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Thermal drying of the solid fraction from biogas digestate: Effects of acidification, temperature and ventilation on nitrogen content

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ABSTRACT

Drying of solids produced from digestate is prone to N losses through NH_3 volatilisation. The applicability of acidification as an NH_3 emission mitigation technique during the drying of solids from digestate was assessed in a drying experiment. Operating conditions comprised four drying temperatures (70–160 °C), two air ventilation rates (natural, 420 ml/min) and three pH levels (9.2, 6.5 and 5.5) of the solids, modified by the addition of concentrated sulphuric acid. Acidification of the solids from digestate significantly decreased the NH_3 emission during drying, irrespective of the drying conditions. A parallel decrease in the organic nitrogen content and an increase in the ammonium content of the solids was observed after acidification of the solids. It was confirmed that acidification before thermal concentration of solids from digestate, minimised NH_3 losses under a wide range of drying conditions.

1. Introduction

Thermal drying is a commercially available post-treatment for the dewatered effluent from the anaerobic digestion (AD) of manure and other biomasses. It is well known that drying facilitates the sanitation, storage and transportation of the solids from digestate (SD) (Arlabosse et al., 2012), however it also alters the nutrient content of the SD and subsequently its agronomic properties (Mondini et al., 1996). In mid-range drying temperatures, the concentration of organic nitrogen (N_{org}) in the solid fraction is only slightly affected (Maurer and Müller, 2012). Nevertheless, the inorganic N (N_{inorg}) content of the solids, mainly as ammonium, is prone to losses through ammonia volatilisation and thus a reduction of the nitrogen (N) fertilising value (Rotz, 2004). In cases where thermal drying is part of the manure or biogas digestate management plan, strategies mainly focus on treatments of the exhausted air, e.g. by scrubbing, to prevent atmospheric N emissions and N recovery rather than on the retention of the inorganic N content in the dried solids (Flotats et al., 2011).

Ammonia (NH_3) volatilisation during drying appears to be unavoidable under normal drying conditions. In manure, ammonium (NH_4^+) and ammonia (NH_3) are in dynamic equilibrium according to the equation:

$$NH_4^+ \leftrightarrow NH_{3g} + H^+$$

Dissociation of non-volatile NH_4^+ to easily volatile NH_3 increases with increased manure temperature and pH, resulting in a higher NH_3 concentration in the manure (Gustin and Marinsek-Logar, 2011). The resulting concentration gradient of NH_3 between manure and the adjacent air is responsible for NH_3 emissions. Nitrogen losses may be enhanced by the enforced aeration commonly applied in modern drying systems. This phenomenon is well documented in a considerable amount of literature reviewed by Sommer et al. (2006). However, there are little available data on N changes during the drying of solid manure or solids produced by dewatering of liquid organic waste. Furthermore, experimental studies on the potential effects of temperature, ventilation rates and pH of manure or solids are so far lacking.

Acidification of animal manure has been proven to be an effective measure to reduce N losses during the storage and field application stages of manure management (Fangueiro et al., 2015). Gradual acidification of animal slurry by the addition of sulphuric acid (H_2SO_4) has been reported to reduce ammonia emission progressively (Stevens et al., 1989; Husted et al., 1991). Strong acidifying agents, such as H_2SO_4, have been proven efficient as NH_3 emission inhibitors due to their ability to maintain a low pH of manure (McCrory and Hobbs, 2001). While acidification as a slurry treatment minimises ammonia emissions, studies have also shown that other physicochemical changes occur in slurry after treatment with strong acids (Hjorth et al., 2012). Specifically, a decrease in the total carbon (C) concentration of manure has been reported, mainly due to C losses through conversions of HCO_3^-/CO_3^{2-} to H_2CO_3 and subsequent gaseous release as CO_2 (Fangueiro et al.,

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2009). Similarly, decrease in the organic nitrogen content of solid fractions of mechanically separated slurry have previously been reported (Fangueiro et al., 2009) due to acid-induced hydrolysis of the least recalcitrant organic matter (Pansu and Gautheyrou, 2007). Furthermore, acidification of slurry before mechanical separation may enhance the dewaterability of the slurry due to the destruction of extracellular polymers and the release of water bonded by the floc matrix (Liu and Fang, 2003). However, the effect of the direct acidification of solids from mechanical separation of digestates, by use of concentrated acid, on their thermal drying behaviour and N content has not yet been investigated in depth.

The objective of the current study was therefore to evaluate how acidification and subsequent thermal treatment affect (i) the drying profile and (ii) the total nitrogen and ammonium nitrogen content of the solids from the mechanical separation of digestate.

The following hypotheses were addressed:

(1) Acidification of SD decreases NH_3 losses during drying, with higher acidification levels resulting in SD with higher inorganic nitrogen content.
(2) Higher drying rates due to higher operating temperatures and ventilation regimes result in higher nitrogen losses.
(3) Acidification of the SD increases the moisture removal rate during drying.
(4) Acidification decreases the organic matter content of the digestate solids, with stronger acidification levels resulting in solids from digestate with lower N_{org} content.

2. Methods and materials

2.1. Solids from digestate

Solids produced from digestate (SD) were collected fresh from Morsø biogas plant, Denmark. The plant receives mainly cow and pig slurry (70% and 20%, respectively) while chicken manure and food waste are used as high bio-methane potential supplements (the remaining 10%). For the separation of the digestate output of the biogas reactor, a decanter centrifuge is installed in the plant. After collection, the solids from digestate were stored frozen (−20 °C) until analysis (in triplicate). Before initiating the experiment the main characteristics of the SD were dry matter content (DM) 26.4% (wet-weight based (w.w)), pH 9.2, NH_4–N 15.1 g kg^{-1}, Total-N 32.5 g kg^{-1}, Total-P 24.7 g kg^{-1} and Total-K 10.6 g kg^{-1} (DM). The day before the experiments, the required amount of SD was thawed overnight at room temperature.

2.2. Analytical methods

To minimise any potential loss of volatile solids, the dry matter (DM) content was determined by drying the SD to constant weight at 80 °C (24 h). The pH was measured by a combined electrode (PHM 210 Meter lab pH meter, Radiometer, Denmark) in a 1:5 (dry matter to volume, DM:vol) solids-to-deionised water ratio. Ammonium and nitrate were analysed by the extraction of wet solids in 1 M KCl (1:20 (DM:vol)). The mixtures were placed in specimen cups (100 ml) and shaken at a 360° vertical shaker for 45 min. The extracts were allowed to settle for 45 min, filtered through grade 44 ashless paper filters (Whatman 44) and kept frozen until analysis. The total N and C content of dried ground solids was determined on an elemental analyser coupled to a mass spectrometer (MS) (ANCA-NT 20-20 system, Sercon, Crewe, UK). Organic N concentration within each pH level of the solids was calculated as:

$$N_{org} = N_{tot} - N_{NH_4d} \quad (1)$$

where N_{org} denotes the organic N concentration of the dried SD, N_{tot} denotes the total N content of the dried SD (as measured by the elemental analyser) and N_{NH_4d} denotes the NH_4–N content of the dried SD. Similarly, total-N concentrations of the fresh solids were estimated as:

$$N_{tot} = N_{org} + (N_{NH_4r} - N_{NH_4d}) \quad (2)$$

where N_{tot}, N_{org} denote the total N and organic N concentration of the SD while N_{NH_4r} and N_{NH_4d} denote the NH_4–N concentration of the raw and dried SD respectively. Total P and other elements were determined in dry samples with ICP-OES after microwave chemical digestion of samples. The digestion media were nitric acid (HNO_3) and hydrogen peroxide (H_2O_2), while hydrogen fluoride (HF) was added in order to improve the dissolution of the solids (Hansen et al., 2013).

2.3. Experimental procedure

The batch drying experiment was performed in a laboratory oven until non-acidified SD reached a DM content of 85%. The option to reach complete drying of the SD was avoided to ensure similar conditions with commercial solid manure driers, where the final product contains approximately 15% moisture (w.w). The specific moisture content is considered as sufficient for storage without significant biological activity. Furthermore it is believed that drying to lower moisture contents could also alter the biophysical properties of the materials (Vesilind and Ramsey, 1996). Drying conditions comprised three factors: drying temperature (70 °C, 100 °C, 130 °C and 160 °C), ventilation (presence or absence of external enforced aeration) and pH of the SD (natural pH or adjusted to two pH levels, 6.5 or 5.5, using sulphuric acid), resulting in a total of 24 different combinations of drying conditions for the SD. The highest operating temperature represented conditions that are easily obtainable in a combined heat and power plant (*e.g.* an engine and generator powered by biogas) and 70 °C was chosen as the lower threshold for partial pasteurisation of the materials. External enforced ventilation was applied to increase the drying rate, and thereby decrease drying time, and evaluate its effect on the nitrogen content of the SD.

Acidification of SD was performed by placing 55 g (w.w) of solids from digestate in a glass beaker (500 ml) and applying concentrated sulphuric acid with a micropipette. Solids were then mixed with the use of a stainless steel spoon to evenly distribute the acid on all surfaces of the solids.

Prior to drying, samples for each acidification level of SD were prepared by placing 13.2 g (DM) of SD in aluminium foil containers (250 ml), which were sealed with their respective lids. All container lids were perforated with 25 holes (Ø = 0.5 mm), evenly distributed across their surface, to facilitate the escape of moisture from the containers and ensure highly reproducible drying conditions, regardless of the passive or active ventilation conditions. Samples under externally ventilated conditions received external air (420 ml min^{-1}; corresponding to a headspace exchange rate of 229 times $hour^{-1}$) from a compressed air supply connected *via* a needle valve regulator and a flow meter through a tube, which was fitted centrally in the lid.

In preliminary trials the time needed to dry the non-acidified SD to a dry matter content of 85% (w.w) under each operational condition was estimated and this time was divided into four drying periods of equal length. A triplicate set of samples remained in the oven for one, two, three or all four drying periods. Samples were then removed, placed in a desiccator and subsequently their weight and pH was recorded. Before being kept frozen for subsequent analyses, part of the SD was removed for immediate extraction of inorganic nitrogen.

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