

Article

Circularity of Bioenergy Residues: Acidification of Anaerobic Digestate Prior to Addition of Wood Ash

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Abstract: The present study investigated the acidification treatment of an agrowaste digestate and a food waste digestate, which is necessary before the addition of the wood ashes to attain the pH of zero point of charge in the blend intended to behave as a slow-release fertilizer. The 336-h acidification treatments of the 2.39 ± 0.35 g of digestates were performed with high and low doses of four commercial acids (sulfuric, hydrochloric, nitric, and lactic acids) in 50-mL capped Corning® tubes. For analytical purposes, after the incubation, ultrapure milli-Q® water was added at a rate of 10 mL for each gram of digestate to create a water-soluble phase that allowed the measurement of the pH and the electric conductivity. The results showed that the optimum dose and type of acid were very dependent on the nature of the anaerobic digestate. The maximum buffer capacity of the agrowaste digestate was $0.07 \text{ mmol H}^+ \text{-H}_2\text{SO}_4/\text{g}$, but this increased by adding the food waste digestate with a greater content of ammoniacal nitrogen. The agrowaste digestate with a greater content of undigested fiber was more easily oxidized by nitric acid. On the other hand, sulfuric acid oxidized the food waste digestate to a greater extent than the other acids did. Since a high dose of acid was required to achieve a greater efficiency in the solid–liquid separation, which would ease any subsequent handling of the digestates, hydrochloric acid was considered to be the most suitable acid. Lactic acid promoted the growth of filamentous microbes in the agrowaste digestate and microbial colonies in the food waste digestate, which is an indication of the poor preservation of the organic matter under these conditions.

Keywords: circular economy; acidification; solid–liquid separation; nitrogen management; waste-derived fertilizer; organic matter



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1. Introduction

The circular economy can be attained by implementing simple treatment processes for the reuse of waste materials (e.g., decrease in the pH of organic manures via the addition of commercial acids [1]), which overall reduces the extraction of raw natural resources [2]. The reprocessing [3], or simple combination of waste streams [4], can enhance the utilization of these materials and minimize the pollution of the environment [5]. Importantly, the selective disposal needs to be assured at the source, as part of the waste management system [6], to avoid cross-contamination of the recyclable materials with the components of the wastes that are not intended to be exploited [7]. The risk of cross-contamination is present at the time of reprocessing [8] and upon utilization of the waste-derived product if the material has not received sufficient upgrading [9]. Valorization of waste materials with a low content of pollutants is possible by direct application to land as soil amendments and fertilizers [10]. As described in the UK regulations, the suitability of a waste-derived product for a particular purpose is assessed by comparing its performance and environmental impact to those of a specifically designed nonwaste material [11]. For residues that are produced in very large amounts (e.g., anaerobic digestate and biomass ash), the

policymakers facilitate the formalities (i.e., interpretation of the regulations) with the entry into force of Quality Protocols [12] (e.g., for biomass ash [13] and anaerobic digestate [14]) and Publicly Available Specifications for the waste-derived products, such as anaerobic digestate [15] and compost [16]. Similarly, in Europe, an action plan and its consequent regulatory framework has been created to promote the circular economy [17]. All of the waste-derived products that meet the end-of-waste (EoW) criteria will be granted with EoW status, according to the EU Directive 2018/851 [18]. In terms of nutrient profile, the EU Regulation 2019/1009 [19] established the benchmark composition that is required for the commercialization of fertilizers.

Organic waste has been traditionally applied to land with fertilization purposes [20]. The anaerobic digestion technology (AD) further exploits this resource via production of bioenergy [21]. The biological strategies that can be present in an AD plant are categorized into upstream, mainstream, and downstream, according to Tabatabaei et al. [22]. The biological pretreatments employed upstream, to enhance the digestibility of the organic waste in the subsequent step of the anaerobic reactor (i.e., mainstream), are very promising [22]. However, these biological innovations are very time consuming and require additional equipment and facilities. On the other hand, the downstream technologies for the biological removal of biogas are expected to replace the physicochemical counterparts on an industrial scale, owing to increasingly stringent environmental regulations [23]. The estimation of the increase in the cost of processing the organic waste and produce biogas is difficult because most investigations are conducted at a lab scale and the assessment of these technologies at commercial plant scale is not often reported [22]. The extracted biogas will no longer contribute to the emissions of greenhouse gases (GHGs) after land application [24], and the mineralization of nutrients during the AD increases the availability of elements such as nitrogen (N) and phosphorus (P) for crops [25].

Reuland et al. [26] assessed the carbon (C) and N mineralization of several anaerobic digestates upon land application and compared them with the profiles found for other soil organic amendments (i.e., pig slurry, compost, and solid fraction of the digestate). They were able to correlate the extent of C and N mineralization with the physicochemical properties of the organic materials. They found that the C to N ratio (C/N) and the ammoniacal nitrogen ($\text{NH}_4^+\text{-N}$) to N ratio were strongly correlated with the extent of mineralization of these elements. This agrees with the findings of Möller and Müller [27]. Reuland et al. [26] found that anaerobic digestates had C sequestration values ranging from 20% to 81% of the total applied organic carbon (C_{org}) to the land, showcasing their potential to contribute to C build-up in agricultural soils. The carbon use efficiency (CUE) was negatively correlated with the content of dissolved organic carbon (DOC), which is the most available form of C_{org} , present in the anaerobic digestates. This means that the catabolic activities and the release of CO_2 were directly promoted by the greater content of DOC in the anaerobic digestates. Reuland et al. [26] concluded that the ratio of DOC to C_{org} and C/N were reliable indicators of the fraction of C that would remain one year after incorporation of the anaerobic digestates to the soil and thus could be used as simple quality parameters to denote the C sequestration potential of digestates prior to their use in the field.

Prado et al. [28] evaluated seven different manures (i.e., three solid manures, two cattle slurries, and two swine slurries) for the production of soil amendments, which would be competitive with the mineral fertilizers, in order to promote the circular economy because farmers are reluctant to use this type of material. The treatments employed by Prado et al. [28] were acidification and solid–liquid separation, or a combination of both (i.e., acidification followed by solid–liquid separation). The impact of the treatments on the nitrogen to phosphorus ratio (N/P) was evaluated. Prado et al. [28] were able to identify which process streams had more potential for valorization as manure-based fertilizers. For example, whilst the liquid fraction of pig slurry cannot be used due to its low nutrient content, the solid fraction is rich in P and has an $\text{NH}_4^+\text{-N}/\text{N}$ of approximately 1. The acidification combined with the solid–liquid separation was employed to produce a liquid

fraction with an N/P around 1 and the remaining solid fraction could be employed as slow N-release material. Importantly, Prado et al. [28] highlighted that some of the treated manures or sub-products obtained after had the usual N/P required by farmers and could be used directly as substitute of mineral fertilizers. However, the blending of some of these materials has a stronger potential for the production of specific manure-based fertilizers.

The acidification is among the most widely adopted downstream technologies to mitigate NH_3 emissions [29], though promotes the leaching of phosphorus in the form of orthophosphate ($\text{PO}_4^{3-}\text{-P}$) [30]. Table 1 contains some additives of a different nature that have been tested to promote sorption [31], coagulation [32], and precipitation processes [33–36]. The current trend is to include the biochar as sorptive agent and to restore the soil as a natural C sink and to minimize the emissions of GHGs [37–39]. However, the processes involving the production of activated carbon-like materials are expensive, whilst wood ashes are produced in larger amounts with a significant share of black carbon (BC) [40–43]. The preparation of blends of wood ashes and anaerobic digestates aims to produce organic soil amendments with a balanced nutrient ratio that enhances the use efficiency of these elements by plants and assimilation by soil microbes [27,44–48]. Achieving the controlled release effect by reducing the availability of nutrients further prevents the air pollution and contamination of groundwaters [49]. A better management of the nutrients also makes the organic manures more competitive with chemical fertilizers [29,50] and directly implies a reduction in the consumption of mineral resources.

Table 1. Additives different from commercial acids that have been tested to enhance the valorization of organic manures, such as anaerobic digestate, and to improve the nutrient management.

Material	Purpose	Reference
$\text{Al}_2(\text{SO}_4)_3$	Coagulation/flocculation, acidification, and mitigation of GHGs after the solid–liquid separation	[51]
FeCl_2	Acidification to reduce the NH_3 volatilization whilst minimizing the leaching of $\text{PO}_4^{3-}\text{-P}$	[35]
CaO	Minimize the leaching of $\text{PO}_4^{3-}\text{-P}$	[36]
Wood ashes	Improve the nutrient profile C/N/P	[52]

Agricultural practices, such as repeated fertilization, impact C, N, and P cycling, and their relationships in the plant–soil continuum, which could have important implications for the magnitude of the GHGs emissions [53]. Gebremichael et al. [53] conducted field-based experiments that assessed the impact of long-term (23 years) P management (0, 15, and 45 kg P/ha) on emissions of nitrous oxide (N_2O) and carbon dioxide (CO_2), following two C + N application events in grass ecosystems with loam and sandy loam soils. Gebremichael et al. [53] found that N_2O emissions were significantly higher in unamended P soils (1.08 ± 0.09 g $\text{N}_2\text{O}\text{-N}/\text{m}^2$) than when a rate of 45 kg P/ha (0.63 ± 0.03 g $\text{N}_2\text{O}\text{-N}/\text{m}^2$) was used. Moreover, loam soil (1.04 ± 0.04 g $\text{N}_2\text{O}\text{-N}/\text{m}^2$) produced significantly higher emissions than the sandy loam soil (0.88 ± 0.05 g $\text{N}_2\text{O}\text{-N}/\text{m}^2$). The authors concluded that P-limitation stimulates N_2O emissions, whereas P-enrichment promotes soil respiration (i.e., release of CO_2) in the temperate grasslands that they assessed [53]. Thereby, a balanced nutrient profile is required to minimize the emissions of GHGs.

The present study investigates the implications of acid treatment of food waste digestate (FWD) and post-harvest vegetable waste digestate (PVWD). This is the first step in the manufacturing of the newfangled blended fertilizer, since the acidifications of the anaerobic digestates were found to be necessary to achieve the optimum combinations with wood fly ash (WFA) and wood bottom ash (WBA) [54], which are sources of phosphorus [55]. In this way, the blending conditions would be further optimized to achieve the pH of zero point of charge (pH_{zpc}) of the sorbents [40,56]. The pH_{zpc} can be achieved upon the addition of the wood ashes to the anaerobic digestates treated with common doses of commercial acids employed in the agroindustry [54,57]. The originality of the present study is in the approach followed for the characterization of (a) the microbial growth, (b) the level of

oxidation of the organic matter (OM), and (c) the extent of the solid–liquid separation due to the acidification treatment of the anaerobic digestates, to potentially prepare granular fertilizers upon addition of the wood ashes [58].

2. Materials and Methods

A detailed description of the bioenergy waste streams employed for the present work can be found in the previous investigation of Moure Abelenda et al. [55]. The greater mineralization that the FWD underwent during the AD, compared to that of PVWD, was the reason for the greater chemical instability of the FWD (i.e., more susceptible to lose NH_4^+ -N and PO_4^{3-} -P via NH_3 volatilization and leaching, respectively). This invited us to test the acidification of the PVWD separately as well as the acidification of a blend with 20% PVWD and 80% FWD (hereinafter denoted as Blend). The setups employed to carry out these experiments were 50-mL capped Corning® tubes; where 2.39 ± 0.48 g of PVWD and 2.38 ± 0.12 g of Blend (80% PVWD and 20% FWD) were charged for the acidification experiments. The pH and electric conductivity (EC) of the digestates were monitored during the 336-h incubation at 21 °C and 100 rpm when using two different doses (i.e., high and low commercial doses for acidification of manure and slurry employed in the agro-industry; [57]) of four acids (H_2SO_4 , HCl, HNO_3 , and $\text{CH}_3\text{CH}(\text{OH})\text{COOH}$). Table 2 shows the doses of acids employed expressed as mmol H^+ /g digestates and mEq acid/g digestates, which are the nomenclatures usually employed for these types of studies [57,59]. The calculation of the dissociation of the protons from the species HSO_4^- and $\text{CH}_3\text{CH}(\text{OH})\text{COOH}$ was based on the values of the acidity constants of 1.02×10^{-2} and 1.38×10^{-4} , respectively [59]. A completely shifted equilibrium towards dissociation of the proton was assumed for all the strong acids. The acidification doses were applied directly to the anaerobic digestates and the ultrapure milli-Q® water was added after the incubation following a sample-to-extractant ratio (S/E) 1/10 g/mL. The water-soluble (WS) phase was generated by stirring for 1 h at 100 rpm and subsequent settling of the suspension was carried out via centrifugation at 4000 rpm for 5 min. Finally, the measurements of the pH and the EC of the supernatant were performed. It is important to mention that the settling is usually required for the measurement of the EC, since the detection limit of the pH meter is much higher. Therefore, the degree of turbidity and particles in suspension did not affect the determination of the concentration of H^+ in the liquid phase. The destructive sampling with replications was the method employed to characterize the pH and the EC over the 336-h incubation of the anaerobic digestates under different acidification conditions. This implied that, for each of the 7 points of incubation (0, 24, 48, 72, 96, 168, and 336 h) and 10 acidification conditions (2 doses of 4 acids plus 2 control experiments that did not involve the addition of acid), 3 replicates were prepared. Therefore, 210 experimental units (7 time points $\times$ 10 acid conditions $\times$ 3 replicates) were prepared for the PVWD and the Blend (80% FWD and 20% PVWD). The 2-way ANOVA test was performed to compare the profiles of the pH and EC of the acidification doses applied to the digestate samples.

Table 2. Doses of commercial acids employed to treat the anaerobic digestates.

Dose $\mu\text{L/g}$	H_2SO_4		HCl		HNO_3		$\text{CH}_3\text{CH}(\text{OH})\text{COOH}$	
	mmol H^+ /g Blend	mEq acid/g Blend	mmol H^+ /g Blend	mEq acid/g Blend	mmol H^+ /g Blend	mEq acid/g Blend	mmol H^+ /g Blend	mEq acid/g Blend
10 μL acid/ 2.67 ± 0.55 g PVWD	0.0687	0.1373	0.0443	0.0443	0.0571	0.0571	0.0001	0.0450
100 μL acid/ 2.12 ± 0.06 g PVWD	0.8628	0.1725	0.5569	0.0557	0.7171	0.0717	0.0016	0.0565
10 μL acid/ 2.32 ± 0.11 g Blend *	0.0788	0.1574	0.0508	0.0508	0.0655	0.0655	0.0001	0.0516
100 μL acid/ 2.44 ± 0.11 g Blend *	0.7488	0.1497	0.4833	0.0483	0.6223	0.0622	0.0014	0.0490

* Blend of 80% FWD + 20% PVWD.

3. Results

Figures 1–4 represent the pH and EC profiles during the acid treatment of the anaerobic digestates (Table 2), from which the time required for stabilization before the addition of the wood ashes could be inferred. The maximum buffer capacity of the PVWD was around 0.07 mmol H^+ - H_2SO_4 /g, as can be seen in Figure 1a. In agreement with the description provided by Fangueiro et al. [30] for the underlying chemistry of animal slurry, the EC increased as the pH decreased (Figure 1b) because the solubility of the metals increases at low pH.

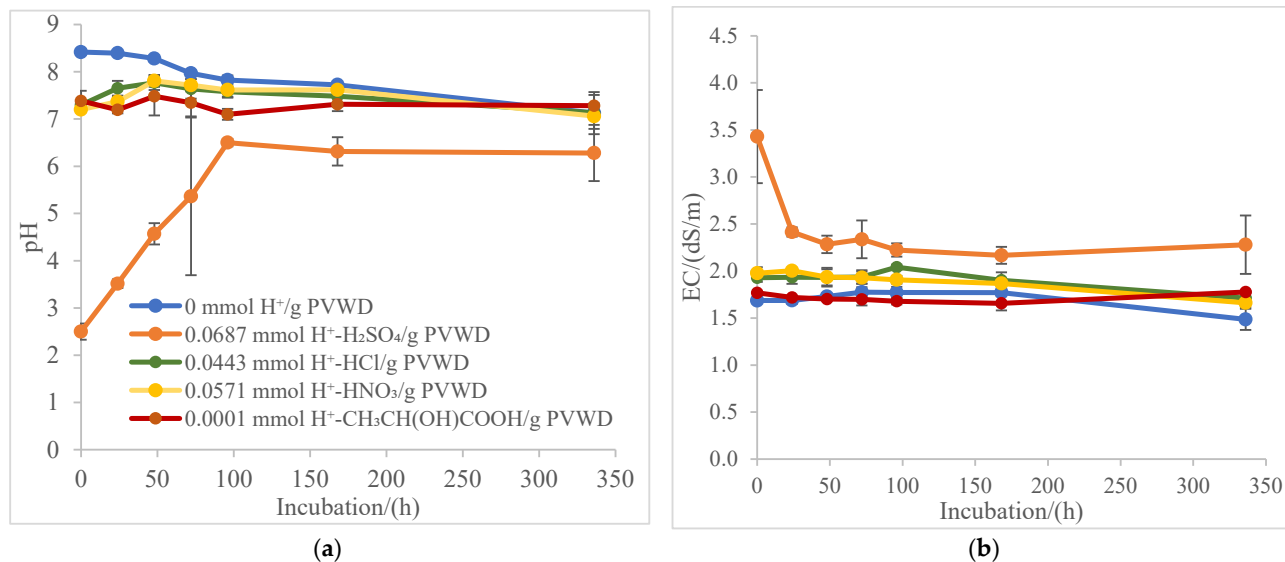


Figure 1. Kinetics of stabilization after mild acidification (Table 2) of 2.67 ± 0.55 g of PVWD incubated at 21 °C for up to 336 h. At the end of the incubation of each destructive replicate ($n = 3$), ultrapure milli-Q® water was added to each sample following a S/E 1/10 g/mL. Subsequent shaking for 1 h at 100 rpm and centrifugation at 4000 rpm for 5 min before measuring in the supernatant (a) pH and (b) EC.

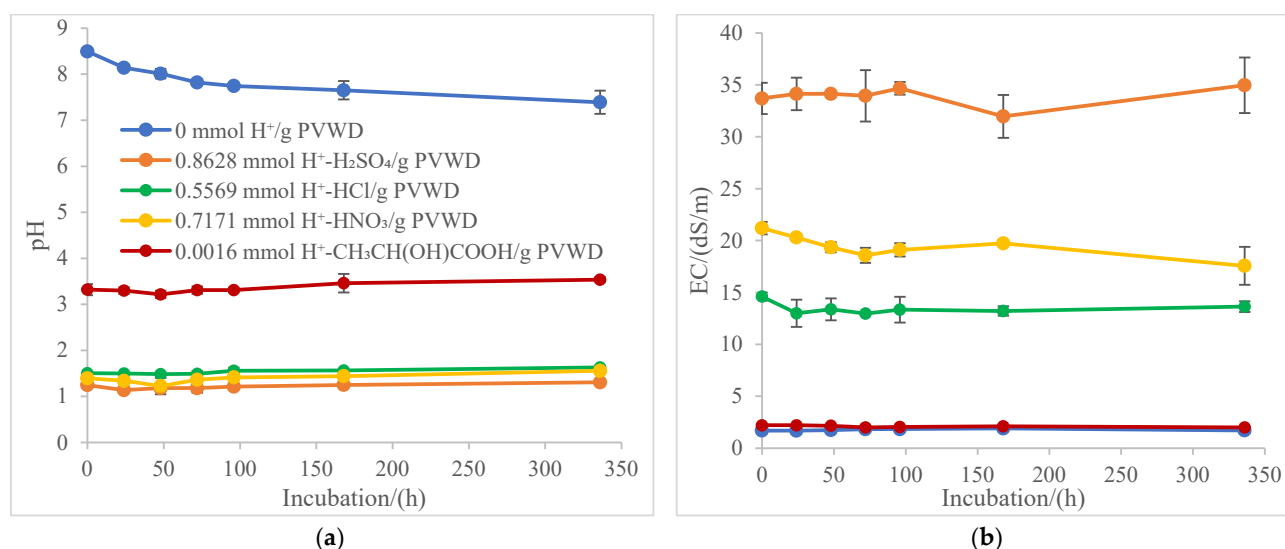


Figure 2. Kinetics of stabilization after severe acidification (Table 2) of 2.12 ± 0.06 g of PVWD incubated at 21 °C for up to 336 h. At the end of the incubation of each destructive replicate ($n = 3$), ultrapure milli-Q® water was added to each sample following a S/E 1/10 g/mL. Subsequently, shaking for 1 h at 100 rpm and centrifugation at 4000 rpm for 5 min before measuring in the supernatant (a) pH and (b) EC.

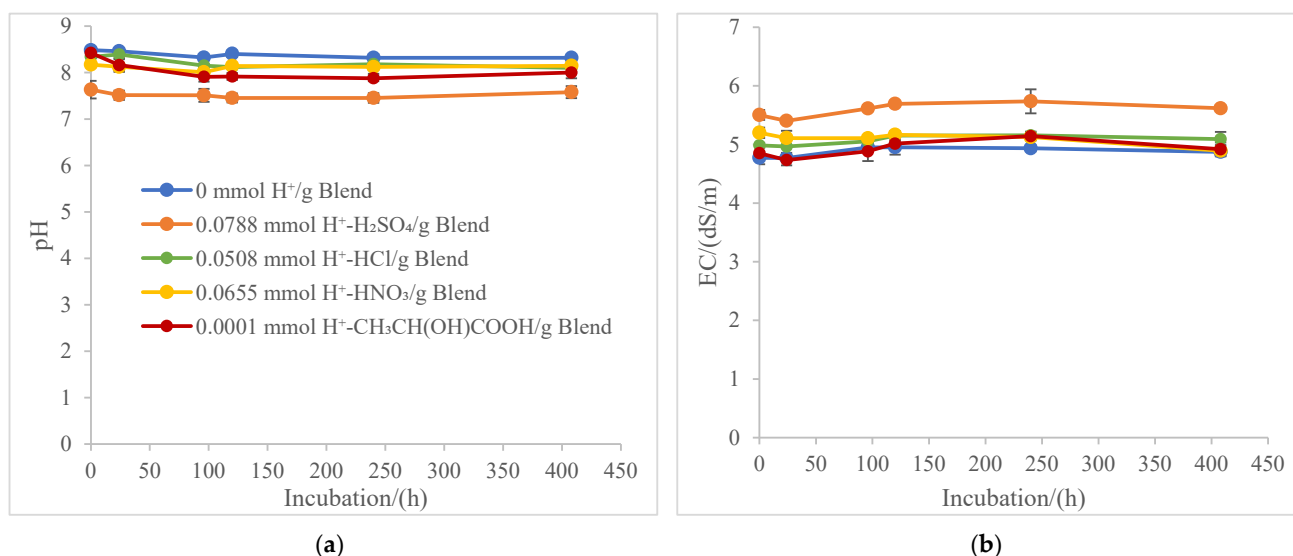


Figure 3. Kinetics of neutralization after mild acidification (Table 2) of 2.32 ± 0.11 g of Blend of 80% FWD and 20% PVWD incubated at 21 °C for up to 408 h. At the end of the incubation of each destructive replicate ($n = 3$), ultrapure milli-Q[®] water was added to each sample following a S/E 1/10 g/mL. Subsequent shaking for 1 h at 100 rpm and centrifugation at 4000 rpm for 5 min before measuring in the supernatant (a) pH and (b) EC.

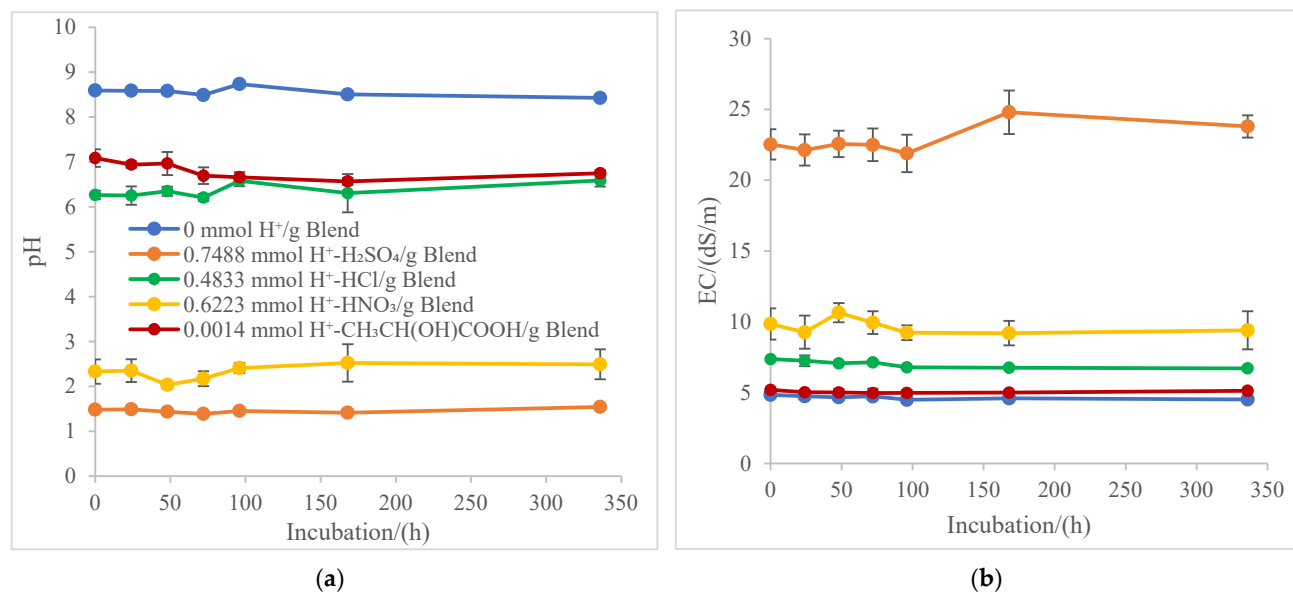


Figure 4. Kinetics of neutralization after severe acidification (Table 2) of 2.44 ± 0.11 g of Blend of 80% FWD and 20% PVWD incubated at 21 °C for up to 336 h. At the end of the incubation of each destructive replicate ($n = 3$), ultrapure milli-Q[®] water was added to each sample following a S/E 1/10 g/mL. Subsequent shaking for 1 h at 100 rpm and centrifugation at 4000 rpm for 5 min before measuring in the supernatant (a) pH and (b) EC.

Even a dose of 0.002 mmol H⁺-CH₃CH(OH)COOH/g PVWD, which decreased the pH from 7.89 ± 0.36 to 3.35 ± 0.14 (Figure 2a), increased the EC of the PVWD significantly ($p < 0.05$) (Figure 2b). The small increase in the EC with CH₃CH(OH)COOH, compared to the other acids, was expected because of the nature of this organic acid that is widely available in the anaerobic systems [60]. Although the acidification with 0.86 mmol H⁺-H₂SO₄, 0.56 mmol H⁺-HCl, and 0.72 mmol H⁺-HNO₃ per gram of PVWD decreased the pH similarly (Figure 2a), the differences in terms of the EC were much more in agreement

with the anion concentrations provided by the acids (Table 2). The pH was less affected by the concentrations of ions due to the smoothing effect by the logarithmic calculation of the concentration of H^+ . On the other hand, the measurement of the electric resistance, which was a proxy of the EC [61], was directly related to the concentration of ions in the solution.

The FWD had greater buffer capacity, around $0.24 \text{ mmol } H^+ - H_2SO_4 / g$ [54], than the PVWD because of the greater $NH_4^+ - N$ content of FWD [55]. The acidification of the Blend of 80% FWD and 20% PVWD was tested (Figure 3a) to evaluate the preparation of the blended fertilizer (Figure 5) with more than one type of digestate, as per the share of the anaerobic digestates in the Blend 2 (Figure 5), while fulfilling $C/N/P \leq 10/1/1$ but with greater nutrient availability. Since the PVWD has undergone poorer anaerobic fermentation due to the higher fiber content (Figures 8a and 11a), it would be more suitable as a slow-release fertilizer because of the lower availability of the nutrients. Even a dose of $0.08 \text{ mmol } H^+ - H_2SO_4 / g$ Blend (Figure 3a) was not able to decrease the pH below 7.

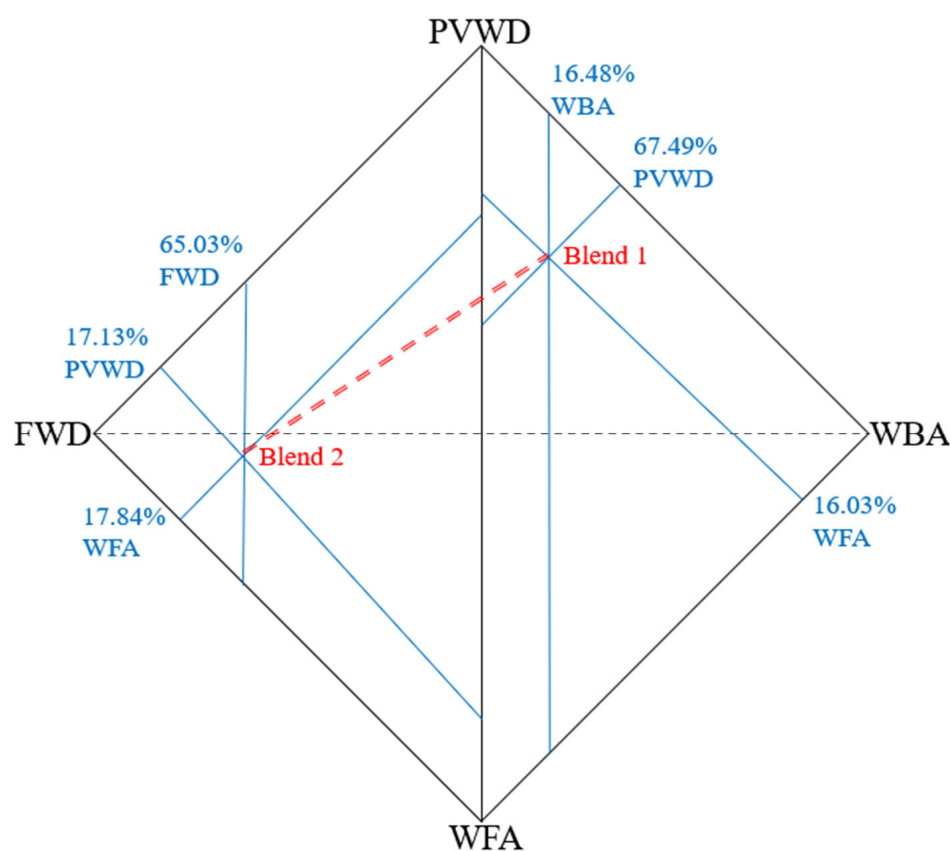


Figure 5. Quaternary diagram (i.e., triangular pyramid with 100% g/g of a component in each vertex) representing all the blends (i.e., red and dashed line between Blend 1 and Blend 2) that could be prepared with the nutrient ratio $C/N/P \leq 10/1/1$ but different levels of chemical stability.

Under the conditions of mild acidification, the PVWD had lower EC (Figure 2b) than that of the Blend of 80% FWD and 20% PVWD (Figure 3b). This could be related to the high $NH_4^+ - N$ and sodium contents of the of the FWD [55], since these chemical species are important contributors to the EC [62]. However, since the Blend required more severe acidification than the PVWD alone, the EC of the Blend (Figure 4b) became greater than that of the PVWD alone (Figure 2b) under the severe acid treatment.

Figure 5 represents all the possible combinations of the samples (i.e., discontinuous line between the Blend 1 and the Blend 2, represented in a quaternary diagram) that could be prepared to maintain a nutrient ratio $C/N/P \leq 10/1/1$. This nutrient ratio is necessary to promote high CUE upon land application [49,63]. There was a difference between the Blend 1 ($67.49 \pm 3.14\%$ PVWD, $16.03 \pm 1.97\%$ WFA, and $16.48 \pm 2.87\%$ WBA) and Blend 2

($65.03 \pm 3.02\%$ FWD, $17.13 \pm 3.23\%$ PVWD, and $17.8 \pm 1.89\%$ WFA) in terms of chemical stability because the FWD had a greater content of $\text{NH}_4^+\text{-N}$ than the PVWD, which had a greater content of undigested fiber. In this way, only by reducing the share of the FWD to zero, it was possible to include the coarser fraction of the wood ashes in the Blend 1. It is important to mention that the greater share of wood ashes in Blend 1 led to higher pH and higher NH_3 volatilization [55]. Blend 2 only contained the WFA because of the smaller particle size and greater surface area of this material compared to the WBA, thus the WFA could play a better role as a stabilization agent. Furthermore, the finer fraction of the wood ashes with greater BC content [55] had better sorptive properties.

The previous acidification of the digestate can be explored as a means to achieve the dewatering of the anaerobic digestates [64]. The dehydration of the organic slurries is important because of the cost of transportation and storage in covered facilities [65–69]. The acids can be employed as cationic surfactants to promote the release of the water molecules bound to the digestate fibers [70]. Figures 6 and 7 show how the severe acidification enhanced the solid–liquid separation more than the mild acidification did. Only the $0.0687 \text{ mmol H}^+\text{-H}_2\text{SO}_4/\text{g PVWD}$, which was able to reduce the pH below a value of 3 at the 0 h of incubation (Figure 1a), presented a clear WS phase (Figure 6(aii)). The WS phase of the $0.0687 \text{ mmol H}^+\text{-H}_2\text{SO}_4/\text{g PVWD}$ became cloudier as the incubation progressed (Figure 6b), in agreement with the buffer capacity observed in the Figure 1a. Note that the WS phase of the experimental unit $0.0687 \text{ mmol H}^+\text{-H}_2\text{SO}_4/\text{g PVWD}$ at the 72 h (Figure 6(biii)) was larger than that of the replicates shown for the 24 h of incubation (Figure 6(bi)) and 48 h of incubation (Figure 6(bii)). The reason for this was the heterogeneity of the sample, which led to inaccuracy in the weighting, and thus a large mass of PVWD was charged in the 50-mL capped Corning® tube for the 72-h incubation. After the 72-h incubation, the corresponding milli-Q® water was added, in agreement with the S/E 1/10 g/mL.

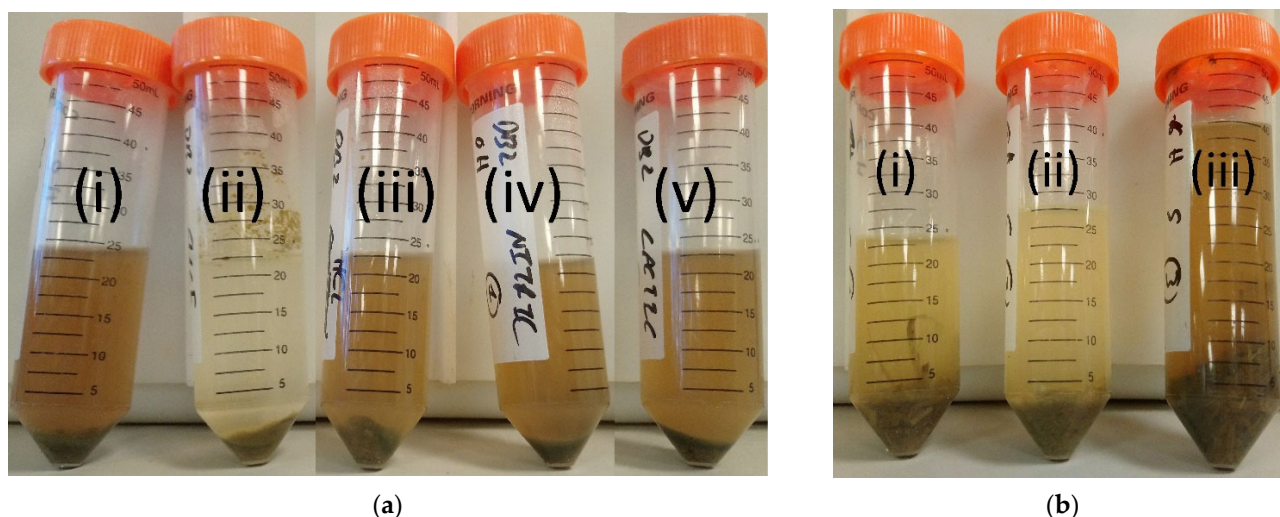


Figure 6. (a) Solid–liquid separation attained at the 0 h of incubation after adding milli-Q® water following a S/E 1/10 g/mL and subsequent centrifugation at 4000 rpm for 5 min. (i) $0 \text{ mmol H}^+/\text{g PVWD}$; (ii) $0.0687 \text{ mmol H}^+\text{-H}_2\text{SO}_4/\text{g PVWD}$; (iii) $0.0443 \text{ mmol H}^+\text{-HCl}/\text{g PVWD}$; (iv) $0.0571 \text{ mmol H}^+\text{-HNO}_3/\text{g PVWD}$; (v) $0.0001 \text{ mmol H}^+\text{-CH}_3\text{CH(OH)COOH}/\text{g PVWD}$. (b) Solid–liquid separation attained at the (i) 24, (ii) 48, and (iii) 72 h of incubation of $0.0687 \text{ mmol H}^+\text{-H}_2\text{SO}_4/\text{g PVWD}$.

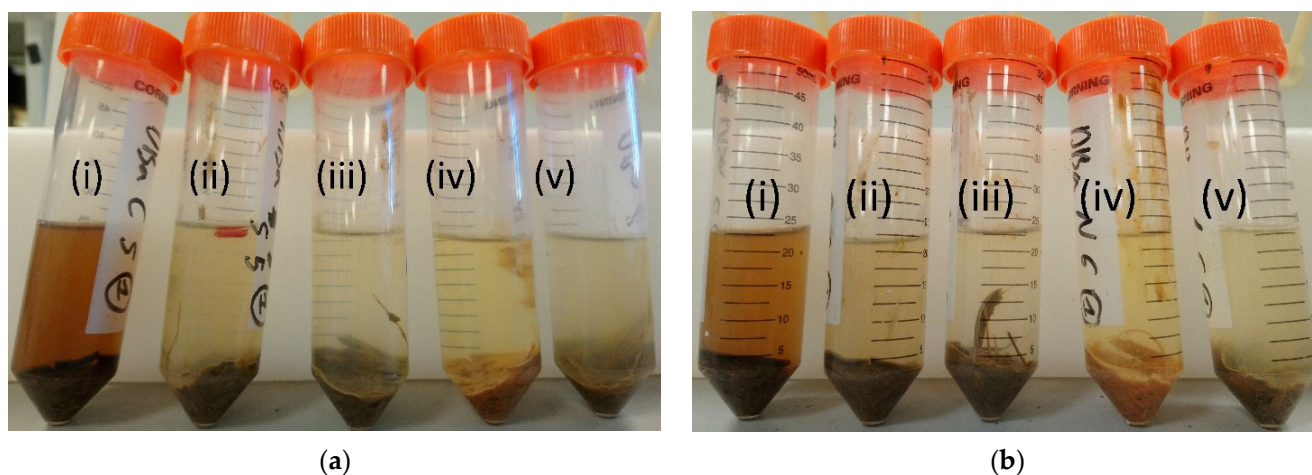


Figure 7. Solid–liquid separation attained at the (a) 168 and (b) 336 h of incubation after adding milli-Q® water following a S/E 1/10 g/mL and subsequent centrifugation at 4000 rpm for 5 min. (i) 0 mmol H⁺/g PVWD; (ii) 0.8628 mmol H⁺-H₂SO₄/g PVWD; (iii) 0.5569 mmol H⁺-HCl/g PVWD; (iv) 0.7171 mmol H⁺-HNO₃/g PVWD; (v) 0.0016 mmol H⁺-CH₃CH(OH)COOH/g PVWD.

As higher doses of all acids were applied to the PVWD (Figure 2a), the clean WS phase was found for all the other acidification conditions, even late in the incubation of the acidified anaerobic digestate, at the 168 h (Figure 7a) and at the 336 h (Figure 7b). The best performance was found for the HCl in terms of attaining a clean WS phase. It should be noted that the yellowish color was due to the oxidizing effect that the 0.7171 mmol H⁺-HNO₃/g FWD had on the OM (Figure 7(aiv) and Figure 7(biv)). The oxidation implied the release of CO₂ throughout the incubation of the 0.7171 mmol H⁺-HNO₃/g PVWD. Tursi [71] described that the anaerobic digestion treatment is enough to improve the management of organic waste, thus the subsequent oxidation due to the addition of the acids is not necessary. It is true that the combination of the fermentation and the thermochemical conversion technology [71], following the biorefinery concept, could lead to more recalcitrant OM contained in the anaerobic digestate, which will help to restore the soil as a C sink.

Both the H₂SO₄ and the HNO₃ are good oxidizing agents due to the high oxidation state of the sulfur and N in each respective acid compound [57]. As per the comparison of Figure 8b,d, the HNO₃ showed a greater detrimental effect on the PVWD fiber. Figure 8 shows how the darker color of the unacidified PVWD (Figure 8a) was only attenuated with the use of 0.8628 mmol H⁺-H₂SO₄/g PVWD compared to the 0.7171 mmol H⁺-HNO₃/g PVWD that turned it to a bright color at 336 h of incubation. The severe acidification with the CH₃CH(OH)COOH did not represent a chemical attack to the PVWD fiber, but filamentous microbial growth (Figure 8e) and the blanch associated with degradation of the OM by microbes (i.e., oxidation) were observed [59]. The acidification is intended to minimize the microbial activity [51], although the use of some organic acids (e.g., citric acid) has been found to have the opposite effect [59]. It should be noted that, although the dose of CH₃CH(OH)COOH was expressed as mmol H⁺/g, digestates were less than 100 times the dose of the inorganic acids, and the amount of acid employed was 10–100 µL in all cases (Table 2).

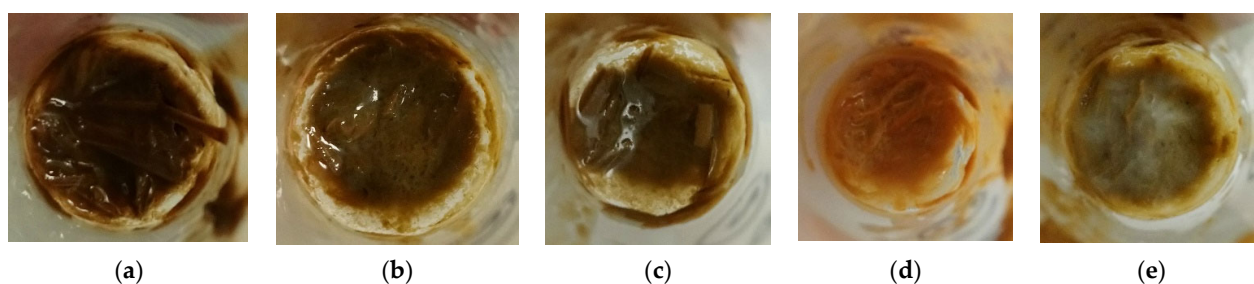


Figure 8. Photographs of the different acidification conditions applied to the PVWD at the end of the treatment (336 h) before the addition of the milli-Q water (S/E 1:10 g/mL) for measuring the pH and the EC. (a) 0 mmol H^+ /g PVWD; (b) 0.7488 mmol H^+ - H_2SO_4 /g PVWD; (c) 0.4833 mmol H^+ -HCl/g PVWD; (d) 0.6223 mmol H^+ - HNO_3 /g ID; (e) 0.0014 mmol H^+ - $CH_3CH(OH)COOH$ /g PVWD.

The reproducibility of the microbial growth due to the acidification with $CH_3CH(OH)COOH$ was high and was found in all replicates, even at earlier time points of the incubation (e.g., 96 h; Figure 9a–c). Although some microbes can be inoculated intentionally as biofertilizers, the growth of pathogens is undesirable because it might lead to phytotoxic effects and plant diseases [72,73]. In the UK, specific microbiological assays conducted by certified laboratories are required to confirm the beneficial microbial activity within an organic manure [74]. Only in a replicate of the 0.0687 mmol H^+ - H_2SO_4 /g PVWD at the 96 h of incubation was it possible to identify some type of microbial growth (Figure 9d), but was much more modest than when using $CH_3CH(OH)COOH$.

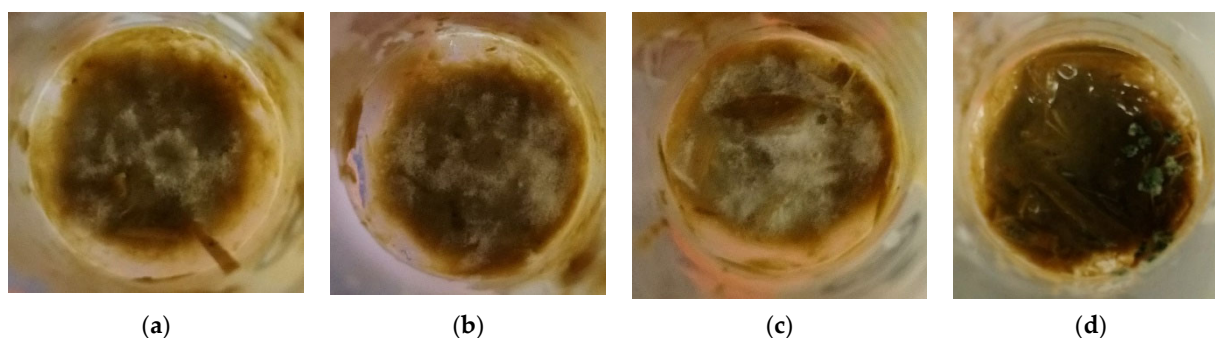


Figure 9. Undesired microbial growth observed in the 3 replicates (a–c) of 0.0016 mmol H^+ - $CH_3CH(OH)COOH$ /g PVWD at the 96 h of incubation. (d) Undesired microbial growth observed in a replicate (right-hand side of the photograph) of 0.0687 mmol H^+ - H_2SO_4 /g PVWD at the 96 h of incubation. These photographs were taken before the addition of the milli-Q[®] water following a S/E/1/10 g/mL.

Due to the lower content of undigested fiber present in the Blend of 80% FWD and 20% PVWD and the greater amount of NH_4^+-N , the effect of the acidification on the processing of the organic material was different than when the PVWD was treated alone. First of all, the cleanest WS phase was obtained using HNO_3 , followed by H_2SO_4 , HCl, and $CH_3CH(OH)COOH$, regardless of the time allowed for the stabilization of the acidification conditions (Figure 10).

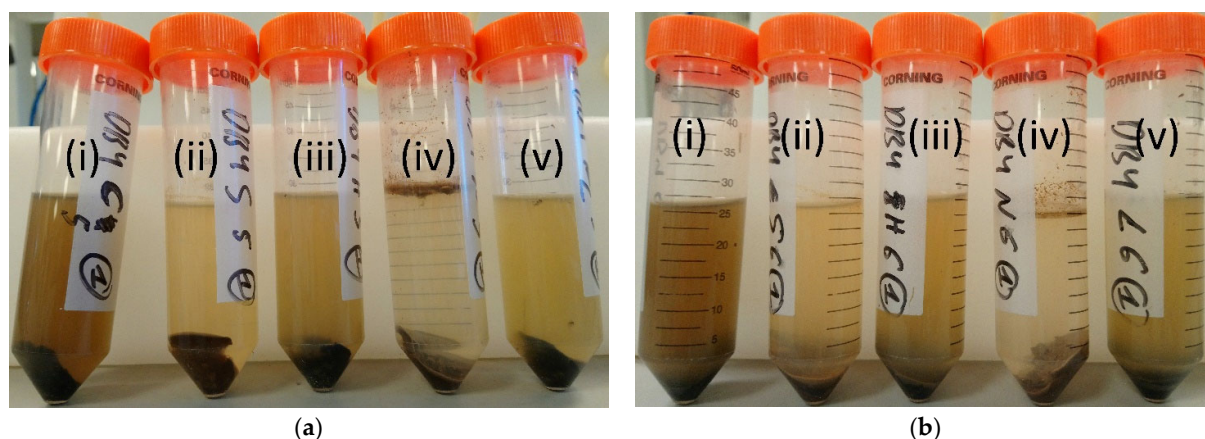


Figure 10. Solid–liquid separation attained at the (a) 168 and (b) 336 h of incubation, after adding milli-Q® water following a S/E 1/10 g/mL and subsequent centrifugation at 4000 rpm for 5 min. (i) 0 mmol H⁺/g Blend; (ii) 0.7488 mmol H⁺-H₂SO₄/g Blend; (iii) 0.4833 mmol H⁺-HCl/g Blend; (iv) 0.6223 mmol H⁺-HNO₃/g Blend; (v) 0.0014 mmol H⁺-CH₃CH(OH)COOH/g Blend.

Furthermore, the H₂SO₄ oxidizes the Blend more than the HNO₃, as per the yellowish color found during the whole incubation of the 0.7488 mmol H⁺-H₂SO₄/g Blend (Figures 11b and 12b), compared to the 0.6223 mmol H⁺-HNO₃/g Blend (Figures 11d and 12d). The greater content of undigested fiber in the PVWD (Figure 8a), compared to the Blend containing 80% FWD and 20% PVWD (Figure 11a), should be noted.

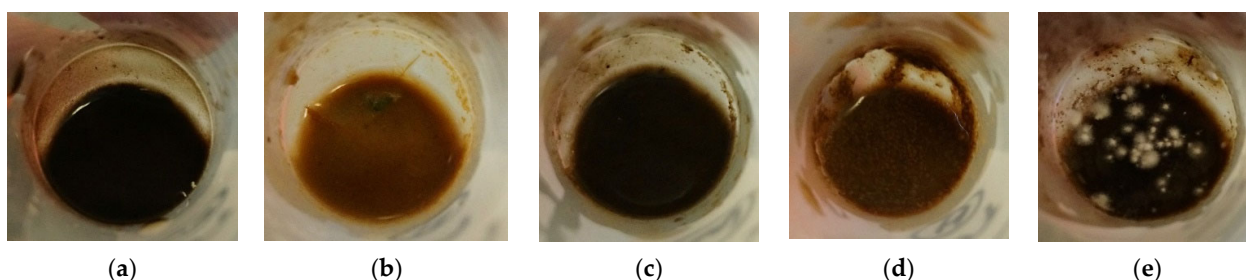


Figure 11. Photographs of the different acidification conditions applied to the Blend (80% FWD + 20% PVWD) at the 168 h of incubation, before the addition of the milli-Q water (S/E 1:10 g/mL) for measuring the pH and the EC. (a) 0 mmol H⁺/g Blend; (b) 0.7488 mmol H⁺-H₂SO₄/g Blend; (c) 0.4833 mmol H⁺-HCl/g Blend; (d) 0.6223 mmol H⁺-HNO₃/g Blend; (e) 0.0014 mmol H⁺-CH₃CH(OH)COOH/g Blend.

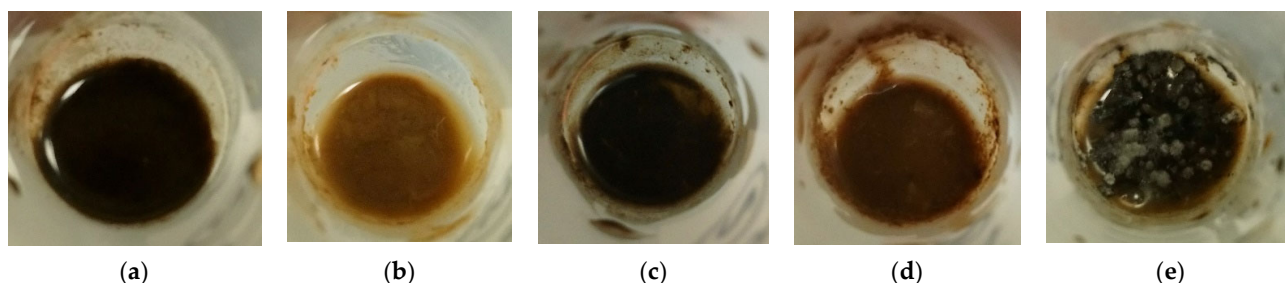
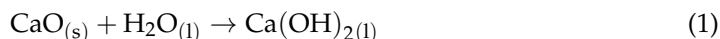


Figure 12. Photographs of the different acidification conditions applied to the Blend (80% FWD + 20% PVWD) at the end of the treatment (336 h), before the addition of the Milli-Q water (S/E 1:10 g/mL) for measuring the pH and the EC. (a) 0 mmol H⁺/g Blend; (b) 0.7488 mmol H⁺-H₂SO₄/g Blend; (c) 0.4833 mmol H⁺-HCl/g Blend; (d) 0.6223 mmol H⁺-HNO₃/g Blend; (e) 0.0014 mmol H⁺-CH₃CH(OH)COOH/g Blend.

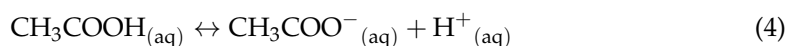
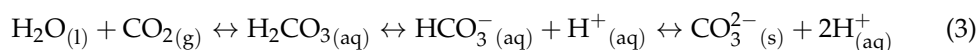
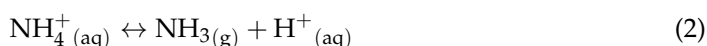
The type of microbial growth promoted by the $\text{CH}_3\text{CH}(\text{OH})\text{COOH}$ in the Blend (80% FWD and 20% PVWD) was not filamentous. Several colonies were observed at the 168 h and after the 336 h of incubation of 0.0014 mmol H^+ - $\text{CH}_3\text{CH}(\text{OH})\text{COOH}$ /Blend (Figures 11e and 12e, respectively).

4. Discussion

Both the pH and the EC are important parameters of fertile soils [75]. Therefore, the organic manures need to be adequately formulated, since these are intended to be suitable for a certain type of soil and crop. The severe acidification hinders the use of the fertilizer as a liming agent, and it should be applied carefully due to the very strong salinity that may exceed the crop tolerance [76]. According to Daliakopoulos et al. [76], any condition with an EC above 8 dS/m can be regarded as strongly saline. It should be noted that the final properties of the waste-derived fertilizers need to be appraised after the addition of the wood ashes. On the one hand, the wood ashes provide the anaerobic digestates with more electrolytes that increase the EC of the novel blended fertilizers. On the other hand, the dewatered blend with only 20% moisture can undergo self-hardening to produce a granular fertilizer [58,77,78] and can reach an EC < 10 dS/m [79]. Anaerobic digestate with high fiber content has already been tested as a construction material [80]. The addition of wood ash could help to limit the water bounded to the OM [70,81,82] due to the hydration and solidification of the calcium oxide (Equation (1)) in the blend for moisture levels up to 30% [82–84]. Alkaline elements, such as calcium and magnesium, are essential components of the wood ashes and the form of these elements (i.e., oxides, hydroxides, or carbonates) depends on the temperature of incineration and conditions of storage [85]. The higher the temperature, the higher the presence of oxides due to the decomposition of hydroxides and carbonates [86]; the oxides achieve their predominant form at an incineration temperature above 1000 °C. Similarly, the reaction with the moisture and the CO_2 of the atmosphere during storage could increase the share of hydroxides and carbonates in the wood ashes [85]. Greater mechanical properties can be expected in the blend of anaerobic digestate and wood ash [87] compared to the digestate fibers alone.



The wood ashes can be employed to achieve a sterilization effect on the anaerobic digestates [88] by maintaining a pH 12 for at least 2 h, as recommended by the UK government [89]. Moreover, a mild dose of wood ash can be used without open-loop acidification (i.e., without using commercial acids: H_2SO_4 , HCl , HNO_3 , and $\text{CH}_3\text{CH}(\text{OH})\text{COOH}$) to achieve the pH_{zpc} by means of NH_3 volatilization (i.e., noninvasive acidification; Equation (2)). Nevertheless, the implementation of a method to recover the NH_4^+ -N is required, such as absorption of the NH_3 volatilized into a H_2SO_4 solution [90,91]. In fact, this is a route for the valorization of the anaerobic digestate and production of a mineral-grade fertilizer [66], which can be marketed as a 40–60% ammonium sulfate solution [64] or as pure crystals of $(\text{NH}_4)_2\text{SO}_4$ [92]. Since the wood ash is a recycled material, the costs of the process of ammonia stripping are reduced from the point of view of the operational expenditure, which is associated with the consumption of alkaline reagents to increase the pH of the anaerobic digestate [64,93]. Less than 1% of the NH_4^+ -N is volatilized as part of the biogas release during the AD [27]. The reason for the costly amount of alkali required is the fact that there are three buffer equilibria responsible for the pH in the anaerobic digestate (Equations (2)–(4); [27]):



It is noteworthy to highlight that two of these equilibria (Equations (2) and (3)) are connected by the precipitation of $(\text{NH}_4)_2\text{CO}_3$ and NH_4HCO_3 , which naturally increases

the pH of anaerobic digestates [94]. Drapanauskaite et al. [95] designed a process for the manufacturing of the NH_4HCO_3 via processing the liquid fraction of the digestate. Unlike the open-loop strategy of the ammonia stripping, which requires commercial grade H_2SO_4 for the manufacturing of the $(\text{NH}_4)_2\text{SO}_4$, the reagents for the preparation of the $(\text{NH}_4)_2\text{CO}_3$ and NH_4HCO_3 are components of the anaerobic digestate [95]. The marketable solid NH_4HCO_3 fertilizer contains 18% of N. In addition to calcium, magnesium, and phosphorus, the wood ash is a source of carbonates [85], which is necessary for the manufacturing of NH_4HCO_3 and $(\text{NH}_4)_2\text{CO}_3$. It is important to mention that the distillation process, as described by Drapanauskaite et al. [95], might be hindered by the alkaline pH that the wood ashes provide to the anaerobic digestates, as this prevents the release of CO_2 . According to the specifications of the process of Drapanauskaite et al. [95], the pH of the anaerobic digestate should be 7.85 (40 °C) at the entrance of the stripping column. Limoli et al. [64] evaluated some of the difficulties associated with a wood ash-like material (i.e., CaO) during the operation of a turbulent mixer with the liquid fraction of the anaerobic digestate. Limoli et al. [64] found that the CaO increases the total solid content and decreased the fluency; hence, in a synergistic approach, these materials might be better combined to ease the dewatering [70].

5. Conclusions and Prospects

The most suitable acidification agent and dose were found to be dependent on the nature of the anaerobic digestate. The novelties of this investigation were the findings of (a) the excessive oxidation of the OM, resulting in color change of the soil organic amendment, (b) the visual characterization of the microbial growth, and (c) the extent of the solid–liquid separation due to acidification. Nevertheless, all the conclusions based on qualitative observations of the photographs are subjected to future in-depth quantitative analysis which was beyond the remit of this paper. While the HNO_3 easily oxidized the undigested fiber of the PVWD, the H_2SO_4 played that role when it was combined with the Blend of 80% FWD and 20% PVWD. The severe acidification (i.e., use of a high dosage of acid) aided the solid–liquid separation but degraded the structure of the OM, which negatively affected the quality of the manure to be employed as a soil amendment. Considering these constraints, the HCl was found to be the most suitable acid to preserve the properties of organic manures. However, individual testing of each material is necessary to optimize the acidification treatment in terms of acid type, dose, and time required for stabilization. Furthermore, the cost of this acid reagent needs to be considered when designing the treatment process, since it might be more expensive than the widely used H_2SO_4 . The $\text{CH}_3\text{CH}(\text{OH})\text{COOH}$ did not negatively affect the OM of the anaerobic digestates but promoted excessive undesired microbial growth. Sterilization of the anaerobic digestates via poisoning with sodium azide (NaN_3) could be performed in future investigations. This method is preferred rather than autoclaving because the latter technique changes the form of C_{org} (e.g., hydrolysis of OM). The NaN_3 poisoning would allow for the study of the chemical effect of the $\text{CH}_3\text{CH}(\text{OH})\text{COOH}$, while avoiding uncontrolled biological activity that otherwise would interfere significantly in the intended outcome of the acidification treatment. The proposed future investigation would help to envisage the best conditions for employing organic acids, such as the $\text{CH}_3\text{CH}(\text{OH})\text{COOH}$. If the outcome would be that sterilization is needed, the wood ashes could aid the pasteurization process and reduce the costs at a scale beyond 50 mL. The addition of the wood ashes was also proposed to finalize the stabilization of the anaerobic digestates in terms of pH, EC, nutrient profile, and for the manufacturing of a granular fertilizer, after performing the solid–liquid separation.

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Abbreviations

AD	anaerobic digestion
Blend	mixture of approximately 20% PVWD and 80% FWD
BC	black carbon
C	carbon
C _{org}	organic carbon
CUE	carbon use efficiency
C/N/P	nutrient ratio
DOC	dissolved organic carbon
EoW	end-of-waste
FWD	food waste digestate
GHGs	greenhouse gases
OM	organic matter
PVWD	post-harvest vegetable waste digestate
PO ₄ ^{3−} -P	phosphorus in the form of orthophosphate
N	nitrogen
NH ₄ ⁺ -N	ammoniacal nitrogen
S/E	sample-to-extractant ratio
WBA	wood bottom ash
WFA	woof fly ash

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