

Article

Comparison of Alum and Sulfuric Acid to Retain and Increase the Ammonium Content of Digestate Solids during Thermal Drying

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Abstract: Aluminum sulphate (alum, $\text{Al}_2(\text{SO}_4)_3 \cdot n\text{H}_2\text{O}$) has successfully been used to reduce ammonia loss from poultry litter, cattle feedlots and manure composting, but has not yet been utilized in the thermal drying process of digestate solids. The objectives of the present study were to evaluate the effects of alum addition on ammonium nitrogen ($\text{NH}_4^+\text{-N}$) content and phosphorus (P) solubility in dried digestate solids in comparison to the addition of concentrated sulfuric acid (H_2SO_4). Manure-based (MDS) and sewage sludge-based (SDS) digestate solids were chosen to conduct a drying experiment at four pH levels (original pH, 8.0, 7.5 and 6.5) and using two acidifying agents (alum, concentrated H_2SO_4). Alum addition increased the final $\text{NH}_4^+\text{-N}$ content significantly from 1.4 mg g^{-1} in the non-acidified control up to 18 mg g^{-1} and 10.8 mg g^{-1} in dried MDS and SDS, respectively, which were higher levels than obtained with the addition of concentrated H_2SO_4 . Moreover, alum considerably lowered the water extractable phosphorus (WEP) in raw and dried SDS by 37–83% and 48–72%, respectively, compared with the non-treated control. In contrast, concentrated H_2SO_4 notably increased WEP in raw and dried MDS by 18–103% and 29–225%, respectively. The comparison between the two acidifying agents indicated that alum had the potential to be an efficient and easy-handling alternative to concentrated sulfuric acid, resulting in higher $\text{NH}_4^+\text{-N}$ content and lower P solubility.

Keywords: aluminum sulfate; ammonia loss; acidification; thermal drying; biosolids



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1. Introduction

Anaerobic digestion is a well-established waste-to-energy technology for treatment of various organic wastes, which also facilitates recycling of valuable nutrient resources like nitrogen (N) and phosphorus (P) in the waste materials [1]. However, the high volume and low nutrient concentrations of the digested effluent make it difficult and costly to utilize. Thermal drying of the dewatered effluent from anaerobic digesters (digestate solids) is an effective post-treatment process for volume reduction and stabilization [2,3]. Unfortunately, up to 95% of the $\text{NH}_4^+\text{-N}$ contained in the solids can be emitted as NH_3 during the drying treatment [4] due to the high pH (>8.0) of the digestate solids and the high temperature (>70 °C) of the drying process. To avoid these massive N losses and improve the fertilizer value of the dried products, concentrated sulfuric acid can be used to acidify the digestate solids before drying [4]. However, special equipment and operation skills are required when handling acids to avoid corrosion of farm installation systems and potential hazards to the health of farm animals and farmers. Furthermore, Roboredo et al. (2012) [5] and Sommer et al. (2015) [6] reported that acidification using concentrated sulfuric acid increased water soluble P in the solid fraction of pig slurry, resulting in a higher risk of P leaching and runoff.

Aluminum sulphate ($\text{Al}_2(\text{SO}_4)_3 \cdot n\text{H}_2\text{O}$), commonly referred to as alum, has been suggested as a practical and economical amendment to reduce ammonia emissions from poultry litter [7], cattle feedlots [8] and animal manure composting [9]. Alum hydrolyzes to the aluminum hydroxide precipitate and a dilute sulfuric acid solution [10], resulting in lower pH of the mixture and thus conserving N in NH_4^+ form to avoid volatilization losses.

In trials conducted in poultry or cattle farming, alum was generally applied at a rate of 2–10% of the weight of poultry litter or cattle feedlot surface material and caused 70–99% lower NH_3 losses than the untreated control [8,11,12]. In manure composting studies, 2.5–10% alum addition reduced NH_3 volatilization by 58–85% [9,13,14]. Furthermore, Moore and Edwards (2007) [15] and Huang et al. (2016) [16] indicated that inorganic and organic P compounds in poultry litter react with Al from alum, leading to lower P solubility and thus resulting in significantly reduced risk for P runoff and leaching after soil application. Therefore, alum has the potential to be an alternative acidifying agent with lower risks of operation safety and P eutrophication. However, alum has not yet been utilized as an acidifying agent in the thermal drying process of digestate solids.

The overall objective of the present study was therefore to evaluate (i) the efficiency of alum as an acidifying agent to retain NH_4^+ -N in digestate solids during thermal drying and (ii) P solubility in alum-treated thermally-dried solids.

It was hypothesized that:

- (1) Alum increases the ammonium nitrogen content after thermal drying of digestate solids to the same extent as concentrated H_2SO_4 ;
- (2) Alum-treated thermally-dried digestate solids have a lower P solubility than the non-treated dried solids;
- (3) H_2SO_4 -treated thermally-dried digestate solids have a higher P solubility than the non-treated dried solids, and P solubility is positively correlated with the acidification level.

2. Materials and Methods

2.1. Digestate Solids

Two kinds of digestate solids derived from anaerobic digestion of either manure (MDS—70% dairy, 20% pig, 8–9% chicken manure and 1–2% food waste) or sewage sludge (SDS—the secondary sludge after chemical removal of P using ClFeO_4S and sludge precipitation with AlCl_3) were freshly collected from Morsø biogas plant (Morsø, Denmark) and Bjergmarken wastewater treatment plant (Roskilde, Denmark), respectively. Sampling was conducted directly at the outlet of the mechanical solid-liquid separator (decanting centrifuge). MDS and SDS were kept frozen at -20°C after collection and the required amount was defrozen at room temperature overnight before further use. The main characteristics of the MDS and SDS are shown in Table 1.

Table 1. Chemical characteristics of manure-based digestate solids (MDS) and sewage sludge-based digestate solids (SDS) used in the experiments.

Material	Dry Matter Content (DM)	pH	NH_4^+ -N	N_{tot}	P_{tot}	K_{tot}	Ca_{tot}	Al_{tot}	Mg_{tot}	C/N	Ca/P	Al/P
	%		g·kg ⁻¹ DM									
MDS	27.3	9.2	7.7	39.4	25.9	10.5	35	1.3	14.4	11.3	1.4	0.05
SDS	27	8.6	8.9	44	36	2.8	64	13.5	7.4	6.8	1.8	0.4

2.2. Experimental Procedure

Drying experiments using MDS and SDS were conducted in a laboratory-scale drying system placed in a laboratory oven, as described in detail in [17]. Drying was operated at a temperature of 130°C and an air ventilation rate of 525 mL min^{-1} , corresponding to a headspace exchange rate of 286 times hour⁻¹. Before drying, caking was removed

from the fibrous MDS material and the sticky SDS material was cut into rectangular blocks ($1 \times 1 \times 2.8$ cm, around 4.5 g per block) to ensure homogeneity of drying time.

In a preliminary experiment, the time for drying was estimated by drying raw MDS/SDS to a DM content of 85% (MDS 200 min and SDS 170 min) and divided equally into four periods (T1–T4). Furthermore, a titration curve was established to determine the amount of alum required to decrease the pH of MDS and SDS to the targeted levels. MDS/SDS was homogeneously mixed with alum and kept at room temperature for 72 h to investigate the evolution of pH before the determination of the titration curve. The titration curve for concentrated H_2SO_4 had already been established in a prior study [17].

In the final experiment, two varying factors were applied to MDS/SDS: (a) initial pH before drying (acidified to pH 8.0, 7.5 or 6.5, respectively) and (b) acidification agents (concentrated sulfuric acid (95–97% H_2SO_4 , EMPARTA, Darmstadt, Germany) and alum (99.99%, $\text{Al}_2(\text{SO}_4)_3$, Sigma-Aldrich, Saint Louis, Missouri, USA). In total, seven treatments were established for one material (one non-acidified control, three treatments acidified using concentrated H_2SO_4 to reach the initial pH levels, and three treatments acidified using alum to reach the initial pH levels). The final amounts added to each material can be found in Table 2. MDS and SDS samples for each acidification level with concentrated H_2SO_4 were freshly prepared before drying as described in Liu et al. (2019) [17]. For alum, a 24 h premix with the materials was performed (see Section 3 for rationale).

Table 2. Application rate (based on fresh weight of digestate solids) of acidifying agents.

Acidification Level		pH Original	pH 8.0	pH 7.5	pH 6.5
application rate					
MDS	$\text{H}_2\text{SO}_4 \mu\text{L g}^{-1}$	0	5	7.5	12.5
	alum %	0	1.2	2	4
SDS	$\text{H}_2\text{SO}_4 \mu\text{L g}^{-1}$	0	1.25	2.5	5
	alum %	0	0.8	1.3	3

Triplicate samples stayed in the oven (at 130 °C) for one, two, three or four drying periods (T1–T4), respectively. Before further measurements, samples were removed and placed in a desiccator until they had reached room temperature (around 15 min). Afterwards, samples were weighed and pH was measured with a PHM 210 Standard pH Meter (Radiometer Analytical, Lyon, France) using a 1:5 (*dw/v*) ratio of solids to deionized water.

MDS/SDS NH_4^+ -N contents from different drying time points were analyzed after extraction with 1M KCl (1:20, *dw/v*, shaking for 45 min on an end-over-end shaker and filtering through Whatman no.5 filter paper) using flow-injection analysis (FIAstar 5000 Analyzer, FOSS, Hilleroed, Denmark). Water extractable phosphorus (WEP) contents from initial and final drying time points were measured after extraction with deionized water (1:100, *dw/v*), shaking for 1 h and filtering through Whatman no.5 filter paper) using flow-injection analysis.

2.3. Statistical Analyses

Statistical analyses of drying curve, pH variation and NH_4^+ -N content during the thermal drying process were conducted using a one-way ANOVA followed by the Tukey test at the 0.05 significance level. For all ANOVAs, the assumption of the homogenous variance of different groups was checked with Levene's test and the assumption of normality was tested using the Kolmogorov–Smirnov test. All statistical analyses were conducted using IBM SPSS Statistics 22 (Armonk, New York, NY, USA).

3. Results and Discussion

3.1. Alum Titration Curve

According to the pH evolution test of MDS and SDS for 72 h after alum addition (Figure 1), the pH decline could be divided into three stages: I, precipitous decline stage,

instantly after alum addition; II, slow decline stage, 0–24 h, and III, relatively stable stage, after 24 h upon addition. In MDS, most of the pH decline (from 9.1 to 7.9) happened in stage I, and pH remained at around 7.8 after 24 h upon addition. For SDS, pH dropped from 8.6 to 7.1 in stage I and gradually declined to 6.4 in stage II. Therefore, MDS and SDS were homogeneously mixed with alum and kept at room temperature for 24 h before titration curve measurement.

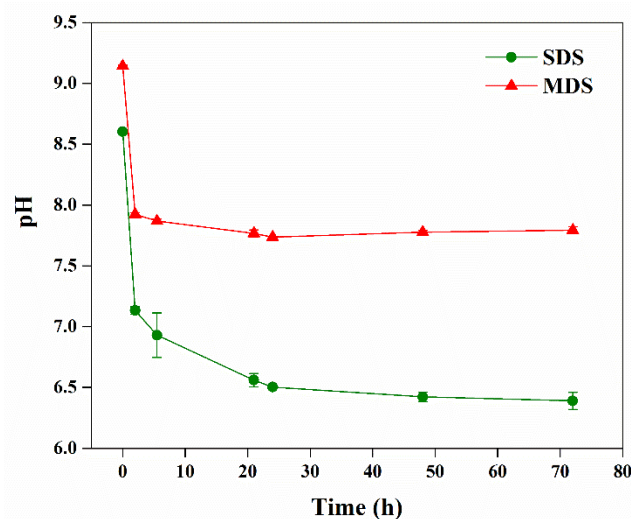


Figure 1. pH evolution pattern of manure-based (MDS) and dewatered sewage sludge-based (SDS) digestate solids after adding 4% (MDS) and 2% (SDS) alum, respectively.

We tested the alum titration curve based on two time points for MDS: I, 24 h after alum addition; II, 50 min after drying at 130 °C (Figure 2), since in the following thermal drying test, MDS and SDS were observed to have different pH variation patterns in response to alum addition. The pH of alum-treated MDS dramatically declined while drying, yet pH of SDS remained stable. An excessive amount of alum (15%, wet weight based) was used to acidify raw MDS to pH 6.5, but pH dropped to 3.8 after 50 min drying (Figure 2). Therefore, the time point II titration curve was chosen for the determination of the necessary amount of alum to be used to acidify MDS. Table 2 shows the required amount of alum to adjust the pH of MDS and SDS from the starting value to pH 8.0, 7.5 and 6.5, respectively.

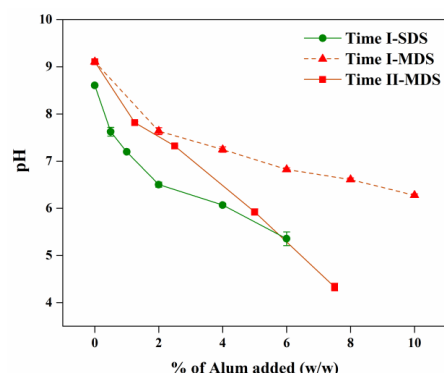


Figure 2. Titration curves of the manure-based (MDS) and dewatered sewage sludge-based (SDS) digestate solids. Error bars represent standard error ($n = 3$) (Testing time, I: 24 h after alum addition, before drying, II: after 50 min drying at 130 °C).

The different pH variation patterns between the two solids during drying were possibly due to the different physical structure of the two materials resulting in a different hydrolysis time of alum. Alum may have hydrolyzed more readily in SDS than in MDS, and a continuous pH decline occurred between 0–24 h after alum addition (Figure 1).

Since alum was applied as powder, the compact and sludgy SDS probably benefited the solid-liquid reactions by providing a large contact area, which led to a considerable rate of hydrolysis. MDS had a more fibrous, porous structure, possibly resulting in non-sufficient contact with a lower rate of hydrolysis during premix (24 h).

3.2. Drying Curve

For MDS and SDS, drying curve patterns under acidification using concentrated H_2SO_4 bore strong similarities to the treatments using alum across all acidification levels (Figure 3a,b and Figure 4a,b). The moisture content declined almost linearly with drying time.

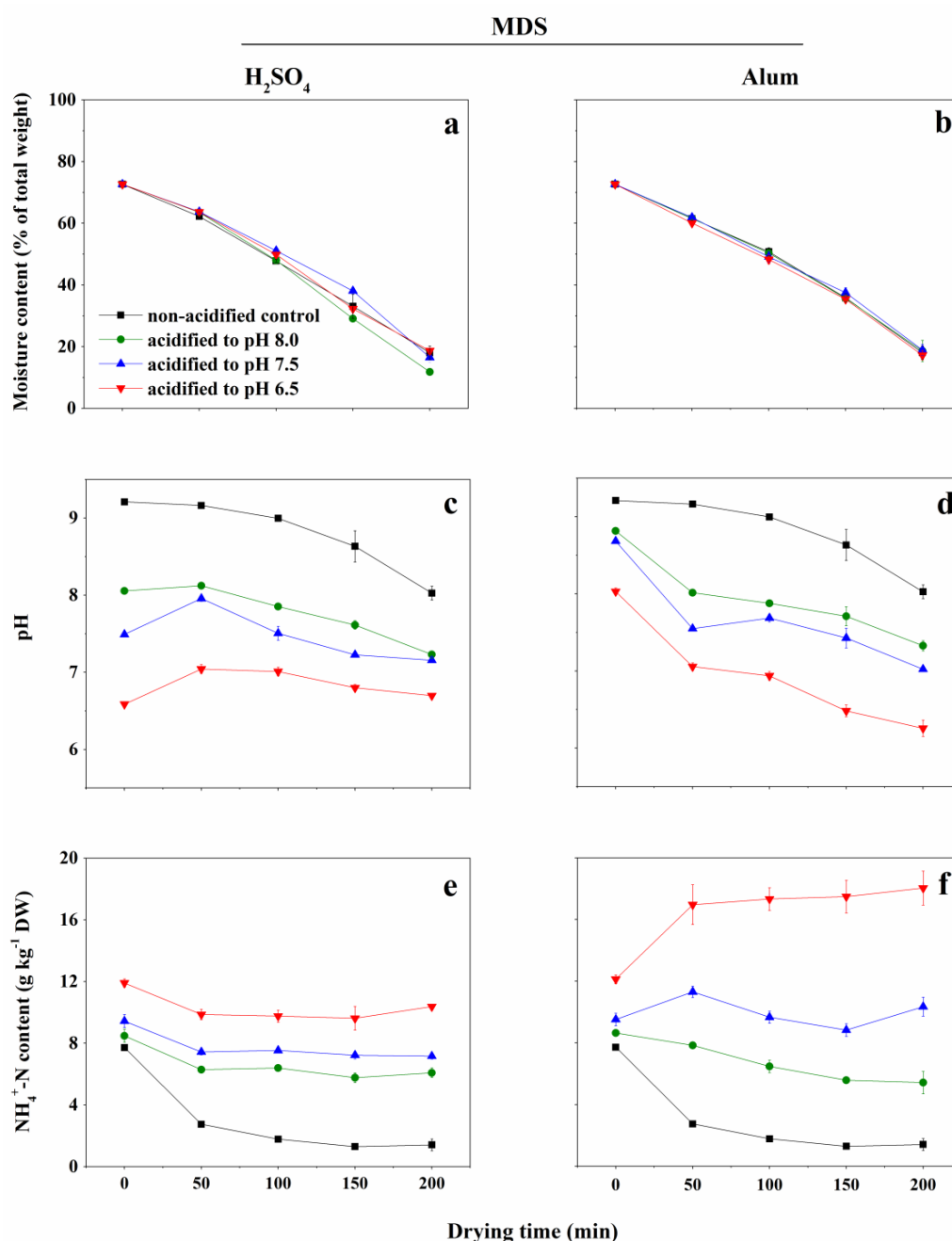


Figure 3. Moisture loss (a,b), pH evolution (c,d) and NH_4^+-N content (e,f) of the manure-based digestate solids (MDS) during thermal drying (ventilated, $130^\circ C$) in the non-acidified control (original pH) and acidified to three different pH levels with H_2SO_4 (left) or alum (right). Error bars represent standard error ($n = 3$); when not visible, error bars are covered by symbols.

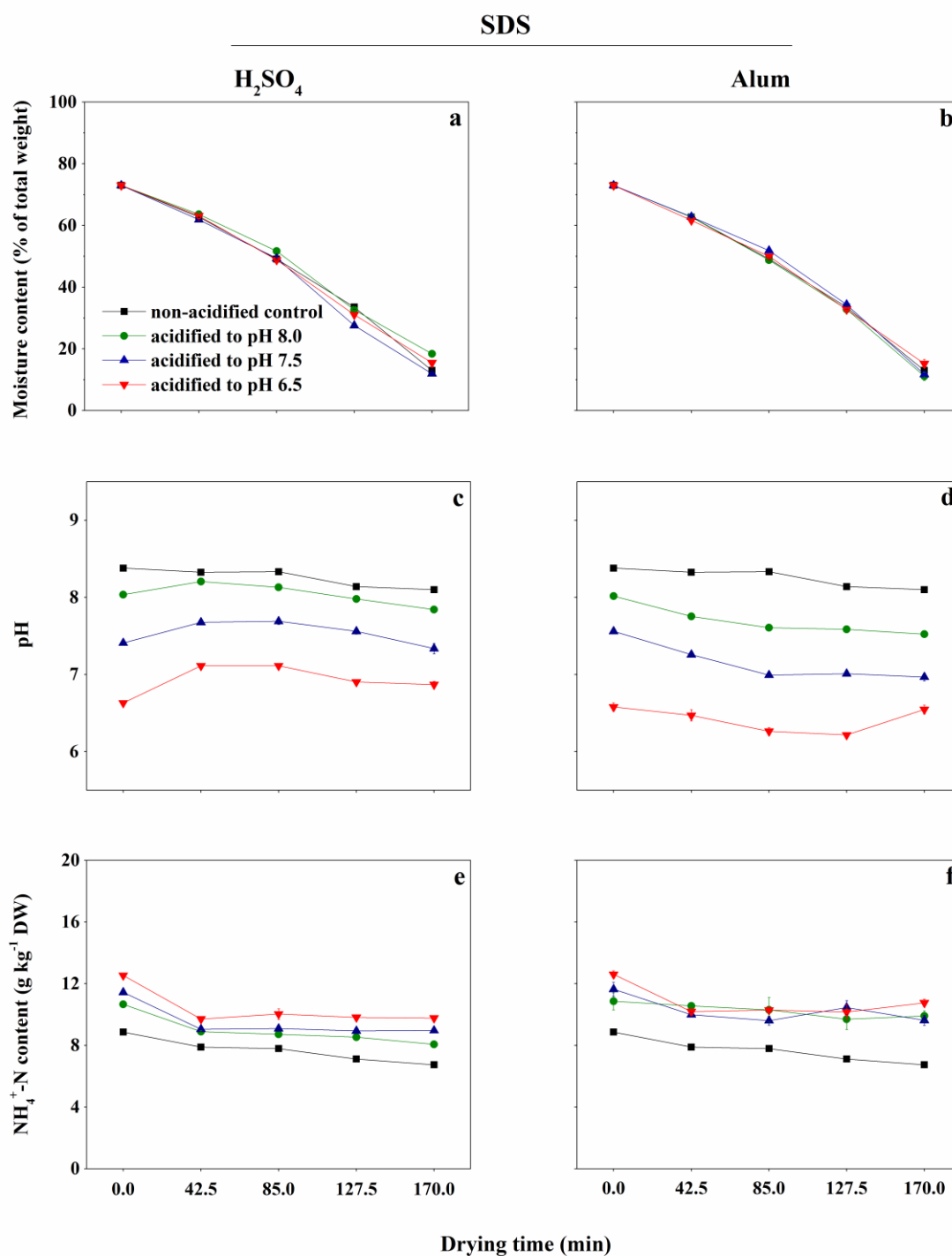


Figure 4. Moisture loss (a,b), pH evolution (c,d) and NH_4^+ -N content (e,f) of the sewage sludge-based digestate solids (SDS) during thermal drying (ventilated, 130 °C) in the non-acidified control (original pH) and acidified to three different pH levels with H_2SO_4 (left) or alum (right). Error bars represent standard error ($n = 3$); when not visible, error bars are covered by symbols.

3.3. pH Evolution during Drying

MDS and SDS showed similar pH evolution patterns upon addition of concentrated sulfuric acid, peaking at T1 and descending later with a variation range of 0.5 and 0.2 units in MDS and SDS, respectively (Figures 3a and 4a). As already pointed out in a previous study [17], this could be attributed to the release of the CO_2 from dissolved bicarbonate of digestate solids resulting in a net increase of pH at T1 [18], and to the subsequent release of

H⁺ from dissociation of NH₄⁺ to NH₃ after bicarbonate depletion, contributing to the later pH decline.

In MDS treated with alum, the pH declined by approximately 1 unit in T1 and then gradually decreased around 0.5 units within T2–4. In contrast, pH did not show a significant decline in SDS during T1, but a mild decrease of pH, around 0.5 units, occurred with drying. As alum hydrolysis is strongly temperature-dependent [19], high temperature and intensified water movement during drying [20] probably promoted the alum hydrolysis, contributing to the sharp decrease of pH in alum-treated MDS (Figure 3d). Thus we hypothesize that alum hydrolysis mainly occurred during the 24 h premix in SDS and during the drying process in MDS, respectively.

3.4. NH₄⁺-N Content in the Materials during Drying

Acidification significantly increased ($p < 0.05$) the initial NH₄⁺-N contents irrespective of the acidifying agents, possibly due to acid-induced hydrolysis of the solids' organic matter [21]. For MDS, the initial NH₄⁺-N content was increased from 7.7 mg g⁻¹ to 8.6, 9.5 and 12.0 mg g⁻¹ at target acidification levels of pH 8.0, 7.5 and 6.5, respectively (Figure 3a,b). Similarly, the initial NH₄⁺-N content of SDS was raised from 8.9 mg g⁻¹ to 10.8, 11.5 and 12.6 mg g⁻¹ (Figure 4e,f).

For MDS, the variation patterns of NH₄⁺-N contents during thermal drying were different between acidification agents (Figure 3e,f). When using concentrated H₂SO₄, NH₄⁺-N declined in T1, probably due to ammonia volatilization from the high initial NH₄⁺-N content. Pantelopoulos et al. (2016) [4] also reported that more than 90% of the total NH₄⁺-N content decline in digestate solids occurred during the early stage of drying at 70–160 °C. In contrast, when acidifying MDS using alum (to pH 7.5 and 6.5), a significant increase of NH₄⁺-N was seen at T1, which was probably due to the pH-induced further hydrolysis of organic N. During the drying process, a considerable decrease of pH occurred because of alum hydrolysis (Figure 4d). Acidification using both agents significantly increased ($p < 0.05$) the NH₄⁺-N content compared to the control, however, alum addition induced a higher NH₄⁺-N content than concentrated H₂SO₄ at each acidification level (Figure 5a).

The different NH₄⁺-N contents at each sampling time (T1–T4) were the net balance between hydrolysis of organic N and NH₃ volatilization losses. Since NH₃ volatilization was not directly measured, no conclusion can be drawn with regard to the total N balance of the acidifying and drying processes.

Many previous studies concerning the reduction of NH₃ emissions from animal manure and slurry documented the efficiency of concentrated H₂SO₄ [21,22]. Regarding alum, Bautista et al. (2011) [9] reported that NH₃ emissions from swine manure treated with 2.5% alum were, on average, 84% lower than those from the control during 18 days of composting. Spiehs and Woodbury (2018) [8] reported that acidifying beef feedlots to below pH 6.5 using alum could completely suppress NH₃ emissions. Early reports also linked reduction of ammonia losses directly to the final pH after acidification [23,24]. Similarly, the present study indicated that the increase of NH₄⁺-N content in dried digestate solids became more pronounced with the increasing acidification level (Figure 5a). Acidifying MDS to pH 6.5 using H₂SO₄ and alum achieved 34% and 134% higher NH₄⁺-N content in the final dried MDS, respectively, relative to the initial NH₄⁺-N content (7.7 mg g⁻¹) in the control (Figure 5a).

Regarding SDS, at drying, comparable NH₄⁺-N content variation patterns were observed with the two acidification agents: almost all the NH₄⁺-N decline occurred in T1 and then NH₄⁺-N content of SDS maintained stable. As mentioned above, alum may undergo a high hydrolysis rate during the 24 h premix period in SDS, resulting in a lower pH decrease during drying compared to MDS. Therefore, acid-induced hydrolysis of SDS organic matter might only happen before drying and the NH₄⁺-N content of SDS did not increase during drying as observed for the alum-treated MDS. Although the relative NH₄⁺-N content reduction in the non-acidified SDS control was much less than for MDS,

acidification using concentrated H_2SO_4 and alum also significantly enhanced ($p < 0.05$) the $\text{NH}_4^+\text{-N}$ content in the final dried SDS (Figure 5b). After drying, alum-treated SDS had a higher $\text{NH}_4^+\text{-N}$ content than H_2SO_4 -treated SDS (Figure 5b). In particular, SDS acidified to pH 8.0 using alum already had a 12% higher $\text{NH}_4^+\text{-N}$ content relative to the initial content (8.9 mg g^{-1}) in the control, while a 9% lower $\text{NH}_4^+\text{-N}$ content was achieved by using concentrated H_2SO_4 relative to the initial content.

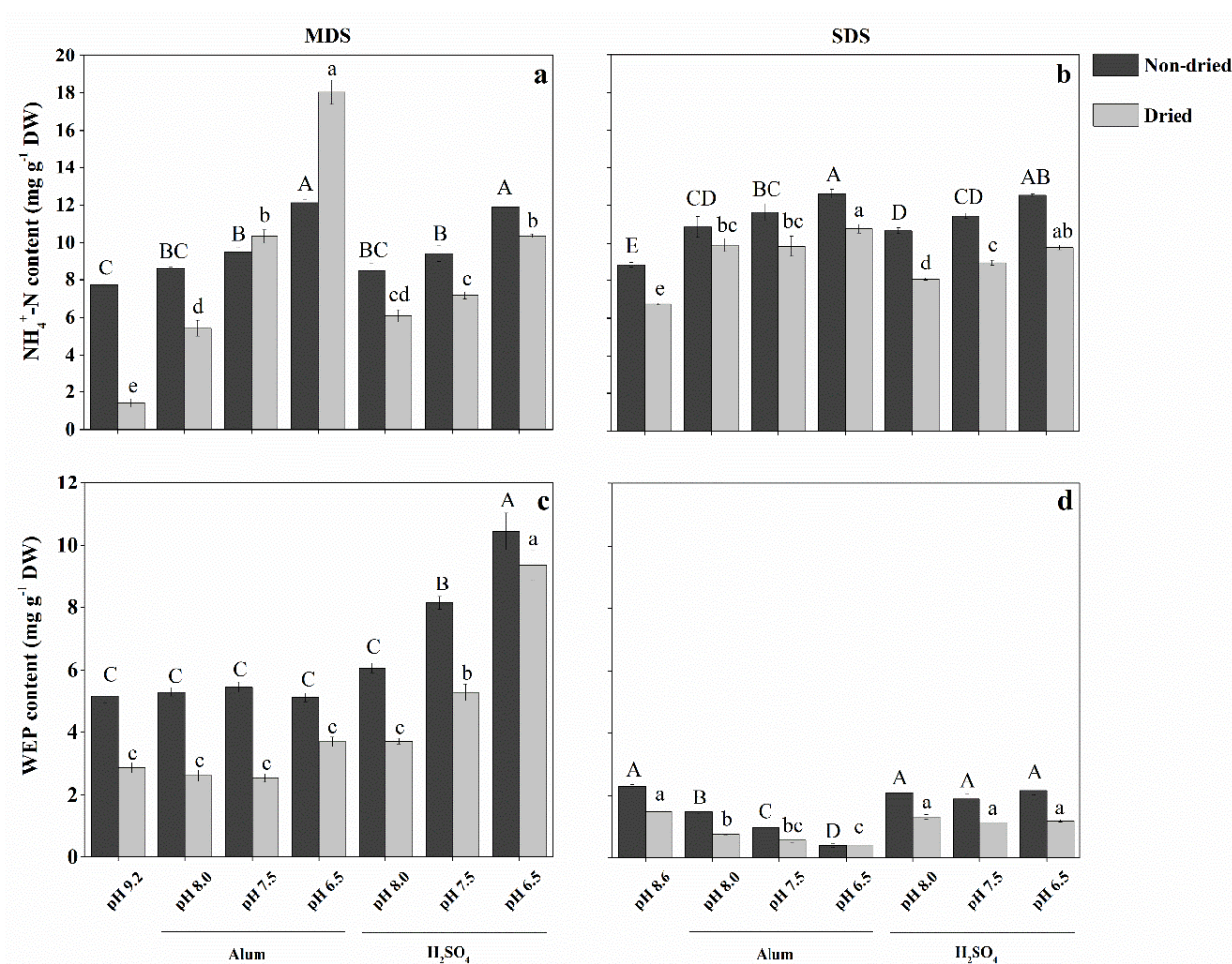


Figure 5. Variations in $\text{NH}_4^+\text{-N}$ (a,b) and WEP (c,d) content between raw and finally dried manure-based (MDS, left) and sewage sludge-based (SDS, right) digestate solids at different acidification levels. Error bars represent standard error ($n = 3$). Different letters denote significant difference ($p < 0.05$) between non-dried treatments (capitals) or between dried treatments (lower case) by Tukey test.

3.5. Water Extractable P before and after Drying

Acidification prior to drying affected the WEP content of MDS, but the effects differed with the two agents (Figure 5c). Compared with the non-acidified control, using concentrated H_2SO_4 significantly increased WEP in raw and dried MD solids by 18–103% and 29–225%, respectively, and WEP content increased along with the increasing acidification level. Using alum as an acidification agent caused no significant enhancement of WEP in raw and dried MDS solids. Furthermore, drying generally led to considerable WEP reduction (44%), but acidification using concentrated H_2SO_4 decreased the decline to 10–39% (Figure 5c), being lowest at the highest acidification level.

However, contrary to MDS, acidification using concentrated H_2SO_4 before drying had no positive effect on WEP in raw and dried SDS solids compared with the non-acidified control (Figure 5d). Using alum even significantly reduced ($p < 0.05$) the WEP by 37–83% and 48–72% in raw and dried SDS solids, respectively, showing an enhanced reduction of

WEP content with increasing alum addition rate (Figure 5d). Additionally, drying caused an average 36% decrease of WEP content across SDS treatments.

The different response of WEP content to acidification using concentrated H_2SO_4 can probably be attributed to different P species present in MDS and SDS, respectively. Since MDS is derived from animal manure, a high content of struvite ($\text{NH}_4\text{MgPO}_4 \cdot 6\text{H}_2\text{O}$) can be assumed [25], while in SDS produced from anaerobic digestion of sewage sludge, Ca-phosphates (e.g., β -tricalciumphosphate, brushite, and dicalciumphosphate) are typically dominant. This is corroborated by the fact that MDS contained twice as much Mg than SDS and a higher Mg/P ratio (MDS, 0.6; SDS, 0.2) while SDS had 53% more Ca than MDS and also a higher Ca/P ratio (MDS, 1.4; SDS, 1.8). The solubility of Mg-P and Ca-P is pH dependent; Mg-P is fully dissolved at a pH below 6.7 and Ca-P is mostly dissolved between pH 6.7–5.5 [26]. In the present study, the digestate solids were not acidified to a pH lower than 6.5, thus struvite in MDS probably dissolved resulting in higher WEP, and less acid-soluble Ca-P in SDS resulted in a constant level of WEP.

Huang et al. (2007) [27] observed the formation of Ca-P (probably brushite) and Al-P precipitation after adding alum as a stabilizer to sewage sludge using electron microscopy (SEM). Furthermore, alum could lower the solubility and mobility of organic P, e.g., myoinositol hexakisphosphate (phytate), in biosolids by forming an aluminum phytate precipitant [16,28]. Consequently, Huang et al. (2016) [16] showed that soil fertilized with alum-treated poultry litter had 74% lower WEP than soil receiving untreated litter after 20 years. Moore et al. (2000) [11] reported that alum additions to poultry litter reduced P runoff by 75% throughout a three-year trial. However, depending on the pH level, acidification caused by alum addition could also lead to the dissolution of Mg-P, Al-P and Ca-P, and acid hydrolysis of organic P [27]. Thus, it can be speculated that in MDS, the acidification effect of alum had a similar positive impact on WEP as H_2SO_4 , but that this effect was counteracted by the addition of Al with alum [15,16], resulting in a similar WEP content of the non-acidified control and alum-treated MDS. For SDS, acidity created by alum addition did not have an influence on WEP, as also observed with H_2SO_4 , and the addition of aluminum contributed to the significantly lower WEP in alum-treated SDS.

3.6. Technology Implementation Options

Concentrated sulfuric acid (95–98% H_2SO_4) and alum had a market price of around € 0.4 per liter and €135 per ton, respectively, on chembid.com.

The lowest alum addition rate of 1.2% (target pH 8.0) would result in $5.4 \text{ mg g}^{-1} \text{NH}_4^+\text{-N}$ in dried MDS (70% of the initial $\text{NH}_4^+\text{-N}$ content) at a cost of €1.38 per ton of MDS, while the minimum concentrated H_2SO_4 level (0.92%, target pH 8.0) would achieve a similar $\text{NH}_4^+\text{-N}$ content of 6.1 mg g^{-1} at a cost of €1.9 per ton of MDS. If aiming for a higher $\text{NH}_4^+\text{-N}$ content in dried MDS, using 2% alum (target pH 7.5) or 1.38% concentrated H_2SO_4 (target pH 6.5) could achieve 10.3 or $10.4 \text{ mg g}^{-1} \text{NH}_4^+\text{-N}$ at a cost of €2.76 or €2.85, respectively.

Regarding SDS, the lowest level of alum addition (0.8%, target pH 8.0) could achieve $9.9 \text{ mg g}^{-1} \text{NH}_4^+\text{-N}$ in dried SDS (12% higher than the initial $\text{NH}_4^+\text{-N}$ content) at a cost of € 0.56 per ton, whereas an addition rate of concentrated H_2SO_4 of 0.46% (target pH 7.5) would result in $9 \text{ mg g}^{-1} \text{NH}_4^+\text{-N}$ in dried SDS at a cost of €0.9 per ton of SDS.

Based on these calculations, using alum would be approximately 30% cheaper than using H_2SO_4 to achieve similar $\text{NH}_4^+\text{-N}$ contents in dried solids.

4. Conclusions

As hypothesized, alum addition (0.8%–4%, target pH: 8.0, 7.5 and 6.5) significantly increased the $\text{NH}_4^+\text{-N}$ content in dried MDS and SDS, even more effectively than concentrated H_2SO_4 , thus raising the level of immediately plant-available N in the dried products. Contrary to our expectations, alum addition had no considerable influence on WEP in raw and dried MDS, but significantly lowered the WEP in raw and dried SDS. On the other hand, H_2SO_4 addition notably increased WEP in raw and dried MDS compared with the

non-acidified control, yet had no obvious effect on raw and dried SDS. The inorganic P species with different solubility present in solid fractions of organic fertilizers are likely to influence acidification effects on WEP, which also depend on target pH. The present study indicated that acidified-dried digestate solids potentially could become valuable products with high N fertilizer value and low environmental impact. Furthermore, alum can be considered as effective, low-cost, easy to handle, and a high safety alternative to concentrated H₂SO₄ addition before drying of digestate solids.

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References

1. Tsui, T.-H.; Wong, J.W.C. A critical review: Emerging bioeconomy and waste-to-energy technologies for sustainable municipal solid waste management. *Waste Dispos. Sustain. Energy* **2019**, *1*, 151–167. [\[CrossRef\]](#)
2. Drosig, B.; Fuchs, W.; Al Seadi, T.; Madsen, M.; Linke, B. *Nutrient Recovery by Biogas Digestate Processing*; IEA Bioenergy: Dublin, Ireland, 2015.
3. Horttanainen, M.; Deviatkin, I.; Havukainen, J. Nitrogen release from mechanically dewatered sewage sludge during thermal drying and potential for recovery. *J. Clean. Prod.* **2017**, *142*, 1819–1826. [\[CrossRef\]](#)
4. Pantelopoulos, A.; Magid, J.; Jensen, L.S. Thermal drying of the solid fraction from biogas digestate: Effects of acidification, temperature and ventilation on nitrogen content. *Waste Manag.* **2016**, *48*, 218–226. [\[CrossRef\]](#)
5. Roboredo, M.; Fanguero, D.; Lage, S.; Coutinho, J. Phosphorus dynamics in soils amended with acidified pig slurry and derived solid fraction. *Geoderma* **2012**, *189–190*, 328–333. [\[CrossRef\]](#)
6. Sommer, S.G.; Hjorth, M.; Leahy, J.J.; Zhu, K.; Christel, W.; Sørensen, C.G.; Sutaryo, S. Pig slurry characteristics, nutrient balance and biogas production as affected by separation and acidification. *J. Agric. Sci.* **2015**, *153*, 177–191. [\[CrossRef\]](#)
7. Choi, I.H.; Moore, P.A. Effect of Various Litter Amendments on Ammonia Volatilization and Nitrogen Content of Poultry Litter. *J. Appl. Poult. Res.* **2008**, *17*, 454–462. [\[CrossRef\]](#)
8. Spiehs, M.J.; Woodbury, B.L. Use of aluminum sulfate (alum) as a feedlot surface amendment to reduce ammonia emissions from beef feedlots. In Proceedings of the 2018 ASABE Annual International Meeting, Detroit, MI, USA, 29 July–1 August 2018; American Society of Agricultural and Biological Engineers: St. Joseph, MI, USA, 2018; p. 1. [\[CrossRef\]](#)
9. Bautista, J.M.; Kim, H.; Ahn, D.-H.; Zhang, R.; Oh, Y.-S. Changes in physicochemical properties and gaseous emissions of composting swine manure amended with alum and zeolite. *Korean J. Chem. Eng.* **2011**, *28*, 189–194. [\[CrossRef\]](#)
10. Moore, P.A.; Miller, D.M. Decreasing Phosphorus Solubility in Poultry Litter with Aluminum, Calcium, and Iron Amendments. *J. Environ. Qual.* **1994**, *23*, 325–330. [\[CrossRef\]](#)
11. Moore, P.A.; Daniel, T.C.; Edwards, D.R. Reducing Phosphorus Runoff and Inhibiting Ammonia Loss from Poultry Manure with Aluminum Sulfate. *J. Environ. Qual.* **2000**, *29*, 37–49. [\[CrossRef\]](#)
12. Zhang, H.-F.; Jiao, H.-C.; Song, Z.-G.; Lin, H. Effect of Alum-Amended Litter and Stocking Density on Ammonia Release and Footpad and Hock Dermatitis of Broilers. *Agric. Sci. China* **2011**, *10*, 777–785. [\[CrossRef\]](#)
13. Delaune, P.B.; Moore, P.A.; Daniel, T.C.; Lemunyon, J.L. Effect of Chemical and Microbial Amendments on Ammonia Volatilization from Composting Poultry Litter. *J. Environ. Qual.* **2004**, *34*, 728–734. [\[CrossRef\]](#)
14. Lefcourt, A.; Meisinger, J. Effect of Adding Alum or Zeolite to Dairy Slurry on Ammonia Volatilization and Chemical Composition. *J. Dairy Sci.* **2001**, *84*, 1814–1821. [\[CrossRef\]](#)
15. Moore, P.A.; Edwards, D.R. Long-Term Effects of Poultry Litter, Alum-Treated Litter, and Ammonium Nitrate on Phosphorus Availability in Soils. *J. Environ. Qual.* **2007**, *36*, 163–174. [\[CrossRef\]](#) [\[PubMed\]](#)
16. Huang, L.; Moore, P.A.; Kleinman, P.J.A.; Elkin, K.R.; Savin, M.C.; Pote, D.H.; Edwards, D.R. Reducing Phosphorus Runoff and Leaching from Poultry Litter with Alum: Twenty-Year Small Plot and Paired-Watershed Studies. *J. Environ. Qual.* **2016**, *45*, 1413–1420. [\[CrossRef\]](#)

17. Liu, J.; de Neergaard, A.; Jensen, L.S. Increased retention of available nitrogen during thermal drying of solids of digested sewage sludge and manure by acid and zeolite addition. *Waste Manag.* **2019**, *100*, 306–317. [[CrossRef](#)]
18. Sommer, S.; Zhang, G.; Bannink, A.; Chadwick, D.; Misselbrook, T.; Harrison, R.; Hutchings, N.; Menzi, H.; Monteny, G.; Ni, J.; et al. Algorithms Determining Ammonia Emission from Buildings Housing Cattle and Pigs and from Manure Stores. *Adv. Agron.* **2006**, *89*, 261–335. [[CrossRef](#)]
19. Petrovic, J.; Thomas, G. *Reaction of Aluminum with Water to Produce Hydrogen: A Study of Issues Related to the Use Aliminum for On-Board Vehicular Hydrogen Storage*; US Department of Energy: Washington, DC, USA, 2008; pp. 1–26.
20. Haghi, A.K.; Ghanadzadeh, H. A study of thermal drying process. *Indian J. Chem. Technol.* **2005**, *12*, 654–663.
21. Fangueiro, D.; Hjorth, M.; Gioelli, F. Acidification of animal slurry—A review. *J. Environ. Manag.* **2015**, *149*, 46–56. [[CrossRef](#)]
22. McCrory, D.F.; Hobbs, P. Additives to Reduce Ammonia and Odor Emissions from Livestock Wastes: A Review. *J. Environ. Qual.* **2001**, *30*, 345–355. [[CrossRef](#)]
23. Dai, X.; Blanes-Vidal, V. Emissions of ammonia, carbon dioxide, and hydrogen sulfide from swine wastewater during and after acidification treatment: Effect of pH, mixing and aeration. *J. Environ. Manag.* **2013**, *115*, 147–154. [[CrossRef](#)]
24. Petersen, S.O.; Andersen, A.J.; Eriksen, J. Effects of Cattle Slurry Acidification on Ammonia and Methane Evolution during Storage. *J. Environ. Qual.* **2012**, *41*, 88–94. [[CrossRef](#)] [[PubMed](#)]
25. Pagliari, P.H. Variety and Solubility of Phosphorus Forms in Animal Manure and Their Effects on Soil Test Phosphorus. In *Applied Manure and Nutrient Chemistry for Sustainable Agriculture and Environment*; Springer Science and Business Media LLC: Berlin/Heidelberg, Germany, 2014; pp. 141–161.
26. Fordham, A.W.; Schwertmann, U. Composition and Reactions of Liquid Manure (Gülle), with Particular Reference to Phosphate: II. Solid Phase Components. *J. Environ. Qual.* **1977**, *6*, 136–140. [[CrossRef](#)]
27. Huang, X.-L.; Chen, Y.; Shenker, M. Solid Phosphorus Phase in Aluminum- and Iron-Treated Biosolids. *J. Environ. Qual.* **2007**, *36*, 549–556. [[CrossRef](#)] [[PubMed](#)]
28. Yan, Y.; Li, W.; Yang, J.; Zheng, A.; Liu, F.; Feng, X.; Sparks, D.L. Mechanism of Myo-inositol Hexakisphosphate Sorption on Amorphous Aluminum Hydroxide: Spectroscopic Evidence for Rapid Surface Precipitation. *Environ. Sci. Technol.* **2014**, *48*, 6735–6742. [[CrossRef](#)]