Comparison of different approaches for ammonia emissions minimization by acidification of dairy and pig slurries.

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Abstract

Different organic and inorganic acids were used to acidify dairy and pig slurries and the effect over a 60 days storage period on pH, ammonia (NH_3) emissions and main slurry characteristics was investigated. Two pH values (pH=3.5 and pH=5.5) were considered. The amount of acid required in each treatment was previously determined allowing an economical comparison of the treatments. Our results showed that acidification process has to consider the slurry type since different results were obtained with pig and dairy slurry. Slurry acidification at pH 3.5 allowed maintaining NH_3 emissions at trace level over the 60 days whereas at pH 5.5, significant NH_3 emissions were observed in most treatments after day 20. Aluminium sulphate can be faced as a good alternative to H_2SO_4 since it efficiently reduced NH_3 emissions at a similar cost when acidifying at pH 5.5.

Introduction

Acidification of animal slurries aims at reducing ammonia by modification of physical and biochemical properties of the slurry [1]. Reducing these emissions is important due to the highly negative effects of NH_3 emissions have on the environment and health of the animals [2]. Moreover, the loss of NH_4^+ via NH_3 emission reduce the fertilizer value of animal slurries [3] Acidification have been studied previously by using sulphuric and nitric acid [4] but no systematic study have been performed until now considering different acids, slurry types and pH values. The influence of the pH value is very significant [5, 6] regarding NH_3 emission and slurry composition modifications.

The efficiency of the acidification process as well as the composition of the resulting material depends on many parameters, such as slurry composition, acidification process or acid used. Sulphuric acid (H_2SO_4) is commonly used for acidification due to economical reasons but strong concerns with acid hazards [7] have limited the implementation of slurry acidification in many countries as Portugal. The parameters to take into account when studying the economical viability of the different acids depend on the amount of acid required to reach the pH at which NH_3 emissions are avoid and the valuable end use of the treated slurry obtained.

The main objective of this study was to compare the efficiency of different acids employed for slurry acidification and for this, NH_3 emissions and pH evolution were followed during 60 days and the cost related to each acid and the composition of the slurry also considered.

Material and Methods

Dairy and pig slurries were acidified to pH 5.5 or 3.5 using lactic acid, sulphuric acid, citric acid, acetic acid or aluminium sulphate. It led to 20 different treatments three times replicates. Acids were added to slurry in small volumes of 0.2 mL while stirring and the pH was measured after each addition by using an electrode pH meter (Metrohm, Germany) until pH value was stabilized. The main characteristics for each treatment and slurry at the beginning and at the end of the storage period are shown in Tables 1 and 2.

Airtight glass bottles containing plastic recipients with 100 ml of 0.1 M orthophosphoric acid (H_3PO_4) used to trap NH_3 emissions were employed to keep the acidified and non-acidified samples. At the beginning and at the end of the experimental period, slurry samples in three replicates were analysed for dry matter (DM), organic matter (OM), Kjedahl N, Ammoniacal Nitrogen (TAN), soluble nitrogen (Nsol), total phosphorus (Pt) and mineral phosphorus (Pmin) using standard methods.

Table 1. Composition of treated and raw dairy slurry at the beginning and the end of the period

	TAN ($mg\ gDM^{-1}$)		Nsol ($mg\ gDM^{-1}$)		Pmin ($mg\ gDM^{-1}$)	
	t_0	t_f	t_0	t_f	t_0	t_f
Raw dairy slurry	19.9	23.1	24.9	27.4	0.2	0.1
Sulfuric acid	27.8	30.8	34.8	38.3	5.7	0.3
Lactic acid	21.8	21.6	26.6	29.7	2.7	0.1
Citric acid	24.5	28.7	25.9	34.1	6.8	0.2
Acetic acid	27.4	21.3	28.8	27.5	3.8	0.1
Aluminum sulfate	19.7	24	27.2	24.9	0	0.1
Sulfuric acid	25.4	24.5	29.5	31.2	7.1	6.1
Lactic acid	16.3	14.7	19.3	19.3	5.5	2.8
Citric acid	27.4	18.5	34.2	24.5	7.2	6.5
Acetic acid	26.1	23.2	31.3	32.2	9.9	8.6

TAN: Total ammoniacal nitrogen; Nsol: soluble nitrogen; Pmin: mineral phosphorus; Pt: total phosphorus

Table 2. Composition of treated and raw pig slurry at the beginning and the end of the period

	TAN ($mg\ gDM^{-1}$)		Nsol ($mg\ gDM^{-1}$)		Pmin ($mg\ gDM^{-1}$)	
	t_0	t_f	t_0	t_f	t_0	t_f
Raw pig slurry	93.6	100.5	96.8	109.1	0.5	0.4
Sulfuric acid	66.7	59.1	74	66.1	9.9	0.5
Lactic acid	51.4	49	52.5	63.1	8.4	0.5
Citric acid	64.5	82.8	66.1	93.6	18.6	0.7
Acetic acid	68.6	61.3	71.8	68.6	11.3	0.4
Aluminum sulfate	51.3	33.4	53.1	34.2	0.1	0.1
Sulfuric acid	60.7	54.2	60.6	61.3	14.5	12.8
Lactic acid	35.7	35.2	38	42.9	12.2	8.9
Citric acid	30.4	30.3	32.5	36.6	11.8	11.3
Acetic acid	78.2	79.6	83.2	98.3	24.7	22.8

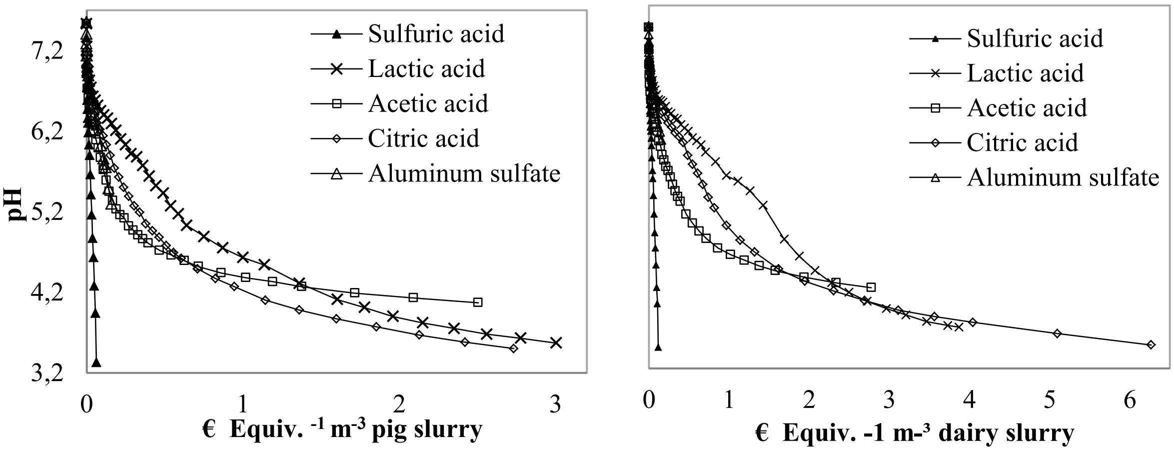
Results and Discussion

Slurry acidification induces a strong increase of Pmin except in the case of aluminium sulphate. The Pmin content decreased drastically to values close to 0 during the storage time when slurries were acidified to pH 5.5 but such decrease was not observed when acidifying at pH 3.5.

The amount of additives needed to reach the two pH values studied depends on the nature of the additive as well as on the slurry type. Indeed, when acidifying at pH 3.5 with sulfuric acid and citric acid, the amounts required for dairy slurry was two times higher than when acidifying pig slurry whereas the same amount of acid was needed when acetic, lactic acid and aluminum sulfate were used. On the other hand, when acidifying dairy slurry at pH=5.5, significantly more citric acid was needed relative to the other additives whereas small amounts of aluminum sulfate or acetic acid were enough.

Our results showed that, the best option regarding amounts required would be aluminum sulfate followed by acetic acid for both slurries when acidifying at pH 5.5; when acidifying at pH 3.5, sulfuric acid would be the best option for both slurries. However, the acid acquisition costs have also to be considered since values to reach pH 5.5 and pH 3.5 vary considerably depending on the acid used and on the slurry to treat but the price of each acid varies also significantly.

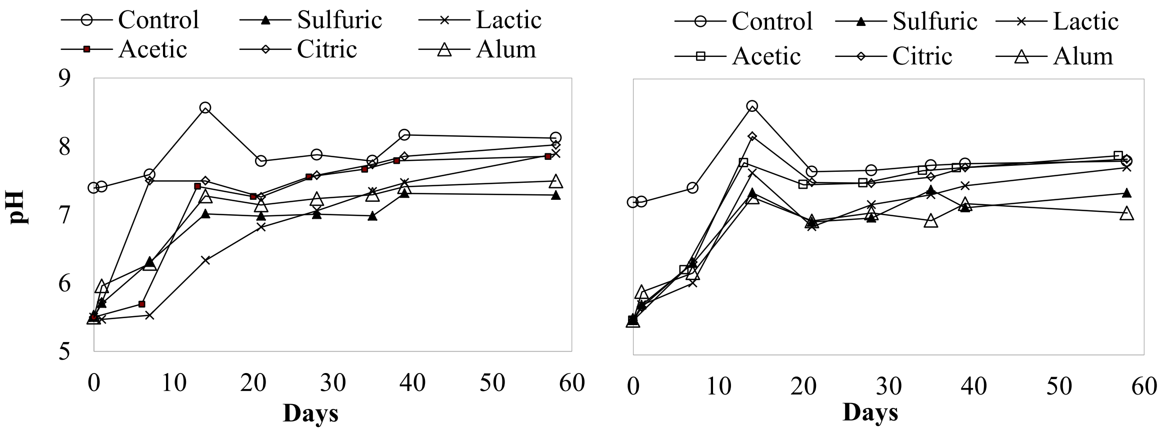
When comparing slurries, it appears that acidification costs in the case of dairy slurry are twice those required for pig slurry. Lactic acid is the most expensive for pig and citric acid is the most expensive for dairy when acidifying at pH 3.5 being sulfuric acid the cheapest one in both cases. When acidifying at pH 5.5 the most expensive acid is lactic acid for both pig and dairy and the cheapest one continue being the sulfuric acid but followed closely by acetic acid and aluminum sulfate in both cases.



(a) (b)

Fig. 1. Acidification costs for pig (a) and dairy (b) slurries acidified at pH=5.5 and pH=3.5

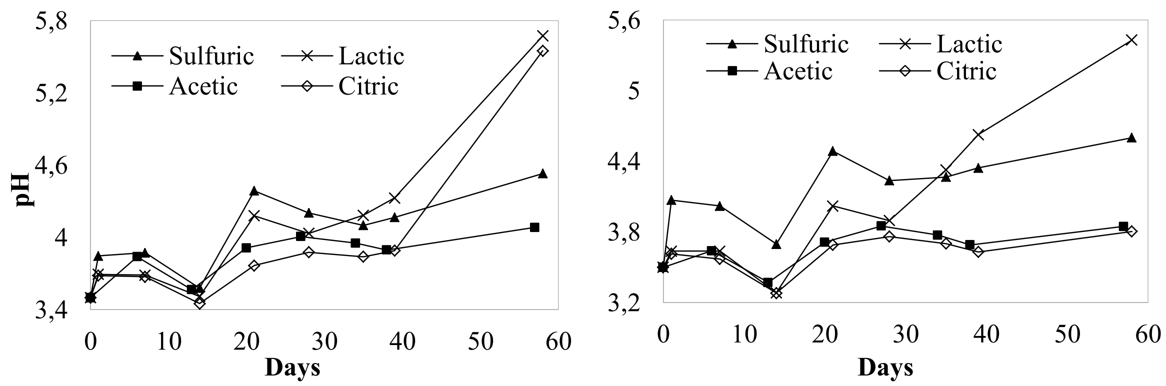
When initially acidified at pH=5.5, pH of the acidified slurries (both pig and dairy) (Fig. 2) increased considerably until day 15 followed by a small decrease and finally reached a constant value close to the initial slurry pH. In dairy slurry, aluminium sulphate showed to be the best treatment to maintain a low pH value over the whole period.



(a) (b)

Fig. 2. pH variations over time for pig (a) and dairy (b) slurries acidified at pH=5.5

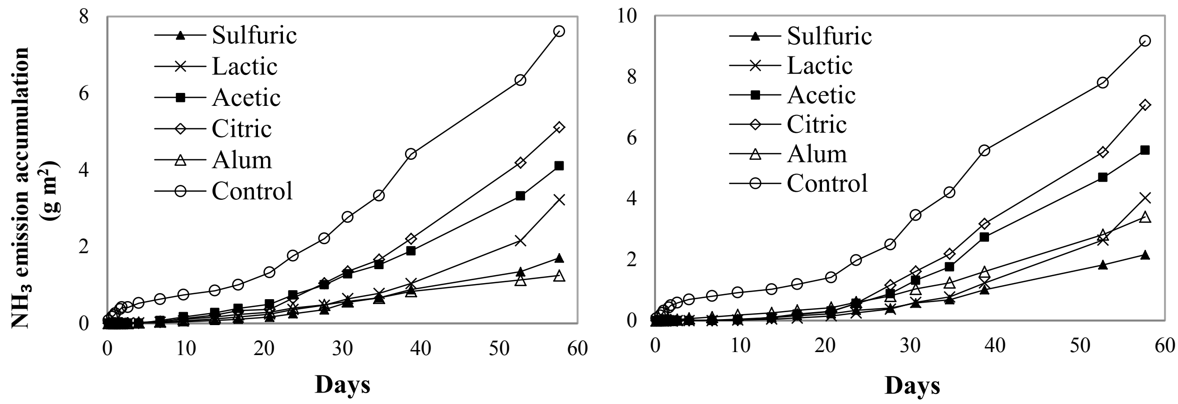
When acidifying at pH=3.5 (Fig. 3) the values increased insignificantly until day 10, decreasing between 10 and 15 and then stabilized between days 20 and 40 at pH close to 4. The final highest values were observed in case of lactic acid in both slurries, maintaining the lowest pH values the acetic acid in dairy slurry and citric acid in pig.



(a) (b)

Fig. 3. pH variations over time for pig (a) and dairy (b) slurries acidified at pH=3.5

All acids used to acidify pig and dairy slurries allowed lower NH_3 emissions in comparison with the non acidified slurries. NH_3 emissions accumulation (Fig. 4) in acidified pig and dairy slurries at pH 5.5 showed to be the lowest when using sulphuric acid, aluminium sulphate and lactic acid in both pig and dairy slurries. At pH 3.5 NH_3 emissions can be considered negligible in both slurries since NH_3 accumulation at the end of the experimental period did not exceed values of 0.35 mg NH_3 m^{-2}.



(a) (b)

Fig. 4.Cumulated NH_3 gaseous emissions for dairy (a) and pig (b) slurry at pH=5.5

NH_3 emissions were not strictly related to pH evolution; it was notice that after day 40 even if pH remained constant, daily NH_3 emissions increased considerably in both acidified pig and dairy slurries.

Conclusion and perspectives

This first study allowed us to investigate different alternatives to the existing ones considering different pH values that were not commonly employed before.

The results obtained over 60 days indicated that all the acids used reduced efficiently NH_3 emissions.

Slurry acidification at pH 3.5 allowed maintaining NH_3 emissions at trace level over the 60 days whereas at pH 5.5, significant NH_3 emissions were observed in most treatments after day 20. Aluminium sulphate can be faced as a good alternative to H_2SO_4 since it efficiently reduced NH_3 emissions at a similar cost when acidifying at pH 5.5.

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