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Corn cobs efficiently reduced ammonia volatilization and improved nutrient value of stored dairy effluents

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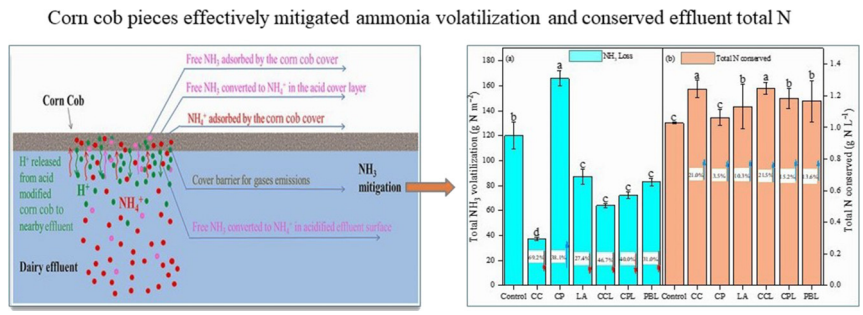
HIGHLIGHTS

- Corn cobs reduced NH_3 volatilization during effluent storage by 69.2%.
- Light expanded clay aggregate stimulated effluent NH_3 volatilization by 38.1%.
- Lactic acid amendment reduced effluent NH_3 volatilization by 27.5%.
- Corn cobs more efficiently retained effluent N during effluent storage.

GRAPHICAL ABSTRACT



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ABSTRACT

Dairy farms produce considerable quantities of nutrient-rich effluent, which is generally stored before use as a soil amendment. Unfortunately, a portion of the dairy effluent N can be lost through volatilization during open pond storage to the atmosphere. Adding of covering materials to effluent during storage could increase contact with NH_4^+ and modify effluent pH, thereby reducing NH_3 volatilization and retaining the effluent N as fertilizer for crop application. Here the mitigation effect of cover materials on ammonia (NH_3) volatilization from open stored effluents was measured. A pilot-scale study was conducted using effluent collected at the Youran Dairy Farm Company Limited, Luhe County, Jiangsu, China, from 15 June to 15 August 2019. The study included seven treatments: control without amendment (Control), 30-mm × 25-mm corn cob pieces (CC), light expanded clay aggregate - LECA (CP), lactic acid (LA) and lactic acid plus CC (CCL), CP (CPL) or 20-mm plastic balls (PBL). The NH_3 emission from the Control treatment was 120.1 g N m^{-2}, which was increased by 38.1% in the CP treatment, possibly due to increased effluent pH. The application of CC reduced NH_3 loss by 69.2%, compared with the Control, possibly due to high physical resistance, adsorption of NH_4^+ and effluent pH reduction. The lactic acid amendment alone and in combination with other materials also reduced NH_3 volatilization by 27.4% and 31.0–46.7%, respectively. After 62 days of storage, effluent N conserved in the CC and CCL treatments were 21.0% and 22.0% higher than that in the Control ($P < 0.05$). Our results suggest that application of corn cob pieces, alone or in combination with lactic acid, as effluent cover could effectively mitigate NH_3 volatilization and retain N, thereby enhancing the fertilizer value of the stored dairy effluent and co-applied as a soil amendment after two months open storage.

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1. Introduction

Livestock production generates an effluent that is a combination of faeces and urine collected from livestock animal houses mixed with water (Kupper et al., 2020; Tullo et al., 2019; Ullman and Mukhtar, 2007). Effluents are the liquid components of dairy cow excreta following liquid-solid separation, with a dry matter content less than 5% (Li et al., 2015; Longhurst et al., 2010). Storage of effluent is needed to allow land application at a suitable time to supply nutrients and water for crops. Effluent storage open to the atmosphere has been found to be a major source of ammonia (NH_3) emissions, amounting to 11.3 Tg NH_3 year^{-1} globally (Cao et al., 2020; Fangueiro et al., 2015; Kupper et al., 2020; Sommer et al., 1993; Xu et al., 2017). In China, annual NH_3 loss from livestock effluent has been estimated at 6.1 Tg, which is equivalent to 49% of total NH_3 volatilization from agriculture in China (Bai et al., 2016). Livestock housing and effluent storage contributed 73% of total NH_3 loss during livestock production (Bai et al., 2017). Ammonia gas is produced through microbial degradation of nitrogen or organic compounds in the bulk effluent (Kupper et al., 2020; Sommer et al., 1993). Depending on the chemical equilibrium between ammonium ions (NH_4^+) and NH_3, which shifts towards NH_4^+ at low effluent pH, the rate of microbial consumption for the NH_3 gas moves to the emitting surface controlled by diffusion and convection (Hjorth et al., 2013; Sommer et al., 2003). Effluent acidification is suggested to be a favourable abatement approach, with the ability to decrease emissions by 75–90% (Berg et al., 2006a; Fangueiro et al., 2015; Regueiro et al., 2016; Wang et al., 2021).

Regueiro et al. (2016) and Cao et al. (2020) have shown that the chemical characteristics of the initial livestock excreta have an important impact on the acidification process and can affect the increase in effluent pH over time due to ammonification during storage. Caceres et al. (2018) and Chen et al. (2020) reported that urea and organic nitrogen in dairy and swine effluents are both substrates for ammonification. Chen et al. (2020) and Karunarathne et al. (2020) found that biogeochemical processes during liquid dairy effluent storages are responsible for the conversion of amine or amide groups into NH_3 or NH_4^+. Acidification of effluents reduces the degradation pathways, regulated by microorganisms, and final effluent characteristics (Shin et al., 2019; Ullman and Mukhtar, 2007). Recent studies have shown that effluent acidification reduced NH_3 volatilization suggesting inhibition of effluent microbial activity and organic matter degradation (Andreev et al., 2017; Berg et al., 2006a; Petersen et al., 2012). Organic acids, such as lactic acids, are generally found in nature as animal and plant components. The use of organic acids is known to have a less detrimental effect on effluent characteristics and the health of farmers compared with inorganic acids such as sulphuric and nitric acid (Dai and Blanes-Vidal, 2013; Regueiro et al., 2016). Although acidification of effluent during storage retains NH_3 as NH_4^+, reduction of effluent pH can potentially stimulate N_2O production by providing more substrates for nitrification and denitrification (Asgedom et al., 2014; Baral et al., 2017; Butterbach-Bahl et al., 2013).

Effluent covering is the placement of natural or synthetic materials on the surface of the effluent and coverings are envisioned to offer resistance to the transfer of NH_3 from the effluent surface to the atmosphere. Biomass covers have hydrophobic sites (Mohan et al., 2014) and higher surface area (Agyarko-Mintah et al., 2017; Peng et al., 2019), which increases their life span and ability to adsorb NH_3 and NH_4^+, respectively. It has also been found that the use of physical covering materials such as light expanded clay particles (LECA), plastic balls, PVC, etc. (Sommer et al., 1993; Hörnig et al., 1999; Xue et al., 1999) cost-effectively reduced NH_3 emission by 37.0–99.5% (VanderZaag et al., 2009; Yagüe et al., 2010). In contrast, some storage covers made of natural materials can also be inexpensive and efficiently prevent diffusivity of NH_3 and these can be incorporated with effluents and applied to crops (Berg et al., 2006a; Holly and Larson, 2017; VanderZaag et al., 2009). These materials include sawdust, rice hulls, wood prunings, clay, corn stalks and grass clippings. The disadvantages of these covers are their biological and chemical degradation potential and their lower capacity to float and maintain adequate effluent coverage during storage.

Recent studies have indicated that corn cobs as an effluent cover can reduce the initial pH of effluent and act as a physical barrier and sorbent to NH_4^+ and NH_3, thereby reducing NH_3 and conserving stored effluent N (Agyarko-Mintah et al., 2017; Fan et al., 2019; Wang et al., 2018). China is the world's second-largest maize producer, with a total production of 257 million tons of dry matter in 2018 (FAO, 2018). As an industry by-product, over 203 million tons of corn cobs are generated annually in the North China Plain growing region (Li et al., 2020; Zhang et al., 2018).

Here the effect of separate and combined treatments of lactic acid and covering materials on NH_3 emission and effluent quality was measured. It was hypothesized that the combined application of corn cobs and LECA would increase the contact with NH_4^+, thereby reducing NH_3 emission and conserving the N source for crop use. Also, using these physical barriers in combination with lactic acid would modify the pH of the effluent and thus, change the chemical equilibrium from NH_3 to NH_4^+. The objectives of this study were: (i) to evaluate the influence of covering materials and lactic acid individually and in combination on NH_3 emission and N conservation; and (ii) identify the optimal method for suppressing NH_3 volatilization from stored effluent.

2. Materials and methods

2.1. Experimental site and design

The field experiment was conducted from 15 June to 15 August 2019 (a time of year when photochemical reactions are due to be active) located at the Youran Dairy Farm Company Limited, Luhe County, Jiangsu Province, China (32°30′N, 118°37′E). The study included seven treatments: control without material amendment (Control), corn cob pieces (CC), light expanded clay aggregate (CP), lactic acid (LA) and lactic acid plus CC (CCL), CP (CPL) or plastic balls (PBL). Corn cobs were collected from the village around the experimental site, air-dried for 5 days and chopped into 30 mm lengths with 25 mm width, producing a density of 0.70 kg m^{-3}. Light expanded clay aggregate (LECA) is clay that has been pelletized and fired in a kiln at a temperature of 400 °C. It was supplied by Borui Environmental Protection Company Limited, Huaian, China. The LECA was granular in nature with a diameter of 10-mm and a density of 0.8 kg m^{-3}. The plastic balls used were expanded polystyrenes made from the moulding of polymeric materials after the application of heat and pressure. The balls had special properties such as low density, low electrical conductivity and toughness (Williams, 2003). They were purchased from a nearby market and had a diameter of 20 mm and a density of 0.87 kg m^{-3} (Table 1).

Analytical grade lactic acid was purchased from Shanghai Macklin Biochemical Company Limited, China. Before starting the experiment, 5 M lactic acid (LA) at a rate of 40 mL L^{-1} was used to adjust the pH of the fresh dairy effluent from 8.11 to approximately 5.00 for the acid (LA, CCL, CPL and PBL) treatments.

Twenty-eight polyvinyl chloride containers (height = 50 cm, surface area = 0.96 m^2, volume = 48.11 L) were buried to 30 cm depth in the ground to simulate ponds for effluent storage.

Fresh (immediately after solid-liquid separation) dairy effluent was collected from the storage ponds at the Youran Dairy Company Limited. Each container was filled with 38.0 L of fresh, homogenized dairy effluent. The application amounts of corn cob, LECA and plastic balls were 3.37, 3.84 and 4.14 kg m^{-2} to form a 5 cm layer over the effluent surface. Treatments were randomized with four replicates and stored under the same conditions. The containers were open to the air, except during NH_3 emission measurements, and closed during rainfall to avoid the effluents overflowing from containers.

Table 1
Physical and chemical properties of effluent and covering materials.

Parameters	Effluent (dry matter)	CC	CP	PB
Organic C (g C kg^{-1})	3.01 ± 0.12	429.15 ± 0.19	1.24 ± 0.00	ND
Total N (g N kg^{-1})	2.10 ± 0.05	10.81 ± 0.30	0.06 ± 0.01	ND
C:N	1.43 ± 0.04	39.77 ± 1.24	20.58 ± 2.67	ND
pH	8.11 ± 0.01	4.65 ± 0.02	6.27 ± 0.08	ND
Density (kg m^{-3})	1.00 ± 0.00	0.70 ± 0.01	0.80 ± 0.06	0.87 ± 0.01
Pore diameter (Å or 10^{-10} m)	ND	8.84 ± 0.96	6.72 ± 0.35	ND
Surface area (m^2 g^{-1})	ND	32.64 ± 3.68	22.14 ± 0.58	ND
Pore volume (cm^3 g^{-1})	ND	0.055 ± 0.00	0.048 ± 0.00	ND
Amount of cover added (kg m^{-2})	ND	3.37	3.84	4.14

Means ± standard errors (n = 4). CC, corn cob; CP, light expanded clay aggregate; PB, plastic balls; ND, not determined.

2.2. NH_3 volatilization measurement

The daily NH_3 volatilization from the effluents was determined twice per day from 09:00 to 10:00 h and from 15:00 to 16:00 h during the first 9 days and subsequently two or three times per week. A continuous air-flow enclosure method was used to measure the NH_3 volatilization. The measuring system comprised a container cover (35 cm diameter and 25 cm height), a vent pipe, a vacuum pump, and a chemical trap bottle, which were connected by plastic pipes. The air in the chamber was pumped through a trap bottle, containing 100 mL of 2% boric acid (H_3BO_3) solution to absorb the emitted NH_3, at an air exchange rate of 15–20 chamber volumes per minute. The NH_3 was titrated with standard 0.10 M sulphuric acid using a combination of bromocresol green and methyl red as an indicator. After each NH_3 measurement, the covers were removed from the storage containers (Cao et al., 2020; He et al., 2018).

2.3. Effluent and cover material analysis

At the start and end of the experiment, effluent samples were taken, after mixing, from three different depths and combined into a composite sample. Total solids (TS) concentrations were determined by drying effluent at 85 °C for 24 h (Misselbrook et al., 2016). Effluent NH_4^+-N and NO_3^--N were extracted by shaking for 1 h with 2 M KCl (effluent/solution of 1:10), and the concentrations of the extracts were determined using a Skalar Segmented flow Analyzer (Skalar, The Netherlands). Effluent DOC was extracted by shaking for 1 h with deionized water at a ratio of 1:10 (v/v), centrifuging, filtering (<0.45 μm) and measuring using a TOC analyzer (Vario TOC, Elementar, Germany). Effluent pH was measured using a pH meter. Effluent organic carbon (OC) and total N (TN) concentrations were determined using the redox titration and Kjeldahl methods, respectively (Horneck and Miller, 1998).

Cover material pH was determined in a 1:100 (w/w) mass to deionized water ratio by agitating for 2 h, filtering and measurement with a pH meter. The surface area, pore volume and pore diameter of the cover materials were determined by nitrogen adsorption/desorption isotherm using a Micromeritics ASAP 2020 (ASAP 2020 Plus Accelerated Surface area and Porosimetry System, Norcross, Georgia, USA). The FT-IR spectra were determined on a Thermo Nicolet 6700 Fourier transform infrared spectrometer using the oven-dried (100–110 °C) KBr pellet technique in a ratio of 1:100 w/w. The total scan number was 32 with a spectral resolution range of 4–8 cm^{-1} (Thermo Fisher Scientific, Alachua, Florida, USA). Cover material C and N concentrations were determined using the redox titration and Kjeldahl TN methods, respectively.

2.4. Data and statistical analyses

The NH_3 fluxes (F, g N m^{-2} day^{-1}) were calculated using the following equation:

$$F = [(2 \times C \times V \times 14)/A] \times (24/t) \quad (1)$$

where V is the volume of H_2SO_4 used in the titration (mL); C is the concentration of the H_2SO_4 (mol L^{-1}); t is the duration of NH_3 collection; and A is the area of the chamber (m^2).

The mitigation efficiencies (ME, %) of the treatments were calculated as follows:

$$ME = [(V_{addition} - V_{control})/V_{control}] \times 100 \quad (2)$$

where $V_{addition}$ and $V_{control}$ are cumulative NH_3 emissions for the material added treatment and Control treatment, respectively. Cumulative NH_3 emissions from each treatment over the storage period were calculated by averaging the net daily flux rates of two consecutive sampling points, multiplying by the time interval between the sampling points and then summing over the whole storage period (Scotto di Perta et al., 2020). The NH_3 emission factor for the effluent total N was calculated by dividing the cumulative NH_3 emissions by the initial effluent N concentration.

Before the data analyses, the assumptions of normality of residuals and constant variance (across the seven treatments) for the ANOVA were checked using the Shapiro-Wilk and D'Agostino kurtosis tests, and the data were Ln transformed if necessary. Differences between treatments were analyzed using one-way ANOVA, followed by Kisher least square differences (LSD) test at a significance of 5%. The correlations between NH_3 flux and pH, DOC, NH_4^+, NO_3^- or TS were determined using Pearson correlation coefficients. Statistical analyses were conducted using SPSS 24.0 for windows (IBM, Inc.).

3. Results

3.1. Effluent characteristics

During storage, the effluent pH in the Control treatment increased from 7.61 to 8.55. The pH increased from 7.27 to 8.30 in the CP treatment, but did not change in the CC treatment (Fig. 2a). As for the lactic acid added treatments, the pH increased from 5.0 at the beginning of the experiment to 7.61, 7.88, 8.08 and 8.14 for the CCL, PBL, LA and CPL treatments, respectively. In the initial phase, the pH tended to increase rapidly in the acidified treatments until day 26 and then remain steady until the end of the storage period, while the Control and CP treatments had values higher than those in the acidified treatments.

The effluent NH_4^+ concentration in the Control treatment decreased from 65.56 to 4.84 mg N kg^{-1} during storage, and decreased from 62.66 to 3.03 mg N kg^{-1} in the CP treatment ($P < 0.05$), while the CC treatment showed a smaller reduction from 60.42 to 17.91 mg N kg^{-1}. With lactic acid addition, the final NH_4^+ concentrations were significantly higher compared with the Control ($P < 0.05$), with reductions from 85.29 to 17.15, 82.68 to 19.36, 84.86 to 15.46 and 89.44 to 20.37 mg N kg^{-1} for the LA, PBL, CPL and CCL treatments during the storage period, respectively (Fig. 2b).

The effluent NO_3^- concentration during the storage period increased from 0.65 to 0.82, 0.74 to 2.11, 0.63 to 5.16, 0.60 to 1.08, 0.71 to 1.05, 0.58 to 1.17 and 0.69 to 1.08 mg N kg^{-1} in the Control, CP, CC,LA, CCL, CPL and PBL treatments, respectively (Fig. 2c). The effluent DOC in the Control treatment slightly decreased from 59.78 to 57.79 mg C kg^{-1}, and decreased from 61.50 to 34.01 and 56.14 to 38.15 mg C kg^{-1} in the CC and CP treatments, respectively. In the lactic acid treatments, effluent DOC was significantly higher compared with the other treatments (Fig. 2d).

Total solids (TS) content in the effluent decreased from 14.48 to 9.46, 15.61 to 9.61 and 15.49 to 10.91 g kg^{-1} in the Control, CC and CP treatments, respectively. In the lactic acid added treatments, TS initially increased and then decreased to 9.35, 5.23, 7.43 and 6.95 g kg^{-1} in the LA, CCL, CPL and PBL treatments, respectively (Fig. 2e).

3.2. Ammonia volatilization

The NH_3 fluxes showed a similar pattern among the treatments during the storage period (Fig. 3a). The NH_3 flux in the Control treatment was 5.00 g N m^{-2} day^{-1} on day 1 and increased to 5.21 g N m^{-2} day^{-1} on day 19 before declining. The NH_3 peak fluxes in the CP treatment were highest, amounting to 5.77 g N m^{-2} day^{-1} on day 19. In contrast, the CC treatment significantly reduced the peak flux to 2.14 g N m^{-2} day^{-1} on day 13. Acidification of effluents significantly ($P < 0.05$) reduced the NH_3 fluxes compared with the Control. The acidified treatments were lower than 0.50 g N m^{-2} day^{-1} until day 19 with subsequent peak fluxes of 1.28, 1.99, 1.31 and 1.48 g N m^{-2} day^{-1} for the LA, CCL, CPL and PBL treatments, respectively.

The NH_3 fluxes were positively correlated with effluent pH in all the treatments (Table 4). The NH_3 fluxes were also correlated with NH_4^+ concentrations in the Control, CC, CP and CCL treatments but negatively correlated with NH_4^+ concentrations in the LA, CPL and PBL treatments. In the Control and CC treatments, NH_3 fluxes were positively correlated with effluent DOC concentration, while negatively correlated with DOC and TS concentrations in the LA, CCL, CPL and PBL treatments.

Cumulative NH_3 volatilization from the Control was 120 g N m^{-2} during the storage period (Fig. 3). The addition of LECA (CP) increased NH_3 emission by 38.1%, but in contrast, application of corn cob (CC) reduced NH_3 losses by 69% ($P < 0.05$) compared with the Control. The reduction was 27% for acid addition alone (LA). The combined application of lactic acid with LECA (CP) or plastic balls (PB) reduced NH_3 loss by 40.0% and 31.0%, respectively, while the reduction was 46.7% for CCL, which was a lesser reduction than with CC alone. During the 62-day monitoring period, 55.0–84.0% of the emitted NH_3 occurred over the first 31 days (Fig. 3a).

The NH_3 emission factor for the effluent total N was estimated at 10.5% for the Control and 14.6% for CP, while reducing to 3.3% for CC. The lactic acid addition effectively reduced the NH_3 emission factor to 7.7%, 5.6%, 6.2% and 7.3% for the LA, CCL, CPL and PBL treatments, respectively.

3.3. Variation of effluent N

The effluent N content decreased from 2.10 to 1.03 g N L^{-1} in the Control, and was close to 1.06 g N L^{-1} in the CP treatment, while it significantly ($P < 0.05$) increased to 1.24 g N L^{-1} for CC after 62 days of storage. As for the lactic acid only treatment, the total N retained in the effluent was 1.13 g N L^{-1}. Compared with the Control, the combination of acid and cover materials significantly increased the conserved total N by 22% in the CCL treatment, while in the CPL and PBL treatments, the increases were 15% and 14%, respectively, although these were not statistically significant.

The highest proportions of effluent N lost as other than NH_3 were 40.6%, 38.5% and 37.6% in the Control, CP and CC treatments, followed by the CCL treatment (35.0%) (Table 2).

Table 2
Effluent N losses during 62 days of storage.

Treatment	NH_3 loss		Total N loss	
	Amount (g N m^{-2})	Proportion (%)	Amount (g N m^{-2})	Proportion (%)
Control	120.13 ± 0.62b	10.54 ± 0.93b	582.77 ± 10.62a	50.92 ± 0.26a
CC	37.03 ± 1.24d	3.25 ± 0.11d	465.80 ± 1.24b	40.86 ± 2.67b
CP	165.94 ± 6.25a	14.56 ± 0.55a	563.05 ± 6.25a	49.39 ± 5.21a
LA	87.16 ± 6.16c	7.65 ± 0.54c	525.65 ± 6.16ab	46.11 ± 6.75ab
CCL	64.00 ± 1.50c	5.61 ± 0.13c	462.84 ± 1.50b	40.60 ± 1.83b
CPL	72.10 ± 2.74c	6.24 ± 0.24c	498.18 ± 2.74a	43.69 ± 2.95b
PBL	82.94 ± 2.83c	7.27 ± 0.25c	506.73 ± 2.83ab	44.45 ± 6.21ab

Means ± standard errors (n = 4). Different letters within the same column indicate significant differences between treatments at $P < 0.05$.

4. Discussion

4.1. Effect of cover materials on NH_3 volatilization

Similar to findings from other studies (Holly and Larson, 2017; Hou et al., 2015), this study observed that corn cobs showed the greatest inhibition of NH_3 emission, by 69.2% compared with Control. Guarino et al. (2006) and Holly and Larson (2017) found that corn cobs and corn stalks reduced NH_3 losses by 60–90% during the storage of liquid cattle and swine manures (Table 5). VanderZaag et al. (2008) and Hou et al. (2015) also reported 60–78% reduction of NH_3 emission by cob based covers during liquid manure storage. The NH_3 emission factor for the effluent N in the CC treatment was 3.25%, which was at the low end of the range of 3.1–21.8% reported previously during storage of pig and dairy effluents with biomass covers (Table 5) (Gronwald et al., 2018; Wang et al., 2016). Our results suggest that applying corn cobs is an effective strategy for reducing NH_3 emission during effluent storage.

This study found that the effluent NH_4^+ concentration in the CC treatments after 62 days of storage was 17.9 mg N kg^{-1}, which was much higher than in the Control (4.8 mg N kg^{-1}). Mao et al. (2017) and Scotto di Perta et al. (2020) also reported that NH_4^+ concentration increased when straw and apple pomace were applied as covers to store and compost dairy effluent and pig manure. Several possible mechanisms are suggested. Firstly, the addition of corn cobs effectively reduced effluent pH from 7.61 to 7.18 initially, with a final pH of 7.64 after 62 days of storage, which was lower by 0.91 units compared with the Control. The additional negatively charged acidic functional groups and Lewis acid phenols might have reduced basic ammonia by reacting with it through an acid-base neutralization reaction, thereby retaining NH_3 in the form of NH_4^+ and decreasing NH_3 emissions (Lanyon et al., 1985; Regueiro et al., 2016). Secondly, the corn cobs were acidic and contained substantial oxygen-containing functional groups (Fig. 1) which could weaken the degradation and ammonification of effluent organic substances through a neutralization effect by adsorbing DOC, thereby reducing the production of NH_4^+ (Agyarko-Mintah et al., 2017; Peng et al., 2019; Yagüe et al., 2010). The neutralization effect of corn cob by adsorbing DOC could be explained by the low effluent DOC in the CC treatment during the storage (Fig. 2d) and further reduced by 41.1% in the final effluent compared with the Control treatment (Table 3). This reduction of DOC in the effluent was attributed to the sorption on corn cob (Xing et al., 2008), which could affect mineralization. The effluent labile organic C could supply energy to microorganisms, which releases NH_4^+ and subsequent NH_3 loss by mineralizing effluent organic N (Chen et al., 2020). Therefore, the sorption of labile C in the effluent on a corn cob (Agyarko-Mintah et al., 2017) could inhibit mineralization, whereas the sorption of NH_4^+ could also decrease NH_3 volatilization. Thirdly, negative carbonate ions and the large surface area and pore volume of the corn cobs were found to adsorb NH_3 (Agyarko-Mintah et al., 2017; Holly and Larson, 2017; Mao et al., 2017). Fourthly, corn cobs directly act as a physical barrier to reduce air movement across the surface of the effluent, thereby increasing the

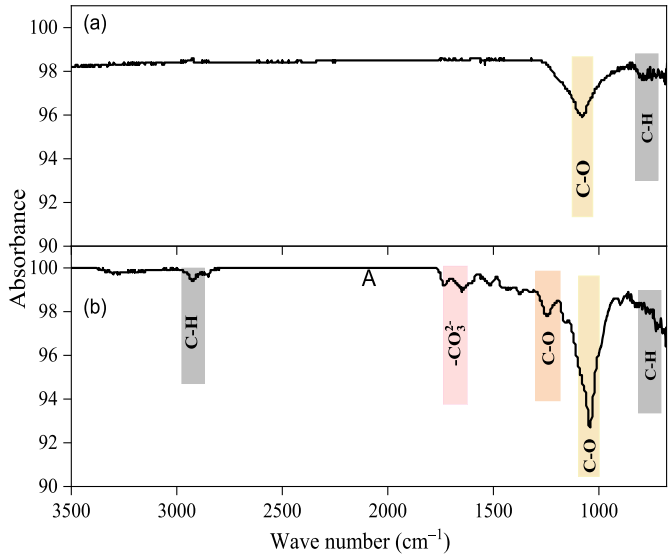

Fig. 1. FTIR spectra of cover materials corn cob (a) and light expanded clay aggregate (b).

surface resistance to NH_3 loss (Sommer et al., 1993; Yagüe et al., 2010). Unfortunately, Yagüe et al. (2010) concluded that biomass covers have short effective duration because the mitigation efficiency could be affected by decomposition of the cover over time. In the current study, the degradation of corn cobs can be seen from the changes in the rate of NH_3 losses from the start of the storage and stabilization from day 32 until the end of the storage period, indicating that decomposition of the corn cob occurred (Peng et al., 2019; VanderZaag et al., 2009). Guarino et al. (2006) and Scotto di Perta et al. (2020) found that a corn stalks cover lasted for 1–4 months depending on the weather, the effluent dry matter content (the greater the effluent dry matter, the longer the cornstalks would float) and the depth of the cover layer. Scotto di Perta et al. (2020) and Smith et al. (2007) found that periodic addition of cover during the storage period sustained the efficacy of the effluent cover. The additional corn cob layer would further decrease ammonia volatilization either via physical barrier or sorption of NH_4^+ and NH_3 (Sommer et al., 1993), but the additional layer could stimulate N_2O emissions (Misselbrook et al., 2016; Sommer et al., 2000). Guarino et al. (2006) found a 15.0% reduction in CO_2 when higher corn cob cover layer (14 cm) was applied, which in turn reduced effluent pH. He et al. (2019) concluded that low pH is conducive for acidophilic denitrifiers. The additional corn cob could create a favourable environment for N_2O producing microorganisms in N (NH_4^+-N and NO_3^--N) rich effluent and an anaerobic zone for denitrification (Xue et al., 1999). More oxygen is available in the interfacial layer between the effluent and corn cob, thereby increasing NH_4^+ nitrification and supplying substantial substrates for denitrification (Zhang et al., 2021), and N_2O emission from the bulk effluent (Sommer et al., 2006). The corn cob is also high in labile organic carbon such as carbohydrate (Sommer et al., 2000), that could supply energy for denitrifiers, hence increasing N_2O and N_2 production (Cao et al., 2020). Thus, we suggest that corn cobs could reduce NH_3 volatilization for approximately 2 months, and efficiency could be further enhanced by adding another corn cob layer during the storage period (Fig. 4).

NH_3 volatilization in the CP treatment increased by 38% compared with the Control. This is consistent with some previous studies showing increased NH_3 losses during effluent storage with permeable covers (Holly and Larson, 2017) but differs from Guarino et al. (2006) who reported a 1.9% reduction in NH_3 volatilization when a 7-cm layer of expanded clay was applied over the storage of liquid dairy manure for 30 days. In the current study, a natural crust was formed in the Control treatment during the storage, as has been reported previously (Chen et al., 2018; Scotto di Perta et al., 2020). Misselbrook et al. (2005)

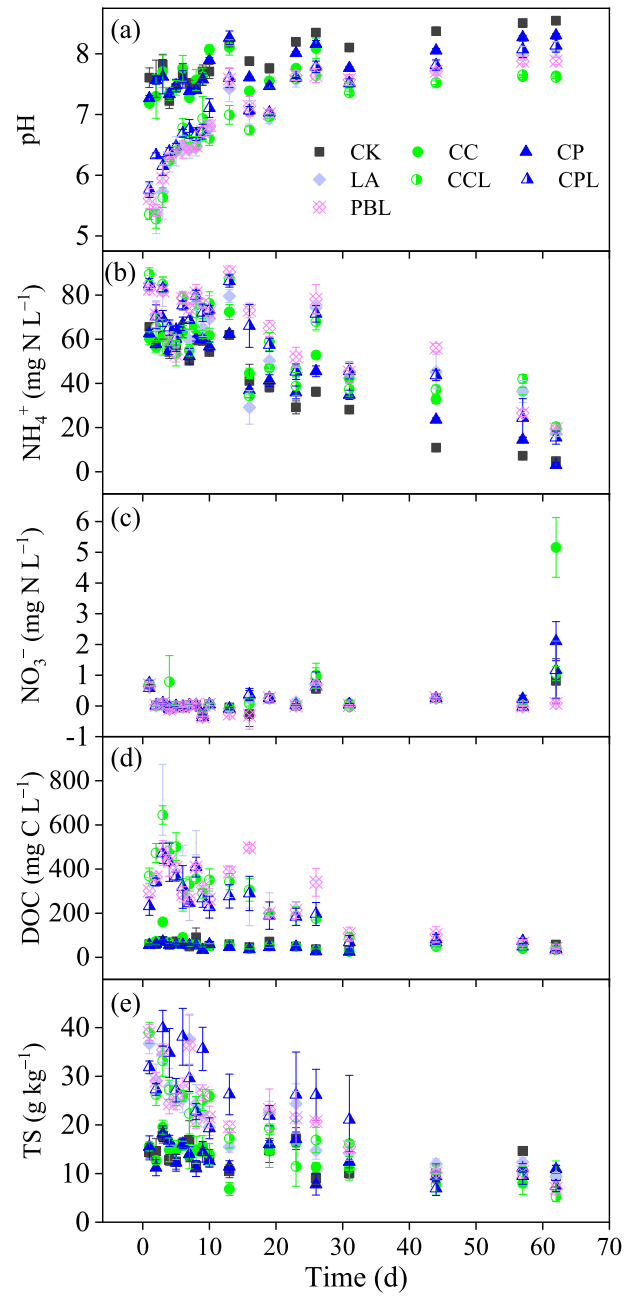

Fig. 2. Effect of treatment on changes in effluent characteristics: effluent pH a, ammonium concentration, NH_4^+ b, nitrate concentration, NO_3^- c, dissolved organic carbon, DOC d, and total solids, TS e, during storage. Vertical bars represent SEMs ($n = 4$). CK, Control; CC, corn cob only; CP, light expanded clay aggregate only; LA, lactic acid only; CCL, lactic acid + corn cobs; CPL, lactic acid + clay particles; PBL, lactic acid + plastic balls.

demonstrated that surface crust formation was accelerated with increasing dry matter content in dairy effluent. On the other hand, effluent natural surface crust development was also enhanced by the release of carbon dioxide (CO_2) and methane (CH_4), produced by anaerobic fermentation processes during effluent storage, as bubbles to the surface (Scotto di Perta et al., 2020; Smith et al., 2007). There have been a few studies that reported enhancement of NH_3 reduction with higher depths of clay covers, unlike the current study with a 5 cm clay cover. For instance, Berg et al. (2006a), Berg and Pazsiczki (2006), Guarino et al. (2006) and Misselbrook et al. (2016) reported that LECA with a depth range of 7–14 cm could reduce effluent NH_3 volatilization by 64–83% during 30–120 days of dairy and swine effluent storage in the absence of a surface crust. The current study, however, found that

Table 3
Variation of effluent characteristics during storage.

		Control	CC	CP	LA	CCL	CPL	PBL
pH	Initial	7.61 ± 0.16a	7.18 ± 0.01b	7.27 ± 0.05ab	5.71 ± 0.15c	5.36 ± 0.09c	5.76 ± 0.13c	5.62 ± 0.16c
	Final	8.55 ± 0.05a	7.64 ± 0.03b	8.30 ± 0.03a	8.08 ± 0.12a	7.61 ± 0.01b	8.14 ± 0.11a	7.88 ± 0.05b
TS (g kg^{-1})	Initial	14.48 ± 1.66a	15.61 ± 2.27a	15.49 ± 2.27a	15.71 ± 2.09a	16.89 ± 2.13a	15.84 ± 1.30a	15.01 ± 1.64a
	Final	9.46 ± 2.22a	9.61 ± 2.98a	10.91 ± 0.81a	9.35 ± 0.87a	5.23 ± 1.02c	7.43 ± 1.15b	6.95 ± 1.37b
DOC (mg C L^{-1})	Initial	59.78 ± 5.52a	61.50 ± 5.62a	56.14 ± 5.34a	60.05 ± 1.18a	63.00 ± 1.56a	59.12 ± 1.30a	60.37 ± 3.95a
	Final	57.78 ± 7.11a	34.01 ± 4.45b	38.15 ± 3.43b	40.63 ± 5.16ab	46.08 ± 4.19b	34.73 ± 4.55b	40.42 ± 0.70b
Total N (g N L^{-1})	Initial	2.10 ± 0.00a	2.10 ± 0.05a	2.10 ± 0.01a	2.10 ± 0.02a	2.10 ± 0.05a	2.10 ± 0.03a	2.10 ± 0.01a
	Final	1.03 ± 0.01c	1.24 ± 0.06a	1.06 ± 0.05c	1.13 ± 0.14b	1.25 ± 0.04a	1.18 ± 0.06b	1.17 ± 0.03b
NH_4^+-N (mg N L^{-1})	Initial	65.56 ± 2.01b	60.42 ± 2.90b	62.66 ± 1.68b	85.29 ± 3.61a	89.44 ± 2.90a	84.86 ± 2.52a	82.68 ± 1.08a
	Final	4.84 ± 0.27c	17.91 ± 0.74ab	3.03 ± 1.31d	17.15 ± 1.12ab	20.37 ± 1.74a	15.46 ± 2.98b	19.36 ± 0.13a
NO_3^--N (mg N L^{-1})	Initial	0.65 ± 0.04a	0.63 ± 0.02a	0.74 ± 0.10a	0.60 ± 0.03a	0.71 ± 0.04a	0.58 ± 0.03a	0.69 ± 0.06a
	Final	0.82 ± 0.72c	5.16 ± 0.97a	2.11 ± 0.64b	1.08 ± 0.03c	1.05 ± 0.23c	1.17 ± 0.91c	1.08 ± 0.03c

Means ± standard errors (n = 4). Different letters within the same row indicate significant differences between treatments at $P < 0.05$. CK, control; CC, corn cob only; CP, light expanded clay aggregate only; LA, lactic acid only; CCL, lactic acid + corn cob; CPL, lactic acid + clay particles; PBL, lactic acid + plastic balls.

even if the LECA amendment formed a surface crust, there existed gaps allowing NH_3 release, likely due to low layer thickness with the low addition rate in this study.

The optimal pH for microbial degradation activity of effluents has been found to range from 7 to 9 (Muck and Steenhuis, 1982; Peng et al., 2019; Xue et al., 1999). The effluent pH following LECA addition increased rapidly and remained at approximately 8.3, which is in line with earlier findings (Andreev et al., 2017; Ni, 1999; Wang et al., 2014). This pH was more favourable for the decomposition of organic acids, uric acids (Yagüe et al., 2010) and amino acids in dairy effluent (Lanyon et al., 1985; Misselbrook et al., 2016; VanderZaag et al., 2009; Wood et al., 2014), which in turn could release NH_4^+, bicarbonate or carbonate (Chen et al., 2018; Misselbrook et al., 2016; Smith et al., 2007), therefore maintaining higher effluent pH and high NH_3 emission. In the current study it was found that the first NH_3 peak flux, on day 1, decreased by 34% compared with the Control, indicating that floating LECA could have initially adsorbed the abundant effluent NH_4^+. The subsequent effluent NH_3 losses were, however, higher, which indicates that the LECA became fully saturated and began to release the initially adsorbed NH_3 with increasing effluent pH, probably due to the 5 cm clay cover addition rate (Dontsova et al., 2005; Witter and Lopez-Real, 1988). Additionally, significantly lower DOC concentration in the CP treatment than in the Control implied that LECA addition stimulated decomposition of DOC. Previous studies have shown that LECA can provide more favourable microsites for proliferation and activity of microbes, which in turn stimulates the decomposition of organic matter and consequently increases NH_4^+ release and NH_3 emission (Miner et al., 2003; VanderZaag et al., 2008). Petersen and Ambus (2006) reported that microbial activity was lower with straw cover and a natural crust, but was increased with LECA covers on stored swine and dairy effluents. The presence of microbial growth could lower LECA performance as an effluent cover due to bio-plugging of the LECA (Clanton et al., 1999; VanderZaag et al., 2008). This process catabolizes NH_3 (Miner et al., 2003), thereby increasing NH_3 volatilization (Mlih et al., 2020). These results suggest that CP is not a reliable option for mitigating NH_3 loss during storage of dairy effluent.

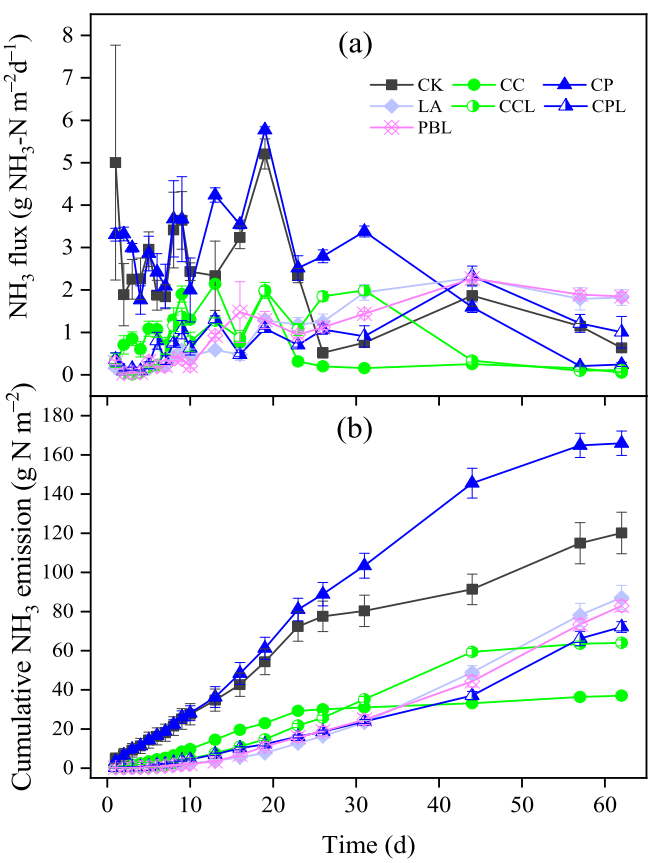

Fig. 3. Effect of treatment on ammonia, NH_3 flux a, and cumulative emission b, during effluent storage. Vertical bars represent SEMs ($n = 4$). CK, Control; CC, corn cob only; CP, light expanded clay aggregate only; LA, lactic acid only; CCL, lactic acid + corn cobs; CPL, lactic acid + clay particles; PBL, lactic acid + plastic balls.

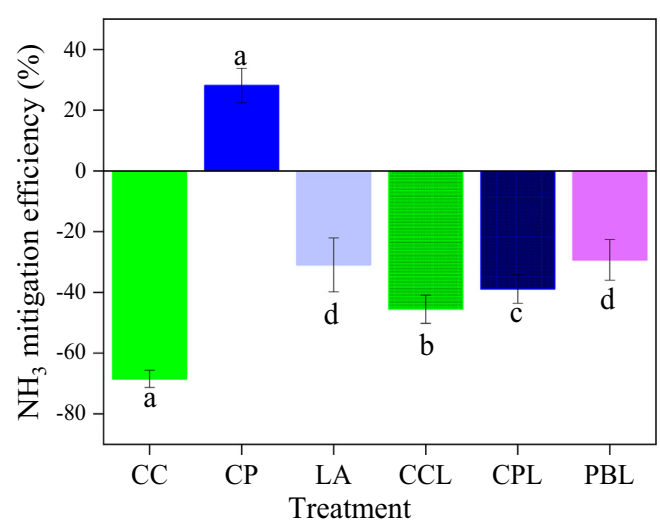

Fig. 4. Effect of material addition on mitigation of NH_3 during effluent storage. Different letters represent significant differences between treatments at $P < 0.05$. Vertical bars represent SEMs ($n = 4$). CC, corn cob only; CP, light expanded clay aggregate only; LA, lactic acid only; CCL, lactic acid + corn cobs; CPL, lactic acid + clay particles; PBL, lactic acid + plastic balls.

Table 4
Correlation between effluent NH_3 fluxes and effluent pH, ammonium (NH_4^+), nitrate (NO_3^-), dissolved organic carbon (DOC) and total solids (TS).

Treatment	pH	NH_4^+	NO_3^-	DOC	TS
Control	0.63**	0.58**	−0.37*	0.38*	0.35
CC	0.30*	0.78**	−0.63**	0.34*	0.15
CP	0.56**	0.72**	−0.55**	−0.15	0.28
LA	0.92**	−0.60**	−0.37	−0.80**	−0.82**
CCL	0.50**	0.27*	−0.13	−0.48*	−0.26
CPL	0.74**	−0.35*	0.18	−0.71**	−0.64**
PBL	0.87**	−0.61**	0.11	−0.66**	−0.83**

* $P < 0.05$.
** $P < 0.01$.

4.2. Effect of lactic acid on NH_3 volatilization

The NH_3 volatilization from the stored effluent was reduced by 27.4% with lactic acid addition alone while by 31.0–46.7% in the CCL, CPL and PBL treatments. The mitigation effects of acids on NH_3 emission are not fully known, varying from greater than 90% to less than 50% (Dai and Blanes-Vidal, 2013; Park et al., 2015; Parkhurst et al., 1974) related to the acid type and rate. Wang et al. (2014) reported a 40.2% reduction of NH_3 volatilization during pig slurry storage when the pH was adjusted to 5.5 with sulphuric acid. Effluent acidification is aimed to minimize NH_3 volatilization by raising the NH_4^+/NH_3 ratio (Fangueiro et al., 2015). As well, effluent organic matter degradation could be decelerated, lowering NH_4^+ production from effluent proteins (Ndegwa et al., 2008; Sun et al., 2014). Hartung and Phillips (1994) concluded that when the temperature is held constant, pH controls the equilibrium between NH_4^+ and NH_3 in aqueous media (Harper et al., 2000; Molloy and Tunney, 1983). The highest NH_3 losses occur between pH 7–10; while NH_3 emissions decrease at pH lower than 7; around a pH of 5, there is almost no quantifiable free NH_3 in effluent (Hartung and Phillips, 1994; Kupper et al., 2020). In the current study, effluent pH was lowered to 5.36–5.76 with the addition of lactic acid and remained below 7 during the first 10 days of storage but was higher than 7.5 from day 26 onward. Misselbrook et al. (2016) also found an increase in pig slurry pH 25 days after slurry acidification. The microbially regulated degradation of effluent DOC under anaerobic conditions depends on hydrolysis (Prado et al., 2020; Regueiro et al., 2016) and is enhanced under acidic conditions (Hjorth et al., 2013). The increased hydrolysis under acidic conditions can release more easily degradable monomers such as low molecular weight carbohydrates through degradation of dissociated organic acids and mineralization of organic N and carbohydrates (Hjorth et al., 2015; Hjorth et al., 2013; Sommer et al., 2017), which in turn increases effluent pH (Eriksen et al., 2008; Regueiro et al., 2016; Wang et al., 2014).

Previous studies have shown that effluent pH buffering capacity is influenced by the type and addition rate of acids (Sommer et al., 2017). In an in-situ study using lactic and sulphuric acids, Petersen et al. (2014) and Regueiro et al. (2016) reported an 80–90% reduction in NH_3 volatilization when H_2SO_4, lactic and citric acid addition rates were 10 kg t^{-1} and pH was reduced to 5.5, but only a 41–49% decrease when pH was lowered to 6.5 using the same acids at lower rates over 60–83 days of dairy and swine effluent storage. More importantly, lactic acid compared with inorganic acids was less effective in reducing NH_3 emissions, since lactic acid was easily decomposed and could not maintain steady effluent pH conditions (Ndegwa et al., 2008; Parkhurst et al., 1974). However, organic acids such as lactic acid have apparent advantages because they do not seriously affect the final effluent characteristics and the health of farmers compared with inorganic acids (Dai and Blanes-Vidal, 2013; Wang et al., 2021). Lactic acids are less expensive useful chemical additive produced by bacteria in organic manure fermentation and has been applied as an acidulant in food, textile and pharmaceutical industries (Hofvendahl and Hahn-Hägerdal, 2000). Additionally, LA bacteria was found to survive below pH 5, compared with other bacteria (Chopin, 1993; Hofvendahl and Hahn-Hägerdal, 2000), which can sustainably release H^+ and reacts with NH_3 during the early stage of the effluent storage (Nie et al., 2020), thereby controlling NH_3 volatilization. Results from the current study indicated that the low reduction effect of lactic acid on effluent NH_3 volatilization was likely to be primarily due to the low addition rate (40 mL L^{-1} effluent). Based on the quantity of lactic acid (134 mL L^{-1} of dairy or swine effluent) required to obtain 87% NH_3 reduction at pH 5.5 in their 60-day storage study (Regueiro et al., 2016), it is likely that a similar rate of 5 M lactic acid would have been required for the two months (62 days) of storage in the current study.

Table 5
Summary of available researches on NH_3 mitigation strategies used in effluent storage.

Method	Region	Mitigation material	Specific parameter modified	Effluent type	Storage duration	Mitigation efficiency	References
Biomass cover	USA	Corn cob	5 cm layer depth	Dairy	49 days	90.0%	Holly and Larson, 2017
	Italy	Corn stalk	7 cm layer depth	Dairy	30 days	60.0%	Guarino et al., 2006
	Netherlands	Straw	5 cm layer depth	Dairy	70 days	78.0%	Hou et al., 2015
	China	Corn cob	5 cm layer depth	Dairy	62 days	69.2%	This study
Clay cover	Italy	LECA	7 cm layer depth	Dairy	30 days	1.9%	Guarino et al., 2006
	Germany	LECA	6 cm layer depth	Pig	120 days	83.0%	Berg et al., 2006a
	England	LECA	7 cm layer depth	Dairy	60 days	64.0%	Misselbrook et al., 2016
	China	LECA	5 cm layer depth	Dairy	62 days	38.0%[a]	This study
Natural crust	England	Natural crust	> 20 cm natural crust	Dairy	180 days	60.0%	Smith et al., 2007
	Denmark	Natural crust	7 cm natural crust	Dairy	60 days	85.0%	Sommer et al., 1993
	China	Natural crust	NB	Dairy	62 days	27.6%	This study
Acidification	England	Sulphuric acid	Acidified to an initial pH 5.5	Dairy	72 days	68.0%	Misselbrook et al., 2016
	Germany	LA	Acidified to an initial pH 4.8	Dairy	92 days	90.0%	Berg et al., 2006b
	Germany	LA	Acidified to an initial pH 4.8	Dairy	168 days	86.0%	Berg et al., 2006a
	China	Sulphuric acid	Acidified to an initial pH 5.5	Pig	95 days	40.2%	Wang et al., 2014
	Portugal	LA	Acidified to an initial pH 5.5	Dairy	60 days	47.4%	Regueiro et al., 2016
	Portugal	LA	Acidified to an initial pH 5.5	Pig	60 days	40.0%	Regueiro et al., 2016
	China	LA	Acidified to an initial pH 5.0	Dairy	62 days	27.4%	This study
Acid + cover	Germany	LA + LECA	Acidified to an initial pH 4.8 + 6 cm LECA	Dairy	92 days	59.0%	Berg et al., 2006a
	Germany	Lactic acid + straw	Acidified to an initial pH 4.8 + 6 cm straw	Pig	92 days	86.0%	Berg et al., 2006a
	England	Sulphuric acid + LECA	Acidified to an initial pH 5.5 + 7 cm LECA	Dairy	70 days	75.0%	Misselbrook et al., 2016
	China	Lactic acid + LECA	Acidified to an initial pH 5 + 5 cm LECA	Dairy	62 days	40.0%	This study
	China	Lactic acid + PB	Acidified to an initial pH 5 + 5 cm PB	Dairy	62 days	31.0%	This study
	China	Lactic acid + CC	Acidified to an initial pH 5 + 5 cm CC	Dairy	62 days	46.7%	This study

CC, corn cob; LECA, light expanded clay aggregate; PB, plastic balls; ND, not determined; LA, lactic acid; value[a], increased NH_3 volatilization.

During the 62 day storage period, the mitigation effect of NH_3 emissions compared with the Control was further increased when LECA or corn cob pieces were added with lactic acid in the CPL and CCL treatments, respectively. This is consistent with Berg et al. (2006a) and Berg and Pazsiczki (2006) who reported a further reduction in cumulative NH_3 with a combined addition of lactic acid with clays or straw. Unexpectedly, NH_3 mitigation efficiency was significantly lower in the CCL treatment than in the CC treatment. From day 25 to 45, the CCL treatment showed higher NH_3 fluxes and lower effluent NH_4^+ concentrations compared with the CC treatment. This may be related to a rapid decrease in DOC during the period. Compared with the Control treatment, effluent DOC was reduced by 20.2% in the CCL treatment (Table 3). Misselbrook et al. (2016), Regueiro et al. (2016) and VanderZaag et al. (2009) found that the addition of labile organic C, such as organic acids, accelerated decomposition of corn cobs (Fangueiro et al., 2015; Kupper et al., 2020). VanderZaag et al. (2009) reported that straw cover could provide additional labile organic C, which reduced bubbling and increased effluent surface layer aerobic microbial activity. The rapid decrease in the effluent's DOC in the CCL treatment could be due to the decomposition of the added labile organic C and dissociated lactic acid, which increased pH and NH_4^+ concentration of the effluent, promoting microbial growth and consequently increasing NH_3 volatilization (Kupper et al., 2020; Petersen et al., 2013; Regueiro et al., 2016). From this study, it was found that the decomposition of corn cobs was more apparent in the CCL treatment than in the CC treatment. Thus, the combined amendment with corncobs and lactic acid was not as effective in reducing NH_3 emission compared with corn cobs alone.

4.3. Effect of acid and cover materials on effluent N

The effluent N concentration after 62 days of storage was highest in the CC and CCL treatments, followed by LA, CPL and PBL, and lowest in the CP and Control treatments. The lowest effluent N loss ratios were 40.6% and 40.9% in the CC and CCL treatments, respectively, and the highest value was 51.1% in the Control. These losses are still very high, possibly due to the high temperature during the study period. The air temperature ranged from 22.5 °C to 32.5 °C, with an average of 27.3 °C. Yagüe et al. (2010), Fangueiro et al. (2015) and Regueiro et al. (2016) reported a 27–77% decrease in total N when corn stalks and organic acids were applied during storage of pig or dairy effluents compared with the Control. Results from the current study indicate that corn cob amendment more efficiently retained effluent N compared with other treatments.

In this study, effluent N was primarily lost via gaseous emission. Unexpectedly, although the CC treatment more efficiently reduced NH_3 volatilization (Fig. 5), it exhibited the highest N losses, possibly via other gases such as N_2O, N_2 and NO_x, apart from the LA and Control treatments. Hou et al. (2015) reported that N_2O emissions were increased 8.6-fold when chopped straw was added to the stored slurry. Sommer et al. (2000) also reported that N_2O emission was higher from straw covers than from LECA covers. The CC treatment not only suppressed NH_3 volatilization, it also reduced oxygen diffusion into the effluent interface developed between the stored effluent and the air-filled corn cob surface layers, which could have facilitated the coexistence of aerobic and anaerobic zones for nitrification and denitrification (Sommer et al., 2000; Wang et al., 2021). More importantly, the corn cobs could have provided a source of energy for denitrification, thereby stimulating N_2O and, especially, N_2 production depending on the NO_3^- concentration of the effluent (Cao et al., 2020; Regueiro et al., 2016). Further study is required to evaluate the influence of corn cobs on N_2O and N_2 production during denitrification.

5. Conclusion

Storage of dairy effluent is a hotspot source of NH_3 volatilization impacting the final effluent fertilizer value. The use of LECA as storage cover on stored effluent resulted in an increase in NH_3 volatilization. In contrast, a corn cob cover layer was effective in decreasing effluent NH_3 and total N losses by 69.2% and 21.0%, respectively, compared with the Control. Lactic acid application alone, at a rate of 40 mL L^{-1} of effluent, also reduced NH_3 losses, by 27.4% and by 31.0–46.7% when co-applied with cover materials, compared with the Control. The use of corn cobs can be seen as a win-win option and an excellent option instead of lactic acid, considering the comparatively low commercial value of corn cobs. Based on this comprehensive study, we recommend that effluent, together with the corn cob cover could be used for soil amendment after 2 months of open pond storage.

CRediT authorship contribution statement

Obemah David Nartey: Conceptualization, Formal analysis, Investigation, Methodology, Writing - original draft, Writing - review & editing. **Deyan Liu**: Methodology, Supervision, Resources, Validation. **Jean Yves Uwamungu**: Conceptualization. **Jiafa Luo**: Writing - review & editing. **Stuart Lindsey**: Writing - review & editing, Validation. **Hong J Di**: Writing - review & editing. **Zengming Chen**: Conceptualization. **Junji Yuan**: Conceptualization. **Weixin Ding**: Conceptualization, Supervision, Resources, Project administration, Validation, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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