalization, J. Clean. Prod. 32 (2012) 227–235. doi:10.1016/j.jclepro.2012.04.003.

 [6] L. Martínez-Suller, A. Azzellino, G. Provolo, Analysis of livestock slurries from farms across Northern Italy: Relationship between indicators and nutrient content, Biosyst. Eng. 99 (2008) 540–552. doi:10.1016/j.biosystemseng.2007.12.002.

[7] E. Dinuccio, W. Berg, P. Balsari, Gaseous emissions from the storage of untreated slurries and the fractions obtained after mechanical separation, Atmos. Environ. 42 (2008) 2448–2459. doi:10.1016/j.atmosenv.2007.12.022.

[8] L. Hamelin, M. Wesnæs, H. Wenzel, B.M. Petersen. Environmental Consequences of Future Biogas Technologies Based on Separated Slurry, Environ. Sci. Technol. 45 (2011) 5869–5877. doi:10.1021/es200273j.

[9] M.S. Romero-Güiza, S. Tait, S. Astals , R. del Valle-Zermeno, M. Martínez, J. Mata-Alvarez, J.M., Chimenos, Reagent use efficiency with removal of nitrogen from pig slurry via struvite: A study on magnesium oxide and related by-products, Water Res. 84 (2015) 286–294. doi.org/10.1016/j.watres.2015.07.043

[10] M.S. Romero-Güiza, S. Astals, J. Mata-Alvarez, J.M. Chimenos, Feasibility of coupling anaerobic digestion and struvite precipitation in the same reactor: Evaluation of different magnesium sources, Chem. Eng. J. 270 (2015) 542–548. doi:10.1016/j.cej.2015.02.057.

[11] M. Cerrillo, J. Oliveras, M. Viñas, A. Bonmatí, Bioelectrochemistry Comparative assessment of raw and digested pig slurry treatment in bioelectrochemical systems, Bioelectrochemistry. 110 (2016) 69–78. doi.org/10.1016/j.bioelechem.2016.03.004.

[12] M. Edström, A. Nordberg, L. Thyselius, Anaerobic treatment of animal byproducts from slaughterhouses at laboratory and pilot scale, Appl. Biochem. Biotechnol. 109 (2003) 127–138. DOI: 10.1385/ABAB:109:1-3:127.

[13] E. Salminen, J. Rintala. Anaerobic digestion of organic solid poultry slaughterhouse waste – a review, Bioresour. Technol. 83 (2002) 13–26. doi: 10.1016/S0960-8524(01)00199-7.

[14] N. Marti, A. Bouzas, A. Seco, J. Ferrer, Struvite precipitation assessment in anaerobic digestion processes, Chem. Eng. J. 141 (2008) 67–74. doi:10.1016/j.cej.2007.10.023.

[15] R. Taddeo, K. Kolppo, R. Lepist. Sustainable nutrients recovery and recycling by optimizing the chemical addition sequence for struvite precipitation from raw swine slurries, J. Environ. Manage. 180 (2016) 52–58. doi: 10.1016/j.jenvman.2016.05.009.

[16] H. Huang, C. Xu, W. Zhang, Removal of nutrients from piggery wastewater using struvite precipitation and pyrogenation technology., Bioresour. Technol. 102 (2011) 2523–8. doi:10.1016/j.biortech.2010.11.054.

[17] APHA, AWWA, WEF, Standard Methods for the Examination of Water and Wastewater., in: 21st ed., Washington, 2005.

[18]   M.F.N. Secondes, V. Naddeo, V. Belgiorno, F. Ballesteros, Removal of emerging contaminants by simultaneous application of membrane ultrafiltration, activated carbon adsorption, and ultrasound irradiation, J. Hazard. Mater. 264 (2014) 342–349. doi:10.1016/j.jhazmat.2013.11.039.

[19]   D. Li, S. Liu, L. Mi, Z. Li, Y. Yuan, Z. Yan, X. Liu, Effects of feedstock ratio and organic loading rate on the anaerobic mesophilic co-digestion of rice straw and pig manure., Bioresour. Technol. 187 (2015) 120–7. doi:10.1016/j.biortech.2015.03.040.

[20]   Y. Liu, J.H. Kwag, J.H. Kim, C. Ra, Recovery of nitrogen and phosphorus by struvite crystallization from swine wastewater, Desalination. 277 (2011) 364–369. doi:10.1016/j.desal.2011.04.056.

[21]   D. Zhang, Y. Chen, G. Jilani, W. Wu, W. Liu, Z. Han, Optimization of struvite crystallization protocol for pretreating the swine wastewater and its impact on subsequent anaerobic biodegradation of pollutants., Bioresour. Technol. 116 (2012) 386–95. doi:10.1016/j.biortech.2012.03.107.

[22]   S.G. Sommer, Ammonia volatilization from farm tanks containing anaerobically digested animal slurry, Atmos. Environ. 31 (1997) 863–868. doi:10.1016/S1352-2310(96)00250-6.

[23]   P. Balsari, G. Airoldi, E. Dinuccio, F. Gioelli, Ammonia emissions from farmyard manure heaps and slurry stores—Effect of environmental conditions and measuring methods, Biosyst. Eng. 97 (2007) 456–463. doi:10.1016/j.biosystemseng.2007.03.033.

[24]   A. Capdevielle, E. Sýkorová, B. Biscans, F. Béline, M.L. Daumer, Optimization of struvite precipitation in synthetic biologically treated swine wastewater--determination of the optimal process parameters., J. Hazard. Mater. 244-245 (2013) 357–69. doi:10.1016/j.jhazmat.2012.11.054.

[25]   J. Prywer, A. Torzewska, Bacterially Induced Struvite Growth from Synthetic Urine: Experimental and Theoretical Characterization of Crystal, Cryst. Growth Des. 9 (2009) 3538–3543. doi: 10.1021/cg900281g.

[26]   E. V. Münch, K. Barr, Controlled struvite crystallisation for removing phosphorus from anaerobic digestern sidestreams, Water Res. 35 (2001) 151–159. doi.org/10.1016/S0043-1354(00)00236-0.

[27]   Z. Ye, Y. Shen, X. Ye, Z. Zhang, S. Chen, J. Shi, Phosphorus recovery from wastewater by struvite crystallization: property of aggregates., J. Environ. Sci. (China). 26 (2014) 991–1000. doi:10.1016/S1001-0742(13)60536-7.

[28]   A. Korchef, H. Saidou, M. Ben Amor, Phosphate recovery through struvite precipitation by CO2 removal: effect of magnesium, phosphate and ammonium concentrations., J. Hazard. Mater. 186 (2011) 602–13. doi:10.1016/j.jhazmat.2010.11.045.

[29]   X. Lu, K. Shih, X. Li, G. Liu, E.Y. Zeng, F. Wang, Accuracy and application of quantitative X-ray diffraction on the precipitation of struvite product., Water Res. 90 (2016) 9–14. doi:10.1016/j.watres.2015.12.014.

[30]   H. Yan, K. Shih, Effects of calcium and ferric ions on struvite precipitation: A new assessment based on quantitative X-ray diffraction analysis, 95 (2016) 310–318. doi.org/10.1016/j.watres.2016.03.032.

[31]   G. Krishna, L. Chen, Comparison on batch anaerobic digestion of five different livestock manures and prediction of biochemical methane potential (BMP) using different statistical models, Waste Manag. 48 (2016) 492–502. doi: 10.1016/j.wasman.2015.10.021.

[32]   M. Kawai, N. Nagao, N. Kawasaki, A. Imai, T. Toda, Improvement of COD removal by controlling the substrate degradability during the anaerobic digestion of recalcitrant wastewater, J. Environ. Manage. 181 (2016) 838–846. doi: 10.1016/j.jenvman.2016.06.057.

[33]   S. Borowski, J. Domansky, L. Weatherley, Anaerobic co-digestion of swine and poultry manure with municipal sewage sludge, Waste Manag. 34 (2014) 513–521. doi.org/10.1016/j.wasman.2013.10.022.

[34]   Jun Zhu, Anaerobic digestion of swine manure with crop residues, (2016). University of Minnesota Extension Engineer.

[35]   M. Cerrillo, M. Viñas, A. Bonmatí, Overcoming organic and nitrogen overload in thermophilic anaerobic digestion of pig slurry by coupling a microbial electrolysis cell., Bioresour. Technol. 216 (2016) 362–72. doi:10.1016/j.biortech.2016.05.085.