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Resource recovery from anaerobic digestate: struvite crystallisation versus ammonia stripping

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ABSTRACT

The wide application of anaerobic digestion for the treatment of organic waste streams and high-loaded wastewater results in the production of high quantities of anaerobic effluents. Such effluents are characterised by high nutrient content, this is why struvite crystallisation and ammonia stripping have gained interest as routes to nitrogen and phosphorus recovery. Pros and cons of both technologies have been analysed in this paper. Ammonia stripping coupled with absorption proved to be a suitable technical solution for the recovery and valorisation of the nitrogen contained in waste streams. Laboratory-scale experiments result in more than 80% of ammonia recovery using this technique. However, since the crystallisation process can simultaneously remove and recover more than 90% P and N in stoichiometric ratio (according struvite formulation) from waste streams, it is considered the preferred technique. Both processes are environmentally friendly and cost-effective in large-scale facilities although economics slightly favour the struvite formation.

Keywords: Ammonia stripping; Struvite crystallisation; Economics; Effluents valorisation; Nutrients recovery

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1. Introduction

Anaerobic digestion of high-loaded waste streams results in the production of effluents characterised by high nutrients content. Consequently, adequate post-treatment of these effluents is required in order to comply with the existing land application and discharge legislation in the European Union countries, when the amount of digestate produced exceeds local demand for its secure use as fertiliser.

Phosphorus and nitrogen are important macronutrients, vital for life, making a major contribution to agricultural and industrial development, but their release to natural water bodies is one of the main causes of eutrophication [1].

On the other hand, phosphorus resource is considerably limited for the utilisation of human society [2].

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Phosphorus is a non-renewable resource and there is no available substitute, nothing that can be synthetically created to replace this vital component of all biological processes.

The current consumption of rock phosphorus is over one million tons yearly as fertiliser and nitrogen fertiliser consumption might be threefold of this, this is why struvite crystallisation [3–5] and ammonia stripping [6,7] have gained interest as routes to nitrogen and phosphorus recovery. 1 kg/d of struvite, for example, would be sufficient to fertilise 2.6 ha of arable land at an application rate of 40 kg/ha/yr of phosphorus as P_2O_5 [8].

Air stripping is a method that has traditionally been used in the treatment of urban and industrial wastewater with low nitrogen concentration [9,10], but, nowadays, its application for ammonia removal in the treatment of wastewater streams with a high content in this component is given excellent results [11,12].

The crystallisation of nitrogen and phosphorus in the form of magnesium phosphate and ammonium phosphate hexahydrate ($MgNH_4PO_4•6H_2O$), also known as magnesium ammonium phosphate or struvite, is one of the techniques that can be used to remove and/or recover nutrients in effluents [13–15]. The result is a white crystalline product that can be used as the base for high quality ecofriendly fertilisers [16]. Depending on the composition of the waste effluent and the process parameters selected, struvite precipitation can be used to remove ammoniacal nitrogen (NH_4-N), phosphate (PO_4-P) or both [17].

Pros and cons of both technologies and optimum operational conditions have been analysed and discussed in this paper.

2. Materials and methods

2.1. Experimental

Lab-scale experiments were carried out to study air stripping and struvite crystallisation as methods for removing nutrients from anaerobic digestion effluents, more specifically in this case, digested pig manure proceeding from a pilot anaerobic reactor.

In the case of the ammonia stripping, a stripping tower for continuous operation (Fig. 1) was designed and constructed with the following dimensions: 102 cm height × 4.2 cm internal diameter. It was packed with plastic rings (8 mm) to promote the down flow of liquid in a thin and gentle stream. Air was supplied from near the bottom of the tower by a forced air blower. The effects of pH, temperature, air-to-liquid ratio flow and liquid recirculation flow on N removal from digested manure were investigated. The details of the experimental conditions are summarised in Table 1.

Influent pH was adjusted to the target value, in all the experiments, by the addition of lime previously to the introduction of this stream into the tower.

In the case of struvite crystallisation, and in order to investigate the effects of pH value, magnesium dosage and calcium concentration on the process, lab-scale batch experiments were carried out. Batch experiments were performed on a magnetic stirrer with a stirring rate of 800–900 rpm at room temperature of 20–22°C. The digestate with a N/P molar ratio of 8 was mixed in a beaker and its pH value was adjusted by addition of NaOH to the designed value. According to the different Mg/P (or Ca/Mg) molar ratios designed, the Mg source (or both, Mg and Ca sources) was added to the above solution. Throughout the reaction, the pH value of the mixture was kept at the defined constant value (±0.02) by NaOH supplement. Samples of the solution were removed at frequent intervals and filtrated with 0.45 μm membranes. Struvite crystals were dried naturally at room temperature.

2.2. Analysis

Ammonium nitrogen, phosphate, Mg, Ca and pH were determined following standard methods [18] recommendation. Ammonium nitrogen and phosphate were analysed colorimetrically with an UV–visible Spectrophotometer (Shimadzu, UV-1603, Japan). Ca and Mg were measured with an inductively coupled plasma optical emission spectrometer (Varian, 720-ES, US). The morphology of the struvite precipitates obtained was analysed by using SEM-EDX microscopy (FEI, Quanta-200, US).

3. Results and discussion

3.1. Precipitation of phosphorus and nitrogen as struvite

The investigations focused on the effects of two controlling factors, solution pH value and initial Mg/P molar ratio, and one main potential inhibiting factor, the concentration of Ca^{2+}, on the crystallisation of struvite. A series of experiments were performed under the conditions of the pH range of 8.5–11.5 and N:P:Mg molar ratio of 8:1:1–1.9.

The average removal efficiencies of N and P at the reaction time of 25 min are shown in Fig. 2(a). The P removal efficiency increases at pH range of 8.5–9.5 up to 90% and slightly decreases at pH range of 9.5–11.5. The profile of the N removal efficiency shows that the

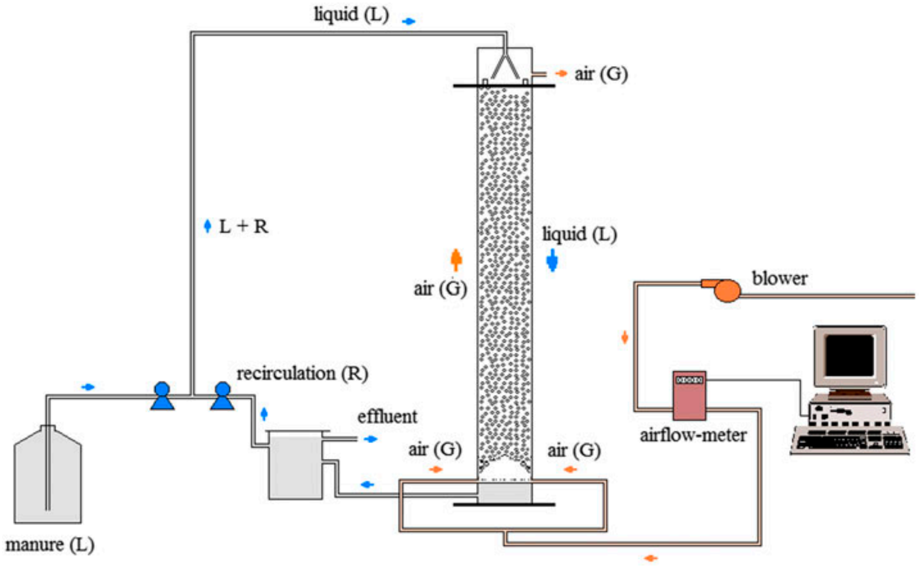

Fig. 1. Schematic diagram of the stripping experimental installation.

Table 1
Air stripping experiments

Run #	Packet size	NH_3 source	NH_3-N (mg/L)	G^a (L/h)	L^b (L/h)	R^c (L/h)	G/L (−)	L/R (−)	pH-L* (−)	pH-(R + L) (−)	$\bar{T}^d$ (°C)	NH_3-N^e (%)
1–2	Pall-8	NH_4Cl	1,718	3,000	0.9	–	3,300	–	10.6	–	20	77.4
2–2	Pall-8	NH_4Cl	1,770	3,000	0.9	3.5	3,300	0.3	10.5	9.8	20	59.5
3–2	Pall-8	Manure	2,480	2,500–3,000	0.6	–	4,200–5,000	–	10.6	–	18	77.4–79.0
4–2	Pall-8	Manure	2,490	700–3,000	0.9	–	800–3,300	–	10.7	–	18	50.0–72.5
5–2	Pall-8	Manure	2,494	500–3,000	0.6	–	800–5,000	–	12.9	–	20	59.3–79.9
6–2	Pall-8	Manure	1,221	3,000	0.9	0–0.3	3,300	−/3.0	10.8	10.5	20	74.9
7–2	Pall-8	Manure	840	2,600–3,000	0.7	0–0.8	3,700–4,300	−/0.9	12.8	12.5	18	79.3–89.0
8–2	Pall-8	Manure	965	2,400–2,800	0.7	0.2	3,400–4,000	3.5	12.7	12.5	20	78.2–84.0
9–2^+	Pall-8	Manure	1,244	3,000	0.9	0.3	3,300	3.0	11.4	11.2	18	75.2
10–2^+	Pall-8	Manure	1,304	3,000	0.9	0.3	3,300	3.0	12.5	12.4	18	75.8
11–2^+	Pall-15	Manure	1,625	3,000	1.5–0.5	–	2,000–6,000	–	10.7	–	18	55.3–79.1
12–2^+	Pall-8	Manure	1,709	3,000	1.5–0.5	–	2,000–6,000	–	10.5	–	18	54.7–73.8
13–2^+	Pall-8	Manure	1,264	3,000	0.9	0.3	3,300	3.0	10.0	9.7	20	16.3

[a] G: air flow at $\bar{T}$ = 17°C.

[b] L: fresh feed flow at T = 16–20°C.

[c] R: recirculation flow.

[d] Effluent average temperature.

[e] Ammoniacal nitrogen removed in the process.

[+] Assay with anti-foaming agent addition.

*By addition of CaO.

removal of N increases sharply during the initial reaction period and then gradually arrives at a plateau, approaching the equilibrium state, but the highest removal efficiency of only 24.3% is reached at pH 10.5.

To study the effect of Mg^{2+} on the struvite crystallisation, Mg/P molar ratios of 1.0 and 1.9 were adopted at pH 10.5, N:P molar ratio of 8:1 and reaction time of 25 min. The average P removal efficiencies at the end of reaction are shown in Fig. 2(b). It shows that the P removal efficiency rises with the increase of Mg/P molar ratio. The P removal efficiencies reach 93.7% at the Mg/P molar ratio of 1.3, but they do not rise significantly any more with further increase of Mg/P molar ratio.

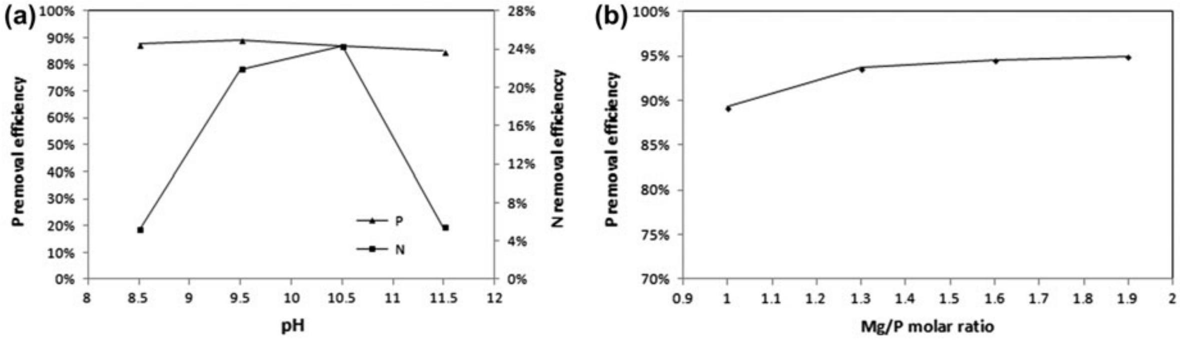

Fig. 2. Average removal efficiencies of phosphate and/or ammonium nitrogen: (a) effect of pH value; (b) effect of Mg/P molar ratio.

In the struvite crystallisation system, the presence of Ca^{2+} may influence the process due to the formation of calcium phosphate precipitate. To analyse the effect of Ca^{2+} concentration, the following solution conditions were designed: pH 10.5 and N:P:Mg molar ratio 8:1:1.6. Ca/Mg molar ratios assayed were 0.5, 1.0 and 2.0. The removal amounts of P, Mg and Ca are shown in Fig. 3. With the increase of Ca/Mg molar ratio, both the removal of Mg and the removal of Ca increase significantly. The amount of removed P decreases slightly.

Fig. 4 shows the SEM analyses of the precipitates obtained. Needle-like crystals are observed and the crystal length is about 20–80 μm. The crystal retention time in the reactor appeared to have a significant effect on the crystal size, hardness and morphology.

3.2. Ammonia stripping and scrubbing

The details of the experimental conditions are summarised in Table 1 where it also shows the range of ammonia removed in each experiment.

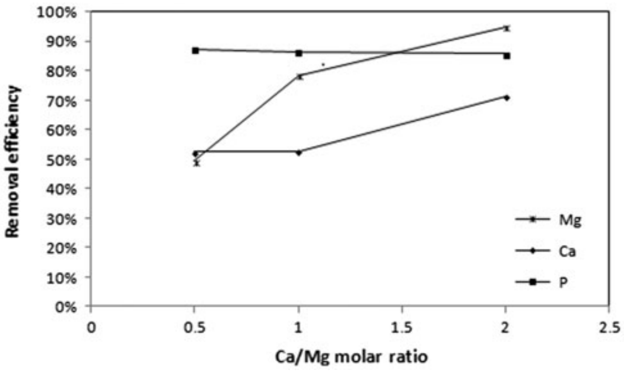

Fig. 3. Effect of Ca/Mg molar ratio on P, Ca and Mg removal.

The rate between ammonia and dissociated ammonium concentrations is a function of pH. Working at high pH values, the balance $[NH_3]/[NH_4^+]$ moves towards the formation of molecular ammonia, favouring its desorption. Nevertheless, an excessive increase of the pH supposes an additional cost of lime that is not advisable for the economy of the process. For this reason, tests at different pH values have been carried out in order to find a balance between efficiency of the process and economic cost.

Experimental results (Table 1) demonstrate that from pH 10.5 down, the higher the influent pH, the higher the removal efficiency achieved. However, above pH 10.5, the ammonia removal efficiency was not greatly influenced by pH, but it supposes a considerable increase in the exploitation costs because of the exponential extra lime consumption required to reach higher pH levels (e.g. around 3 g CaO/L extra per unit of pH increased for a digestate stream with 2,500 mg NH_3-N/L) and the appearance of heavy calcium carbonate scale within the stripping tower.

In regard to the air flow entering the system, all the results show higher levels of ammonia removal when an increase of air-to-flow ratio occurs (Fig. 5). Fig. 6 shows the air-to-liquid rate influence on ammonia desorption, as a function of feed pH. It can be observed that, for low *G*/*L* rate values, an increment of pH of the feed over 10.6 increases, in an appreciable way, the amount of desorbed ammonia. Nevertheless, at higher values of *G*/*L* rate, the influence of pH is lower.

Liquid recirculation in the system supposes, besides the extra cost of a new pump, the risk of pH decreasing in the final liquid stream entering the tower, with the consequent decrease in the yield of the desorption process (Table 2). There are two ways in order to avoid that the pH value decreases below 10.5 (value defined as optimal) when the system is

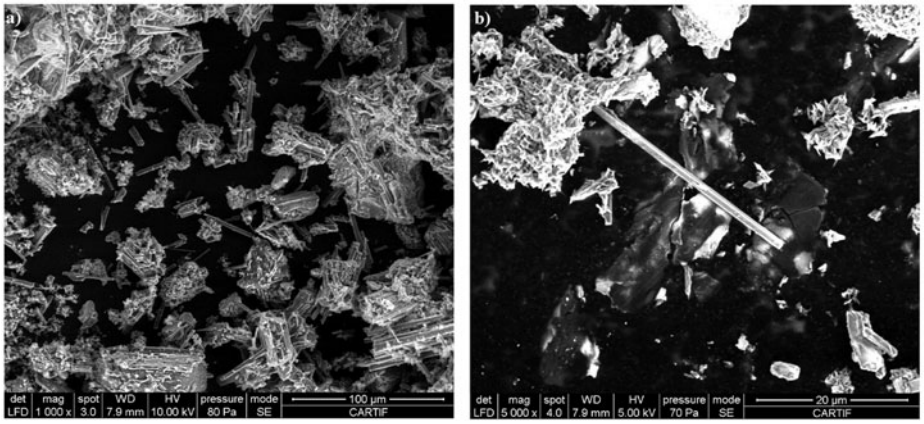

Fig. 4. SEM images of struvite crystals: (a) 1,000×; (b) 5,000×.

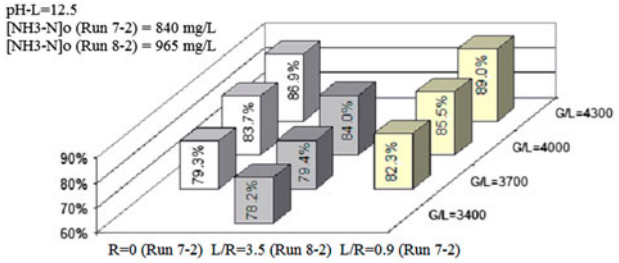

Fig. 5. NH_3-N removal at different L/R and G/L rates.

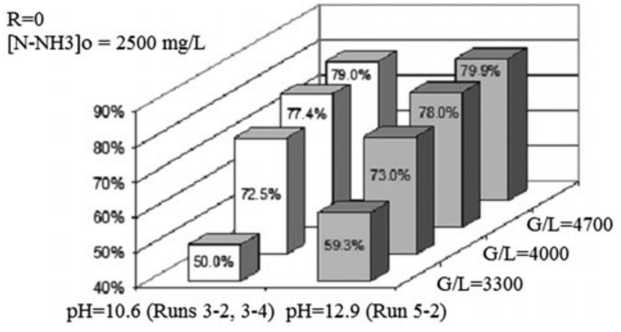

Fig. 6. NH_3-N removal at different pH levels and G/L rates.

working with recirculation: operating at low recirculation flow, do not altering too much the pH of the original feed; or using a feed with pH higher than 11, but this option increases the lime consumption and the risk of scaling. The two mentioned options allow obtaining nitrogen removal yields slightly higher than the obtained when the system works without recirculation (Fig. 5); however, the recirculation of the liquid in the desorption tower is not economically or operationally justified. The additional expenses that suppose to increase pH over 10.5, by the excessive lime consumption or by the increase of the cleaning necessities and maintenance of the tower, cause that this option is unacceptable.

Table 2
Effects of liquid recirculation in the ammonia stripping process

	pH-L	pH-(L + R)	% NH_3-N
Run 1–2 (R = 0)	10.6	10.6	77.4
Run 2–2 (L/R = 0.3)	10.5	9.8	59.5

The gas phase, charged with ammonia was then put in contact with a strong acid solution (H_2SO_4 or HNO_3). The result was a nitrogen fertiliser without added P (which may otherwise not to be necessary), that is stable and can be sold or applied by the farmer when and in quantities beneficial to the crop.

3.3. Comparative economic feasibility study

Methods of recovery nutrients such as fertilisers vary, not only in efficacy, but also in costs. In the case of ammonia stripping, the action of recovering nitrogen from waste effluents will produce financial benefits to farms or organic waste digesters of sufficient size [19]. Ammonia has been traditionally recovered with sulphuric acid to produce ammonium sulphate but, in terms of net revenue and requirements for storage of the product, nitric acid is, in most of the cases, preferable to sulphuric acid as a medium for ammonia capture. Furthermore, the high N-concentration of ammonium nitrate makes it a higher value product, even as liquid fertiliser. Average market prices for ammonium nitrate-based fertilizers (26%) and ammonium sulphate-based fertilizers (21%) in 2013 were 295

Table 3
Comparison of struvite crystallisation and ammonia stripping techniques

	Products	% recovery	Operational problems	Economical viability	Estimated N and P recovery costs
Struvite crystallisation	Struvite crystals (slow-release fertiliser)	90–94% P 20–25% N	Crystallisation in piping/equipment interferences (Ca^{2+}, CO_3^{2-}, …)	Can be profitable in large-scale facilities (economy of scale)	1,753 €/kg [22]
Ammonia stripping	$(NH_4)_2SO_4$ or $(NH_4)NO_3$ (fertiliser solutions)	0% P 80–90% N	Scaling corrosion	Can be profitable in large-scale facilities (economy of scale)	1,927 €/kg [21]

and 255 €/t, respectively [20]. A detailed economic analysis of manure stripping and recovery with nitric acid [21] estimated the cost of NH_4^+-N recovery as 1,927 €/kg $NH_4^+\text{-}N_{removed}$.

The cost of recovering nitrogen and phosphorus as struvite depends on several factors, such as the initial concentration of nitrogen in the effluent, recovery percentage, molar ratio of chemicals used in the process, and the type of chemicals selected as the sources of Mg and Yetilmezsoy et al. [22] carried out a detailed economic analysis of struvite crystallisation process and demonstrated that the cost of N and P recovery was estimated as 1,753 €/kg $(NH_4^+\text{-}N+PO_4\text{-}P)_{removed}$. On the other hand, struvite produced by recovering phosphate is sold in the UK, Japan and Canada as a "green recycled" product at 600 €/ton [23]. However, in certain markets (i.e. in Japan) much higher sales prices (i.e. 2,500 €/ton) can be achieved for specialised applications. This process is, thus, viable when associated environmental benefits and the market value for struvite is taken into account in large-scale facilities.

4. Conclusions

The results show essential and practical knowledge on the process of struvite crystallisation, which would be important for the practice of N and P recovery from AD digestate: the optimum pH value for struvite crystallisation is in the range of 9.5–10.5; the phosphorus removal efficiency increases with the increase of Mg/P molar ratio; the optimum Mg/P molar ratio is 1.3, and excessive Mg dosage does not show significant effect on the efficiency improvement of struvite crystallisation; the co-existing of Ca in solution does not strongly affect P removal but could disturb the morphology and purity of the product.

The tests undertaken showed that the air-stripping method achieves very high yields of ammonia removal from the digested liquid fraction of swine manure, operating at moderate temperatures (16–20°C). The best result obtained from the study was 89% ammonia reduction at 18°C, pH of 12.5, without liquid recirculation and with a G/L rate of 4,300.

A summary of the experimental results is presented in Table 3.

Nitrogen and phosphorus in waste effluents are a burning environmental issue of the present world since they are considered highly polluting when discharged into the environment. However, effluents which contain a high amount of phosphorus and nitrogen would be a good source of fertilisers if these elements are properly recovered.

Ammonia stripping coupled with absorption proved to be a suitable technical solution for the recovery and valorisation of the nitrogen contained in waste streams. However, since the crystallisation process can simultaneously remove and recover N and P from waste streams, it is considered the preferred technique. This process is environmentally friendly and cost-effective in large-scale facilities. Struvite contains 12.6% P, 5.7% N and 9.9% Mg, has slow release rate, and has less evaporative loss of N compared with other N-rich fertilisers.

For both techniques, it is essential to put attention on fertilising value of the end-products and marketing value towards industrial end-users. To be economically profitable, the price allocated to the recovered nutrients should be in accordance to the market price of N and P in mineral fertilisers.

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