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Air stripping of ammonia from pig slurry: characterisation and feasibility as a pre- or post-treatment to mesophilic anaerobic digestion

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Abstract

The objective of the present paper has been to study the effect of pig slurry waste type, fresh or anaerobically digested, and the effect of initial pH on ammonia air stripping from pig slurry waste at high temperature (80 °C). Stripping process as pre- or post-treatment to anaerobic digestion has been also evaluated. Treatment performances differ according to pig slurry type. When fresh pig slurry is used, despite working at 80 °C, a high initial pH (11.5) is required for complete ammonia removal. On the other hand, for digested pig slurry, complete ammonia removal without pH modification is possible and organic matter significantly less contaminates recovered ammonia salt. Batch anaerobic tests showed that ammonia air stripping is not an advisable pre-treatment to pig slurry anaerobic digestion.

1. Introduction

Processing pig slurry, whether on a single-farm or regional scale, involves several basic treatment steps. The inclusion of anaerobic digestion in pig slurry treatment strategy offers several advantages. However, its low hydrolysis and biogas production rates may limit its economic feasibility. The high ammonia nitrogen content of pig slurry has been reported as the main reason for this low biogas production (Angelidaki and Ahring, 1993, 1994; Bonmatí, 1998; Hansen et al., 1998). When energy cogeneration is applied, the feasibility of the process also depends on possible profitable uses for the recovered heat.

The recovery of valuable products for applications outside the agricultural sector or for improving crop nutrient management efficiency has become a necessity in geographical areas with high animal farming density (Rulkens et al., 1998). Treatments for nitrogen removal or recovery have become processes of concern for improving waste management in areas with a structural nitrogen surplus. Ammonia removal as a pre-treatment of anaerobic digestion could also enhance its performance, decreasing its concentration in the feeding substrate

Air stripping in combination with absorption, can be used to remove and recover ammonia from pig slurry. Ammonia is transferred from the waste stream into the air, then absorbed from the air into a strong acid solution (typically sulphuric acid), thereby generating an ammonium-salt, which can be crystallised.

The amount of ammonia that can be stripped from a liquid waste, or absorbed in the acidic solution is, to a great extent, dependent on two thermodynamic equilibria: ammonia gas/liquid equilibrium and ammonia dissociation equilibrium in the liquid. Ammonia equilibrium in aqueous solution is pH and temperature dependent, and free ammonia concentration is expressed with the following equation,

$$[NH_3] = \frac{[NH_3 + NH_4^+]}{1 + \frac{[H^+]}{K_a}} = \frac{[NH_3 + NH_4^+]}{1 + 10^{pK_a - pH}}, \quad (1)$$

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where $[NH_3]$ is the free-ammonia concentration, $[NH_3+NH_4^+]$ is the total ammonia concentration, $[H^+]$ is the hydrogen ion concentration, and K_a is the acid ionisation constant for ammonia. pK_a can be expressed as function of temperature T by the following equation,

$$pK_a = 4\times10^{-8}\times T^3 + 9\times10^{-5}\times T^2 - 0.0356 \times T + 10.072, \quad (2)$$

obtained by polynomial regression of data from Lide (1993). The higher the pH and temperature, the higher the free ammonia fraction.

Ammonia air stripping in combination with absorption has been considered a good option when treating different types of waste: liquid fraction of dewatered sewage sludge (Janus and van der Roest, 1997; Thorndahl, 1992; Watergroup, 1990), urea fertiliser plant wastes (Minocha and Prabhakar, 1988; Kabdasli et al., 2000), landfill leachate (Cheung et al., 1997) and condensates from a sugar beet factory (Schiweck and Nähle, 1990; González and García, 1996). In all these cases, the process was performed at high pH values.

Liao et al. (1995) and Viel (1996) studied ammonia air stripping from pig slurry at room temperature (22 °C). At this temperature, a high pH (10.5–11.5) was required to obtain high ammonia removal efficiencies, and the excess lime caused problems of calcium carbonate scaling and, as a result, the efficiency of the system decreased and severe maintenance problems arose (Liao et al., 1995). However, if air stripping is performed at high temperature, the high buffering capacity of the pig slurry could probably maintain pH at the needed value, and the amount of alkali could be reduced.

The main limiting factor for ammonia air stripping at high temperature is the availability of a cheap thermal energy source. When combining anaerobic digestion with a stripping/absorption process, the biogas produced during anaerobic digestion can partially or totally provide the heat needed for stripping at high temperature. The aim of the present investigation was to evaluate the effects of pig slurry type (fresh or anaerobically digested), and of pH on ammonia air striping from pig slurry at high temperatures (80 °C), and to study the feasibility of the process as a pre- or post-treatment to mesophilic anaerobic digestion.

2. Methods

2.1. Raw material

Two types of pig slurry were used: fresh slurry from a pig farm, and effluent from a lab scale mesophilic anaerobic continuous stirred tank reactor (CSTR), fed with similar pig slurry (Table 1). Before the stripping process, the slurries were filtered through a 200-μm sieve. pH was adjusted with calcium hydroxide. After 12 h of sedimentation, the pH of the clarified stream was re-adjusted to the desired value.

2.2. Air stripping/absorption experiment

An isothermal wet wall glass column was used for air stripping tests (97.5 cm height×5 cm internal diameter), in semi-batch conditions, batch for the liquid phase and continuous flow for the gaseous phase (Fig. 1). Four litres of pig slurry were used in each experiment. The effluent was collected at the bottom of the column and recycled to the top using a peristaltic pump. Air was supplied by an air blower. Temperature was set at 80 °C. Pig slurry stream and air were preheated in a thermostatic bath. The column was insulated to maintain the desired temperature. Air and liquid flows were set at 20 and 0.266 ml/min, respectively. Air charged with ammonia was bubbled through a strong acid solution. Two serial ammonia traps were used to ensure that all the ammonia was recovered. The absorption process was performed at room temperature. Slurry was sampled every hour at the slurry sample port (8 in Fig. 1). Ammonia recovered in the two ammonia traps was sampled and analysed at the end of the experiment (3 and 4 in Fig. 1).

Six treatments were carried out (three replications of each). Two types of pig slurry, previously described, were used and three different initial waste stream pHs were tested. In order to contrast the effect of the usual components of pig slurry against the specific ones controlling primarily the stripping process (ammonia and alkalinity), three more treatments were carried out with a reference ammonia solution (RAS). The composition of the RAS was as follows: 3.5 gNH_4^+–N/kg and 15

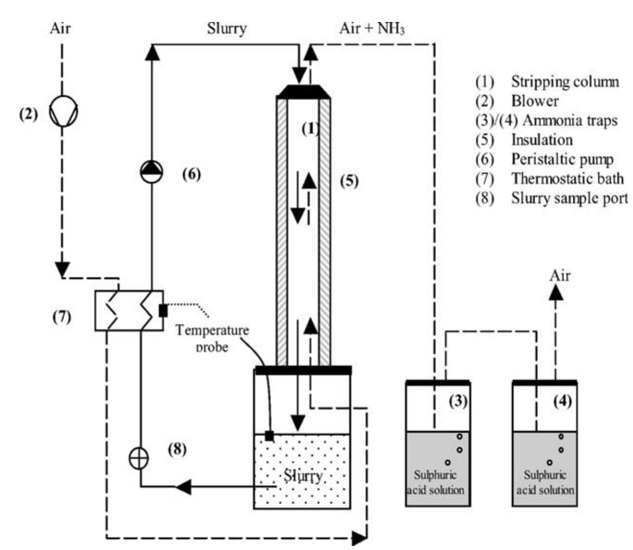


Fig. 1. Schematic representation of the laboratory set up of the semi-batch stripper/absorber system.

$gCaCO_3$/kg. The main characteristics of the treatments are shown in Table 2.

Ammonia removal efficiencies were calculated by performing a mass balance. In order to compare the ammonia removal rate of the different treatments, ammonia nitrogen evolutions through time (per cent removal) were fitted to a non-linear model, expressed as

$$E(t) = Em \cdot \left(1 - e^{-kt}\right), \tag{3}$$

where E (t) is the ammonia removal efficiency (%) as a function of time t (h), k is the ammonia removal rate (h^{-1}), and Em is the maximum ammonia removal efficiency, set initially at 100%.

2.3. Batch anaerobic test

A batch anaerobic test was performed, as described later, in order to determine whether ammonia air stripping had a positive effect on further slurry anaerobic digestion.

The batch reactors were 120-ml glass vials filled with 54 g of substrate and 6 g of inoculum, and flushed with N_2/CO_2 (80:20) for 3 min. These were tightly closed with rubber stoppers and aluminium crimps and placed in an incubator for 80 days at 35 °C. The inoculum used came from a steady state sewage sludge anaerobic reactor. The headspace gas composition was analysed every 3–4 days. Volatile fatty acids (VFA) were analysed each week. At the beginning and at the end of the experiment the following parameters were analysed: total Kjeldhal nitrogen (TKN), ammonia nitrogen (NH_4^+–N), total and partial alkalinity (TALK, PALK), alkalinity ratio (RALK), and chemical oxygen demand (COD). Additionally, calcium (Ca), copper (Cu) and zinc (Zn) were analysed at the beginning of the experiment.

Four treatments were carried out, as can be seen in Table 3, and a further treatment with water and inoculum was used as a control. Three replications per treatment were made.

Volumetric methane production rates referred to the initial substrate, to the initial volatile solids (VS) and to the initial COD, as well as the substrate conversion rates to methane (M%), VFA (VFA%), and acidification (A%), according to Field et al. (1988), were used for the comparative analysis.

Table 1
Characterisation of the pig slurries used in the air stripping experiments (average of three samples)

	Units	Fresh slurry	Anaerobically digested slurry
pH		7.5	8.4
Total solids (TS)	g/kg	52.97	31.72
Volatile solids (VS)	g/kg	35.18	17.17
Chemical oxygen demand (COD)	g/kg	70.59	41.23
Ammonia nitrogen (NH_4^+–N)	g/kg	3.39	3.68
Total Kjeldahl nitrogen (TKN)	g/kg	5.63	4.73
Organic nitrogen (Norg)	g/kg	2.24	1.05
Total alkalinity (TALK)	g $CaCO_3$/kg	13.42	14.51
Partial alkalinity (PALK)	g $CaCO_3$/kg	5.92	11.76
Alkalinity ratio (RALK)		0.55	0.19
Total volatile fatty acids (TVFA)	g acetate/kg	10.84	0.24

Table 2
Treatment characteristics of the air stripping experiments

Treatment identification	Raw material	Initial pH	Duration of experiment (h)	Replications
T1	RAS[a]	7.5	3	3
T2	RAS	9.5	4	3
T3	RAS	11.5	5	3
T4	Filtered fresh slurry	Non modified (7.7)	4	3
T5	Filtered fresh slurry	9.5	4	3
T6	Filtered fresh slurry	11.5	4	3
T7	Filtered ana. dig. slurry	Non modified (8.5)	5	3
T8	Filtered ana. dig. slurry	9.5	4	3
T9	Filtered ana. dig. slurry	11.5	4	3

[a] RAS, reference ammonia solution.

2.4. Analytical methods

TKN, ammonia nitrogen, pH, total solids (TS), VS, and COD were all analysed by standard methods (APHA, 1995). Partial and total alkalinity (PALK, TALK) were analysed by titration with HCl to pHs 5.75 and 4.3, respectively. Alkalinity ratio (RALK) was calculated according to Iza (1995). Ca, Cu and Zn were analysed with a flame atomic absorption spectrometer (FAAS). Volatile fatty acids were analysed by capillary gas chromatography with a FID detector. Biogas composition was determined with a packed column gas chromatography with a TCD detector.

2.5. Statistical analysis

Statistical analysis was performed using the SAS software (SAS Institute, 1989). A one way ANOVA test was carried out. When this analysis indicated significant differences and interaction was significant, least square means test was performed, with a significance level of $\alpha = 0.05$. Non-linear regression analysis was performed using Statgraphics Plus software and using the Levernberg–Marquardt algorithm.

3. Results and discussion

3.1. Filtration and pH adjustment of the raw material

When fresh pig slurry was filtered, a decrease in COD and total P was observed in the liquid fraction. However, as expected, since ammonia nitrogen is a soluble substance, its concentration in the liquid fraction increased (Fig. 2a). Similar results were reported by Møller et al. (2000). The behaviour of the digested pig

Table 3
Characterisation of the different treatments in batch anaerobic tests

Treatment identification	P1	P2	P3	P4
Air stripping pre-treatment	NO	YES (initial pH = non-modified)	YES (initial pH = 9.5)	YES (initial pH = 11.5)
pH	7.7	8.5	8.8	9.9
TS (g/kg)	50.73	44.27	62.92	79.13
VS (g/kg)	33.11	27.43	38.36	44.88
COD (g/kg)	70.59	64.69	83.12	77.30
TKN (g/kg)	5.31	4.32	4.48	3.42
NH_4^+–N (g/kg)	3.24	2.40	2.15	1.18
TALK (g $CaCO_3$/kg)	8.90	7.88	6.50	5.48
PALK (g $CaCO_3$/kg)	4.30	2.95	2.18	2.10
RALK	0.52	0.62	0.67	0.62
TVFA (g acetate/kg)	10.84	11.57	13.65	15.06

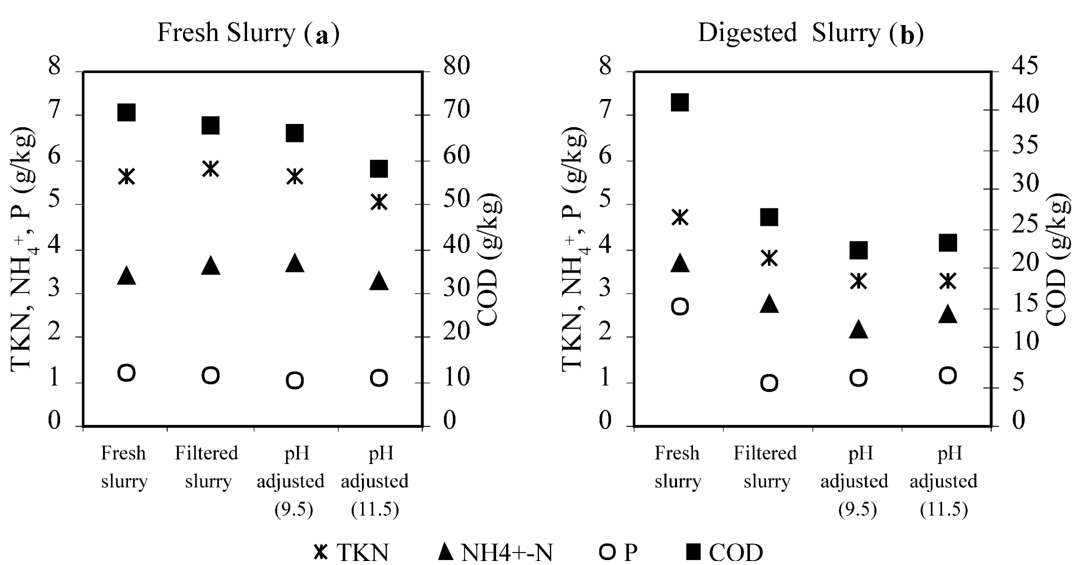


Fig. 2. Effect of filtration and pH adjustment on fresh pig slurry (a) and digested pig slurry (b). Average of three replications.

slurry was very different. The observed decrease in COD and total P was much larger than that with the fresh slurry. Moreover, ammonia nitrogen concentration in the liquid fraction also decreased (Fig. 2b). This could be explained by the high biomass content of the digested slurry, which could lead to ammonia becoming trapped or adsorbed in the matrix of the suspended solids removed by the sieve. Experiments performed by the authors (results not shown) with a pilot plant centrifuge also resulted in a decrease in the ammonia concentration in the liquid fraction when treating anaerobic digested slurry.

pH adjustment of the fresh slurry led to a decrease in TKN, COD and total P. This decrease was larger when pH was adjusted to 11.5 than when it was adjusted to 9.5 (Fig. 2a). This was in accordance with experiments performed with landfill leachate (Cheung et al., 1997). pH adjustment with $Ca(OH)_2$ led to a reduction in total P (85–93%) and COD (20–48%) in the liquid fraction. However, these values were much higher than those reported with fresh slurry (total P removal = 7.4–12% and COD removal = 2.8–15%). The large amount of organic matter and the observed poor settleability of precipitates and formed flocs in fresh manure could explain this difference. The effect of pH adjustment on the digested slurry also differed from that on the fresh slurry. When pH was adjusted to 11.5 no further TKN, COD and total P decrease was reported for digested slurry (Fig. 2b). The different nature of the organic matter in the digested slurry could explain this different behaviour.

pH adjustment led to a slight decrease in ammonia nitrogen content, in both kinds of slurry. This decrease could be attributable to its volatilisation during the settling process, as pointed out by Watergroup (1990).

3.2. Ammonia removal

Results obtained in the performed experiments are presented separately for each substrate. Ammonia nitrogen, pH and alkalinity evolutions are discussed in this section.

3.2.1. Reference ammonia solution

The evolutions of ammonia concentration and ammonia removal in the experiments with the reference ammonia solution are shown in Fig. 3. In spite of the different initial pHs, ammonia was totally removed in all treatments. However, the initial pH greatly affected ammonia removal rates. On increasing the initial pH from 7.5 to 11.5, the time needed for complete ammonia removal diminished from 5 to 3 h.

On increasing temperature (pre-heating step) there was a change in pH (Fig. 4). In treatment T1, pH increased to 8.2, in treatment T2 and T3 pH decreased to 8.8 and 10.5, respectively. Changes in pH could be expected as temperature affects the chemical equilibria between substances leading to a new chemical equilibrium that modifies the pH.

In spite of the observed ammonia removal, the pH increased slightly throughout the process in treatment T1 and T2, but did not change in treatment T3. This could possibly be explained by the simultaneous evaporation of water that was also observed. Water evaporation led to an increase in the concentration of $CaCO_3$, thereby causing a slight increase in pH. The fact

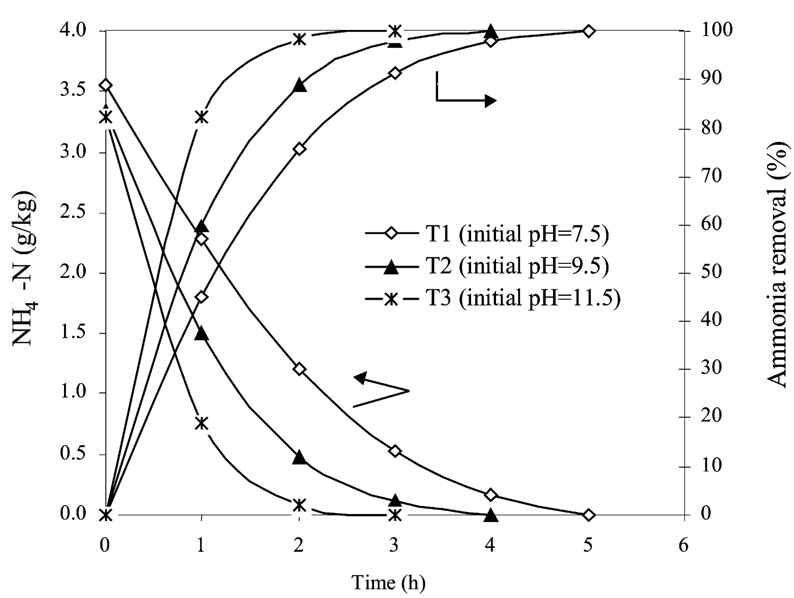


Fig. 3. Ammonia nitrogen concentration and ammonia removal in experiments with the reference ammonia solution ($T = 80$ °C).

that pH did not increase in treatment T3 could be explained by the formation of $CaCO_3$ precipitates, leading to a stable equilibrium and therefore a stable pH.

These results showed that when ammonia stripping is performed at high temperature (80 °C) and there are no other components modifying chemical equilibria, an initial pH of 7.5 is enough for total ammonia removal.

3.2.2. Fresh pig slurry

Results of the experiments with fresh pig slurry are shown in Fig. 5. Ammonia nitrogen concentration decreased with time. After 3 h, a slight increase in ammonia concentration was observed in treatment T4 and T5 (Fig. 5a). This could be explained by the evaporation of water, throughout the stripping process, and by the low ammonia removal rate due to the fall in pH (Fig. 5c) which reduced the ammonia volatility by shifting its dissociation reaction towards the ionic form.

This was in accordance with the different ammonia removal efficiencies observed depending on the initial pH (Fig. 5b). A final (after 4 h) removal efficiency of 65, 69 and 98.8% was recorded for treatments T4 (non-modified pH), T5 (initial pH = 9.5) and T6 (initial pH = 11.5), respectively.

Alkalinity also decreased in all treatments (Fig. 5d). The formation and precipitation of salts (Cheung et al., 1997) and/or CO_2 stripping (Collivignarelli et al., 1998) may explain this reduction. This loss of buffering capacity during the stripping process together with the high VFA concentration (see Table 1) resulted in the observed fall in pH. Moreover, the low VFA volatility at these pHs together with water evaporation, led to a slight increase in its concentration.

3.2.3. Digested pig slurry

Results from the experiments performed with anaerobic digested slurry are shown in Fig. 6. Ammonia nitrogen concentration greatly decreased with time (Fig. 6a). Final ammonia concentrations below 0.12 g/kg, and ammonia removal efficiencies above 96%, were reported in all treatments (Fig. 6b). Experiments performed with landfill leachate showed that it was possible to achieve high ammonia removal efficiencies even without base dosage, if temperature was maintained at between 60 and 70 °C (Collivignarelli et al., 1998).

pH evolution (Fig. 6c) showed a similar pattern to that reported in the reference ammonia solution experiments. pH slightly increased in treatment T7 (non modified pH) and T8 (initial pH = 9.5), and remained practically constant in treatment T9 (initial pH = 11.5).

However, alkalinity decreased with time (Fig. 6d), as reported with fresh slurry, but this did not lead to a fall in pH. The low concentration of VFA (see Table 1) could explain this fact, and also the differences in behaviour between the two slurry types.

3.3. pH effect on ammonia removal rates

Results from ammonia air stripping were fitted to a non-linear model [Eq. (3)], in order to compare the ammonia removal rates of the different treatments performed.

The removal rates (k) obtained were statistically analysed with double factorial design (initial pH and stream type) and three levels for each. The results from the statistical analysis are shown graphically in Fig. 7.

As seen in Fig. 7, the different pH levels had different effects on ammonia removal rates, according to the

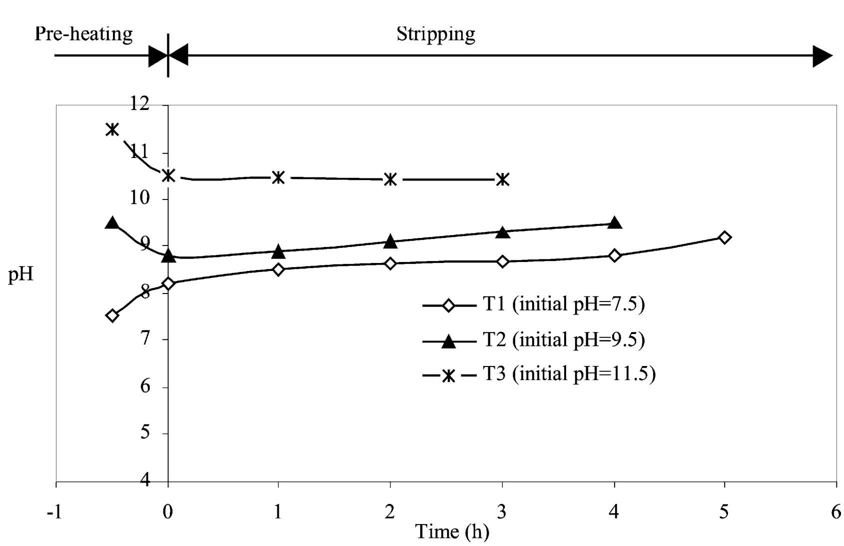


Fig. 4. pH evolution in experiments with the reference ammonia solution.

substrate. When the reference ammonia solution was used, an increase in the initial pH led to an increase in ammonia removal rates. This was in accordance with experiments performed by other authors with similar reference ammonia solution (Katehis et al., 1998). When ammonia air stripping was performed at 75 °C, the process became pH insensitive with a pH of between 10 and 10.5. The pH value in treatment T3 was 10.5 during stripping process (see Fig. 4).

In the experiments performed with fresh pig slurry, although the initial pH was set at 9.5, ammonia removal rates did not increase significantly (letters a–c in Fig. 7). A high initial pH (11.5) was necessary to obtain a significant increase in the ammonia removal rate. The anaerobically digested slurry showed a different behaviour. On setting the initial pH at 9.5 the ammonia removal rate increased significantly, but no further increase was reported when initial pH was set at 11.5. It can be therefore concluded that air stripping of digested pig slurry at 80 °C became independent of pH with a pH of around 9.5, under these experimental conditions.

As it can be seen in Fig. 7 (letters x–z), at a certain pH, ammonia removal rates for the reference ammonia solution were significantly higher than those reported for pig slurry. Digested pig slurry showed faster removal rates than fresh pig slurry, except at the initial pH of 11.5.

A final hypothesis could be made from the results obtained in the experiments with fresh pig slurry. In treatment T4 (initial pH = non-modified) and T5 (initial pH = 9.5), the observed fall in pH, and the subsequent decrease in free ammonia, could not allow a complete ammonia removal. In such a case the assumption that the maximum ammonia removal efficiency (*Em*) is 100% would not be valid. In order to test this hypothesis, experimental data were fitted to the same model [Eq. (3)] but taking *Em* as a parameter.

Results from the non-linear regression analysis showed that in all the treatments except T4 and T5, the predicted parameters did not significantly differ with respect to the predicted parameters previously reported. The predicted *Em* in treatments T4 and T5 were 79 and

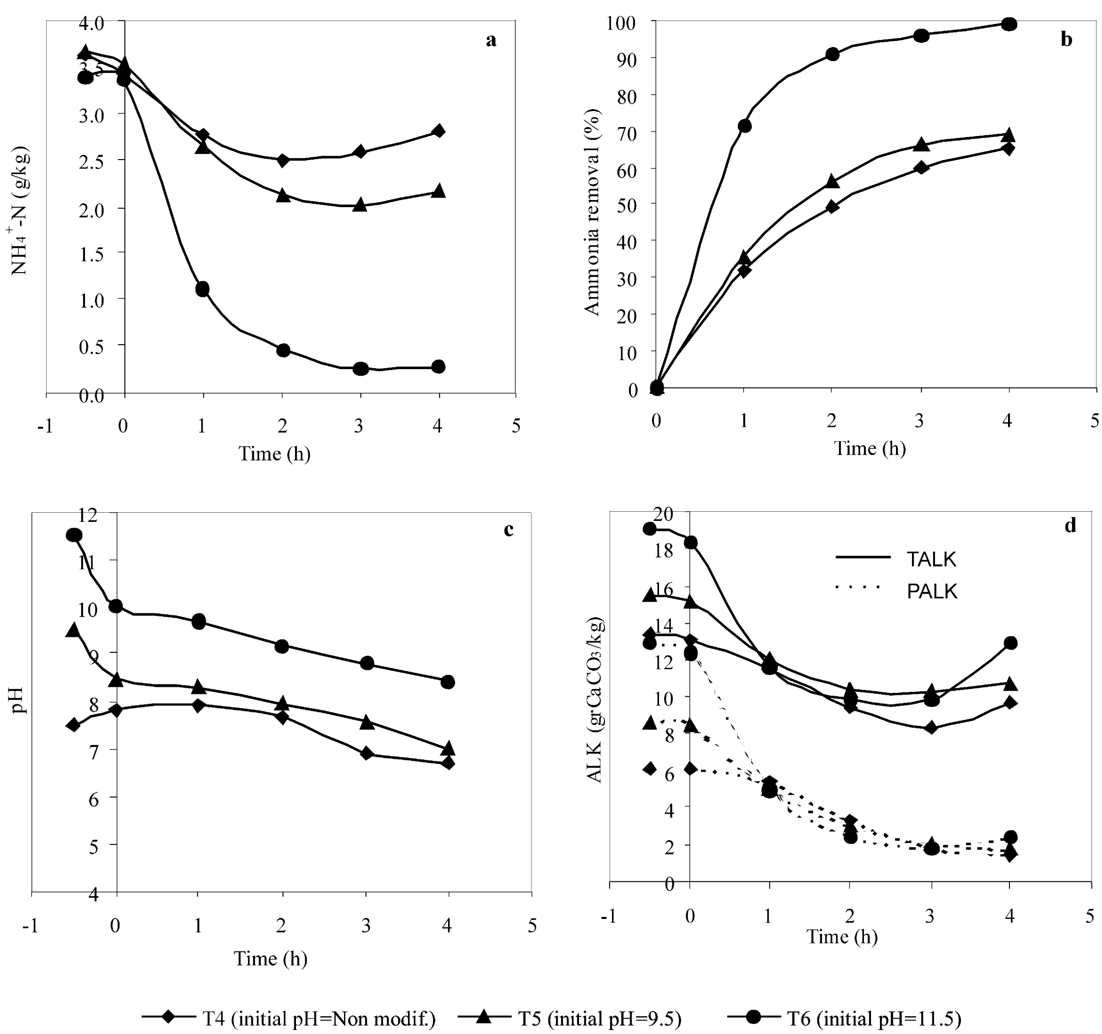


Fig. 5. Ammonia nitrogen concentration, percentage ammonia removal, pH, TALK and PALK evolutions in fresh pig slurry experiments.

87%, respectively. This shows that if air stripping is performed with fresh pig slurry, a high initial pH is necessary in order to achieve a complete ammonia removal. Markos et al. (1997) reported similar results: when a stream with a high content of acidic substances was air-stripped an increase in ammonia concentration was reported.

3.4. Characteristics of the ammonia-salt water

Air charged with ammonia and volatile organic matter was bubbled into a strong acid solution (H_2SO_4). Two serial ammonia traps were used (see Fig. 1).

Water evaporation led to an increase in COD concentration in the slurry. Even so, the mass balance showed that 26–30% of the COD was removed by air stripping in experiments with fresh pig slurry and 20–21% in experiments with digested pig slurry. This is worthy of comment, because this organic matter should, in theory, have been transferred to the ammonia-salt water obtained in the absorption process.

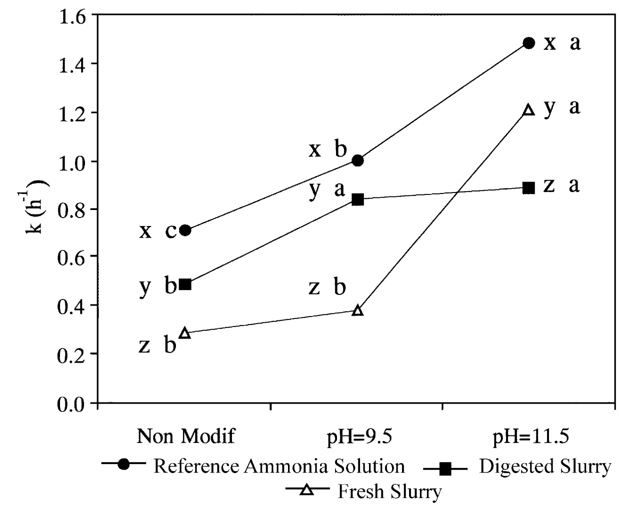


Fig. 7. Ammonia removal rates for the different pHs and substrate types. Values with the same letter are not statistically different using the least squares means test (5% significance), letters "a–c" are used to compare initial pHs for the same substrate, letters "x–z" are used to compare substrates with the same initial pH.

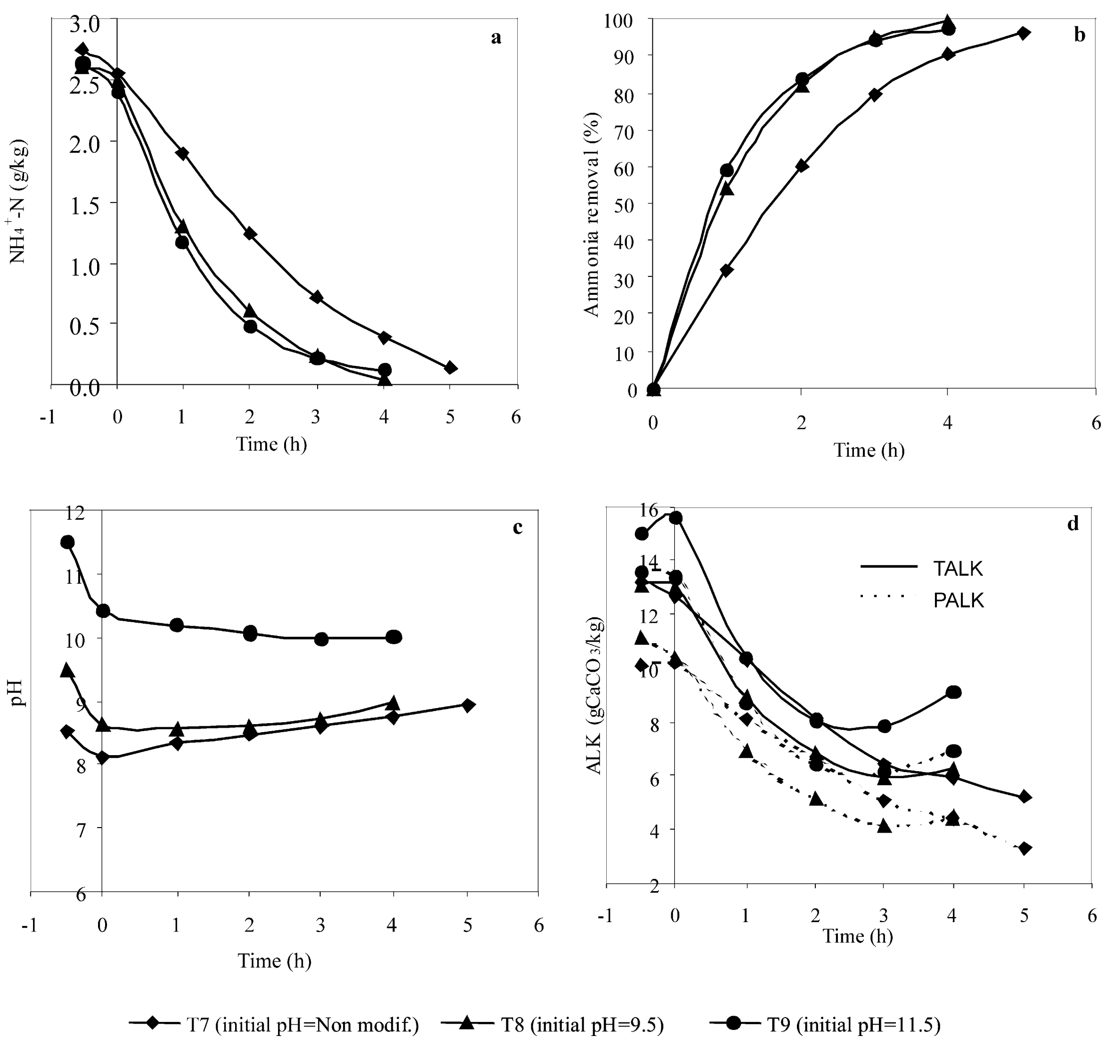


Fig. 6. Ammonia nitrogen concentration, percentage ammonia removal, pH, TALK and PALK evolutions in anaerobic digested pig slurry experiments.

The ammonia mass balance showed that between 6 and 16% of the ammonia was not recovered. This could have been attributable to experimental error since ammonia was not detected in the second ammonia trap in any of the experiments. On the other hand, only 1.8–5% of the COD removed in the air stripping process was recovered in the absorption process. This showed that the majority of the COD could not be fixed in the strong acid solution used. A supplementary treatment (i.e. biofilter) would therefore be necessary to control volatile organic matter emissions.

Water containing ammonia-salt was crystallised (see photo in Fig. 8). As can be seen, in spite of the low COD recovery, the crystallised ammonia salt, proceeding from slurry experiments, had a different colour than that from synthetic water. Moreover, the higher COD content of the water–ammonia salt coming from the fresh pig slurry resulted in a darker colour than that from digested slurry.

3.5. Batch anaerobic test

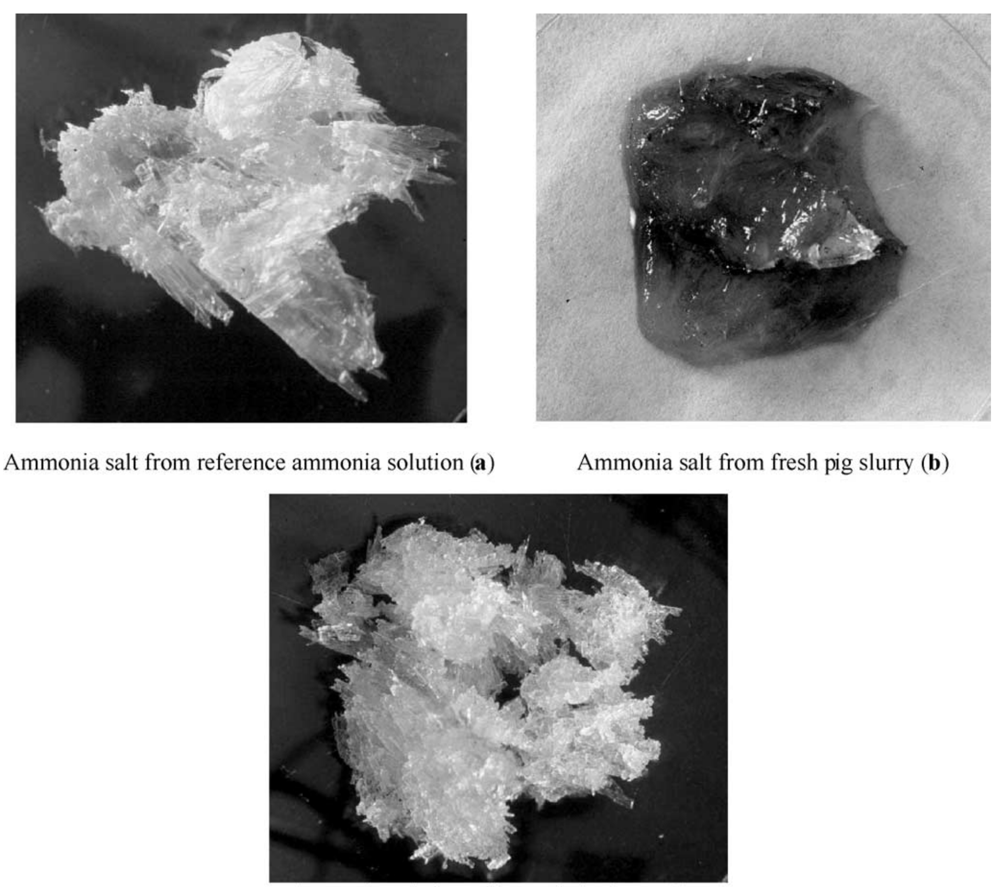
A batch anaerobic test was performed in order to determine whether ammonia air stripping had a positive effect on further anaerobic digestion of the slurry. The initial characteristics of the treatments are reported in Table 3.

As shown Table 3, P2, P3 and P4 treatments (air-stripped slurry) had a lower concentration of ammonia nitrogen and alkalinity than P1 (non pre-treated slurry). Moreover, the observed water evaporation during the air stripping process led to a higher COD and TVFA in the treatments involving air stripped slurry than in the one with non pre-treated slurry.

The initial pH in treatments P2, P3, and P4 were also interesting. In spite of the observed fall in pH (on-line measurement at high temperature), during the air stripping process (Fig. 5c), pH measurement at room temperature showed a higher value than the fresh slurry (P1 treatment). The generation of basic substances due to thermal organic matter degradation during air stripping and the different chemical equilibria depending on temperature, could explain these pH values (Bonmatí et al., 2001).

3.5.1. Methane production

There were significant differences in the volumetric methane production rates for the different treatments



Ammonia salt from reference ammonia solution (**a**)

Ammonia salt from fresh pig slurry (**b**)

Ammonia salt from digested pig slurry (**c**)

Fig. 8. Crystallised ammonia salt obtained in the absorption process and further crystallisation from the following experiments: (a) reference ammonia solution, (b) fresh pig slurry and (c) digested pig slurry.

(Table 4). The production rates were higher in the treatment with non-pretreated slurry (P1) than in those with pretreated slurry (P2, P3 and P4). This suggests that air stripping is not advisable as a pre-treatment to pig slurry anaerobic digestion.

However, the low methane production rates of treatment P1, together with the low substrate conversion rates to methane, suggested that the process could be inhibited by the presence of inhibitor or toxic substances. Furthermore, the high VFA% showed that the system could not consume all the VFA generated, thus confirming the hypothesis that the process was inhibited.

3.5.2. Inhibition phenomena

As free ammonia has been suggested as the active compound responsible of ammonia inhibition (Hashimoto, 1983), the initial and final free ammonia concentrations were calculated applying Eq. (3); Table 5. In treatments P2, P3 and P4, despite a lower initial ammonia nitrogen concentration than in treatment P1, their high initial pHs led to a higher free ammonia concentration. The VFA accumulation during anaerobic digestion led to a decrease of pH in those treatments, and therefore to lesser final free ammonia concentration. Treatment P1 showed the contrary, the final ammonia concentration was higher than the initial one.

The free ammonia concentration described in the literature as inhibiting anaerobic digestion is between 0.1 g (Henze et al., 1995) and 0.7 g NH_3/kg when inoculum has been previously adapted to high ammonia nitrogen concentrations (Angelidaki and Ahring, 1994). As can be seen in Table 5, free ammonia concentration was above the inhibitory threshold in all treatments. However, this did not completely explain the observed differences between the treatments nor the extremely low methane yields reported in all cases, which suggests that another inhibitory phenomena was at work.

Other inhibitory compounds usually present in pig slurry are Cu and Zn (normally used as additives in pig feed). Since these are non-volatile compounds, water evaporation observed during air stripping may increase their concentrations and thereby their inhibitory or toxic effect. Calcium could also be the cause of inhibition, since high amounts of $Ca(OH)_2$ were added in the stripping pre-treatment.

The concentration of Cu, Zn and Ca and their inhibition thresholds are shown in Table 6. With respect to Ca concentration, P4 was the only treatment with a

Table 4
Methane production and substrate conversion rates in batch anaerobic tests

Treatment	Methane production rates			Substrate conversion rates		
	CH_4/substrate (l/kg)	CH_4/VSi (l/kg)	CH_4/CODi (l/kg)	%M (COD_{CH4}/COD_i)	%VFA (COD_{VFA}/COD_i)	%A ($COD_{CH4+VFA}/COD_i$)
P1	2.9 **a**	88.8 **a**	38.4 **a**	10.0	22.1	32.1
P2	1.5 **b**	47.7 **b**	20.5 **b**	5.4	22.2	27.6
P3	0.9 **b**	22.0 **b**	10.5 **b**	2.8	24.2	26.9
P4	1.5 **b**	30.6 **b**	17.6 **b**	4.6	23.6	28.2

Different letters, in columns, show statistically significant differences between means (5% significance).

Table 5
Initial and final concentration of total ammonia nitrogen, free ammonia and pH in batch anaerobic test

Treatment	Initial (0 days)			Final (80 days)		
	$[NH_3–N+NH_4^+–N]$ (g/kg)	pH	$[NH_3–N]$ (g/kg)	$[NH_3–N+NH_4^+–N]$ (g/kg)	pH	$[NH_3–N]$ (g/kg)
P1	3.24	7.7	0.16	3.93	8.3	0.75
P2	2.40	8.5	0.68	3.11	8.0	0.30
P3	2.15	8.8	0.89	2.99	7.7	0.18
P4	1.18	9.9	1.06	2.13	7.9	0.17

Table 6
Cu, Zn and Ca concentration in batch anaerobic test

	P1	P2	P3	P4	Inhibition threshold	
					Values	Reference
Ca (g/kg)	1.47	1.34	2.73	10.32	4–6	Kugelman and Chin (1971)
Zn (g/kg)	0.81	0.70	1.02	0.91	0.40–0.60	Hayes and Theis (1978)
Cu (g/kg)	0.035	0.037	0.050	0.047	0.04–0.07	Hayes and Theis (1978)

higher concentration than that reported as inhibitory. Treatments P1 and P2 were close to the Cu inhibitory threshold and those in treatments P3 and P4 were above it. In all these treatments, Zn concentration was above the reported inhibitory concentration.

This showed that the observed anaerobic digestion inhibition could not only be explained by ammonia concentration, but also by the high concentration of Zn, Cu and Ca, and by the high initial pH, which led to a more complex inhibitory phenomenon. Other inhibitory compounds, produced during thermal hydrolysis induced by stripping at 80 °C can explain also the behaviour of anaerobic digestion, as was described by Bonmatí et al. (2001).

3.6. Air stripping evaluation as a pre- or post-treatment to anaerobic digestion

The results obtained in the present experiment showed that ammonia air stripping has many advantages if it is performed as a post-treatment to pig slurry anaerobic digestion. It is possible to achieve high ammonia removal efficiencies without pH modification and the ammonia-salt water obtained in the absorption process has a low COD concentration.

On the other hand, when air stripping is performed before anaerobic digestion, a high initial pH is required for complete ammonia removal and the ammonia-salt water obtained has a high COD concentration, not contributing to the anaerobic digestion process. Furthermore, the effluent obtained (stripped slurry) did not lead to any improvement in anaerobic digestion and, if necessary, stripping without base addition could be preferable, accepting a decrease in biogas potential. Even so, it must be emphasised that, the pig slurry used did not allow a clear evaluation of the negative effects on air stripping. Therefore, further studies are required.

4. Conclusions

Air stripping is a very efficient process for removing ammonia. Treatment performances vary depending on the pig slurry type. In all cases, as expected, the higher the pH, the higher the removal rates. When fresh pig slurry is used, in spite of working at 80 °C, a high initial pH (11.5) is required for complete ammonia removal. With digested slurry it was possible to completely remove ammonia without pH modification.

Ammonia air stripping is not advisable as a pre-treatment to pig slurry anaerobic digestion. In spite of the ammonia removal during the air stripping pre-treatment, the observed pH increase did not lead to a decrease in free ammonia nitrogen concentration. Consequently there was no reduction in its inhibitory effect.

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