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Evaluation of a Tomato Waste Biofilter for the Retention of Gaseous Losses from Pig Slurry Hygienization by pH Modification

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Abstract: The use of pig slurry as organic fertilizer in intensive horticulture could be possible after hygienization to avoid contamination of products. This research aimed to evaluate a mixture of tomato waste and rice husk as biofilter media to reduce NH$_3$, N$_2$O, CO$_2$, and CH$_4$ losses from a simple and low-cost solution for slurry hygienization by pH modification. The experiment was made in a system of laboratory scale biofilters connected to jars filled with raw slurry as control and three treatment methods: acidified slurry, alkalinized slurry, and neutralized slurry. The gas concentrations were measured for 35 days, and the composition of slurries and biofilters were determined. The results of this study showed that the mixture of biofiltering media, composed of tomato waste and rice husk, has the potential to retain NH$_3$ and greenhouse gases (GHG) from a simple and low-cost solution for slurry hygienization by pH modification. Compared to the treatment raw slurry biofilter, the treatment neutralized slurry biofilter, subjected to a combined treatment by alkalinization/neutralization, retained 19% NH$_3$ and 4% CO$_2$, and 83% CH$_4$ losses and had no impact on N$_2$O and global warming potential. Thus, the use of tomato waste biofilter during alkalinization did not increase the loss of NH$_3$ and reduced GHG compared to raw slurry, avoiding the subsequent neutralization of slurry for environmental reasons, and could be used as an organic fertilizer in horticulture. However, using the combined alkalinization/neutralization treatment will improve the fertilizer value of the slurry by adjusting the pH from 9.5 to 7.5.

Keywords: ammonia; biofilter; GHG emissions; mitigation measure; pH adjustment; tomato waste

1. Introduction

The industrialization of livestock production over Europe led to specialized farms with a slurry (liquid manure) based system, that are generally dissociated from crop production [1,2]. In the EU-28, close to 1.2 billion tons of manure are produced annually, mainly from 89.5 million bovine animals, 147.8 million pigs, and 1.7 billion poultry animals [3]. Consequently, while livestock production continues to increase (duplication in 2050 [4]), the surface of agricultural soil available to receive the derived animal slurry tends to diminish. The dissociation of the two systems strengthens the problem related to slurry management [1], and the efficiency of integrated productive systems were outlined in several studies [5,6]. A frequent consequence of this dissociation is the over-application of slurry in some fields and consequent environmental problems, such as nitrate leaching and greenhouse gases (GHG) and ammonia (NH$_3$) emissions.

Slurry treatment has been pointed out as a solution to improve slurry management. Namely, solid–liquid separation leads to a solid fraction rich in organic matter and phosphorus (P) that can easily be transported to other farms [7]. Such techniques are now
widely used at farm scale, but interest in the resulting liquid fraction is still scarce and many farmers mix it back in the slurry store. Anaerobic digestion is another solution to improve slurry management, but it requires strong investment and, consequently, is marginally used in Portugal. The challenge is therefore to find some new soil areas to apply raw slurry or the derived liquid fraction. In Europe, slurry is mostly applied on grasslands and cereals [8–11]. The use of slurry for soil fertilization in industrial horticulture has been considered but remained marginal [12–14]. Minimizing the use of chemical fertilizers is essential for integrated horticultural production [15], but also for environmentally friendly development. Furthermore, some alternatives to mineral P fertilizer are needed since current global reserves of P rocks may be depleted in 50–100 years [16]. Fertilization using slurry has the advantage of providing nitrogen (N) and P, but also a significant part of organic matter that contributes to soil productivity. Mineral fertilizers replacement by slurry in industrial horticulture should therefore be a successful solution.

The main limitation is the fact that land application of untreated livestock manures increases the health risk for the animals and people, because of the diffusion of pathogens into the soil and the air, and because it creates unpleasant odors [17]. A wide range of pathogenic microorganisms exists in slurry [18], and slurry treatment is recommended before soil application to minimize the risk of human or animal contamination since some microorganisms and bacterial zoonosis survive for long periods after soil application [19,20]. Pathogen survival relies on several factors such as initial level of contamination, time, pH, salinity, dry matter content, competing microbiota, and temperature [17]. The only sanitation process used at farm scale before application to cereals or grass is slurry storage during a specific period (almost 60 days in summer and 90 days in winter), before application to grazing land [21]. However, even if storage for 90 days might be enough to solve the pathogens issues [22], the bacteria survival is more complex, and some studies have reported survival well more than 90 days [23].

When considering slurry application to horticulture products, a deeper slurry sanitation must be guaranteed to avoid human health problems, but also for marketing reasons. Chemical treatment of slurry by pH modification has proved to be efficient at eliminating most pathogens and bacteria present in slurry. Disinfection of slurry by addition of ash, lime, urea, and NH₃ has been tested [24–26], but the selection of the chemical agent must consider the time necessary for adequate treatment, the anti-microbial effectiveness, and the agronomic value of the product [26]. Indeed, a quick rise of pH and consequent die-off of pathogens can be achieved by lime addition, but the effect is temporary due to pH decreasing over time and potential regrowth of some pathogens [27]. However, very limited data are available relative to the effect of slurry acidification on pathogenic microorganisms. Furthermore, slurry acidification has proved to be efficient at delaying the nitrification process after soil application [28,29]. Slurry treatment by urea or NH₃ addition showed to be the most suitable animal waste disinfectants, despite concerns about NH₃ emissions and the environmental impact [20,24].

An advantage is the fact that it is possible to recycle the N as fertilizer after the treatment. However, the increased NH₃ content in the treated material leads to a risk for NH₃ gas emissions during treatment and storage. A solution to minimize such impact might be the use of NH₃ scrubbers or biofilters, which have been shown to be efficient at avoiding NH₃ emissions and minimizing odors [28]. The use of raw materials generally used for growing media as packing material in the biofilter could allow its subsequent soil application. Similarly, the acid solution used in the scrubber could be used to acidify the treated slurry immediately before soil application to minimize NH₃ emissions [29]. However, the impact of such treatment on the slurry characteristics, namely its fertilizer value and nutrients availability, on GHG emissions during storage or after field application, have not been considered and need to be studied to avoid the so-called pollution swapping. Similarly, the impact of treated slurry application on the soil quality must be monitored to avoid any negative effect.
This research aimed to evaluate a mixture of a tomato waste and rice husk as biofilter media to reduce NH$_3$, nitrous oxide (N$_2$O), carbon dioxide (CO$_2$) and methane (CH$_4$) losses from a simple and low-cost solution for slurry hygienization by pH modification.

2. Materials and Methods

2.1. Slurry Treatments

The untreated (raw) pig slurry used in this study (Table 1) was collected from the outdoor pipe of a fattening pig building located in Viseu, Portugal. We considered four treatments, namely untreated slurry as control (raw slurry) and the following three treated methods: acidified slurry, alkalinized slurry, and neutralized slurry. The three treatment slurries were obtained by the methodology described in Rodrigues et al. [30]. For raw slurry, a sample of 4000 g of untreated raw slurry without any additive was retained in closed plastic containers at 20 °C for 24 h. For alkalinized slurry, another sample of 4000 g of raw slurry was subjected to alkalinization with pH 9.5 that was achieved by adding 28 g of concentrated KOH, 85% (w/w) and d = 2.04 g cm$^{-3}$ (Macron Fine Chemicals, Radnor, PA, USA), with continuous mixing. For neutralized slurry, a sample of 4000 g of raw slurry was alkalinized to pH 9.5 (as previously described), and after 24 h, the slurry sample was neutralized to pH 7.5 by adding 16 mL of concentrated H$_2$SO$_4$, 95% (w/w) and d = 1.84 kg L$^{-1}$ (AppliChem GmbH, Darmstadt, Germany), under continuous mixing. For acidified slurry, another sample of 4000 g of raw slurry was acidified by adding 32 mL of concentrated H$_2$SO$_4$, 95% (w/w) and d = 1.84 kg L$^{-1}$ (Chem-Lab, Zedelgem, Belgium) to the target pH of 5.0, with continuous mixing.

Table 1. Physicochemical characteristics of the packing materials and pig slurry used in the experiment (mean ± standard deviation) ($n = 3$).

| Wastes                  | pH ± SD | DM ± SD | TC ± SD | TN ± SD | NH$_4^+$ ± SD | NO$_3^-$ ± SD | C/N ± SD | BD ± SD | PO ± SD |
|------------------------|---------|---------|---------|---------|------------|-------------|---------|--------|--------|
| Tomato waste           | 5.7 ± 0.1 c | 842.2 ± 3.8 b | 779.8 ± 1.7 a | 39.6 ± 5.4 b | 14.9 ± 0.7 b | 7.3 ± 0.6   | 19.9 ± 2.7 b | 90.6 ± 0.1 c | 87.4 ± 0.1 b |
| Rice husk              | 7.0 ± 0.1 b | 895.6 ± 7.7 a | 843.4 ± 0.5 a | 3.3 ± 0.4 c  | 0.2 ± 0.1 c  | 4.3 ± 3.4   | 257.4 ± 31.9 a | 149.3 ± 0.1 b | 44.4 ± 3.2 a  |
| Tomato + rice husk     | 7.1 ± 0.1 b | 500.0 ± 0.1 c | 774.4 ± 6.0 a | 29.8 ± 5.0 b | 26.7 ± 2.9 b | 6.4 ± 0.8   | 26.4 ± 4.5 b | 105.3 ± 0.1 c | 88.0 ± 6.8 b  |
| (biofilters) Pig slurry| 8.3 ± 0.1 a | 222.0 ± 0.3 d | 493.3 ± 31.8 b | 59.4 ± 1.0 a | 25.0 ± 82.6 ± 4757.5 a | 5.8 ± 0.5 | 8.3 ± 0.6 b | 1000.0 ± 0.1 a | nd |

Note: $n = 3$ (three replications per treatment), pH: pH (H$_2$O), DM: dry matter (g kg$^{-1}$), TC: total C (g C kg$^{-1}$ DM), TN: total N (g N kg$^{-1}$ DM), NH$_4^+$: NH$_4^+$-N (mg N kg$^{-1}$ DM), NO$_3^-$: NO$_3^-$-N (mg N kg$^{-1}$ DM), C/N: C:N ratio, BD: bulk density (kg m$^{-3}$), PO: porosity (%), nd: not determined. Values presented with different lowercase letters within columns are significantly different ($p < 0.05$) by Tukey test.

Slurry samples of the four treatments (three replications per treatment), were subdivided into doses of 1000 g and used in the laboratory experiment. Other subsamples of each treatment (three replications per treatment) were retained and analyzed by standard laboratory methods to the parameters shown in Table 2. Summarizing, pH (H$_2$O) was determinate by potentiometry (EN 13037, Brussels, Belgium), dry matter content by the gravimetric method (24 h at 105 °C (EN 13040, Brussels, Belgium), total C by the Dumas method, total N by the Kjeldahl method (EN 13654-1, Brussels, Belgium), NH$_4^+$ and NO$_3^-$ by absorption spectrophotometry (EN 13652, Brussels, Belgium), bulk density by the volumetric method, and biochemical oxygen demand by incubation over 5 days at 20 °C (ISO 5815-1, Geneva, Switzerland).

2.2. Biofiltration

The tomato waste was collected from an agricultural greenhouse located in Viseu, Portugal and the rice husk was supplied from a rice industry located in Aveiro, Portugal. The tomato waste was naturally dehydrated, cut by hand in small pieces (<5 mm), and mixed with rice husk at a ratio 3:1 (tomato waste:rice husk) for the biofilter packing material. The composition of these two packing materials are given in Table 1, being analyzed by standard laboratory methods [31]: pH (H$_2$O) was determined by potentiometry (EN 13037, Brussels, Belgium), dry matter content by the gravimetric method (EN 13040, Brussels,
Belgium), total carbon by the Dumas method, total nitrogen by the Kjeldahl method (EN 13654-1, Brussels, Belgium), \( \text{NH}_4^+ \) and \( \text{NO}_3^- \) by absorption spectrophotometry, and bulk density and porosity by the volumetric method.

**Table 2.** Physicochemical characteristics of each slurry treatment at the beginning of the experiment (mean ± standard deviation) (\( n = 3 \)).

| Treatments       | pH (mean ± standard deviation) | DM (g kg\(^{-1}\)) | TC (g C kg\(^{-1}\)) | TN (g N kg\(^{-1}\)) | \( \text{NH}_4^+ \) (mg N kg\(^{-1}\)) | \( \text{NO}_3^- \) (mg N kg\(^{-1}\)) | C/N | BOD (mg O\(_2\) L\(^{-1}\)) |
|------------------|--------------------------------|---------------------|----------------------|----------------------|------------------------------------------|------------------------------------------|-----|-----------------------------|
| Raw slurry       | 8.3 ± 0.1 b                     | 22.2 ± 0.3 a        | 493.3 ± 51.8         | 59.4 ± 1.0 a         | 25.1 ± 4.8                                | 5.8 ± 0.5                                | 8.3 ± 0.6 | 1535.0 ± 25.4 a             |
| Acidified slurry | 5.0 ± 0.1 d                     | 23.8 ± 0.3 a        | 473.9 ± 2.8          | 46.9 ± 3.0 b         | 21.4 ± 3.6                                | 4.2 ± 0.5                                | 10.2 ± 0.5 | 26.7 ± 2.9 d                |
| Alkalinized slurry | 9.5 ± 0.1 a                  | 21.6 ± 0.5 b        | 442.1 ± 18.8         | 52.3 ± 0.9 ab        | 24.5 ± 3.4                                | 0.6 ± 0.7                                | 8.4 ± 0.5 | 155.0 ± 17.5 c              |
| Neutralized slurry | 7.5 ± 0.2 c                | 23.3 ± 0.7 a        | 440.0 ± 39.8         | 52.1 ± 1.1 ab        | 23.5 ± 1.3                                | 5.2 ± 0.5                                | 8.4 ± 0.6 | 1040.0 ± 13.3 b             |

Note: \( n = 3 \) (three replications per treatment), pH: pH (H\(_2\)O), DM: dry matter (g kg\(^{-1}\)), TC: total C (g C kg\(^{-1}\) DM), TN: total N (g N kg\(^{-1}\) DM), \( \text{NH}_4^+ \): \( \text{NH}_4^+\)-N (g N kg\(^{-1}\) DM), \( \text{NO}_3^- \): \( \text{NO}_3^-\)-N (mg N kg\(^{-1}\) DM), C/N: C:N ratio, Biological oxygen demand: BOD (mg O\(_2\) L\(^{-1}\)). Values presented with different lowercase letters within columns are significantly different (\( p < 0.05 \)) by Tukey test.

### 2.3. Experimental Design

The experiment was made in a climatic room using a laboratory system developed by Pereira et al. [31] to mimic scale biofilters (Figure 1). Briefly, a system of twelve laboratory scale biofilters (\( H = 3.5 \) cm, \( \Omega = 9.5 \) cm) was connected to Kilner glass jars (\( H = 23.0 \) cm, \( \Omega = 10.5 \) cm, volume = 2000 mL) filled with 1000 mL (\( H = 11.5 \) cm) of pig slurry each and under a constant airflow rate (2500 mL min\(^{-1}\)). A flow meter (Aalborg TM FT10201SAVN, Aalborg, Denmark) connected to a small pump (KNF, model N010.KN.18, Neuberger GmbH, Freiburg, Germany) assured the constant airflow rate of each jar. The \( \text{NH}_3 \), \( \text{N}_2\text{O} \), \( \text{CO}_2 \), and \( \text{CH}_4 \) concentrations from the outlet air were monitored under constant temperature (20 °C), and in the next 35 days to the application of 100 g of the biofilter mixture, being composed by 75% tomato waste and 25% rice husk. Each one of the four treatments with three replications were added to each Kilner jar (1000 mL of slurry), leaving an equal volume of empty headspace between the slurry surface and the lid. A first Teflon tube (\( \Omega = 3000 \) µm) was inserted into a septum for air inlet (20 mm of paste surface) and a second Teflon tube was symmetrically positioned in another septum for air outlet. The inlet air came from inside the climate room and passed through \( \text{NH}_3 \) retention filters coated with oxalic acid, while the exhaust air from the biofilters was expelled out of the climate room through a hood.

**Figure 1.** Schematic view of the laboratory system developed by Pereira et al. [31] and used in this study.
Air samples from each biofilter were collected sequentially (every 2 min with a Teflon tube) by a multipoint sampler (INNOVA 1409-12, Lumasense Technologies, Ballerup, Denmark), followed by analysis to the gas concentrations using a photoacoustic multigas monitor (INNOVA 1412i-5, Lumasense Technologies, Ballerup, Denmark) and controlled by a LumaSoft Gas Multipoint 7870 Software (Lumasense Technologies, Ballerup, Denmark). The monitor was previously calibrated by the manufacturer and operated in a mode that compensates water interference and cross interference, being equipped with an optical filter for water vapor (filter type SB0527, Lumasense Technologies, Ballerup, Denmark) and with the following detection limits: 152.1 µg m\(^{-3}\) for NH\(_3\) (filter type UA0973, Lumasense Technologies, Ballerup, Denmark), 58.9 µg m\(^{-3}\) for N\(_2\)O (filter type UA0985, Lumasense Technologies, Ballerup, Denmark), 2947.1 µg m\(^{-3}\) for CO\(_2\) (filter type UA0982, Lumasense Technologies, Ballerup, Denmark), and 286.4 µg m\(^{-3}\) for CH\(_4\) (filter type UA0969, Lumasense Technologies, Ballerup, Denmark).

The NH\(_3\), N\(_2\)O, CO\(_2\), and CH\(_4\) concentrations from the outlet air of each biofilter were expressed per hour and day. The NH\(_3\), N\(_2\)O, CO\(_2\), and CH\(_4\) elimination efficiency (EE, %) and pollutant elimination capacity (EC, mg m\(^{-3}\) s\(^{-1}\)) of each biofilter used in treated slurries (acidified slurry, alkalinized slurry, and neutralized slurry) were determined by comparing the daily gas concentrations of the biofilter used in raw slurry and each biofilter of treated slurries. A detailed description of the procedure to calculate EE and EC could be found in Pereira et al. [31].

2.4. Statistical Analysis

The data were analyzed by the statistical software package STATISTIX 10 (Analytical Software, Tallahassee, FL, USA). The one-way analysis of variance (ANOVA) was used to test the effects of each treatment on the composition of slurries and biofilters and gaseous losses, and the statistical significance (p < 0.05) of the means difference between treatments was determined by the Tukey’s Honest Significant Difference test.

3. Results

3.1. Composition of the Treated Slurries and Biofilters

The initial (0 day) composition of the untreated (raw) and treated (acidified, alkalinized, and neutralized) slurries are shown in Table 2. The initial values of pH decreased significantly (p < 0.05), from 5.0 to 9.5, by the following order of treatments: acidified slurry < neutralized slurry < raw slurry < alkalinized slurry (Table 2). The initial content of dry matter (DM), total C, total N, NH\(_4^+\), NO\(_3^-\), and C/N ratio did not differ significantly (p > 0.05) among untreated and treated slurries, but with a numerical decrease of pH and total N and a numerical increase of DM, total C, and C/N ratio in the three treated slurries when compared with raw slurry (Table 2).

The initial values of biological oxygen demand (BOD) decreased significantly (p < 0.05) in the following order: raw slurry < neutralized slurry < alkalinized slurry < acidified slurry (Table 2).

The final (35 days) composition of the biofilter media mixtures are shown in Table 3. The final values of pH, DM, total C, total N, NH\(_4^+\), NO\(_3^-\), and C/N ratio were not significantly different (p > 0.05) among untreated and treated slurries, but with a numerical decrease of pH and total N and a numerical increase of DM, total C, and C/N ratio in the three treated slurries when compared with raw slurry (Table 3).

3.2. Ammonia and Nitrous Oxide Losses

The daily concentrations of NH\(_3\) from treatments are shown in Table 4 and varied significantly (p < 0.05) among untreated (raw) and treated (acidified, alkalinized, and neutralized) slurries. Comparatively to all other treatments, the daily NH\(_3\) concentrations were significantly higher (p < 0.05) in the first 5 days for the treatment alkalinized slurry (46 to 21 mg NH\(_3\) m\(^{-3}\)), followed by a progressive decrease between days 6 and 30 and with significantly higher (p < 0.05) values (6 to 12 mg NH\(_3\) m\(^{-3}\)) for treatment raw slurry.
(Table 4). From day 26 until the end of the experiment, the daily NH$_3$ concentrations did not differ significantly ($p > 0.05$) among all treatments and varied from 2 to 7 mg NH$_3$ m$^{-3}$ (Table 4). Comparatively to treatments raw slurry and neutralized slurry, the daily NH$_3$ concentrations of treatment alkalinized slurry increased about four times in the first 5 days of experiment, while these same concentrations were reduced to about half in treatment acidified slurry and during the same period (Table 4). The mean NH$_3$ concentrations (0–35 days) did not vary significantly ($p > 0.05$) among treatments raw slurry and neutralized slurry, being significantly reduced ($p < 0.05$) by 48% in treatment acidified slurry and significantly increased ($p < 0.05$) by 46% in treatment alkalinized slurry (Table 4).

Table 3. Physicochemical characteristics of the biofilter of each treatment at the end of the experiment (mean ± standard deviation) ($n = 3$).

| Treatments (Biofilters) | pH     | DM    | TC    | TN    | NH$_4^+$ | NO$_3^-$ | C/N   |
|-------------------------|--------|-------|-------|-------|----------|----------|-------|
| Raw slurry              | 8.1 ± 1.0 | 286.2 ± 35.0 | 460.1 ± 13.2 | 37.4 ± 0.9 a | 92.1 ± 0.5 a | 5.6 ± 0.5 | 12.3 ± 0.5 b |
| Acidified slurry        | 7.4 ± 1.6 | 363.9 ± 30.5 | 476.7 ± 16.4 | 29.6 ± 3.7 b | 40.3 ± 6.5 b | 5.1 ± 0.5 | 16.3 ± 1.1 a  |
| Alkalinized slurry      | 7.0 ± 0.4 | 349.0 ± 39.1 | 469.9 ± 5.7 | 32.0 ± 1.9 ab | 62.4 ± 7.6 ab | 4.6 ± 0.5 | 14.7 ± 0.5 ab |
| Neutralized slurry      | 7.7 ± 0.9 | 298.5 ± 38.8 | 462.3 ± 2.7 | 34.5 ± 1.0 ab | 72.9 ± 5.1 ab | 5.2 ± 0.5 | 13.4 ± 0.5 ab |

Note: $n = 3$ (three replications per treatment), pH: pH (H$_2$O), DM: dry matter (g kg$^{-1}$ DM), TN: total N (g N kg$^{-1}$ DM), NH$_4^+:$ NH$_4^+$-N (mg N kg$^{-1}$ DM), NO$_3^-$: NO$_3^-$-N (mg N kg$^{-1}$ DM), C/N: C:N ratio. Values presented with different lowercase letters within columns are significantly different ($p < 0.05$) by Tukey test.

As can be observed in Table 5, the NH$_3$ elimination efficiency was not significantly different ($p > 0.05$) among treatments raw slurry and alkalinized slurry, although being observed a numerically increase of 5% in treatment alkalinized slurry. Comparatively to treatment raw slurry, the NH$_3$ elimination efficiency was significantly reduced ($p < 0.05$) by 43% in treatment acidified slurry and by 19% neutralized slurry (Table 5). The NH$_3$ elimination capacity of biofilter follow the same trend than NH$_3$ elimination efficiency, being significantly reduced ($p < 0.05$) in the three treated slurries relative to untreated (raw) slurry and with higher reductions in treatments acidified slurry and neutralized slurry (reduction of 169 µg NH$_3$ m$^{-3}$ s$^{-1}$ for acidified against reduction of 82 µg NH$_3$ m$^{-3}$ s$^{-1}$ for neutralized) (Table 5). In addition, no significant differences ($p > 0.05$) were found among treatments raw slurry and alkalinized slurry on the NH$_3$ elimination capacity (Table 5).

The daily concentrations of N$_2$O from all treatments did not vary during the 35 days of experiment (Table 4). The daily N$_2$O concentrations, including the average values (0–35 days), from untreated (raw) and treated (acidified, alkalinized, and neutralized) slurries did not differ significantly ($p > 0.05$) (430 to 460 µg N$_2$O m$^{-3}$), although numerically higher values in treated slurries were observed at most measurement days (Table 4). Comparatively to treatment raw slurry, the mean N$_2$O concentrations (0–35 days) of treated (acidified, alkalinized, and neutralized) slurries did not differ significantly ($p > 0.05$) but were numerically higher in treatment alkalinized slurry (517 µg N$_2$O m$^{-3}$ for alkalinized against 506 µg N$_2$O m$^{-3}$ for all other treatments) (Table 4).

The N$_2$O elimination efficiency did not reduce significantly ($p > 0.05$) in treated (acidified, alkalinized, and neutralized) slurries relative to untreated (raw) slurry, with a numerical increase observed in the following order: acidified slurry > neutralized slurry > alkalinized slurry (Table 5). Comparatively to the untreated (raw) slurry, the N$_2$O elimination capacity was not significantly reduced ($p > 0.05$) in treated (acidified, alkalinized, and neutralized) slurries, with an increase observed in the elimination capacity that ranged from 0.1 to 0.5 µg N$_2$O m$^{-3}$ s$^{-1}$ of increase (Table 5).
### Table 4. Average gas concentrations in the biofilter outlet air of each treatment (mean ± standard deviation) (n = 3).

| Treatments (Biofilters) | Days of Experiment |
|------------------------|--------------------|
|                        | 1–2    | 3–5    | 6–10   | 11–15  | 16–20  | 21–25  | 26–30  | 31–35  | 0–35   |
| **NH₃ concentrations**  |        |        |        |        |        |        |        |        |        |
| (mg m⁻³)               |        |        |        |        |        |        |        |        |        |
| Raw slurry             | 5.8 ± 0.4 b | 8.8 ± 1.3 b | 8.4 ± 1.1 a | 6.4 ± 0.8 a | 7.5 ± 1.2 a | 11.2 ± 1.6 a | 7.0 ± 0.5 | 3.9 ± 0.2 | 7.4 ± 0.8 b |
| Acidified slurry       | 3.9 ± 0.5 c | 3.8 ± 0.7 c | 3.4 ± 0.7 c | 2.9 ± 0.6 b | 3.3 ± 0.6 b | 5.6 ± 0.4 b | 4.3 ± 0.5 | 3.0 ± 0.4 | 3.8 ± 0.5 c |
| Alkalinized slurry     | 45.7 ± 4.5 a | 20.8 ± 1.5 a | 2.6 ± 0.5 c | 1.7 ± 0.1 c | 2.2 ± 0.2 c | 6.2 ± 1.2 b | 4.4 ± 0.6 | 2.7 ± 0.2 | 10.8 ± 1.0 a |
| Neutralized slurry     | 7.5 ± 1.4 b | 6.3 ± 0.7 b | 4.2 ± 0.1 b | 3.6 ± 0.4 b | 4.7 ± 0.2 b | 8.9 ± 0.6 b | 6.9 ± 0.8 | 4.4 ± 0.3 | 5.8 ± 0.1 b |
| **N₂O concentrations** |        |        |        |        |        |        |        |        |        |
| (µg m⁻³)               |        |        |        |        |        |        |        |        |        |
| Raw slurry             | 535.8 ± 3.7 | 533.2 ± 0.8 | 479.2 ± 0.7 | 527.3 ± 2.0 | 484.5 ± 7.1 | 429.8 ± 10.4 | 508.2 ± 4.5 | 536.3 ± 5.0 | 504.3 ± 3.3 |
| Acidified slurry       | 558.4 ± 2.5 | 551.3 ± 3.2 | 484.7 ± 1.4 | 528.1 ± 1.1 | 496.6 ± 7.4 | 449.4 ± 7.4 | 520.9 ± 2.5 | 543.9 ± 2.0 | 516.7 ± 2.9 |
| Alkalinized slurry     | 551.5 ± 11.5 | 546.0 ± 4.8 | 480.2 ± 0.5 | 528.1 ± 1.4 | 486.0 ± 7.9 | 431.1 ± 3.3 | 507.0 ± 1.5 | 533.7 ± 2.0 | 508.0 ± 0.6 |
| Neutralized slurry     | 534.7 ± 2.9 | 531.3 ± 3.1 | 479.1 ± 0.5 | 529.1 ± 0.7 | 495.5 ± 6.6 | 439.4 ± 9.3 | 514.6 ± 1.7 | 537.9 ± 0.9 | 507.7 ± 1.7 |
| **CO₂ concentrations** |        |        |        |        |        |        |        |        |        |
| (mg m⁻³)               |        |        |        |        |        |        |        |        |        |
| Raw slurry             | 973.3 ± 12.6 b | 907.6 ± 13.6 a | 906.7 ± 13.4 a | 931.5 ± 26.9 | 1111.4 ± 64.3 | 1288.3 ± 72.9 | 1058.7 ± 66.5 | 973.4 ± 58.4 | 1018.9 ± 40.7 |
| Acidified slurry       | 1158.1 ± 49.3 a | 814.8 ± 1.3 b | 848.8 ± 0.5 b | 937.6 ± 11.6 | 1100.0 ± 29.7 | 1178.5 ± 73.4 | 961.9 ± 32.6 | 900.0 ± 25.0 | 987.4 ± 16.9 |
| Alkalinized slurry     | 842.5 ± 2.1 b | 811.2 ± 6.0 b | 845.6 ± 3.0 b | 882.7 ± 20.6 | 1062.4 ± 62.0 | 1304.0 ± 84.0 | 1095.8 ± 13.4 | 984.3 ± 10.3 | 978.6 ± 16.8 |
| Neutralized slurry     | 1139.8 ± 33.7 a | 883.0 ± 7.8 a | 885.6 ± 2.2 b | 889.6 ± 1.9 | 994.7 ± 19.5 | 1161.1 ± 58.4 | 1005.0 ± 18.3 | 920.7 ± 14.4 | 984.9 ± 5.6 |
| **CH₄ concentrations** |        |        |        |        |        |        |        |        |        |
| (µg m⁻³)               |        |        |        |        |        |        |        |        |        |
| Raw slurry             | 173.6 ± 52.5 a | 191.6 ± 20.4 a | 7.0 ± 2.4 | 1.3 ± 0.9 | 7.8 ± 3.9 | 158.8 ± 26.2 a | 8.2 ± 1.6 | 3.6 ± 2.0 | 69.0 ± 6.3 a |
| Acidified slurry       | 60.4 ± 52.3 b | 161.7 ± 16.4 a | 0.7 ± 0.9 | 0.9 ± 0.9 | 3.7 ± 1.6 | 72.1 ± 12.7 b | 3.3 ± 1.5 | 0.9 ± 0.9 | 37.7 ± 2.6 b |
| Alkalinized slurry     | 59.2 ± 15.8 a | 122.9 ± 10.6 a | 3.2 ± 1.2 | 0.9 ± 0.9 | 0.9 ± 0.9 | 108.5 ± 16.4 b | 2.9 ± 2.5 | 0.9 ± 0.9 | 37.2 ± 2.9 b |
| Neutralized slurry     | 0.9 ± 0.9 b | 44.7 ± 16.5 b | 2.6 ± 0.9 | 0.9 ± 0.9 | 0.9 ± 0.9 | 147.6 ± 13.5 a | 0.9 ± 0.9 | 0.9 ± 0.9 | 24.4 ± 3.9 b |

Note: n = 3 (three replications per treatment). For each gas, values presented with different lowercase letters within columns are significantly different (p < 0.05) by Tukey test.
Table 5. Gas elimination efficiency and pollutant elimination capacity in the biofilter outlet air of each treatment (mean ± standard deviation) \((n = 3)\).

| Treatments (Biofilters) | Gas Elimination Efficiency (EE) (%) | Pollutant Elimination Capacity (EC) \((\mu g m^{-3} s^{-1})\) | GWP |
|-------------------------|-----------------------------------|-------------------------------------------------------------|-----|
|                         | \(\text{NH}_3\)  | \(\text{N}_2\text{O}\) | \(\text{CO}_2\) | \(\text{CH}_4\) | \(\text{NH}_3\) | \(\text{N}_2\text{O}\) | \(\text{CO}_2\) | \(\text{CH}_4\) |      |
| Raw slurry              | 0.01 ± 0.01 c | 0.01 ± 0.01 | 0.01 ± 0.01 b | 0.01 ± 0.01 c | 0.01 ± 0.01 | 0.01 ± 0.01 b | 0.01 ± 0.01 b | 0.01 ± 0.01 b | 0.01 ± 0.01 b |
| Acidified slurry        | ↓42.74 ± 12.87 a | ↑2.41 ± 1.16 | ↓3.55 ± 5.37 a | ↓74.45 ± 0.24 a | ↑168.89 ± 63.41 a | ↑0.52 ± 0.25 | ↓2154.65 ± 2910.84 a | ↓1.13 ± 0.12 a | ↓2049.52 ± 2847.93 a |
| Alkalized slurry        | ↑4.61 ± 0.89 c | ↑0.48 ± 0.76 | ↓2.78 ± 2.70 a | ↓78.46 ± 1.98 a | ↓10.07 ± 14.17 c | ↑0.10 ± 0.16 | ↓1362.01 ± 1447.63 a | ↓1.05 ± 0.05 a | ↓1363.82 ± 1406.19 a |
| Neutralized slurry      | ↓18.54 ± 4.75 b | ↑0.95 ± 0.59 | ↓4.15 ± 3.29 a | ↓83.29 ± 4.75 a | ↓82.04 ± 32.13 b | ↑0.20 ± 0.13 | ↓2397.28 ± 1756.46 a | ↓1.28 ± 0.29 a | ↓2382.39 ± 1737.65 a |

Note: \(n = 3\) (three replications per treatment), (↓): reduction of gas emission in comparison to raw slurry, (↑): increase of gas emission in comparison to raw slurry. Values presented with different lowercase letters within columns are significantly different \((p < 0.05)\) by Tukey test. GWP: global warming potential as \(\text{CO}_2\)-equivalents and expressed in \(\mu g (\text{CO}_2\)-equivalents) m\(^{-3}\) s\(^{-1}\) = 0.01 \times [\text{NH}_3] + 265 \times [\text{N}_2\text{O}] + 1 \times [\text{CO}_2] + 28 \times [\text{CH}_4].\)
3.3. Carbon Dioxide and Methane Losses

As can be observed in Table 4, during the 35 days of experiment, the daily concentrations of CO₂ are very close between untreated (raw) and treated (acidified, alkalinized, and neutralized) slurries. Comparatively to all other treatments, the daily CO₂ concentrations were significantly higher \((p < 0.05)\) in the first 2 days for the treatments acidified slurry and alkalinized slurry (1140 to 1150 mg CO₂ m⁻³), followed by significantly higher \((p < 0.05)\) values (907 mg CO₂ m⁻³) from day 3 to 10 for treatment raw slurry (Table 4). From day 11 until the end of the experiment, the daily CO₂ concentrations did not differ significantly \((p > 0.05)\) among all treatments, although numerically higher (970 to 1290 mg CO₂ m⁻³) in treatment raw slurry (Table 4). The mean CO₂ concentrations (0–35 days) were reduced, but not significantly \((p > 0.05)\) in treated (acidified, alkalinized, and neutralized) slurries relative to untreated (raw) slurry (985 mg CO₂ m⁻³ for treated slurries against 1019 mg CO₂ m⁻³ for untreated slurry) (Table 4).

The CO₂ elimination efficiency and capacity were significantly reduced \((p < 0.05)\) in the three treated slurries relative to untreated (raw) slurry, and numerically higher reductions in treatments acidified slurry and neutralized slurry were observed (reductions of 3.6–4.2% for elimination efficiency and 1362–2397 µg CO₂ m⁻³ s⁻¹ for elimination capacity) (Table 5).

The daily concentrations of CH₄ peaked twice in all treatments and during the 35 days of experiment, with a first peak (45 to 192 µg CH₄ m⁻³) in the first 5 days followed by a second peak (72 to 159 µg CH₄ m⁻³) between days 26 and 30 (Table 4). The daily concentrations of CH₄ were not significantly reduced \((p > 0.05)\) in treated (acidified, alkalinized, and neutralized) slurries when compared to untreated (raw) slurry, despite being numerically higher in treatment raw slurry during the 35 days of experiment (Table 4). The mean CH₄ concentrations (0–35 days) were significantly higher \((p < 0.05)\) in treatment untreated (raw) slurry (69 µg CH₄ m⁻³) when compared with treated (acidified, alkalinized, and neutralized) slurries (24 to 38 µg CH₄ m⁻³) (Table 4).

The CH₄ elimination efficiency and capacity decreased significantly \((p < 0.05)\) in the three treated slurries comparatively to the untreated (raw) slurry, with average reductions of 78.9% for elimination efficiency and 1.1 µg CH₄ m⁻³ s⁻¹ for elimination capacity (Table 5) observed. In addition, the global warming potential elimination efficiency decreased significantly \((p < 0.05)\) in the three treated slurries relative to untreated (raw) slurry, with a numerically higher reduction observed in treatments acidified slurry and neutralized slurry (reduction of 2216 µg CH₄ m⁻³ s⁻¹ for elimination capacity) (Table 5).

4. Discussion

4.1. Gaseous Losses from Treated Slurries

The acidification of pig slurry to decrease the slurry pH to an acidic range (3.5–5.5) leads to a modification of the ratio NH₄⁺:NH₃, with about 98.00–99.98% of NH₄⁺, and therefore reduces NH₃ volatilization and preserves NH₄⁺ in slurries [32,33], being in line with this study, where NH₃ losses were reduced in treatment acidified slurry (Table 4). Regueiro et al. [33] reported higher concentrations of total solids in acidified pig slurry relative to non-acidified slurry, and in this study higher concentrations of DM and TC were observed in raw slurry (Table 1). However, an increase in the population of \(E.\ Coli\) is expected after acidification to pH = 5.5 of pig slurry and therefore an increased risk of its leaching after application to soil [34,35]. Also, to comply with Regulation (EU) 2019/1009, the European microbiological rule for fertilizers requires the absence of \(Salmonella\) spp. in 25 g of material and less than 1000 colony-forming units of \(E.\ Coli\) per g of fresh material. Alkalinization of pig slurry to raise the manure pH to a basic range (9.0–11.0) has been shown to be effective in reducing the number of pathogens at pH 9.0–13.0; particularly, the level of \(E.\ Coli\) was below the sanitation threshold for all samples [30]. However, as observed in this study (Table 4), such treatment increases the volatilization of NH₃ in the treatment alkalinized slurry (pH = 9.5) in relation to the treatment raw slurry, which decreases the NH₄⁺ in the pulps and increases the environmental impact. In addition, successive applications of alkalinized slurry in non-acidic soils can pose an additional...
A problem for agricultural production. The neutralization of pig slurry to decrease the pH from 9.5 to 7.5 reduced the risks described above, particularly the reduction of NH$_3$ losses to values below those of the treatment raw slurry (Table 4).

4.2. Gaseous Losses from Biofiltration

Previous studies [31,36] have reported great potential for NH$_3$ retention using a wide range of packing materials as biofilters, with reductions ranging from 64 to 78% for woodchips and 51 to 77% for tomato-based biofilters. This retention of NH$_3$ by the biofilter packing material can be explained by the removal of NH$_3$ dissolved in the aqueous phase by nitrifying bacteria and by the accumulation in the organic packing material itself [37]. Pereira et al. [31] developed tomato based biofilters and obtained 77% and 908 µg m$^{-3}$ s$^{-1}$ of NH$_3$ elimination efficiency and capacity, respectively, in packing material with 75% tomato waste and 25% rice husk. It is noteworthy that the composition of this biofilter packaging material was like that used in the present study, with the same efficiency in NH$_3$ retention being observed for the alkalinized slurry as for the raw slurry (Table 5). However, this same biofilter was more effective on NH$_3$ retention from neutralized slurry (19% of reduction) relative to alkalinized slurry (82 µg m$^{-3}$ s$^{-1}$ elimination capacity for neutralized against 10 µg m$^{-3}$ s$^{-1}$ elimination capacity) (Table 5). Overall, the use of this biofilter packing material in the treatment neutralized slurry retained about 96% of NH$_3$ losses when compared to whole slurry without a biofilter.

In recent studies [31,38], an increase in N$_2$O emissions from biofilters has been reported regardless of packaging material, with increases from 0 to 400% for woodchips and 10 to 61% for tomato-based biofilters. The N$_2$O emissions were produced in the biofilter from both nitrification and denitrification processes [37]. In the present study, the biofilter (packing material with 75% tomato waste and 25% rice husk) did not increase the N$_2$O emissions from the three treated slurries in relation to the untreated (raw) slurry (Table 5), being related to the release of compounds from acidified/alkalinized slurries that can inhibit nitrifiers/denitrifiers from packing materials.

Published studies [31,39] have reported equal efficiency and CO$_2$ scavenging capacity between different biofilter packaging materials (e.g., agroforestry wastes). The CO$_2$ emissions coming from the microbial oxidation of gaseous contaminants of the packing material and also from the urea hydrolysis and methanogenesis in slurries. In the present study, a decrease in CO$_2$ losses from the biofilter of the treated slurries was observed in relation to the untreated slurry (Table 5), which may be related to the pH modification by the acidification/alkalinization processes that reduced the microbial activity.

Other studies [31,40,41] found up to 85% CH$_4$ removal efficiency using different biofilter packaging materials, including 69% reduction for the same type of biofilter packaging material used in this study. The mechanisms responsible for the high removal of CH$_4$ from the biofilter are its adsorption by packing materials and conversion to CO$_2$ and H$_2$O by methanotrophic bacteria [31,42]. Compared with the untreated slurry, high CH$_4$ removal efficiencies (74 to 83% reduction) were observed in the three treated slurries, with high values for neutralized slurry (Table 5), which may be due to an inhibition of methanotrophic bacteria by acidification/alkalinization processes.

Although the results of this study suggest that the biofilter packaging material, with 75% tomato waste and 25% rice husk, has the potential to retain NH$_3$ and GHG from a combined alkalinization/neutralization treatment, further studies are needed under real conditions to confirm these findings.

5. Conclusions

The results of this study showed that the mixture of biofiltering media, composed of tomato waste and rice husk, had the potential to retain NH$_3$ and GHG from a simple and low-cost solution for slurry hygienization by pH modification. Compared to the treatment raw slurry biofilter, the treatment neutralized slurry biofilter, subjected to a combined treatment by alkalinization/neutralization, retained 19% NH$_3$, 4% CO$_2$, and 83% CH$_4$. 

losses and had no impact on N$_2$O and global warming potential. Thus, the use of tomato waste biofilter during alkalinization did not increase the loss of NH$_3$ and reduced GHG compared to raw slurry, avoiding the subsequent neutralization of slurry for environmental reasons, and could be used as an organic fertilizer in horticulture. However, using the combined alkalinization/neutralization treatment will improve the fertilizer value of the slurry by adjusting the pH from 9.5 to 7.5.

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